

AN ABSTRACT OF THE THESIS

Kais S. Ebrahem for the degree of Doctor of philosophy in Horticulture presented on October 16, 1992

Title: FACTORS INFLUENCING STORAGE QUALITY OF HAZELNUT VARIETIES

Abstract approved: \_\_\_\_\_

Dr. Daryl G. Richardson, Professor of Horticulture

This thesis research is a series of five studies dealing with various aspects of hazelnut quality:

1. Identification of kernel mold and its incidence among hazelnut varieties.
2. Seasonal development and composition of kernels.
3. Hazelnut oil composition (fatty acids and tocopherols) of seventeen varieties.
4. Hazelnut oil composition compared to 14 other nuts and oilseeds.
5. Storage and roasting effects on lipid oxidation.

Barcelona, Daviana, and Ennis varieties of hazelnuts used to study white mold showed that mold incidence was highest in 1986, and much less in 1987 and 1988. Ramularia spp was the only fungus that was identified in all samples with kernel mold and was usually found at high percentages. Temperatures for drying, storage, and numbers of nuts per cluster had no significant effect on percent mold.

The second part of this study measured fatty acid and vitamin E concentrations during the growing season. Samples were collected from seven varieties (Barcelona, Daviana, Ennis, Tonda Romana, Tonda Gentile della Langhe, Tombul, and Tombul Ghiaghli). Kernel oil and vitamin E (tocopherol) concentrations increased with time, while moisture decreased. Oleic acid was the major fatty acid (ca.75%) found in hazelnuts, followed by linoleic(ca.20%). Linolenic was high at the beginning of the season but then decreased to about 1% at harvest. Alpha-tocopherol was the major form of vitamin E found, composing almost 95% of total tocopherols. Hazelnuts are a rich source of vitamin E, with about 350  $\mu\text{g/g}$  oil.

Fourteen types of nuts, oil seeds, and seventeen varieties of hazelnuts were compared for oil content, fatty acid, and tocopherol composition. Macadamia nuts were the highest in oil content (77%) and chestnuts were the lowest (3%). Oil concentrations in oil seeds ranged from 5% in corn to 50% in sesame seeds. Oil concentration also varied among hazelnut cultivars. Hall's Giant had low concentrations (58%) of oil and Tombul had high concentrations (66%) of oil. Gamma-tocopherol was the dominant form in pistachios, English walnuts, black walnuts, pinenuts, and Brazil nuts. All four tocopherols were found in oil seeds and tocotrienols were found in some. Hazelnut varieties were stable during storage for up to two years with only slight loss in vitamin E.

FACTORS INFLUENCING STORAGE QUALITY  
OF HAZELNUT VARIETIES

by

Kais S. Ebrahim

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Typed by Amy Ellingson for Kais S. Ebrahim

# بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

And in the Earth are neighbouring tracts, vineyards and ploughed lands, and date-palms, like and unlike,<sup>2</sup> which are watered with one water. And We have made some of them to excel others in fruit. Lo! herein verily are portents for people who have sense.

وَفِي الْأَرْضِ قِطْعٌ مُتَّجِرَةٌ وَجَدْتُمْ مِنْ آعْنَابٍ  
وَزَرْعٌ وَنَخِيلٌ صِنَوَانٌ وَغَيْرُ صِنَوَانٍ يُسْقَى بِمَاءٍ  
وَاحِدٍ تَنْفَضُّلٌ بَعْضُهَا عَلَى بَعْضٍ فِي الْأَكْلِ إِنَّ  
فِي ذَلِكَ لَآيَاتٍ لِقَوْمٍ يَعْقِلُونَ ④

IN THE NAME OF ALLAH, THE MOST BENEFICENT, THE MOST  
MERCIFUL.

## DEDICATION

This thesis is dedicated to three special persons. The first person, to whom I am indebted for my education, is my father who died on March 16, 1990. I lost a wonderful father. Father, you are not around us but you will always live in my heart; while I have missed you, I have tried hard to achieve the goals that I would told you about. (MAY GOD BLESS YOU FOR ALL THINGS YOU DID FOR THE THREE OF US).

The second person is my lovely and devoted mother, who very early in my childhood, taught me that a little extra effort at the right time can prove profitable in the long run. Words are not inadequate to express my love and respect for her. I will never forget what you did for me during my study in high school, university, and how much it is difficult on you being far away from you (**I LOVE YOU SO MUCH, YOU ARE A WONDERFUL MOTHER**).

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## **FACTORS INFLUENCING STORAGE QUALITY OF HAZELNUT VARIETIES**

### **Chapter 1. Introduction**

Three countries produce 94% of the worlds hazelnut production. Turkey is first and Italy is second in hazelnut production. Table 2.1 shows the top five countries in hazelnut production (Mehlenbacher, 1989) and Oregon, USA is 4th. The cultivation of hazelnuts is very important to Oregon's agricultural economy. There are at least 29,000 acres of prime hazelnut land in the Willamette Valley. The processed value of hazelnuts for 1987 was 36 million dollars (Crabtree, 1987), and Willamette Valley orchards produce 98% of the U.S. Hazelnut crop (Mehlenbacher, 1991). The hazelnut industry of Oregon has grown dramatically over the last twenty years. There seem to be a lot of new products being developed, particularly in the breakfast cereal industry and with a lot of food processors. More than one million pounds of hazelnuts have been used since the introduction in the U.S. of the breakfast cereal Mueslix in fall of 1987 (Martin, 1988).

Hazelnuts are harvested in the fall, but sold throughout the year. The tree is susceptible to alternate bearing, which often results in a large crop every other season. In order to smooth out the supply, the nuts (usually in shell) are stored in warehouses from one season to the next. Since the hazelnut kernel has a low respiration rate it might be expected to be a relatively stable commodity. However, due to large amounts of unsaturated fatty acids, (mainly oleic), oxidative

rancidity is a potential threat to the stability of the kernel. Therefore, it is desirable to reduce the kernel moisture to about 6% and store at fairly low (5 °C to 10 °C) temperatures in order to extend hazelnut shelf life.

Mold and rancidity are two factors which can strongly affect the market acceptability of hazelnuts. Oregon hazelnut quality was reduced because of the high incidence of kernel mold. Extra costs were incurred because of the necessity of carefully controlling in-shell quality and removing large numbers of moldy kernels from shelled nuts.

Lipid oxidation is one of the primary mechanisms of quality deterioration in stored foods regardless of whether oil content is high or low. The changes in flavor, color, texture, and nutritive value and the production of toxic compounds are all important quality considerations (Kanner et al., 1988; Ladikos and Lougovois, 1990). During the past 40 years, a great deal of experimental evidence has accumulated suggesting that lipid peroxidation in cellular membranes is implicated in a variety of pathological conditions (Pompella et al., 1987).

The ratio of (oleic, linoleic, and linolenic acids) to one another is important to the economic value of the nut. Low linoleic and linolenic acid content might improve the shelf life, but a higher linoleic acid content might be nutritionally desirable. It is not known how these might affect flavor compared to other constituents of nuts.

There is every indication that in the future hazelnut growers will be subject to even greater competition from growers of other kinds of nuts. With the rapidly increasing almonds, English walnuts and pecans in the United States and a steadily increasing importation of cheaply produced Brazil nuts and Cashew nuts from abroad, it appears likely that the consumer will be looking for bargains.

Among the important characteristics needed in new hazelnut varieties are high percentages of kernel, well formed nuts, good texture and good flavor. Attention must also be given to nut shape and to such factors as yield, disease resistance, hardiness, and bearing habits. Introduced with some of these improvements may be other genetic changes which affect the nutrient value of the hazelnut in positive or negative ways.

The current interest in the human demand for vitamin E as well as the trend toward preferred consumption of high unsaturated fats, has emphasized the need for surveys of the tocopherol and fatty acid content of hazelnuts and other kind of nuts.

From the optimum time of harvest, the kernels begin to undergo a series of irreversible biochemical changes which may be detrimental to quality. Management of these changes, which are mainly a function of the kernel's unique composition, presents a series of challenges which vary considerably from

the post-harvest problems encountered with many other horticultural crops.

Several pre-harvest and post-harvest factors can dramatically influence the quality, and thus market acceptability of hazelnuts. Among the pre-harvest factors are kernel fill, and moisture conditions while the nuts are on the tree. Post-harvest factors are: moisture content, nut drop delays between harvest and drying, drying temperature, temperature of storage, shelling, roasting, and blanching.

Past research on the hazelnut has been limited largely to a few areas of study that have been projects of commercial importance such as breeding and processing (Woodroof, 1967). The hazelnut breeding program at Oregon State University was initiated in 1969 by Dr. Maxine Thompson. The objectives of the OSU breeding program include increasing the yield of kernels per acre and improving kernel quality (Thompson, 1982), and better commercial propagation (Lagerstedt and Hubert, 1975; Lagerstedt, 1982; Stebbins and Kent, 1982; Bassil et al., 1991; Mehlenbacher and Smith, 1992), compatibility and incompatibility between cultivars (Thompson and Richardson, 1978; Thompson, 1979a,b,c; Mehlenbacher and Miller, 1988; Mehlenbacher and Smith, 1988; Mehlenbacher and Thompson, 1991; Mehlenbacher et al., 1991), disease resistance, brown-stain (Stebbins, 1984), and eastern filbert blight (Mehlenbacher, 1988; Stone et al., 1988). Studies on germination, gibberellic acid, sterol production in

germination of hazelnut seeds were done by Shewry and Stobert (1974) and Shewry et al. (1974). Other studies characterized changes in phospholipid fatty acids in germinating hazelnuts by Shewry et al. (1973) and Shewry and Stobert (1973). The chemical composition and nutritional aspects of nutmeats have largely been ignored in these programs, and only limited reports are available in which newly developed and standard cultivars have been compared.

### **Objectives**

The objectives of this research were to determine those pre-harvest and post-harvest factors which lead to the ability to store hazelnuts in-shell and as free kernels for the longest time without sacrificing quality. This involves the study of factors leading to kernel mold and rancidity development in the stored nuts both in and out of shell.

1. Identification of the fungi responsible, and the time of infection of the kernels will be attempted, and whether or not there are any major differences in susceptibility of the major commercial varieties.

2. To study the accumulation of fatty acids and vitamin E during kernel development for seven varieties of hazelnuts.

3. To evaluate the concentrations of vitamin E, fatty acids, and peroxide value of sixteen varieties of hazelnuts stored for various times up to three years.

4. To study the effect of temperature, moisture, and vitamin E on storage quality of hazelnuts.

Table 2.1. Top five countries in production of hazelnuts.\*

Country	Production (metric tons)	%
Turkey	480,000	65.0
Italy	50,000	23.0
Spain	33,000	6.0
USA	20,000	4.0
France	1,500	0.4

\*From (Stumbs, 1987; Hansberry et al., 1988; Erridge et al., 1989 ; Mehlenbacher, 1991)

## Chapter 2. Review of Literature

### **The Hazelnut**

#### History

According to a manuscript found in China dating back to 2838 B.C., the hazelnut takes its place among the five sacred nourishments God bestowed to humanity and has been going on for 4798 years. In olden times the hazelnut was used as a medicine and a tonic. The Greek physician Dioscorides, 1800 years ago, in his book "Materia Medica" (Kitabul Hasayis) emphasizes the properties of hazelnut as a medium of remedy for coughs, colds, and baldness.

In "The Law" the manuscript of Ibn Sina, registered under number 3748 in the St. Sophia library located in Turkey, the following information has been given about hazelnuts.

Ibn Masu, In his work "Eccamul Mufredatul Ediviye Liebnul Baytar" volume 1, p. 119, registered in Cairo library under number 3870, says "filbert is more nutritious than walnut and it strengthens the intestines. Also it purifies the intestines by removing all the harmful waste and gasses in them. Its advantages increase if it is eaten with some figs after meals."

According to more modern books, "Filbert oil is valuable as a remedy for tape worms in the intestines of children and also used as a hair tonic." The person who suffers from indigestion should eat dried fruits like hazelnuts, walnuts, and pistachios (Peker, 1962a,b). There is historical evidence

that nuts formed parts of human nutrition long before recorded history. In recorded history hazelnuts are described as an ingredient of the Chinese diet 5000 years ago (Lauer, 1986).

The hazelnut was introduced into Oregon in 1885 by Felix Gillet. The term filbert and hazelnut are used interchangeably to include all plants in the genus Corylus. Geoschke (1887) in his monograph on Corylus used the term hazel-nut. The L.H. Bailey (1949) and Rehder (1956) manuals of cultivated plants give hazelnuts as the preferred common name for the genus. In Great Britain, a distinction is made between filberts, which have the husk longer than the nut, and cob nuts in which the husks are shorter than the nuts (Howes, 1948). In the United States, filbert is commonly used to designate nuts derived from European species while native American genotypes are called hazelnuts (Slate, 1930). The Oregon state legislature recently passed a resolution proclaiming the hazelnut as Oregon's official state nut (ANON, 1989a).

The name filbert is supposed by some to have originated from "fullbread" referring to the fact that in some cultivars the husk entirely covers the nut. By others, it is thought to have been derived from St. Philibert, as August 22 is dedicated to him, a date that corresponds in England to the ripening of the earliest filbert (Anon, 1963).

The most important sources of commercial cultivars are Corylus avellana and C. maxima, both of European origin. The

American species Corylus americana has been hybridized with the European hazelnuts to produce cold hardy cultivars of some commercial promise (Woodroof, 1979). Table 2.2 Oregon shows hazelnut trees and production percentage by varieties in 1989 (ANON, 1989b; Williamson, 1991).

### Areas of Production

World commercial hazelnut production for 1989-1990 is expected to reach a new high of 645,300 tons (in shell basis), exceeding last seasons record harvest by nine percent, according to the U.S.D.A. Foreign Service. Turkey is the largest producer of hazelnuts in the world with 480,000 tons, (65%) of all output (Mehlenbacher, 1991). It is the leading kernel supplier as far as the major markets in Europe are concerned. Turkey is also the price leader, or the price discounter (Stumbs, 1987). There are two growing areas, the smaller Akcakoca region near the Bosphorous Straits in the northwest and the larger Black Sea region along the north shore of Turkey (Hansberry, et al, 1988). In Turkey, 'Tombul' is reported as the leading cultivar with 'Sivri' and 'Badem' used as pollinizers (Zielinski, 1959).

Italy is also an important producer with 23% of total production. Italy produces 150 thousand tons in-shell and consumes 90 thousand. This leaves 60 thousand tons of hazelnuts that Italy must export (Erridge et al, 1989).

Spains' production for 1989-1990 was 33,000 tons. Spain does not have a price support for hazelnuts.

Table 2.2. Hazelnut varieties and  
Oregon production, 1989.

Variety	%*	Production (tons) †
1. Barcelona	80.5	16,10
2. Ennis	10.1	2,020
3. Daviana	4.6	920
4. Butler	1.2	240
5. DuChilly	1.2	240
6. Royal	0.5	100
7. Casina	0.4	80
8. Hall's Giant	0.3	60
9. Others	1.2	240
		Total 20,000

\*Williamson, 1991

†ANON, 1988

There are three main varieties grown in France, 'Barcelona', 'Segorbo', and 'Ennis'. The 'Segorbo' variety comprises 30% of French planting, the other 70% is comprised of 'Ennis' and 'Barcelona'. Current production is around 1500 MT and the industry has set a goal of 3,000 to 5,000 tons (Hansberry et al, 1988).

Considerable quantities are also produced in parts of Germany, and England (Anon, 1916), but are consumed mostly in the countries where they are grown.

Hazelnuts are grown throughout western Oregon. The predominant variety planted is 'Barcelona' and other varieties cultivated to a lesser extent are 'Ennis', and the pollinizers 'Daviana', and 'Butler'. The different varieties vary in size, shell characteristics and composition. The Willamette Valley produces 98% of the US hazelnuts and ranks 4th in the world in total production (Mehlenbacher, 1991). Hazelnut acreage in Oregon has grown markedly and should increase even more rapidly as new varieties with improved kernel quality are developed. The processed value of Oregon hazelnuts for 1987 was 36 million dollars (Crabtree et al, 1987). Table 2.1 shows the top five countries productions and percentages of world production (Stumbs, 1987; Hansberry et al., 1988; Erride et al., 1989; Mehlenbacher, 1989). Table 2.3 shows production of the major types of nuts. Almonds were the highest in USA production, walnuts in consumption.

Table 2.3. U.S. production, consumption, price, and oil content of main kinds of nuts, 1980.\*

Nuts	USA production	consumption per cap/lb	\$/lb	oil%
Almond	260,000	0.45	1.75	54.2
Walnut	197,000	0.50	2.00	64.0
Pecan	92,000	0.30	2.75	71.2
Hazelnut	15,000	0.08	1.40	62.4
Macadamia	15,000	0.03	5.50	71.6
Pistachio	14,000	0.04	3.30	53.7

\*From (Rosengarten, 1984; Duke, 1989)

'Barcelona' continues to be the predominant variety, accounting for over 80 percent of the total trees in Oregon. 'Ennis' has become the second most popular variety accounting for over 10 percent of the trees. More than one-third of all trees planted during the past four years have been 'Ennis'. 'Daviana' has dropped into third place, less than five percent of the total, primarily due to its susceptibility to Eastern filbert blight. 'DuChilly', 'Butler', and 'Royal' collectively account for about three percent of the trees. Casina has become increasingly popular in recent plantings. It represents only 0.4 percent of the total trees but more than three percent of new plantings in 1987 and 1988 (ANON, 1989b).

The most recent Oregon survey (1988) showed a total of 3,731,500 trees planted on 28,820 acres; over one-third of the trees have been planted since 1981. The current survey listed 989 commercial hazelnut operations. Yamhill continued to be the leading county with 782,600 trees and Marion county second with 704,200 trees. Washington and Clackamas counties ranked third and fourth. Together these four counties accounted for nearly 75 percent of Oregon's hazelnut trees (Anon, 1989a).

In Washington, tree numbers declined 11 percent to 45,000 planted on 360 acres. Nearly half of the state total is located in Clark county, with much of the remainder near the Canadian border in Whatcom county (ANON, 1989b).

Hazelnut acreage increased at only a slightly slower rate

than tree numbers. The number of trees per acre, at 129 for the 1988-1989 inventory, was up only one tree per acre from four years earlier. In the 1980-81 survey, orchards averaged 116 trees per acre. The current average of 129 trees per acre is approximately what would be obtained from a spacing of 17 by 20 feet (ANON, 1989b).

### Composition

The biochemical constituents of hazelnuts are indicative of their nutritional value and possible post-harvest changes. The approximate composition is: fat 60.9%, carbohydrate 14.3%, protein 12.7%, crude fiber 3.4%, ash 2.7%, calcium 0.287%, phosphorous 0.354%, and water 4.4% (Wigand, 1943). In other studies the nuts contain 5.4% water, 16.5% protein, 64% fat, 11.7% carbohydrates, and 2.4% ash (Smith, 1977). Duke and Atchley (1986) reported that hazelnut(per 100g), contained 620 to 634 calories, 16.4 to 20.0 g protein, 54.3 to 58.5 g fat, 21.4 to 22.9 g total carbohydrates, 3.3 to 5.9 g fiber, 1.8 to 3.7 g ash, 201 mg Ca, 462 mg P, 4.5 mg Fe, 1044 mg K, 10.8  $\mu$ g beta-carotene equivalent, 0.17 mg thiamin, 0.44 mg riboflavin, 5.4 mg niacin, and 2.2 mg ascorbic acid.

Table 2.4 shows proximate analysis of some nuts. Hazelnut is the highest in ascorbic acid (2.2 mg/100g) and K (1044 mg/100 g).

Fifty to sixty percent of the hazelnut kernel is oil

Table 2.4. Proximate analyses of nine nuts.

Content	Almond	Brazil-nut	Cashew	Hickory	Maca-damia	Pecan	Pista-chio	Walnut	Hazel-nut <sup>†</sup>
H <sub>2</sub> O g	4.7	4.6	5.2	3.3	3.0	3.4	5.3	3.1	5.4
Protein g	18.6	14.3	17.2	13.2	7.8	9.2	19.3	20.5	13.2
Fat g	54.2	66.9	45.7	68.7	71.6	71.2	53.7	59.3	64.0
Carbo-hydrate g	19.5	10.9	29.3	12.8	15.9	14.6	19.0	14.8	11.7
Fiber g	2.6	3.1	1.4	1.9	2.5	2.3	1.9	1.7	3.3
Ash g	3.0	3.3	2.6	2.0	1.7	1.6	2.7	2.3	2.4
Ca mg	234.0	186.0	38.0	Tr	48.0	73.0	131.0	Tr	201.0
P mg	504.0	693.0	373.0	360.0	161.0	289.0	500.0	570.0	462.0
Fe mg	4.7	3.4	3.8	2.4	2.0	2.4	7.3	6.0	4.5
K mg	773.0	715.0	464.0	---	264.0	603.0	972.0	460.0	1044.0
B-carotene $\mu$ g	---	Tr	60.0	---	---	78.0	138.0	180.0	10.8
Thiamin mg	0.3	1.0	0.5	---	0.4	0.9	0.7	0.2	0.2
Vit C mg	Tr	---	---	---	---	2.0	---	---	2.2

Duke, 1985

<sup>†</sup>Smith, 1977

(Fang et al., 1949). Wiegand (1943) indicated that the level of free fatty acid is very low in the hazelnut, and therefore, the fatty acid must exist largely in the form of triglycerides. Hazelnut oil contains a high level of unsaturated fatty acid and as a consequence, may be susceptible to autoxidation. Research conducted by Cecil (1957), (for the Oregon Agricultural Experimental Station) indicates however, that the hazelnut kernel is relatively resistant to rancidity. Hazelnuts stored at room temperature did not develop an off flavor until after 7 to 9 months. Cecil also noted that 'Barcelona' samples stored under refrigeration or freezing temperatures (2 °C and -10 °C) remained indistinguishable from fresh hazelnuts when evaluated during the ninth month of storage.

Fang and Butts (1950,1953) evaluated the amino acid content of two hazelnut globulins in order to ascertain the nutritional quality of these proteins. The experiment employed a microbial assay technique. The proteins were shown to be low in lysine and methionine and unable to support growth when used as the sole source of protein for experimental diet during a 28 day test. However, in 1920, Cajori observed that satisfactory growth could be obtained with young rats using partly de-fatted, ground hazelnuts as a protein source. Prompted by these results, Fang et al., (1953), measured the amino acid levels in oil free hazelnut meal. They concluded that the amino acids showed exceptional

balance for a plant protein. In comparison to casein, hazelnut protein was shown to be high in arginine and serine, but low in lysine, proline, and tyrosine.

Food flavor is the result of an interplay of many organic compounds. Jennings and Sevenants (1969), broadly classified these compounds into two categories, "contributing flavor compounds", and "character impact compounds." The literature contains an ever growing list of components which have been identified and associated with the development of heat induced flavors. These compounds arise largely through interactions involving the carbohydrate, protein, and lipid components within the food.

The qualitative and quantitative analyses of the headspace volatiles yielded ten positive and two tentative identifications. The compounds were positively identified by comparing their mass spectra with known fragmentation patterns. GLC relative retention times were used to confirm the mass spectral interpretations as 38 compounds were positively identified and twelve compounds were tentatively identified from roasted hazelnuts. These compounds positively identified include acetaldehyde, propanol, 2-methyl propanol, 2-methyl butanol, hexanol, benzaldehyde, phenylacetaldehyde, acetic acid, hexanoic acid, methyl acetate, ethyl acetate, 2-pentylfuran, 2-furfural, acetyl-2-furan, 5-methyl furfural, furfuryl alcohol, 2,5-dimethyl-4-hydroxy-3-(2h)-furanone, 2-methyl, tetra hydro furan-3-one, 2-methyl pyrazine, 2-ethyl-5-

methyl pyrazine, 2-ethyl-3, 6-dimethyl pyrazine, 2-ethyl-3,5-dimethyl pyrazine, 2-ethyl-3,6-diacetyl, dimethyl sulfide,  $\gamma$ -butyrolactone, acetyl-2-pyrrole, 2-pyrrole aldehyde, 3-hydroxy-2-methyl-4-pyrone, methanol, benzene, toluene, xylene (m- or p-), and n-decane. Compounds tentatively identified include ethanol, heptanal, octanal, ethyl methylpyrazine, 2,6- or 2,5-diethyl-3-methyl pyrazine, thiazole, N-furfurylpyrrole, N-methyl-2-pyrrole aldehyde, 3-pentene-2-one, methyl formate, allyl crotonoate, and 1,2,4 trimethyl benzene. The aldehydes, acids, furans, and pyrazine derivatives were considered to be essential to the roasted flavor (Sheldon et al., 1972).

### Quality

There are several factors effecting hazelnut quality. These factors are : appearance, texture, flavor, nutritional value, and safety (Richardson, 1988).

Appearance includes size, shape, uniformity, color, freedom from defects (such as shell staining, adhering husks, insect damage, mold, kernel shrivel, kernel discoloration, blanching etc.) and cleanliness.

Texture includes crispness, crunchiness, chewiness, and mouth feel. They are all affected by moisture and oil content. Texture of the kernel is related also to hazelnut genotype, and to circumstances that affect development and maturity of the kernel. The texture is based largely on the cohesiveness of the kernel and is usually described as crunchy but without brittleness. If moisture percentage is low, the

kernel can become excessively brittle, if it is high they tend to be spongy (Richardson, 1988).

Factors known to affect color include seasonal variation in growing conditions, delayed harvesting, and moisture level of the soil and air during harvest, particularly the pellicle (skin). Nuts that are left on the ground have a much greater chance of being discolored if the soil surface is moist. Damage during harvest and handling operations has also resulted in a slight increase in darkening of the kernels of pecan (Reid and Heaton, 1977). While more research reportedly published on pecans, the following descriptions are also expected to apply more or less to hazelnuts.

After harvesting, conditions of storage in warehouses, marketing channels, and the home drastically affect the color quality of pecan kernels. Temperature, oxygen, air composition, light, type of light, and moisture may affect color stability of the kernel. Lowering the kernel moisture level to 3.5 - 4% as rapidly as possible after harvest is essential for minimizing the rate of color changes (Heaton and Woodroof, 1970). If pecan kernel moisture content is above 4.5 percent, there is danger of mold development, whereas if the moisture content is lower than 3.5 percent, oxidative rancidity progresses at a faster rate (Heaton and Beuchat, 1980). Under fair weather conditions, the nuts will dry naturally in the grove, but a considerable amount of kernel

discoloration may result when the nuts are allowed to remain on the ground or in direct sunlight.

The highest quality is obtained by harvesting the pecan nuts as soon as possible after maturation (Heaton et al, 1975). At this time the kernels are lighter and more uniformly colored, and have superior color and flavor stability when placed in storage. If harvest is delayed until after full maturity is reached the quality of the nuts declines (Woodroof, 1967).

Storage of dried pecans at 60 to 70% relative humidity results in an equilibrium moisture level in the kernels of 3.5 to 4% (Kays, 1979). The lower the storage temperature the greater the stability of the kernel color (Brison, 1945). Storage temperatures above 5°C result in relatively rapid discoloration, while -16°C or less will maintain quality for several years.

Many factors affecting kernel color also affect the flavor of the pecan. Thus a relationship has been assumed between the color and the flavor. Partly for this reason the USDA uses color as the basis for the quality standards of pecan kernels. The four classifications are light, light amber, amber, and dark amber (USDA, 1976).

Flavor of pecan kernel is related to the oil content, volatile constituents, and possibly to the carbohydrates, especially sugars. Generally the higher the oil content, which may vary from 50 to 75%, the higher the flavor ratings

(Heaton et al, 1977). The major components of the pecan aroma have been identified as four low molecular weight alcohols, (1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol) five low molecular weight aldehydes (hexanal, heptanal, octanal, nonanal, and decanal). These compounds most probably resulted from the enzymatic oxidation of unsaturated fatty acids (Rudolph, 1971).

#### Incidence of Mold on Nuts

Nuts as well as dried grain crops are potentially attacked by Aspergillus spp. The aflatoxins which may or may not be produced by fungi are among the most potent carcinogens known. Thus, it is very important to take every measure to avoid or detect this deadly contaminant.

Aflatoxins occur at varying concentrations throughout the tissue of contaminated dry nut and grain products and can occur at concentrations over 1,000 ppm in individual peanut kernels (Cucully et al., 1966, and 1977). Aflatoxins are fairly resistant to heat and to chemical treatments that do not destroy the nutmeat (Lee et al, 1968). The solution to the aflatoxin problem in particulate foods such as seeds is to remove the contaminated units from the products, since the toxins are confined to a relatively few units (Fuller et al, 1977; Cucully et al, 1966; Schade et al, 1975).

Aflatoxins are secondary metabolites produced by certain strains of Aspergillus flavus and A. parasiticus in a variety of agricultural commodities. The highly carcinogenic nature

of aflatoxins requires that constant monitoring (usually under ultra-violet light) be made to detect them in marketed products to minimize public health hazards.

Although data have been published concerning aspects of mold growth and toxin contamination during pecan production, upon entry into the shelling plant, and during storage (Heaton, 1975), no information is available describing the incidence of mold in general, potential aflatoxin producing molds in particular, on nut meats as pecans are sequentially subjected to various mechanical harvesting procedures. Substantial physical damage and exposure to field dirt may occur when nuts are mechanically shaken from the tree, swept in windrows, transported to shelling plants, and cleaned in preparation for cold storage. It has been suggested that increased levels of molds on nutmeats as they enter the processing plant may be a result of specific mishandling procedures at some point during the harvesting scheme. Knowledge of increased contamination by A. flavus or A. parasiticus associated with specific harvesting procedures might enable modifications to be made which would ultimately reduce the potential for aflatoxin contamination (Escher et al., 1974).

In a survey of the almond crop in California it was estimated by statistical analysis that before processing about one kernel in 26,500 in shell almonds is contaminated with aflatoxin and that these few kernels have, on the average,

very high levels of aflatoxin (Schade and King Jr., 1984). Aflatoxin has also been found in palm nuts and brazil nuts (Raymond, 1966; Wehner and Rabic, 1970).

Hazelnuts were collected randomly from different commercial stores over a one month period. The samples of hazelnuts showed molds belonging to Penicillium and Aspergillus groups and to the genus Cladosporium (Notermans et al, 1988). However, Oregon and Washington have had substantial monitoring programs and aflatoxin is essentially absent.

### Roasting

For centuries people have known that roasting accentuates the full development of the flavor of many foods. It is only in the last 25 years, however, that food researchers have shown that the roasted or toasted flavor characteristics of many diverse foods are due to relatively few chemical substances.

Roasting hazelnut at 191°C for 12 to 15 minutes, alters and substantially improves the flavor, texture, color, and appearance, and is one of the forms of processing for hazelnuts. These nuts contain large amounts of lipids (60%) which may undergo a number of degradative changes during heat processing and thus impact their palatability and wholesomeness. Heated lipids are unavoidably exposed to adverse conditions during the roasting procedure which may produce certain undesirable as well as desirable changes. The

unsaturated fatty acids and possibly the nutritive value of such lipids are decreased (Morton, 1977). There is also the added possibility that the undesirable changes which occur in heated lipids may have a detrimental effect on human health (Kashani and Valadon, 1983).

### Rancidity

A plant species can be called "oleaginous" when its fruit, seeds or other plant parts contain at least 15-20% oil. Hazelnut kernels are 55-67% lipid. While being a major factor in the unique flavor and nutritional qualities of the nut, this presents a series of post-harvest problems in that the oil is potentially susceptible to rancidity.

Lipid oxidation has three important effects: loss of essential fatty acids, decrease in flavor stability, and toxicity (Emken, 1980). The most common cause of flavor change is rancidity. Oxidative rancidity occurs when unsaturated oil reacts directly with oxygen (enzymatically or non-enzymatically) to produce products which lead to an off flavor. Also, a second type of rancidity, hydrolysis of the triglycerides produces glycerol and free fatty acids which can also produce a disagreeable flavor (Farmer et al, 1942). Toxicity from consumption of oxidized fats, especially severely abused fats includes growth depression, lower fat absorption, enlarged livers and kidneys, diarrhea, and increased liver lipid content. Animal feeding experiments showed that oxidized fat could cause cancer (Emken, 1980). Therefore, lipid oxidation is a very critical factor for consumer acceptability both for flavor and for health as well as for profitability of farmer and processors.

Lipid oxidation in foods and other biological systems is associated almost exclusively with unsaturated lipids and is

an autocatalytic process. That is, oxidation products themselves catalyze the reaction so that the rate increases with time (Scharch, 1980). Lipid oxidation occurs both by enzymatic and chemical methods. Chemical oxidation is very difficult to control because of low activation energy (Sonntag, 1979). Initiation, propagation and termination are three steps in oxidative chemical rancidity resulting from free radical oxygen attack on organic molecules.

Initiation:



Propagation:



Termination:



Where RH= lipid, R= lipid radical, ROO= peroxy radical, RO= Lipid alkoxy radical.

These reactions indicate that an unsaturated fatty acid (RH) reacts with oxygen and a free radical (R) is formed when a labile hydrogen is extracted from the carbon atom adjacent to the double bond. The free radical can then react with oxygen to form a peroxy radical (ROO), which in turn may extract a hydrogen from another fatty acid, and this propagates the chain reaction. The process reaches

termination when the free radicals are joined together (RR), a peroxy radical (ROO) reacts with a free radical (R), or two peroxy radicals react with each other (ROOR) (Lillard, 1985; Lillard, 1987; Peng, 1985; and Younathan, 1985). Lipid oxidation has been extensively studied in triplet oxygen free radical oxidation to improve the oxidative stability of lipid foods for the last 50 years. However, it does not fully explain the initiation step of lipid oxidation (Frankel, 1980).

Recently, the role of singlet oxygen at the initiation step of lipid oxidation was suggested because singlet oxygen can directly react with double bonds of fatty acids and its reaction rate with linoleic acid is at least 1450 times greater than that of triplet oxygen (Rawls and Vansanten, 1970)

The highly complex nature of food and other biological systems virtually ensures the presence of many factors which affect not only the rate and course of lipid oxidation but also, by extrapolation, the potential of oxidizing lipid to induce free radicals in proteins and other biologically important molecules.

Factors which generally affect the rate and course of oxidation in food, may be summarized as follows (Lea, 1962): Accelerating factors are high temperatures, irradiation, light (UV and blue), ionizing radiation, peroxides (including oxidized fat), organic metal catalysts (e.g., hemoglobin), Fe,

Cu, Ni, and trace metals, photosynthetic tissues (e.g., chlorophyll), low levels of natural antioxidants, i.e., tocopherol, phenolic, and ascorbate; high oxygen partial pressure, monolayer dispersion, poly-unsaturation, and conjugation, free fatty acids and water. Table 2.5 shows factors effecting lipid peroxidation.

Inhibitory factors are refrigeration, exclusion of oxygen, blanching, antioxidants (e.g., tocopherols), metal deactivators, or chelators, opaque or colored packaging, water, and dilution (Scharch, 1980).

#### Measurement of Rancidity

The measurement of rancidity in oils and fats may be carried out by both physical and chemical means. However, these should be distinguished from methods which measure the resistance of an oil or fat to rancidity, rather than the rancidity itself.

Two types of rancidity should be taken into consideration; namely, oxidative rancidity and hydrolytic rancidity. Oxidative rancidity is clearly caused by oxygen attack on the fat, with the development of oxidized products and the associated off-flavors. Hydrolytic rancidity, on the other hand, is caused by hydrolysis of the triglycerides, in the presence of moisture, and the liberation of free fatty acids. These free fatty acids are particularly troublesome in the lauric oil and the fatty acids liberated (namely capric, lauric, and myristic) have much stronger off-flavors.

Table 2.5. Factors effecting lipid peroxidation.

Promotion	Suppression
Unsaturated fatty acids (especially cis-methylene interrupted)	Reduction to saturated fatty acid
active oxygens	Gas exchange, oxygen removal, vacuum packaging,
Heavy metal ions and compounds	Removal of metal ions metal chelation
Light and dyes	Removal of dyes, shielding
Radiation	Radical scavenger
Peroxide-free radical	Antioxidant
Heating	Refrigeration
Moisture content	Intermediate moisture
Lipoxygenase	Enzyme inactivator

In both cases rancidity is a question of off-flavor. The first line of measurement is therefore by taste panel and subjective evaluation of an oil. The organization of taste panels, in order to overcome the problems of subjective judgement and personal preference, is a subject in its own right. The organization must be carried out carefully if the results are to be reliable, and detailed information on this topic is provided by Rossel (1983). Just as there are statistical sampling problems in the aflatoxin problem, rancidity development is also a difficult sampling problem, particularly at the early stages of development, when only a very few nuts are affected.

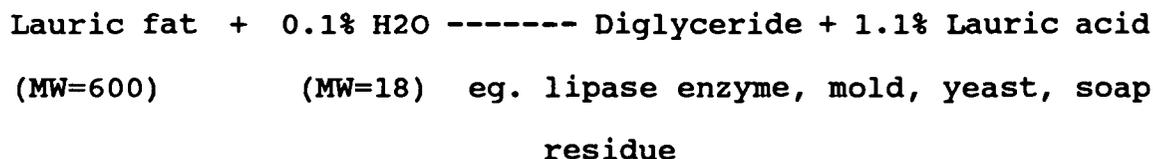
#### Hydrolytic Rancidity

Hydrolytic rancidity is a problem mainly encountered in lauric products, which are fatty products based on palm kernel or coconut oil. The rancidity is due to the liberation of free fatty acids from the parent oils, which are diacyl glycerols with large amounts of capric, lauric, and myristic acids. These acids have a distinctly soapy flavor, which is why hydrolytic rancidity is often referred to as soapy rancidity (Forss, 1972; Heimann, 1980). The acids also have lower flavor threshold values than the longer chain fatty acids found in most other oils and fats, such as palm oil, soybean oil, or beef tallow.

Hydrolytic rancidity is generally caused by a combination of micro-organisms and moisture. It is worth remembering the

molecular weight relationships of the reacting species during the development of hydrolytic rancidity. The following equation shows the liberation of lauric acid from fat containing as little as 0.1% moisture.

catalyst



A generalized scheme for hydrolysis is shown below:



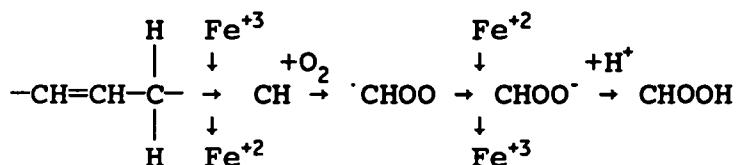
Where hydrolytic rancidity is suspected, there are three factors which are commonly measured: moisture, catalytic agent, and the free fatty acid level. The moisture and catalytic agent are, of course, the factors causing the hydrolytic rancidity, while the free fatty acid, if present, is the product of the hydrolysis (Law et al, 1979).

### Enzymatic Oxidation

Polyunsaturated fatty acids are susceptible to oxidative deterioration as the result of attack by animal and plant derived lipoxygenases. Only free acids are attacked, which have been liberated by the action of lipase. Stearic acid and other monoenoic fatty acids are unaffected. Typical plant lipoxygenases may be found in soybean, vegetables, and grains,

and attacks the polyunsaturated fatty acids through methylene groups, with the formation of radicals which further react to form hydroperoxides (Gunstone and Norris, 1983). The mechanism of enzymic oxidation has been studied and reported (Han and Liston, 1987; McDonald and Hultion, 1987).

Lipoxygenases contain non-heme iron. Hydroperoxidation probably occurs through the following series of one electron changes:



The number of products now known available from arachidonic acid (20:4) as a result of the action of animal lipoxygenases are so numerous that they have been described as the "icosanoid cascade" (Gunstone, 1984).

### Autoxidation

By far the most important cause of lipid deterioration at ambient and sub-ambient temperatures in food stuffs is autoxidation, ie. lipid oxidation by molecular oxygen in a process that is autocatalytic. Although light can be involved in the initiation stage of autoxidation, photo-oxidation and autoxidation are distinctly different processes that proceed by different reaction mechanisms, at different rates giving rise to similar but not identical product mixtures. A comparison of oleate autoxidation and photo-oxidation is shown in Fig. 2.1. The primary product, hydroperoxides, may further

react or decompose to give a whole host of secondary and related products (Billek, 1983). The relative rates of autoxidation of oleate, linoleate, and linolenate have been reported as 1:27:77, respectively (Gunstone and Norris, 1983). Thus oils with high levels of linoleate and/or linolenate are especially prone to rancidity. Autoxidation is a free radical chain process involving initiation, propagation, and termination, the concept developed by Farmer in the 1940's (Paquette, et al., 1985 and references therein). Initiation takes place by loss of an allylic hydrogen radical in the presence of trace metals, light, or heat. The resulting lipid free radicals (1) then interact with oxygen to form peroxy radical (2). These then react further with other lipids to form lipid hydroperoxides (3).

#### Primary Products

Hydroperoxides are the primary products of autoxidation. Hydroperoxide formation from oleate, linoleate, and linolenate is shown in Fig. 2.2. Hydrogen abstraction in each case is indicated and the resulting hydroperoxide structure is given. The percentage production of each product has been studied by HPLC and GLC-MS (Frankel, 1984). Unsaturated hydroperoxides that are capable of further oxidation can react with a second oxygen molecule to produce dihydroperoxides or hydroperoxy cyclic peroxides. The former requires the presence of an independent pentadiene unit.

Fig. 2.1. Comparison of oleate autoxidation and photo-oxidation.  
(Frankel, 1985; Gunstone, 1984)

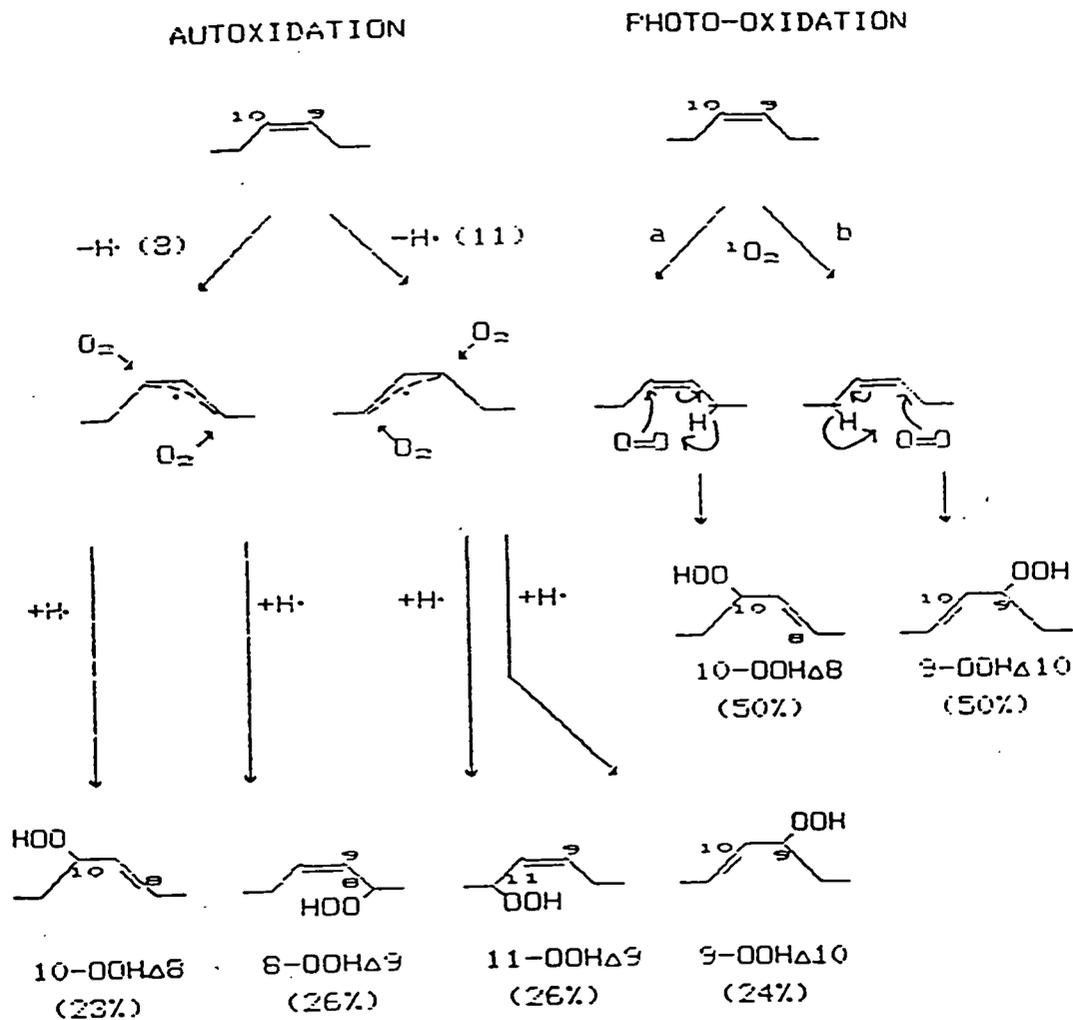
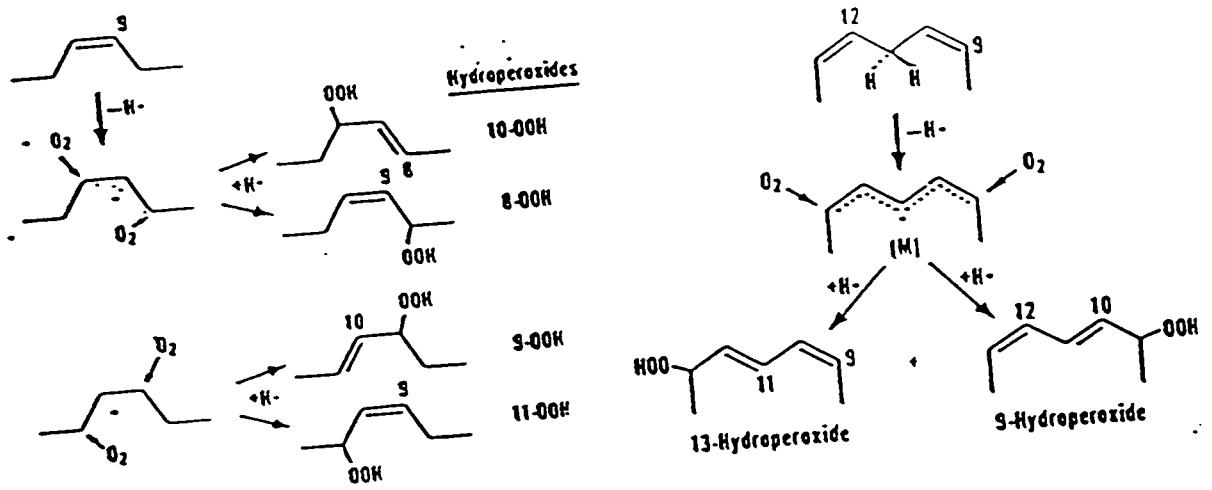
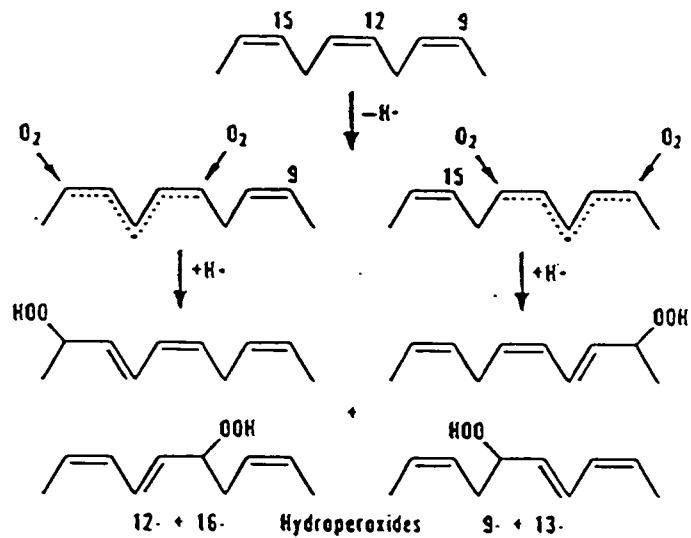


Fig.2.2. Mechanisms of oleate, linoleate, and linolenate autoxidation. (Frankel,1985)



Mechanism of oleate autoxidation.

Mechanism of linoleate autoxidation.



Mechanism of linolenate autoxidation.

The formation of hydroperoxides in edible oils leads to a decrease in the bio-availability of essential dietary components and a possible toxic effect as the result of their ingestion (Gunstone and Norris, 1983).

### Secondary products

The stability of the hydroperoxides formed is poor and under conditions of continuing oxidation, further reaction may occur. In addition, a hydroperoxide may undergo cyclization which may in turn lead to the formation of malondialdehyde. Recent studies have confirmed the formation of monocyclic peroxides from autoxidised linolenate and arachidonate (Frankel, 1984). Malonyldiadehyde reaction with thiobarbituric acid (TBA) is the basis for one type of test for rancidity products, but depends upon high linolenate and/or arachidonate or higher unsaturation.

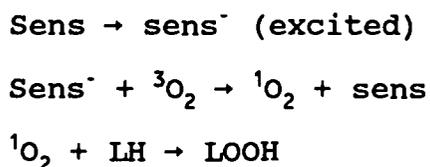
Malondialdehyde is claimed to be an important breakdown product of five-member cyclic peroxides of linoleate and linolenate because of its cross-linking ability with amino groups of proteins, enzymes, and DNA (Tappel, 1986). Not surprisingly, monoenoic and saturated fatty acids do not yield malondialdehyde and thus are not reactive with TBA.

Fat hydroperoxides are generally tasteless and odorless, but their products of decomposition have a great impact on flavor. Some volatile aldehyde cleavage products are extremely potent and can affect the flavor of vegetable oils

at concentrations lower than 1 ppm (Frankel, 1983). Fig. 2.3 shows the typical autoxidation of a polyunsaturated lipid.

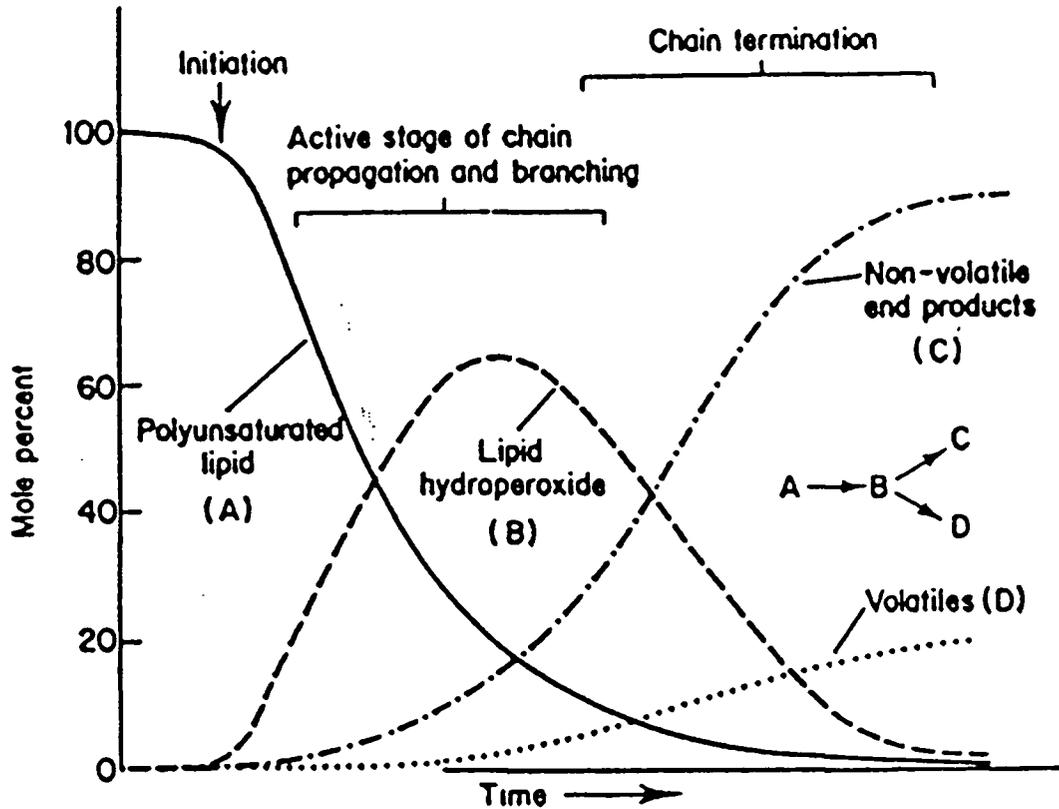
### Photo-oxidation

Photo-oxidation involves the reaction of an alkene (unsaturated fatty acid) with oxygen in the presence of light and a suitable sensitizer, such as chlorophyll, riboflavin, erythrosine, rosebengal, or methylene blue (Gunstone and Norris, 1983). However, before oxygen and fatty acids react, one of them must be activated. In the case of photo-oxidation the oxygen is raised to the more reactive singlet state. Light energy is absorbed by the sensitizer and then passed to the oxygen:



This then leads to a concerted 'one' reaction where the singlet oxygen reacts with an allelic carbon producing hydroperoxides with a trans-double bond. With methyl linoleate this reaction has been reported to be at least 1500 times more rapid than the reaction with singlet oxygen of normal triplet oxygen (Frankel, 1984). The reaction is unaffected by antioxidants but is inhibited by singlet oxygen quenchers such as carotene. Photo-oxidation proceeds at a much faster rate than autoxidation. It has been suggested that the slower autoxidation reaction is initiated by photo-oxidation made possible by traces of pigments found in oils

Fig. 2.3. Typical autoxidation of a polyunsaturated lipid as a function of time showing the various stages in the reaction. (Chan, 1987)



(Gunstone, 1984; Kiritsakis and Dugan, 1985). The rates of photo-oxidative reactivity of oleate, linoleate, and linolenate have been measured in one study as 1.0:1.3:2.3 (Gunstone and Norris, 1983) and in another as 1.0:1.7:2.3 (Terao and Matsushita, 1977). Detailed studies of photo-oxidative processes concerning olive oil, unsaturated esters and linoleate have been reported (Kiritsakis and Dugan, 1985; Chiba et al., 1981).

### Oxidative Rancidity

In comparison to hydrolytic rancidity, oxidative rancidity is a more complex subject, and one to which a considerably greater amount of work has been devoted (Gray, 1978). Oxidative rancidity is clearly caused by oxidation of the fats and takes place through several intermediates including hydroperoxides and peroxides, eventually leading to aldehydes and ketones, as well as other breakdown products. These secondary oxidation products, especially aldehydes, have the off flavors associated with rancid oil. It is generally accepted that the first product formed by oxidation of an oil is a peroxide, or hydroperoxide. The most common method of measurement of oxidative rancidity is therefore the peroxide value (PV), which is reported in units of milliequivalent of oxygen reacted per kilogram of fat. Table 2.6 shows different methods to measure lipid peroxidation.

Table 2.6. Measurements of lipid peroxidation.

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1- Peroxide Value (POV)



2. Measurements of decomposition products

Carbonyl value (Colorimetry with thiobarbituric acid)

Gas chromatography

GC-MS method

3. Measurements of oxygen consumption

Dissolved oxygen meter

Weighting method

Warburg manometer

4. Physicochemical methods

UV absorption (conjugated double bonds)

IR spectrometry

ESR spectrometry

Fluorescence

Chemiluminescence

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## Antioxidants

Modern methods of food processing and handling often require the addition of certain chemicals in order to ensure high quality and a shelf life equal to, if not greater than, the normal distribution and marketing time of foods. Antioxidants, as a class of chemicals, are ubiquitous in their presence by addition to foods including cereals, bakery products, snack foods, animal feeds, intermediate moisture and dehydrated foods, as well as incorporation into packaging materials. They do not improve the initial quality of the product, but, rather maintain it by preventing oxidation of labile lipid components. They are also effective at very low concentrations, as would be expected for inhibition of a free radical chain reaction (Labuza, 1971).

To prevent autoxidation from occurring, or at least to minimize it, several types of antioxidants can be utilized. Table 2.7 shows three types of antioxidants (Scott, 1965).

Type I- Free radical chain stoppers, BHA (butylated hydroxy anisole), BHT (butylated hydroxy toluene), PG (propyl gallate), tocopherol, TBHQ (tert-butyl hydroquinone) and gum guaic are examples, in foods. These are primarily phenolic compounds which can donate a hydrogen to a radical.

Type II- Free radical production preventors in foods, such as the chelating agent EDTA (ethylenediaminetetra-acetic acid), citric acid, and various forms of ascorbic acid.

**Table 2.7. Functions of Antioxidants.**

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Radical scavenger

Hydrogen donor

Electron donor

Peroxide decomposer

Singlet oxygen quencher

Enzyme inhibitor

Synergist

Metal chelating agent:

Reducing agent

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These act mainly by tying up metal catalysts (mainly  $\text{Fe}^{+2,+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$  ).

Type III- Environmental factors, such as lowering of oxygen partial pressure in the package or holding the package at a critical moisture content for a dehydrated food.

Type I antioxidants work primarily by breaking the free radical chain reaction through removal of either the alkylperoxyl or alkyl radicals from the chain step according to the reactions below:



Where AH is the antioxidant, and X is some other moiety. The type of protection afforded is a large increase in the induction period and a slowing of the rate during this period (Emanuel and Lyaskov, 1967).

The relation between the antioxidant activity and the vitamin E potency of the tocopherols has been studied by several authors. The antioxidant activity appears to vary with temperature (Parkhurst et al, 1968).

### Natural Antioxidants

Life forms living in the earth's atmosphere must be equipped to tolerate the action of oxygen on living matter. Plants that are exposed to visible and ultraviolet light and radiation are susceptible to damage by active oxygen and oxygen toxicity. Plant constituents; including tocopherol,

carotenes, and phenolics, act as antioxidants to counter oxygen radicals and excited molecules. Oxidation of phenols, especially polyphenols by polyphenoloxidase, also leads to the formation of polymers that act to protect tissue, as well as to the formation of structural lignin (Namiki, 1990).

The high resistance of sesame oil to oxidation compared with other equally polyunsaturated vegetable oils has long been known. It has been attributed to the presence of the phenolic compound sesamol, which is produced from sesamol, a lignin characteristic of sesame (Budowski et al., 1950; Budowski, 1964; Fukuda and Namiki, 1988; Namiki and Kobayoshi, 1989).

Germ of rice seeds is rich in oil and is known to contain oryzanol, isovitexin, and tocopherol (Tsuchiya, 1970, 1982; Ramaratham et al., 1988, 1989). These showed strong antioxidative activity in storage tests at room temperature and at 60°C showed a low peroxide value (POV) and low residual free radical formation. Isovitexin, one of the active antioxidants in rice hull, is as active as  $\alpha$ -tocopherol in antioxidative activity and effectively scavenged the OH radical (Ramaratham et al., 1989).

The use of spices has been highly valued from prehistorical times not solely because of their flavor, but also because of their food-preserving power. First Dubois and Tressler (1943), showed antioxidative action of sage, mace, black pepper, and others on frozen meat. Then Chipault et

al., (1956), showed effective antioxidative activity of solvent extracts of perilla plants (rosemary, sage, thyme, etc) on lard. Recently several tasteless and antioxidative constituents have been isolated from turmeric and two of them had the same skeletal structure as curcumin, the yellow pigment of turmeric (Toda et al., 1985).

Antioxidative activities of phenolic flavonoids in plants have long been known and studied. Quercetin is representative and widely distributed (Letan, 1966a,b). Also often studied are the antioxidants in soybeans, the isoflavones genisetin, diadzein, and glycitein, which are active in decreasing order, but their activities are weaker than quercetin (Pratt, 1980). Recently, mechanistic studies on antioxidative activity of flavonoids have been conducted using spin trapping and other advanced techniques. Robak and Gryglewski (1988), showed that flavonoids can effectively scavenge superoxide anion radical and the activity was in the order quercetin> myricetin> rutin. Husain et al (1987), examined reactivity with the OH radical generated in a hydrogen peroxide- UV system, and flavonoids were shown as effective scavengers in the order myricetin> quercetin> rhamnetin> merin> diosmetin> naringenin and others, and the activity increased with the number of HO groups in the B-ring.

Flavonoids (flavonols and flavones) are pigments occurring most abundantly in plants. They are universal in leaves, petals, and other organs such as fruits, roots, and

sepals. The major function of flavonoids is to provide color in flowers and fruits, and they have been used as food coloring substances (Herrmann, 1976). Their formation normally depends on light so they are mainly concentrated in the outer tissues. The concentration of flavonols in free-standing leaves and skins of fruits was found to exceed that in other parts of the same plant, except in onions (Herrmann, 1976). Some flavonoids have characteristic pharmaco-dynamic activities such as rufinic acid which is used in a number of medical preparations. Because of their biological activities, certain flavonoids (flavonol glycosides), were known as vitamin P (P= permeability vitamin) (Herrmann, 1976).

Lee (1984), described flavonoids as multi-functional antioxidants combining in their molecule both chain-breaking and metal deactivating properties, each of which can operate at several points. The relationship between the structure of flavonoids and their antioxidant properties has been investigated by several researchers (Crawford et al., 1961; Letan, 1966b; Hudson and Lewis, 1983). Letan (1966a), found that the 3-hydroxy-4-keto group was the most powerful metal-complexing group in the quercetin molecule. The 5-hydroxy-4-keto group had some activity, but was considerably weaker. Hudson and Lewis (1983), evaluated the antioxidant properties of a series of polyhydroxy flavonoid and related compounds. According to these investigators fisetin ( $R_1 = R_3 = R_4 = R_5 = \text{OH}$ ,  $R_2 = \text{H}$ ) and quercetin ( $R_1 = R_2 = R_3 = R_4 = R_5 = \text{OH}$ ), which are

flavones, and contain the 3-OH group, showed better primary antioxidant activity than luteolin ( $R_2 = R_3 = R_4 = R_5 = \text{OH}$ ,  $R_1 = \text{H}$ ), which is a flavone, containing only the 5-OH group. Moreover, Hudson and Lewis (1983) found that dihydro-flavones (flavanones) are more active in chelating metal than the corresponding flavones. The metal complexes formed by flavanones are different from those formed by flavones.

Flavonols were found to stabilize ascorbic acid of black currant juice in the presence of heavy metal ions such as copper which can destroy ascorbic acid rapidly. Flavonols in the juice contribute to the protection of vitamin C (Clegg and Morton, 1968). In another study Harper et al., (1969), reported that quercetin (a flavonol) showed increasing antioxidant activity and protection of ascorbic acid in black currant juice. However, anthocyanin showed slight antioxidant activity in the presence of copper ions. The ability of flavones and flavanones to chelate metal ions through the carbonyl group at c-4 and the hydroxyl group at c-3 and c-5 may explain their protection of ascorbic acid in the presence of copper ions. Takahama (1985), reported that quercetin inhibits soybean lipoxygenase-1 and that 50% inhibition may occur with addition of two to three  $\mu\text{M}$  quercetin. Under this experimental condition, quercetin acted as the primary antioxidant.

Flavonoid substances are recognized for their importance in stabilizing autoxidation in the lipids of vegetable tissue

(Herrmann, 1976; Hudson and Mohgoub, 1980; Hudson and Mohgoub, 1981). Lipid extracts that were obtained from the leaves of rye grass, broad beans, and alfalfa were found to have marked antioxidant properties. This was related to the natural phenolic antioxidants extracted from leaves in the lipid fraction. Upon identification of phenolic and polyphenolic compounds, the main antioxidant compounds were found to be tocopherol, ferulic acid, and quercetin. The effectiveness of these antioxidants has been examined in a model system, their effect on delaying the oxidation of soybean oil heated at 100°C. Quercetin was found to be the most effective and was superior to alpha-tocopherol (Hudson and Mohgoub, 1980).

The safety of flavonoid compounds has been investigated (Pamukou et al., 1980; Nagao et al., 1981; Morine et al., 1982; and Takanashi et al., 1983). Morine et al (1982), determined the carcinogenic effect of quercetin at different concentrations (1-10%) and rutinic acid at 10%. Under experimental conditions, rutinic acid was found not to be carcinogenic. Also, quercetin was not carcinogenic when given at concentrations of 1% and 4%. In another study quercetin (0.1%) and kaempferol (0.04%) were shown not to be carcinogenic to either sexes of rats under experimental conditions (Takanashi et al., 1983).

Tannins are widely distributed in roots, bark, and nuts, sometimes reaching several tens of weight percent. They are assumed to be antioxidative from their polyphenol structures.

Esters of gallic acid, the main structure of the tannins, are in practical use as food antioxidants. Their activities, can be shown either in a methyl linoleate autoxidation system or a rat liver microsome system (Okuda et al., 1983). Su, et al (1986; 1988), screened 230 Taiwanese traditional medicinal plants for antioxidative activity in relation to their medical effects and found 22 plants that contained strong antioxidants.

Many eucalyptus plants with a high content of essential oils have a thick layer of leaf wax, which was examined for antioxidative activity by Osawa and Namiki, 1981. Among many active leaf waxes found, that of Eucalyptus globulus, much of which is found in Japan, was used for isolation of the active components, and n-tritriacontandione and its homologues were identified as new  $\beta$ -diketone type antioxidants (Osawa and Namiki, 1985).

Chlorophyll could act as an effective antioxidant under dark conditions, presumably by its hydrogen-donating action. Nishibori and Namiki (1988), noted the strong antioxidative nature of the lipid fraction of seaweeds and isolated pheophytin as the effective constituent that is a strong antioxidant in the dark.

The Maillard reaction, which is highly important to food quality, is also related to antioxidative action. Strong antioxidative activities found with a molecular weight of approximately 5000 (Lingnert and Erikson, 1983) and in low-

molecular weight sugar and dicarbonyl compounds such as methylglyoxal, glyceraldehyde, di-hydroxyacetone, and dehydroascorbic acid with amino acids (Kawashima et al., 1977; Namiki et al., 1982).

L-ascorbic acid, its sodium salt and palmitoyl ester are unique and versatile chemical compounds. Ascorbic acid, a naturally occurring compound, is vitamin C. All three compounds are biologically active and hence can serve as vitamin C dietary sources. Due to the molecular structure, particularly at carbons 2 and 3, these compounds are oxygen scavengers, antioxidants and synergists. Thus when added to fat-base or water-base foods they serve a technological role by themselves. In the presence of the tocopherols, another class of natural compounds in fatty type foods, they inhibit or retard deteriorative changes and extend palatability and appearance of the food (Bauernfeind, 1986; Johnson, 1971, and Johnson and Pye, 1979).

A substance with antioxidant properties was obtained from the hexane extract of root of Rumex japonicus Houtt. The active component of the hexane extract was isolated and as 2-acetyl-1,8-dihydroxy-3-methyl naphthalene, trivially named musizin (MUS). The antioxidant activities of MUS in six types of fats and oils were higher than that of butyl hydroxyanisole (BHA) and  $\delta$ -tocopherol ( $\delta$ -TOC). Together, TOC and MUS have a synergistic affect, because comparable amounts of either alone

had lower antioxidant activity than various combinations of the two antioxidants (Nishina et al., 1991).

### **Synthetic Antioxidants**

The effectiveness of synthetic antioxidants in stabilizing fats and oils has been confirmed by Gregory (1984) and Coppens (1985). BHA and BHT are used widely in stabilizing fats and oils particularly at room temperature, and in a variety of food products such as baked goods, cereals, nuts, and milk powder (Min and Wen, 1983).

According to FAO specifications, the purity of BHA must be 98.5% to be used in commercial products, while the purity of BHT must be 99% (Hathway, 1967). BHA is a mixture of 15% tert-butyl-4-hydroxyanisole and 85% 3-tert-butyl-4-hydroxyanisole. At low temperature the active component is likely to be the former compound (Hathway, 1967). BHA and BHT can be used individually or in combination with each other because of their synergism. It was found that 100 ppm BHA plus 100 ppm BHT has more effect than 200 ppm of either BHA or BHT (Coppens, 1985).

An antioxidant is considered safe if it meets two conditions: 1) Its LD 50 must be not more than 1000 mg/kg animal body weight, and 2) It must not have a significant effect on growth when fed to an experimental animal for a long period, up to 2 years, at a level 100 times the level proposed in fats for human consumption (Dacre, 1960).

The toxicity of synthetic antioxidants, BHA and BHT, in particular, have been extensively investigated because of concern for public health. The metabolism of BHA and BHT in humans were found to be very close to that of the rat and rabbit. Therefore, the rat or the rabbit is often used to study the toxicity of these synthetic antioxidants.

There is some conflicting evidence in the literature about the carcinogenicity of BHA and BHT. Some studies (Slaga and Bracker, 1977; Hirose et al., 1981; Cohen et al., 1984) showed that BHA and BHT have a protective effect against carcinogens under experimental conditions. However, there are some studies that showed BHA and BHT may be carcinogenic, acting as initiators or promoters under certain conditions (Peraina et al., 1977; Imida et al., 1983; Maeura et al., 1984). Because of this conflicting evidence, the Scientific Committee for Food (SCF) of the European Community (EEC) suggested that the consumption of these synthetic antioxidants should be restricted (Haigh, 1986). The levels of BHA and BHT suggested by this committee are 0-0.5 mg/kg body weight (Haigh, 1986). The maximum recommended concentration of antioxidants in fats and oils for direct consumption is 0.02% either BHA or BHT or mixtures of these two (Johnson, 1971).

## **Vitamin E**

### **History**

Around 1922, it was discovered that a purified diet containing adequate amounts of proteins, fats, carbohydrates, mineral salts, and the vitamins A, B, C, and D (no other vitamins were known at that time) would support growth and well being of laboratory rats, but not the male and female reproductive functions (Bieri and Farrell, 1967). The animals displayed an atrophy of the reproductive organs, and fetal death and resorption were frequent. In 1922, H.M. Evans and K.S. Bishop reported the existence of a new, fat-soluble nutritional factor, they first called it factor X, which prevented fetal death. The same authors found that wheat germ and lettuce were good sources of this fat-soluble factor. Three years later (in 1925), Evans wrote "We have adopted the letter E as the next serial alphabetical designation, the antirachitic vitamin now being known as vitamin D." By about 1927, vitamin E was finally recognized as an essential dietary factor required for the establishment and maintenance of fertility in male and female rats (Lubin and Machlin, 1982).

The first thoughts on the role of vitamin E as an antioxidant were published in 1931 (Olcott and Mattill, 1931). About the same time, encephalomalacia in vitamin E deficient chicks and "alimentary muscular dystrophy" in vitamin E deficient guinea pigs and rabbits were described (Pappenheimer and Goettsch, 1931).

Tocopherols and tocotrienols in the pure form are pale yellow viscous oils, but darken on exposure to oxygen (Ball, 1988). Vitamin E is insoluble in water; readily soluble in alcohol and other organic solvents (including acetone, chloroform, and ether), and in vegetable oils. Vitamin E acetates are less readily soluble in ethanol than the unesterified vitamins (Desai and Machlin, 1985).

Vitamin E in the unesterified form is slowly oxidized by atmospheric oxygen to form mainly biologically inactive quinone, such as  $\alpha$ -tocopherol-quinone. Small amounts of various dimers and trimers are also formed (Nilsson et al., 1968).

#### Recommended Dietary Allowances RDA

In 1950, Harris et al estimated the average alpha-tocopherol intake per capita in the US to be about 14 mg/day, of which over 50% was contributed by oils and fats. In 1963 Harris and Embree arrived at a similar figure of 15 mg/day, based on 1960 per capita food consumption in US and food composition tables for alpha-tocopherol.

Vitamin E daily allowances for people as recommended in the 1974 and 1980 N.A.S.N.R.C. food and nutrition board publication are as follows: infants - 4 to 5 international unit (IU), children (age 1 to 14 years)- 7 to 14 IU, males (15 to 51 plus years)- 15 IU, females (15 to 51 plus years)- 12 IU, and pregnant and lactating women 15 IU. U.S.F.D.A. vitamin E daily allowances used in the nutritional labeling of

commercially produced foods and vitamin supplements, in the US are as follows: infants - 10 IU, adults and children 30 IU, and pregnant and lactating women 30 IU (NAS - NRC, 1974 and 1980).

The current recommended dietary allowance (RDA) for vitamin E ranges from 5 IU in children, 8 IU in females, and 10 IU in males (NRC-RDA, 1989). The reason for this low recommended level appears to be based on the fact that in most western people, no overt clinical deficiency syndrome has been observed (Anon, 1988a; Weisburger, 1991).

### **Structure**

Vitamin E occurs in nature as a group of substances including eight chemically similar compounds which are derivatives of 6 - chromanol. Two to four methyl groups are bound to the chromanol ring, and in position two there is also a saturated or unsaturated isoprenoid C16 side chain. The eight natural vitamin E compounds fall into two groups, the four tocopherols ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ - tocopherol) with a saturated side chain (Fig. 2.4); and the four tocotrienols ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ -tocotrienol) with an unsaturated side chain (Fig. 2.5) (Pennock, 1964). The number and position of the methyl groups and the common nomenclature has been defined (Strum, 1966, and IUPAC-IUB, 1973).

The most biologically active of these compounds is 2R, 4R, 8 R- $\alpha$ -tocopherol (RRR- $\alpha$ -tocopherol) most commonly known as d- $\alpha$ -tocopherol. As shown in various animal bioassays, this

Fig. 2.4. The structure of tocopherol.

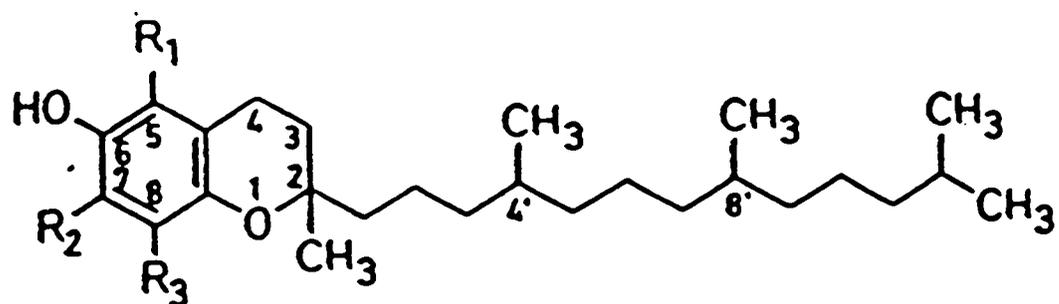
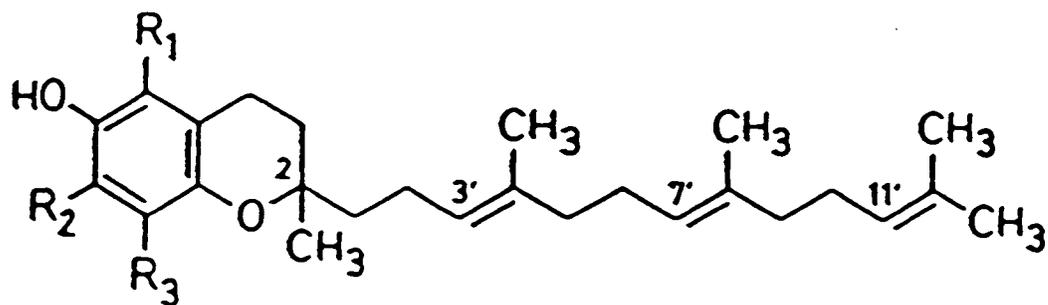


Fig. 2.5. The structure of tocotrienol.



compound is also more active than synthetic 2RS, 4RS, 8RS- $\alpha$ -tocopherol (all-rac- $\alpha$ -tocopherol), most commonly known as dl- $\alpha$ -tocopherol, which is an equimolar mixture of eight possible stereoisomers (Scott, 1978; Weiser and Vecchi, 1982; Behrens and Madere, 1991).

<u>Position of methyl group</u>	<u>Tocopherol</u>	<u>Tocotrienol</u>
5,7,8 trimethyl	$\alpha$ -T	$\alpha$ -T3
5,8 dimethyl	$\beta$ -T	$\beta$ -T3
7,8 dimethyl	$\Gamma$ -T	$\Gamma$ -T3
8 monomethyl	$\delta$ -T	$\delta$ -T3

Vegetable oil usually contains only the saturated members. Variation in tocopherol content within a given oil type can be caused by different handling, processing and storage condition. It is suggested, however, that the method of oil extraction may be more important than other factors in determining tocopherol content of an oil (Carpenter et al, 1976, and Carpenter and Pilam, 1979).

Tocopherols are apparently nature's choice of an antioxidant, as is indicated by high correlation between the total tocopherol level and the combined level of linoleic and linolenic acid. From the available data, Hoves et al (1951), calculated that the correlation coefficient of the two values is  $r = +0.79$ . The ratio of alpha-tocopherol to polyunsaturated fatty acid has been suggested as a measure of adequacy of dietary vitamin E. The recommendation has been made that the ratio of 0.6 mg of alpha-tocopherol to one gram

of poly-unsaturated fatty acids be maintained (Ferrando et al., 1971; Harris and Embree, 1963; Horwitt, 1961). There are two properties of vitamin E which are leading to its use for better physical performance. On one side it promotes an economical energy metabolism, on the other side it acts as a stabilizing antioxidant in membranes (Schnass and Pabst, 1988).

### Antioxidant Activity

Witting (1975) described the general scheme of reactions occurring during lipid peroxidation in the presence of an antioxidant. The capability of terminating the chain reaction is dependent upon the type of tocopherol. The rate and the extent of tocopherol destruction during the stabilizing process as a free radical acceptor varies with the type of natural fats being protected.

An antioxidant (AH) competitively terminates the cyclic chain reaction by withdrawing free radicals from the system via dimerization or through the formation of the tocopherol quinone. Two principal reactions may be considered to control the fate of tocopherols in autoxidizable fats (Frankel et al., 1959): the reaction between tocopherol and reactive hydroperoxides, and the spontaneous oxidation of tocopherol by atmospheric oxygen (Kleiui, 1971). The former reaction is more important. The second reaction may be unimportant because of the relatively high stability of tocopherol as observed in inert solvents (Lips, 1959). Tocopherols present

in vegetable oil also can be oxidized by iron (Pennock et al, 1964) and other metal ions present as contaminants (Luan et al, 1977).

In a study of antioxidant activity of tocopherols and other compounds on several substrates including vegetable oils and animal fats, Cort et al (1974) measured the increase in the number of days required for the peroxides to reach 20 MEQ/kg substrate. They found that di-gamma-tocopherol had more activity than the alpha form, and that activity increased as the concentration increased. This fact corroborates the findings in many previous publications (Griewahn and Daubert, 1948; Lea and Ward, 1959; and Parkhurst et al, 1968). DL-alpha-tocopherol was more active than BHT and BHA in oleic acid, while in linoleic acid, BHT and BHA were more active than tocopherols.

Parkhurst et al (1968), made a comparison of alpha, gamma, and delta-tocopherols at various concentrations and a mixture of these tocopherols representing the average tocopherol content of peanut oil on the oxidative stability of lard at 97 C. Uptake of oxygen was used to indicate the length of the induction period. The antioxidant effectiveness of tocopherols was found to increase in the order of alpha, gamma, delta. The antioxidant efficiency decreases with increasing concentration of tocopherols such that addition of any single tocopherol above a concentration of 250  $\mu\text{g/g}$  of fat has little effect on oxidative stability. A mixture

equivalent to that of an average peanut oil sample, containing 150  $\mu\text{g/g}$  of  $\alpha$ -tocopherol, 250  $\mu\text{g/g}$  of  $\Gamma$ -tocopherol, and 15  $\mu\text{g/g}$  of  $\delta$ -tocopherol was found to be no more stable than one containing 250  $\mu\text{g/g}$  of  $\Gamma$ -tocopherol alone. In a more recent study using a model system of methyl linoleate free from natural antioxidants and metals, Ikeda and Fukuzumi (1977) also observed that relative activities at equivalent molar concentration were in the order of  $\alpha < \Gamma < \delta$ -tocopherol. In a review of antioxidant activity, however, Johnson (1971), concluded that the order of tocopherol activity is affected by temperature. Under mild physiological conditions around 37°C, the tocopherols exhibit antioxidant effectiveness in the order of their biological activity  $\alpha > \beta > \Gamma > \delta$ . If the temperature is raised to between 50°C and 100°C, the order of antioxidants activity is reversed, i.e.  $\delta > \gamma > \beta > \alpha$ . The action of tocopherols was described (Lea, 1960) as dependent on the fatty acid composition of the substrate and the temperature. Alpha tocopherol was shown to be the most effective as an antioxidant in systems with unsaturation greater than that of linoleic acid and with temperatures lower than 37 C. Rao et al, (1967) showed that in sunflower oil, considered by them to have the highest linoleic acid content of the commercial oils, oxidation protection by tocopherols ranked  $\Gamma > \alpha > \delta$  at 63°C. This is the only system besides that of linseed and cod liver oil (Lea, 1960) in which  $\alpha$ -tocopherol has been shown to have greater activity than  $\delta$ -

tocopherol. Based on the insignificant difference in the tocopherol compositions, either in the nature and distribution of individual tocopherols or in the total tocopherol content, Fore et al, (1953) concluded that the relative linoleic acid content of peanut oil is one of the major factors affecting the variation in stability. Tocopherol loss at the end of the induction period was considerably greater in lard ( 75%) than in soybean oil ( 2.7%). Frankel et al (1957) also reported that the loss of tocopherol in different oxidized soybean oils at the end of the induction period was less than 10%. It was suggested that hydroperoxides formed in the highly unsaturated vegetable oils decomposed rapidly before they reacted with tocopherol. Antioxidants that react more rapidly than tocopherol with polyunsaturated fat hydroperoxides are needed to stabilize highly unsaturated vegetable oils.

In an emulsion system, antioxidant degradation is accelerated by the increase of the oxidation state of the fat components and the emulsifier, and by heavy metal ions (Kroll and Roloff, 1974). Inhibition of peroxide formation was optimal at a DL-alpha-tocopherol concentration of 50 mg/100 g. Metal contaminants appreciably increase the extent of tocopherol oxidation. The effect can be eliminated by the addition of citric acid at a level of about 0.01%.

Using chromatographic methods to separate oxidation product fractions of alpha-tocopherol based on their polarity and molecular size, Luan et al (1977) identified the final

oxidation products of tocopherols as predominantly various types of oligomers, so that in vegetable oils stored for a long time the tocopherols are converted into various polymeric derivatives. The quinoid oxidation products of tocopherol were observed to be able to react with amino acids such as L-lysine in a model system and give rise to a number of colored compounds. The mechanism of condensation reaction is probably similar to that of the reaction of the quinoid oxidation products of tocopherol with protein.

#### Effect of Processing

The destruction of tocopherol by oxidation is usually accelerated by exposure to light, heat, and the presence of certain trace metals such as iron ( $Fe^{+2}$ ), and copper ( $Cu^{+2}$ ) (Bauernfiend, 1977; Cort et al., 1978). Natural drying by exposure to the sun reduces the level of tocopherols more rapidly than when the drying is undertaken in the shade. High moisture content accelerates the deterioration of alpha tocopherol as indicated by a rapid rise in peroxide value. Komoda and Harada, (1969), found that addition of water to raw soybeans resulted in extensive oxidation of tocopherols within seven days.

Some form of heating during processing, such as that applied to oil, destroys tocopherol considerably (Chow and Draper, 1974; Ramanujan, 1958). The oxidative stability of the natural tocopherols and tocotrienols was investigated in corn and soybean oil heated at 70 C and aerated at a rate of

100 ml/minute (Al- Kishtaini, 1971). In corn oil,  $\alpha$ -tocopherol and  $\alpha$ -tocotrienol were destroyed faster than  $\Gamma$ -tocopherol and  $\Gamma$ -tocotrienol. In soybean oil,  $\Gamma$ -tocopherol was destroyed faster than  $\delta$ -tocopherol. The baking process also destroys a portion of the tocopherols (Moore et al, 1957). About 36% of the total tocopherols were destroyed and  $\alpha$ -tocopherols were the most easily destroyed. Similar results on the stability of individual tocopherols were observed by Lehmann et al., (1976). Under autoxidative conditions, stability of tocopherols increases in the order of  $\alpha$ -T=  $\alpha$ -T3 <  $\Gamma$ -T3 <  $\delta$ -T3 <  $\Gamma$ -T <  $\delta$ -T =  $\beta$ -T. Blanching was also reported to cause tocopherol loss. Blanching of almonds caused a loss of about 20% of the initial tocopherol content while 80% destruction occurred during roasting of the nuts (Tappel, 1957). Both  $\alpha$  and  $\Gamma$  tocopherol are sensitive and degraded in the presence of  $\text{Fe}^{+3}$  and  $\text{Cu}^{+2}$  (Cort, 1974). However, ascorbic acid can completely prevent the  $\text{Fe}^{+3}$  and EDTA the  $\text{Cu}^{+2}$  oxidation (Cort et al.,1978).

#### Analysis of Vitamin E

Numerous methods are available for analysis of vitamin E. Biological methods are based on the ability of certain animals to respond, especially rapidly and specifically measurement of lipid peroxidation in vitamin E deficient animals. Finally, there are physical-chemical methods available; especially HPLC, chromatography, and spectrophotometry are essential tools.

### General Biological Methods

Many animal species react sensitively, and often quite specifically, to dietary vitamin E deficiency. Table 2.8 gives several examples. Administration of vitamin E can prevent the occurrence of the symptoms.

Comparison of the effects of known amounts of vitamin E and the test sample with unknown vitamin E activities allow the latter to be estimated (Chow, 1985). The preparation of the test animals for the analysis is usually time consuming. There are numerous criteria which can be used to evaluate the biological activities of vitamin E samples (Chow, 1985). The following are most often used; the test animals are usually rats and chicks:

1. Resorption gestation test.
2. Encephalomalacia test.
3. Myopathy test.
4. Liver storage test.
5. Erythrocyte hemolysis test.

### Physical-Chemical Methods

The following methods are used for determination of vitamin E, especially in preparations with sample compositions:

1. UV spectroscopy. It is suitable only for relatively pure, highly concentrated preparations with little foreign material which interferes with UV absorption. The

Table 2.8. Pathology of vitamin E deficiency  
(simplified from Chow, 1985).

Affected tissue; observed change	Animal species
Embryonic degeneration (damage to vessel systems)	Female rats, sheep, hens, turkeys
Degeneration of male gonads	Male rats, guinea pigs, hamsters, dogs
Encephalomalacia	Chickens
Myopathy	Rabbits, guinea pigs, monkeys, ducks, rats, chickens, turkeys
Erythrocyte hemolysis	Rats, chickens
Liver necrosis	Rats, pigs

determination of the difference in absorption of  $\alpha$ -tocopherol and  $\alpha$ -tocopherylquinone (after oxidation) has proven useful (Bunnell, 1971; Parrish, 1980; Bukouits and Lezerovich, 1987).

2. Emmerie-Engle reaction. This is based on the reduction of two  $\text{Fe}^{+3}$  ions to  $\text{Fe}^{+2}$  ions by one molecule of free  $\alpha$ -tocopherol. The  $\text{Fe}^{+2}$  is determined colorimetrically at 520 nm as a red complex with 2,2 dipyridyl. More recently, 4,7 diphenyl-1, 10- phenanthroline, which gives a still more intense color, has been used instead of 2,2-dipyridyl (Draper, 1970; Emmerie and Engel, 1938; Booth, 1964).

3. Polorgraphic determination of  $\alpha$ -tocopherol after its oxidation to  $\alpha$ -tocopherylquinone (Podlaha et al., 1978).

4. Fluorescence measurement. Solutions of free (non-esterified) tocopherols and some of their reaction products have an intense fluorescence in the UV range, which can be measured. The method is specific and sensitive (Thompson, 1982).

5. Gas chromatography (GC) and high-pressure liquid chromatography (HPLC). These are excellent methods for separation, and are used preferentially for pharmaceuticals. All vitamin E mixtures can be separated by HPLC (Piitonen, 1983,1985,1986, and Hakanson et al., 1987).

Initially, the tocopherols were separated by column chromatography (Dick, 1967) and then by paper chromatography (Russell and Ward, 1953), thin layer chromatography (Stowe, 1963), and most recently by high performance liquid

chromatography (HPLC). The first HPLC systems for the separation of the four tocopherols were comprised of silica columns with hexane eluant containing a polar modifier such as diisopropyl ether (Van Niekerk, 1973).

The use of HPLC in organic analysis has increased greatly in the past 20 years. The major developments which moved this were the introduction of microparticulate (commonly 5 micron) column packings and large improvements in detectors. Today, C-18 reverse phase columns are used for separating  $\alpha$ -tocopherol from its esters and other fat-soluble vitamins. Whereas silica and other modified normal phase columns are used for the separation of tocopherol isomers and their tocotrienol counterparts (Tan, 1989, and Tan et al., 1980).

The sample preparation for the analysis of tocopherols in edible oils and fat by HPLC is achieved simply by dissolving the sample in hexane (normally 0.5 g in 50 ml). It is not necessary to remove the glycerides as they do not give a signal either in ultraviolet or fluorescence detectors (Taylor and Barnes, 1981).

HPLC is generally the method of choice for the analysis of alpha-tocopherol in government and industrial laboratories (Desai and Machlin, 1985). Many different HPLC methods for alpha-tocopherol have been reported, using either reversed-phase (DeLeenheer et al., 1978) or normal-phase (Tangney et al., 1979), as well as HPLC with fluorometric detection (Desai and Machlin, 1985; Hatam and Kayden, 1979).

Tocopherols were separated by HPLC with a C-18 column with methanol-water (96:4, V:V) as the mobile phase. Alpha and  $\Gamma$ - tocopherols were detected by fluorescence (excitation 291 nm, emission 330 nm) with a flow cell attachment and were quantified by comparison to commercially available standards.

#### Vitamin E Content of Foods

Both tocopherols and tocotrienols are found in various components of the human diet. Tocopherols are found in polyunsaturated vegetable oils and in the germ of cereal seeds, whereas tocotrienols are found in the aleurone and subaleurone layers of cereal seeds and in palm oil, rice bran oil, wheat germ oil, barley oil, coconut oil, and rubber seed oil (Gould et al., 1991; Yamaoka et al., 1991; Tan, 1989).

Meats do not contain large amounts of vitamin E, which is to be expected, since animals do not manufacture the vitamin but acquire it from their food. The level of tocopherol in animal tissue depends on the amount in the animal's diet. Mammalian muscles generally contain less than 1 mg total tocopherol per 100 g muscle tissue. The liver or heart may contain slightly more, 1 to 2 mg per 100 gm tissue (McLaughlin, 1979).

In eggs, all of the vitamin E is in the yolk. One average chicken egg (50 gm edible content) would contain 0.53 mg of total vitamin E. Chicken eggs differ from most animal products in that about one-third of the vitamin E is in the  $\Gamma$ -tocopherol form. The concentration of vitamin E in dairy

products varies with the cow's feed. The vitamin E content of fish muscle varies with the species and is mainly in the form of  $\alpha$ -tocopherol (McLaughlin and Weihrauch, 1979).

With regard to animal nutrition, most fresh green forage crops are good sources of vitamin E; the vitamin content tends to vary in parallel with that of carotenoids. The vitamin E content of grasses reaches a peak at flowering time and then drops considerably as the plants reach maturity. Wilting destroys a certain amount of vitamin E by oxidation in the presence of heat and light (Meissonnier, 1983; Albers et al., 1978, and 1984).

Most fruits contain low amounts of vitamin E, ranging between 0.1 and 2 mg per 100 g of the edible portion. Wild blackberries are exceptionally high, having about 13 mg per 100 g. Apples and pears have 0.59 mg/100g and 0.48mg/100g respectively. A greater concentration of vitamin E is in the skin than in the flesh (Draper, 1970). Cereal grains and some of their milled products are relatively good sources of vitamin E. Among the whole grains, corn has the highest total vitamin E content, nearly 8 mg per 100 g (Slover, 1971).

Sunflower seeds are among the highest, with 52 mg/100 g. The predominant form is  $\alpha$ -tocopherol in some species and  $\Gamma$ -tocopherol in others. The plant oils are very high in vitamin E. The oil of orange flavedo, rye germ, and wheat germ have over 200 mg per 100 g. Among commercial oils, the averages are lowest in coconut (3.5 mg per 100 g) and palm kernel oil

(6.2 mg per 100 mg). Palm oil is the only food material reported to contain  $\delta$ -tocotrienol (Tan et al., 1989).

Plants synthesize tocopherols ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  tocopherols) and tocotrienols ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  tocotrienols). No chlorophyll a containing higher plant tissue has been proved devoid of tocopherols (Booth, 1963). Alpha-tocopherol is the major tocopherol in chlorophyll containing tissue, and it is mainly localized in chloroplasts (Booth, 1963, Janiszowska and Korezale, 1987). Tocopherols other than  $\alpha$ -T, are situated mainly in non-green tissues such as vegetable oils, nuts, fungi, and cereal grains (Newton and Pennock, 1971), and in chlorophyll containing tissue they are localized mainly outside the chloroplast. Tocotrienols have been found in carrots, kale, broccoli, mushrooms, vegetable oil, and cereal grains (Piironen et al., 1985 and Syvaaja et al, 1986). However, generally only alpha tocopherol is determined, and knowledge of the tocopherol and tocotrienol composition of vegetables, fruits, and berries is poor.

Alpha tocopherol concentrations have been shown to be high in dark green tissues, moderate in fast growing leaves, light green tissues, and colored fruits, and low in roots, etiolated tissues, and colorless fruits. Alpha tocopherol content is high (1.8- 14.5 mg/100 g, fresh weight) in, for example, dandelion leaves, mint leaves, nettle leaves, spinach, parsley, and asparagus. Large amounts of  $\alpha$ -tocopherol were also found in wild blackberries and pepper

fruit. Variation in the  $\alpha$ -tocopherol values of vegetables, fruits, and berries can be caused by variation between species, as well as many other factors. Another factor is the uneven distribution of tocopherols, while richer in edible parts, such as the dark green parts of brassicae and leeks of yellow senescent leaves, are variously discarded (Booth, 1963). Maturity of the tissue, as well as growing conditions such as the weather, growing season, intensity of sunlight, and soil condition, also influence the tocopherol values (Piironen et al, 1986).

The relationship of maturity stage of corn grain to its  $\alpha$ - tocopherol and  $\Gamma$ -tocopherol content was examined. Whether expressed as  $\alpha$ -tocopherol/g of fat or  $\alpha$ -tocopherol/g dry weight of corn, there was no correlation between  $\alpha$ -tocopherol content and the time required to reach maturation. Gamma tocopherol, however, declined as time to maturity increased. The amount of  $\Gamma$ - tocopherol was 1 to 4 times that of  $\alpha$ -tocopherol (Combs and Combs, Jr, 1985).

### Biological Activity

From several statements on the biological activities it is possible to derive activities of the various forms relative to that of  $\alpha$ -tocopherol. If  $\alpha$ -tocopherol is made equal to 1.0, the typical activity factors are:  $\beta=0.4$ ,  $\Gamma=0.1$ ,  $\delta=0.01$  and  $\alpha$ -tocotrienol 0.3,  $\beta=0.05$ ,  $\Gamma=0.01$  (Hjarde et al., 1973 and Syvaaja et al., 1986). These activity factors can be used to calculate the total biologically active tocopherols expressed

as the equivalent weight of alpha- tocopherol (the sum of the milligrams of each form multiplied by the appropriate factor). Food that contains a high proportion of alpha-tocopherol tends to have high activity (Bieri, 1973).

The antioxidant activity depends on the molar ratio of antioxidants to unsaturated lipids, with one molecule each of the  $\alpha$ ,  $\beta$ ,  $\Gamma$ , and  $\delta$ -tocopherol protecting, respectively 220, 120, 100, and 30 molecules of polyunsaturated fatty acids (Fukuzawei et al., 1982, and 1989).

#### Health related applications

The normal blood plasma level of vitamin E (> 80% as  $\alpha$ -tocopherol, 10% as  $\Gamma$ -tocopherol and 2% as  $\beta$ -tocopherol) is 0.7-1.6 mg/dl. Less than 0.4 mg/dl is considered a deficiency. The recommended daily consumption requirement of  $\alpha$ -tocopherol is 10-15 mg.

Alpha tocopherol acetate ( $\alpha$ -T-AC) is the most common form of vitamin E used for oral supplementation in humans. In the gut, the acetate is hydrolyzed with the aid of pancreatic enzymes and bile to yield free alpha tocopherol ( $\alpha$ -T-OH) which is then partially absorbed through the intestinal wall into the lymph. No measurable  $\alpha$ -T-AC is found in blood serum. Naturally occurring vitamin E is present in food as the free phenol (Burton et al, 1988).

A nutritional interrelationship exists between vitamin E and the trace element selenium. For example, selenium substitutes completely for vitamin E in the prevention of

muscular dystrophy in vitamin E deficient sheep and cattle, while both nutrients are required for preventing liver necrosis in the rat. Selenium is an essential trace element because it is a constituent of glutathione peroxidase, an enzyme which protects the integrity of cell membranes by reducing fatty acid peroxides to hydroxy acids. The biosynthesis of this enzyme is prevented under a vitamin E deficiency. At higher concentrations of selenium, where an excess remains after enzyme synthesis, the metal will act as a free-radical donor, and so may be carcinogenic. Vitamin E, being an antioxidant, will tend to counteract this free radical damage (Johnson, 1979). These observations further support the concept that vitamin E acts to stabilize unsaturated lipids in biological membranes.

Vitamin E has also been implicated in a variety of other functions. These include the regulation of muscle metabolism and the DNA and RNA control of specific proteins in muscle cells, regulation of the development and function of the gonads, and the preparation for and protection of pregnancy (Meissonnier, 1983; Albert et al., 1984).

Vitamin E, being fat soluble, accumulates in the body, especially in the liver and pancreas. Unlike vitamins A and D, however, vitamin E at high doses is regarded to be essentially non-toxic, although daily doses of 800 IU of  $\alpha$ -tocopherol have been reported to induce severe weakness, fatigue, and other side effects in otherwise healthy adults.

Excess vitamin E may also interfere with the normal blood clotting process, producing a need for more vitamin K (Omaye, 1984). Many people now take vitamin E in large doses on their own initiative. In a double blind trial this showed no benefits on work performance, sexuality, or general well-being (Truswell, 1985).

Vitamin E appears to have no toxic side effects for the general population, even at levels that are at least one order of magnitude higher than the RDA. One exception is that very high levels of vitamin E should not be recommended for people on anti-coagulant therapy (Pryor, 1991). Vitamin E has multiple protective effects in a variety of conditions. Vitamin E destroys nitrite, a component in the food chain associated with the production of glandular stomach cancer, cancer of the esophagus, and in some instances cancer of the liver (Bright-see, 1983; Chen et al., 1988; Miruishi, 1986). Vitamin E, especially together with vitamin C, is an excellent nitrite trapping agent. Recently, concern was also expressed about the increasing ozone level, particularly in cities, where high automobile traffic generates ozone and other oxidant compounds like nitrogen oxides. Experimental studies have shown that the toxic effect of ozone on the lung is efficiently prevented by vitamin E. Vitamin E protects the circulating red cells and no doubt other essential cell systems against oxygen, and also against adverse effects mediated through hydroxy radical toxicity (Weisburger, 1991).

### Biosynthesis of Vitamin E

Vitamin E (or tocopherols) are a major group of naturally occurring chromanols in plants tissues (Morton, 1970). Aromatic compounds in plants and bacteria are synthesized via one of the two main metabolic pathways. The major one known as "the shikimate pathway" was elucidated in a long series of studies on the biosynthesis of aromatic amino acids in several laboratories. The work was initiated by Davis (1950) who found that certain mutants of the micro-organism Escherichia coli would grow only when the normal culture medium for the wild strain was supplemented with certain aromatic compounds, such as the aromatic amino acids and p-aminobenzoic acid. The biosynthetic pathways in higher plants such as spinach and peas were found to be the same (Mitsuhashi and Davis, 1954). The synthesis of shikimic acid from isotopically labelled intermediates of carbohydrate metabolism was elucidated by Srinivasan et al. (1958) and Srinivasan and Sprinson (1959).

The second method of assembling aromatic compounds such as 6-methyl salicylic acid involves condensation of acetate with malonate units rather than of metabolites of glucose (Birch and Donovan, 1953; Birch et al., 1955). It would appear that a polyketo intermediate is assembled on a multienzyme complex which then cycles in the manner as suggested by Lynen (1961), to yield either orsellinic acid or 6-methyl salicylic acid. Although certain substituted benzoquinones can be synthesized by this latter "acetate-

polymalonate pathway" it is not involved in the synthesis of the well known biologically active quinones containing substituent long-chain polyisoprenoid side-chains (Glover, 1965), such as ubiquinone, phylloquinone and plastoquinone.

Among the biologically active quinones undergoing investigation, the biosynthetic pathway of ubiquinone received attention first and it was shown that the aromatic ring of this group of substances was synthesized from the key intermediate p-hydroxybenzaldehyde (Rundney and Parson, 1963) or p-hydroxybenzoic acid (Parson and Rudney, 1964), derived in turn via the Shikimate pathway.

The biosynthesis of the quinone, plastoquinone, phylloquinone, and tocopherols was studied in maize shoots by Whistance et al. (1967). They found that: a) the aromatic nuclei of all the above were formed via the Shikimic acid pathway of biosynthesis, and, b) the ubiquinone nucleus is synthesized from p-hydroxybenzoic acid as in micro-organism and animals, but the aromatic rings of plastoquinone,  $\alpha$ -tocopherol quinone, and  $\alpha$  and  $\Gamma$ -tocopherols are derived from p-hydroxyphenyl pyruvic acid.

The polyprenyl portions of phytoquinones and tocopherols have been shown to be formed from mevalonic acid by Threlfall et al. (1976) and Dada et al. (1968). The structure relationship between the various naturally occurring tocopherols and tocotrienols as clarified by Pennocks et al. (1964), suggests that methylation of the aromatic nucleus and

reduction of the side-chain possibly occurs after the polyprenyl moiety has become attached to the ring nucleus.

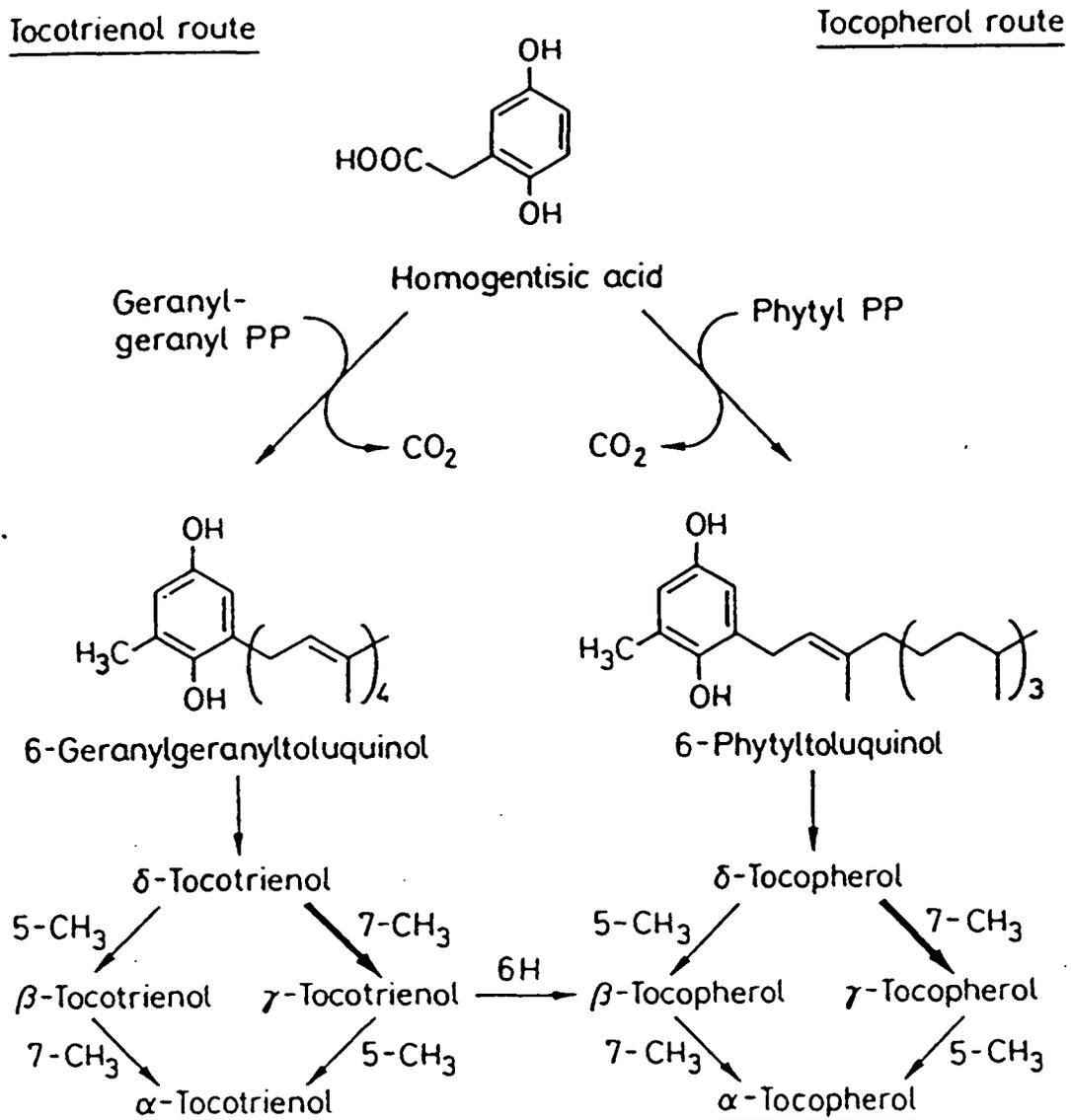
The aromatic carbon atoms and the  $\delta$ -methyl carbon atom of plastoquinone,  $\alpha$ -tocopherol and  $\alpha$ -tocopherol quinone have been demonstrated to be derived from exogenous tyrosine (Whistance and Threlfall, 1968), while the remaining nuclear methyl groups are formed by the transfer of methyl groups from L-methionine (Threlfall et al., 1967) in the form of S-adenosylmethionine. Whistance and Threlfall (1968) postulated these compounds might be synthesized by the pathway: prephenic acid  $\rightarrow$  p-hydroxyphenyl-pyruvic acid  $\rightarrow$  homogentisic acid (possibly as its  $\beta$ -glucoside)  $\rightarrow$  homoarbutin  $\rightarrow$  plastoquinone and tocopherols.

Pennock et al. (1964), suggested the final stages of  $\alpha$ -tocopherol biosynthesis involves the methylation of  $\delta$ -tocotrienol to  $\beta$  or  $\Gamma$ -tocotrienol, a further methylation to  $\alpha$ -tocopherols occurs, then saturation occurs at the required step (solid line, figs. 2.6 and 2.7).

Theoretically the members of the tocotrienols and tocopherols constitute a metabolic grid, providing six alternative pathways of hydrogenation and methylation for biosynthesis of  $\alpha$ -tocopherol from  $\delta$ -tocotrienol (solid and dashed lines, Fig.2.7) (Wellburn, 1970).

Tracer studies with L-[Me-C<sub>14</sub>]-Methionine (Whistance et al., 1968), have clearly established that the nuclear methyl

Fig. 2.6. Probable course of the biosynthesis of tocopherols and tocotrienols. (Janiszowska and Pennock, 1967)



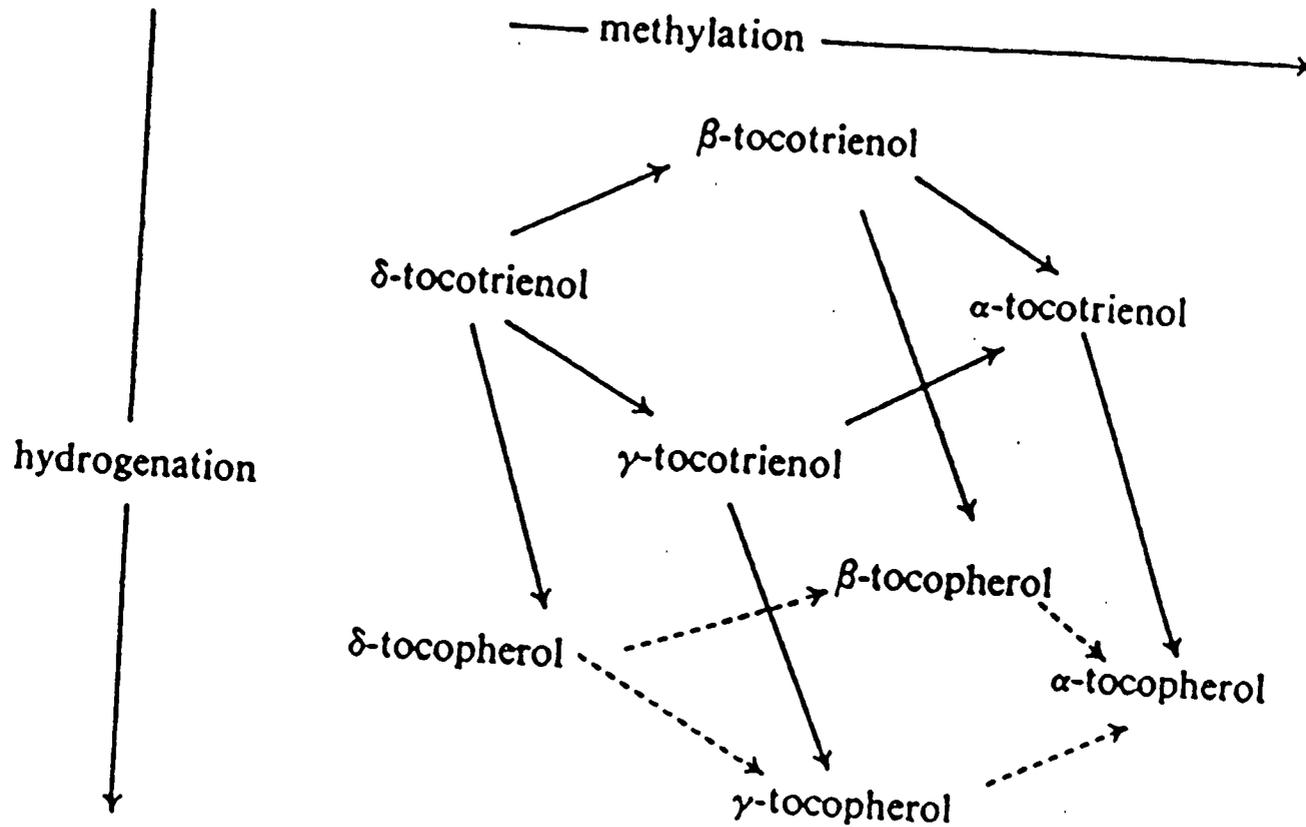


Fig.2.7. Methylation and hydrogenation of tocopherol and tocotrienol. (Wellburn, 1970).

groups other than at position 8 of the tocopherol arise by methyl transfer from s-adenosylmethionine (Cantoni, 1953).

Green (1958), determined the concentration of the different tocopherols in the various stages of growth of wheat, barley, rye, maize, and pea from germination through seedlings to mature plants. Wheat grains contain mainly  $\alpha$ - and  $\beta$ -tocopherols and tocotrienols. As the seedlings develop in the dark, Green found that the levels of the tocotrienols and  $\beta$ -tocopherol declined whereas that of  $\alpha$ -tocopherols increased. Similar studies with the pea, which contains 92%  $\Gamma$ -, 4%  $\alpha$ - (Green, 1958) and a little  $\delta$ -tocopherol (Baszynski, 1961) before germination, showed that  $\delta$  and  $\Gamma$  forms were replaced almost entirely by  $\alpha$ -tocopherol when the plants were about 10-12 cm high. It would seem that the tocotrienols were reduced to form the corresponding tocopherols which in turn became methylated to yield  $\alpha$ -tocopherol, but the actual situation is more complicated since in the plant there are separate sites of biosynthesis of terpene, inside and outside the chloroplast.

Booth (1963), observed that in plants, chlorophyll was accompanied by  $\alpha$ -tocopherol inside the chloroplast whereas  $\Gamma$  and  $\delta$ -tocopherols when present were usually outside. Small amounts of  $\beta$ - and  $\Gamma$ -tocopherols, however, have been detected within chloroplasts (Dilley et al., 1962). Thus methylation of tocopherol may occur more readily within the chloroplast (Newton and Pennock, 1971).

Three methylated derivatives of tocol, 8-monomethyl-7,8-trimethyltol (δ, Γ, and Γ-tocopherols, respectively) have been found in Calendula officinalis leaves. Studies on the distribution of these tocopherols in five purified cellular subfractions (chloroplast, mitochondrial, golgi membranes, microsomal, and cytosol) have shown that δ and Γ-tocopherols were present in chloroplasts, mitochondria, and microsomes, whereas α-T was found only in the chloroplasts. No tocopherols have been found in golgi membranes or cytosol (Janiszowska and Korczak, 1980; Janiszowska, 1987).

The distribution of tocopherols and α-tocopherol and tocotrienol was investigated in 28 spruce (Picea) species and Norway spruce (Picea abies) seedlings. Alpha-tocopherol was detected in all living organs. Beta-tocopherol and Γ-tocopherol were restricted to seedlings and seeds respectively, while traces of α-tocotrienol were detected in primary needles of seedlings and one-year old needles of mature trees, indicative of the tocotrienol pathway for vitamin E biosynthesis in spruce (Franzen et al., 1991). While α-tocopherol was found in all organs, β and Γ tocopherol and α-tocotrienol was present depending on species and state of development (Franzen and Haab, 1991).

## **Fatty Acids**

### **Introduction**

For many years it has been known that fatty acids are important constituents of phospholipid cellular membranes which serve not only as boundaries between individual cells but also to compartmentalize several major biochemical processes within the cell. Apart from the well established role of fatty acids in membrane structure (Singer and Nickolson, 1972), there is now increasing support for a different role of polyunsaturated fatty acids involved in the control of cellular activity and metabolism (Volp and Vageles, 1976).

### **Function of Food Lipids**

The various components of food lipids perform many desirable organoleptic, physical, nutritional, and biological functions (Table 2.9) that must be considered in making broad recommendations regarding dietary lipids (Kinsella, 1988). Lipids are very important components in determining food selection and the properties they impart account for their general desirability in foods. The organoleptic or sensory attributes of lipids in foods include their contribution to aroma, flavor, color (carotenoid), texture (chocolate, flaked pastry), mouth feel (smoothness, juiciness, lubricity, cooling), and overall sensory satisfaction and satiety effects. The flavor, taste, and textural attributes of foods

Table 2.9. Important functions of food lipids.

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Food quality

Color-carotenoids  
 Texture, structure-cocoa butter  
 Flavor, aroma-carbonyl compounds  
 Lubricity-mouthfeel  
 Satiety

Nutritional

Source of energy via  $\beta$  oxidation  
 Carriers of fat-soluble vitamins  
 Source of essential fatty acids  
 Physical functions-micelle formation/bile;  
     facilitate  
 absorption of fat-soluble vitamins

Biological

Vitamins A,D,E, and K-numerous effects  
 Cholesterol-precursor of vitamin D<sub>3</sub>,  
     corticosteroids, bile acids  
 Linoleic acid-component of skin  
     acylglucoceramides  
 Inositol phospholipids-receptor  
 signaling, signal transduction  
 Arachidonic acid-eicosanoids and lipoxins  
 Docosahexaenoic acid-specific membrane functions  
 n-3 Polyunsaturated fatty acids-modulators of  
     eicosanoid synthesis  
 Acetyl ether phospholipids-platelet-aggregating  
     factor; antitumor agent

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are important components of the quality and enjoyment aspects of foods (Min and Smouse, 1988).

### **Nutritional and Biological Effects**

In the context of diet and nutrition, food lipids serve as a very concentrated source of energy, provide essential nutrients (linoleic acid, linolenic acid, and vitamins A, D, E, and K), and facilitate the absorption of fat-soluble vitamins (Mead et al., 1986; Linschneer and Vergroeson, 1988).

Vitamin A, carotenoid, and the retinoid are extremely insoluble in water and require polar lipids to facilitate their absorption into the intestinal mucosa, whence they are transported by the various retinol carrier proteins (Sporn et al., 1984; Ong, 1985). The requirement for vitamin A is approximately 20  $\mu\text{g}/\text{kg}/\text{day}$  (approximately 1-4 mg/day), while the current average intake is >1-5 mg/day and the body pool is around 700 mg. Dairy food, meats, and edible fats and oils provide about 60% of the vitamin A in the USA (NAS/NRC, 1982; and 1988). Vitamin D is the original antirachitic agent, since it is a regulator of calcium and phosphorus metabolism (Deluca, 1988a,b). Hence, reduction in consumption of these foods could adversely effect vitamin A and D status (Kim and Wolf, 1987).

The dietary effects of food fats are determined largely by the relative concentrations of the component fatty acids, digestibility, and stereospecific distribution of the fatty acids on the glyceride (Kritchevsky, 1988).

Oleic acid is the major mono-unsaturated fatty acid in most dietary fats, amounting to 35% of the fatty acids consumed in the American diet, i.e. approximately 14% of dietary calories (NAS/NRC, 1988). The unsaturated fatty acids with more than one double bond are generally classified as PUFAs (polyunsaturated fatty acids). The important dietary PUFAs mostly belong to two separate families, n-6 and n-3 or omega-6 and omega-3 (Crawford, 1987; Kinsella, 1987).

### **Fatty Acids Synthesis**

Acetyl-CoA is generally regarded as a major precursor for fatty acid synthesis. Although it is well known that acetyl-CoA can be generated by the action of the pyruvate dehydrogenase decarboxylase complex, until recently it was disputed whether plastids contained sufficient enzyme to provide enough acetyl-CoA for fatty acid synthesis. In particular, one postulated alternative involved the mitochondrial generation of acetyl-CoA, cleavage of this to free acetate that could then move to the plastid and be reconverted to acetyl-CoA. This indirect pathway was proposed from experiments with spinach leaf fractions (Murphy and Stumpf, 1981), and its applications to plant tissues in general.

For non-green plastids the situation is much clearer. These organelles contain not only an active fatty-acid-synthesizing system but also contain all necessary glycolytic enzymes and pyruvate dehydrogenase. A variety of plastids,

including leukoplasts, chromoplasts, and plastids from seed cotyledons, have been studied (Harwood, 1987).

The de novo synthesis of fatty acids requires the concerted operation of two enzyme complexes, acetyl-CoA carboxylase and fatty acid synthetase. In leaves, acetyl-CoA carboxylase is localized in chloroplasts (Harwood, 1987), where its activity is stimulated markedly by light (Hellyer et al., 1986). Several results suggest that the activity of acetyl-CoA carboxylase may be rate limiting for de novo fatty acid synthesis. Indeed, in seeds, the level of acetyl-CoA carboxylase activity correlates well with accumulation of lipid in developing tissues (Harwood, 1987; Pollard and Singh, 1987). Although the enzyme is "soluble", it may well be associated with plastid membranes in vivo (Finlayson and Dennis 1980; Mohan and Kekwick, 1980), in a similar manner to the plant fatty acid synthetase (Walker and Harwood, 1985).

Fatty acid synthetase activity results normally in the production of palmitoyl-ACP that, by virtue of specific arsenite-sensitive (Harwood and Stumpf, 1971) condensing enzyme (Shimakata and Stumpf, 1982), is chain-lengthened to stearoyl-ACP . This is in keeping with the fact that the vast majority of plant fatty acids are C16 or C18. However, there are cases where novel fatty acids accumulate in seed oils and in some of these, medium chain fatty acids (C8-C14) are prominent. The generation of such fatty acids must involve some modification of the normal fatty acid synthetase.

Stearate is the longest chain fatty acid produced by fatty acid synthetase. To produce very long chained fatty acids, plants must utilize other elongation systems. It is recognized that these elongases are located on the endoplasmic reticulum and since fatty acids are produced de novo in the plastid, some movement of the acyl chains out of the latter organelle must take place for further modification (Stumpf, 1981).

Not all elongases are involved in forming saturated fatty acids for wax, cutin, or suberin synthesis. In some developing seeds, the accumulating oil contains significant amounts of very long chain fatty acids. The erucate of rape seed oil is a good example, in such tissues the trans-double bond appears to be introduced at the C18 (oleoyl) level and retained during elongation. Acetyl-coA substrates seem to be used and several systems have been studied (Harwood, 1988).

The most common plant fatty acids are the C<sub>18</sub> molecules: oleic, linoleic, and  $\alpha$ -linolenic acids. These compounds are produced by the sequential desaturation of stearate (McKean and Stumpf, 1982).

Typically, seeds accumulate storage lipids in a discontinuous manner. In the initial period after flowering there is little or no accumulation of oil, and analyses of seeds in such stages shows a preponderance of membrane (including chloroplast) lipids (Appelquist, 1975). A period of rapid oil accumulation then follows during which most of

the storage triacylglycerol is produced. The final stage is that in which seed dehydration takes place but there is relatively little further synthesis of lipid. Thus, the study of enzymes involved in triacylglycerol and fatty acid formation require seeds in stage 2 of development. Examination of enzyme activity during oil seed development has always shown that enzymes such as acetyl-coA carboxylase (Hellyer et al., 1986), and fatty acid synthetase (Ohlrogge, 1987) have maximal activity during stage 2. Moreover, some seed types such as linseed or soybean also progressively accumulated unidentified inhibitors of enzymes involved in lipid synthesis during stage 2 (Stymne and Stobart, 1987). Therefore, in these cases, seeds in the initial phase of stage 2 have to be utilized.

When triacylglycerol accumulation is sufficient, oil bodies become visible. There is some controversy about the structure and mechanism of formation of these bodies (Gurr, 1980; Stymne and Stobart, 1987; Wanner et al., 1981; Theimer et al., 1989).

The types of diverse environmental factors that affect other poikilotherms also alter the membrane lipids of higher plants. Thus, temperature, water stress, nutritional deprivation, and salt stress have all been shown to produce effects. In addition, certain chemicals (including pollutants and herbicides) may, in some cases, bring about large changes in lipids and lipid metabolism. Moreover, light also causes

significant changes in metabolism, particularly during the development of photosynthetic tissues (Harwood, 1983; 1984).

It is well known that growth at different temperatures can alter the proportions of fatty acids in poikilotherms. For plants, this usually manifests itself in a change in the ratio of saturated to unsaturated fatty acids (Hitchcock and Nichols, 1971; Harwood, 1984; Wintermans et al., 1982). The effects are more obvious in non-photosynthetic tissues because leaves contain such a high amount of unsaturation anyway. However, even in leaves, growth at low temperatures has been shown to increase the unsaturation of phosphoglyceride acyl chains (Chapman and Barber, 1980).

The phenomenon of salt tolerance has been linked to the role that certain lipids may play in the regulation of membrane permeability. In a number of experiments, a salt-induced decrease in chloroplast lipids has been seen (Harwood, 1983). Sometimes this is linked to a reduced unsaturation index (Erdel et al., 1980).

Adaptation of plants to drought has been shown to lead to an increase in phospholipid content and phospholipid synthesis. Changes in fatty acid constituents of the phospholipid and sulfolipid were also noted (Stuiver et al., 1982) and to lower the levels of  $\alpha$ -linolenate and trans-3-hexadecenate in cotton leaves (Pham et al., 1982).

Light has many effects on lipids or lipid metabolism. Monocotyledons have often been used for such studies because

their leaves expand well even in the dark. Greening has been shown to involve an initial degradation of proplastid lipids followed by an accumulation of plastid glycosyl glycerides and phosphatidyl glycerol (Bahl, 1976). Light quality also has been shown to play a significant role in regulating lipid synthesis. Tevini (1977), has summarized some of the differences between exposure to red or blue light. Blue photoreceptor caused an inhibition of linoleate desaturation (Heath, 1984).

**Chapter 3 Occurrence and identification of white mold on hazelnut kernels.**

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**Abstract**

Barcelona, Daviana, and Ennis varieties of hazelnuts were sampled in commercial orchards between Corvallis and Portland for incidence of kernel white mold . What was thought to be storage mold actually occurred on the trees even when the nuts were in early development. There were significant differences between the three years. Mold incidence was highest in 1986, and lower in 1987 and 1988. There were some differences in mold percent between the samples from tree and ground. Ramularia was the only species of fungus that was identified in all samples and was found at high percentages. No incidence of any Aspergillus species were found. Temperatures for drying and storage had no effect on mold percentage nor did number of nuts per cluster.

## Introduction

Nuts, seeds, and dried fruits are subject to microbial contamination at various stages during development and processing (Frazier, 1967). Growth of some of these organisms may take place before the fruits or nuts reach the processing plant if environmental conditions are conducive, and may continue in the plant tissues up to the time of drying, when equipment and workers may also contaminate the products (Wehner and Rabie, 1970). Some pre-treatments may reduce the numbers of organisms and others may increase them, but the fruits and nuts may be contaminated during any of the treatments. After packing, the chances of microbial contamination are very low, as the products are usually packed in containers impermeable to microorganisms capable of causing disease or toxin (such as aflatoxins).

Aflatoxin producing strains of Aspergillus flavus have been isolated from moldy pecan kernel (Escher et al., 1973, 1974) and occur commonly on plants. When incubated under improper condition, both in-shell and shelled pecans supported extensive mold growth and toxin production (Lillard et al., 1970; Benson et al., 1975). Notermans et al., (1988) found a high percentage of mold on hazelnut kernels. Most of the molds belonged to the Penicillium / Aspergillus group and to the genus Cladosporium (Blaser and Lorenz, 1981) but species identification was not done in this study. Most of the mold on walnuts and pistachios belonged to the genus Penicillium

(Fuller et al., 1977; Schade and King, 1984; Sanchis et al., 1986). The highly carcinogenic nature of aflatoxin requires that constant monitoring be made for its presence in marketed products to minimize public health hazards and this is not important in plants (Beuchat, 1975; Ayres, 1977).

Oregon is ranked fourth worldwide in terms of hazelnut production, with three percent of the total (Mehlenbacher and Smith, 1988). The value of hazelnut kernels at harvest is substantially reduced by the presence of mold. Kernel mold is one of the main problems affecting quality of the hazelnut crop state wide. Earlier observations suggested that mold may develop in the hazelnut during the growing season, but no systematic study had been done.

In traditional practice, hazelnuts develop and cure naturally on the trees, then fall to the ground where they further dry. Harvesting is begun when nearly all the nuts have dropped. A period of three weeks or more is often required from the time of maturation of the earliest cultivars such as Daviana to late cultivars such as Ennis. Weather conditions lead to variant nut moisture levels and this may impact storage quality. More recently, warm air dryers have been used to establish uniform kernel moisture in the desired 6-7% range.

Mold and rancidity are two factors which can strongly affect the market acceptability of hazelnuts. The 1985-1986 Oregon in-shell quality was reduced because of the high

incidence of kernel mold. Extra costs were incurred because of the necessity of inspecting in shell quality and removing large numbers of moldy kernels from shelled nuts.

Several years of severe kernel mold and the resulting economic losses to the industry and the lack of microbial information for Oregon hazelnuts, led to undertaking of this study. Hazelnuts may be good substrates for the growth of certain microorganisms, possibly even including aflatoxin-producing Aspergillus flavus. The overall objectives of this study were to identify the fungi involved, find the time of occurrence of kernel mold (whether pre or post-harvest), and to quantify the frequency of mold during storage. Further factors to be evaluated included observations to see if moldy nuts might drop earlier or later than normal nuts, and a better position in the canopy or microclimate (such as nuts per culester) might influence mold incidence. Information of this type might be applied to control the fungus, either through a chemical spray program, or through modified cultural practices or harvest methods to selectively remove contaminated (rotted) nuts.

The overall objectives of this study were to:

- 1- Identify the fungus as fungi causing kernel mold.
- 2- Find the time of occurrence or infection by the mold whether pre or post-harvest.
- 3- Quantify differences in kernel mold incidence between varieties, growing locations, microclimates in the

tree canopy, and whether infected nuts dropped earlier or later than uninfected nuts.

4- Evaluate storage drying condition, and storage time to see if mold increases .

Information of this type will be useful to plant pathologists to develop control programs based upon life cycle of the fungus, and timing of last infection, may allow some reduction in kernel mold through modified cultural or tree management practices or harvest timings, or relate to optimum storage conditions and duration when kernel mold is prevalent.

### Material and Methods

To meet the first objective, to identify the infecting fungi, we were fortunate to have the cooperation of Dr. Jeff Stone, recently hired in the Department of Plant Pathology, OSU. Forty samples of unshelled hazelnuts were surface-sterilized with a solution of 6% sodium hypochlorite, 20% ethanol and 60% sterile water for two minutes (Beuchat, 1975). The hazelnuts were then washed with sterile water and dried on sterile filter paper. Individual hazelnuts (40) were cracked and the nutmeat was cut with a sterile knife. For each sample (variety) 4-6 pieces were then transferred to an Erlenmeyer flask for 3 minutes, two additional decimal dilutions were made. Three samples (2 x 0.5 ml, 1 x 0.5 ml) were taken from each dilution and seeded onto the surface of malt extract agar in petri dishes. Dishes were incubated at 26°C and fungi growing from these seeds were identified directly or were sub-cultured onto other media. The identification was made by Dr. Jeff Stone a special effort was made to check for Aspergillus spp. that might be aflatoxin produceres.

The second objective was to determine the time of mold infection of the hazelnut kernels. This was done by sampling throughout the nut development stages beginning in May, when developing nuts could first be seen, until nut drop in late September. We were also interested to see if varieties and orchard sites had much effect on mold incidence. There were four methods of collecting nut samples: specifically marked

trees, ground, and randomized trees, randomized ground. Samples from specific trees and randomized trees were collected from June until the second week of September, and samples from the ground and randomized ground were collected from the last week in August or the beginning of September until the last week of harvesting. Sampling from the horticulture farm was made only from specific trees.

To meet the third objective, that of quantifying /determining incidence of kernel mold by variety and location, samples of 3 varieties of hazelnuts (Barcelona, Ennis, and Daviana) were collected from four different locations (Corvallis to Portland, Oregon) to represent the growers in the Willamette Valley. Hazelnuts were collected from each of 18 selected trees at weekly intervals in three tree replicates for each treatment. The sampling period extended from June to September in three consecutive years (1986-1988). Another sampling was made from the OSU Department of Horticulture farm (breeding program) on seven different varieties starting when the nuts became visible in May to the end of the season in late September or early October.

To determine kernel mold incidence from commercial orchards and from the OSU hazelnut breeding collection, after the kernel was developed, nuts were cracked manually to inspect the kernels. Two-hundred and fifty nuts were taken from each sample and examined with the aid of a 10X magnification hand lens. Nuts were evaluated for mold

incidence and severity and ranked from 0 to 5, (0 = no mold, 1 = least severe, small area visible under hand lens infected with mold and 5 = most severe, large area infected with mold).

At the end of each year, we collected ten bags from the four commercial farms after they swept all the nuts from the ground. We then cracked ten bags, with 250 nuts each and compared them to our sampling which we took (before they swept), at the end of the season, to compare percent mold from the two sampling methods.

Another study examined the effect of number of nuts per cluster on mold frequency. We sampled Barcelona from two different farms. We picked 250 clusters, three replicates having 1, 2, 3, 4, and 5 nuts per cluster. Sampling was done every other week from mid-June to mid-September, 1987 and 1988.

All the samples were also evaluated for blanks, shriveled kernels, undeveloped kernels, worms, black tips, double kernels, and split kernels.

The purpose of the fourth part of the study was to evaluate the relationship between mold frequency and storage time, storage temperature, cleaning, and two drying temperatures. Samples of Barcelona and Ennis were taken from commercial farms after nut harvest, and samples were divided into four lots. The first and second lots were taken from the farm and then dried in the lab at 32-38°C (90-100°F). These samples were not washed but leaves, twigs, dirt, and stones

were discarded by the sweeping machine. The third and fourth samples were washed, cleaned, and dried at 32-38°C. All four samples were placed in plastic bags and stored at 0, 10, or 20°C. Then 250 nuts were examined for mold after 0, 3, 6, 9, and 12 months storage. This was done for 1987 and 1988.

## Results

### Identification of Mold

Many species of mold were found on samples of hazelnuts from the horticulture farm. Many of the isolated molds failed to sporulate in culture and hence were unidentifiable. Such isolates however, tended to be infrequent and irregular in occurrence from sample to sample. Based on colony characteristics in the absence of spores, these isolates probably comprise numerous infrequent species.

Ramularia was the only species consistently isolated from nuts from all trees and all sampling periods. This species also invariably comprised the greatest proportion of isolates for each tree in every sample. The remainder of isolates, few in number and most not identifiable, were comprised of a wide range of incidental species (Cladosporium, Ulocladium, Alternaria, Epicaceum, Chactonium. and Asperguills, non aflatoxins producing species) that were not isolated consistently throughout the sampling period. The percentage of Ramularia on five different hazelnut varieties are presented in Table 3.1. While Koch's pastulates were not rigarously applied, it appears that Ramularia is the most likely fungal candidate associated with hazelnut kernel white mold.

### Mold Incidence

The percentages of mold over three consecutive years (1986, 1987, and 1988) are shown in Table 3.2. The mold

always began at the tips of the kernels where the funiculus attaches to the embryonic tissues. The mean represents four different farms, three different varieties, and four different methods of sampling. Mold percentage was highest in 1986 (7.6%), less in 1987 (2.6%) and 1988 (1.8%). Barcelona was more susceptible mold than the other two varieties in all three years. For example, mold incidence was 8.3% on Barcelona and 7.2% on Daviana in 1986. Ennis was lower in mold in 1987 and 1988 than either Barcelona or Daviana.

#### Sampling Methods

Nuts sampled from trees (randomized and specific trees) showed higher mold percent than nuts picked from the ground (both randomized and specific). Table 3.3 and Appendix Table A.1 show percentage of mold in all three varieties, four different sampling methods, and three years. Barcelona had the highest mold incidence in all cases. For example Barcelona was 9.4% and Ennis was 7.8%. Samples taken from the trees were slightly higher in mold than those taken from the ground.

#### Timing of Mold Development

Figures 3.1, 3.2, and 3.3 show that visible kernel mold occurs on the trees as early as June, the time of formation of nuts. The percentage of mold varies slightly during the growing season from June to the end of September on nuts that dropped on the ground. The percentage of mold from the ground sampling was essentially the same as the tree sampling, a

little less in some years and more in other years, such as in 1987 when the ground sampled kernel mold was slightly higher than the tree kernel mold in Barcelona and Daviana. However, the difference was not significant. In either method (trees vs. ground) even though percentage of mold was variable from one week to another, differences were not significant. Figs. 3.4, 3.5, and 3.6 show the mean mold incidence both ground and tree samples of three varieties over three years. In 1986, percentage of mold was higher in all three varieties. Appendix Fig. A.1. shows the mean of all three varieties combined together for each year.

Table 3.4 shows the kernel mold percentages at the last ground sampling and the sweeping (pick-up) of the hazelnuts by the four farms at the end of the season. The data shows no significant differences between the two samples. In 1986 mold percent was somewhat higher (7.9%) in our samples at harvest than from the farmers' samples, (7.3%).

#### Effect of Number of Nuts per Cluster

Table 3.5 shows the percent of mold relative to numbers of nuts per cluster for 1986 and 1987. The highest percent existed in clusters containing 3-4 nuts, mold percent was 4.1% in 1986. There were statistical differences in incidence of kernel mold between the two years, but there was no significant effect of cluster number on kernel mold. We conclude that number of nuts per cluster does not influence mold incidence.

### Horticulture Research Hazelnut Trees

Table 3.6 Shows the mold incidence was high in some genotype groups and low in others. In both groups, mold was evident on the samples as early as we started sampling in June.

At the OSU farm, mold incidence was about the same (5.2%) in all three years. In 1986 research hazelnut tree mold percent was, less than mold percent from commercial farms, which was 7.6%. In 1987 and 1988 the kernel mold incidence from commercial farms was significantly less than kernel mold from the horticulture research farm.

### Quality study

Table 3.7 shows that there are no significant differences in several quality measurements in three years (1986, 1987, and 1988). The percent of blanks, undeveloped kernels, and shriveled kernels were higher than other parameters. Brown tip was 0.05% and was the lowest percent in all parameters measured. Table 3.7 is a comparison between Barcelona and Ennis for three years. The percent of blanks, undeveloped kernels, and shriveled kernels were lower in Ennis for all three years.

### Storage Study

Tables 3.8 and 3.9 show the percentage of mold on hazelnuts under different storage temperatures and drying temperatures. Storage of two varieties of hazelnuts (Barcelona and Ennis) under three different temperature

levels, at 7-8% moisture content, had only a small effect on mold percentage. However, the lower temperature (0°C) and the combination of drying with cleaning, exhibited slightly less mold than the others.

Mold percentage decreased with increasing storage times, up to 12 months especially at lower storage temperatures. Mold percent was 6.3 at the beginning of storage with cleaning and drying treatment, but was only 3.5% after 12 months storage at the same temperature.

## Discussion

Identification of Ramualaria spp. as the most likely causal agent of hazelnut kernel mold, and establishment of its presence at very early stages of nut formation (or earlier) will allow plant pathologists to focus on this fungal species in order to establish (Koch;s postulates) its pathogenic role and ultimately to control it.

Samples of hazelnut kernels not showing visible mold were highly contaminated with mold species, mostly saprophytic. This was also observed with pecans (Beuchat and Heaton, 1980). The percent of mold on hazelnuts showed slight increases and decreases during the growing season because of fluctuation of temperature and relative humidity of the atmosphere and this is similar to reports on almonds (King et al., 1983; Purcell et al., 1980). Also, changes in kernel moisture were correlated with variations in relative humidity and temperature. One might expect higher moisture in kernels to provide conditions more favorable for growth of fungi and this may be another reason there is a slightly higher mold percent on the trees, compared with fallen nuts. The exact moisture content at which fungal growth ceases may vary with temperature, oil content, or pellicle phenolics of the kernel during the growing season. It was found that with almonds moisture, temperature, and oil content had an effect on fungal growth (Phillips et al., 1976; Schade and King, 1984; Schade et al., 1975).

There has been no research done with hazelnuts to determine where on the kernel and when white mold initially appears. Visual inspection of hazelnut kernels at the time they were taken from the shell and the incidence of mold were high in 1986 and much less in 1987 and 1988. Higher mold in 1986 was associated with increased rainfall during the growing season. In 1987 and 1988 there was less rainfall than in 1986 during the late growing and sweeping seasons. Another reason may be due to fungicide effectiveness. Due to the increased rain in 1986 fungicides would not stay on the trees long enough to prevent mold growth or that it may not have been applied early enough. Also, perhaps different kinds of field practices, such as increased pruning, which allowed more sunlight in the trees, might also result in decreased mold. Barcelona was higher in mold than Daviana and Ennis, and it appears that Barcelona is more susceptible.

Different numbers of nuts per cluster (table 3-4) showed negligible effects on mold percentage. This suggests that the mold does not move from one nut to another and each nut is infected separately.

Sampling of hazelnuts from the horticulture farm showed that mold incidence was nearly the same in all three years (not significantly different). This may be due to the fact that these trees are under the same applications for treatment and the same field practices by removing old growth and thinning the branches, as commonly practiced on an

experimental station. Another reason could be because the means of mold came from two different groups, one highly susceptible and the second, less susceptible. Another reason could be that the horticulture trees are small and have plenty of distance from each other, this would prevent shading. This is not true of the other four farms from which we sampled. Commercial hazelnut trees were so close to each other that some of the lower branches receive no direct light.

The low percentage of blank nuts shows that the pollinators are in good compatibility and in sufficient numbers to cover all the trees in the field, and the environmental factors such as temperature and humidity were good. A high percentage of blanks were found in Barcelona and this was in agreement with that reported by others (Lagersted and Thompson, 1967; Mehlenbacher, 1991). The low percentage of undeveloped kernels showed that water and nutrients were adequate. The low percentage of shriveled kernels in Barcelona and high percents in Ennis may be due to their size differences. Ennis is a large nut and there is a lot of blank space inside the shell and when it loses water it shrinks. However, Barcelona is a small nut with relatively little space inside the shell, so the kernel maintains its shape better when dried, as also reported by Mehlenbacher (1991). The fact that all other quality parameters were very low implies good control of worms and decay with insecticides and fungicides.

The storage study (Tables 3.8 and 3.9) showed that

cleaning and drying significantly lowered mold percentage possibly due to high temperatures killing or stopping the fungi from developing during storage (Christensen, 1957; El-Bahadli, 1975). The presence of tannins inside hazelnuts shells and in the pellicle may protect the kernel from pathogens and herbivores (Prestone and Sayer, 1992). One would expect that higher moisture in kernels would provide conditions favorable for fungal growth, so drying the nuts to moisture levels of 6-7% does not allow fungi to grow. The recommended hazelnut kernel moisture is 6-7% (Richardson, 1988). It has been traditionally advisable for processors to reduce pecan nutmeat to 4-5% moisture or lower before storage to control mold growth (Heaton and Woodroof, 1970; Heaton et al., 1977). This moisture level results in 0.70 water activity. The moisture content of almonds influences growth of fungi (Phillips et al., 1976; King et al., 1970; King and Schade, 1986). The time for visible mold to appear on almond kernels was related to moisture and water activity. No mold growth was observed after 1.5 years on almonds stored at 4.5 - 5.5% moisture content (King et al., 1983).

Hazelnuts stored at 0°C had less mold than those stored at 10°C and 20°C and clearly shows that lower temperatures can control the activity of mold.

Literature Cited

- Ayres, J.L. 1977. Aflatoxin in pecans: problems and solutions. J. Amer. Oil Chem. Soc.. 54:229A-230A.
- Benson, M.W., R.H. Kurtzman Jr., W.U. Halbrook, and R.M. McCready. 1975. A research note: Aflatoxin production on some feeds and foods. J. Food Sci. 40:1085- 1086.
- Beuchat, L.R. 1975. Incidence of molds on pecan nuts at different points during harvesting. Appl. Microbiol. 29:852-854.
- Beuchat, L.R. and E.K. Heaton. 1980. Factors influencing fungal quality of pecans stored at refrigeration temperatures. J. Food Sci. 45:251-253.
- Blaser, P. and W.S. Lorenz. 1981. Aspergillus flavus kontamination von nussen, Mandeln und mais mit bekannten Aflatoxin-gehalten. Lebensm-Wiss U-Technol. 14:252-259.
- Christensen, C.M. 1957. Deterioration of stored grain by fungi. Bot. Rev. 23:108-134.
- El-Behadli, A.H. 1975. Mold contamination and infection of prunes and their control. Ph.D Dissertation. University of California, Davis. pp.80.
- Escher, F.E., P.E. Koehler, and J.C. Ayres. 1973. Effect of roasting on aflatoxin content of artificially contaminated pecans. J. Food Sci. 38:889-892.
- Escher, F.E., P.E. Koehler, and J.C. Auyres. 1974. A study on aflatoxin and mold contaminations in improved variety pecans. J. Food Sci. 39:1127-1129.
- Frazier, A.C. and J.G. Lines. 1967. Studies on changes in flour tocopherol following ageing and treatment of the flour with chlorine dioxide. J. Sci. Food Agric. 18:203-207.
- Fuller, B., W.W. Spooncer, A.D. King, J. Schade Jr., and B. Mackey. 1977. Survey of aflatoxins in California tree nuts. J. Amer. Oil Chem. Soc.. 54:231-234.
- Heaton, E.K. and J.G. Woodroof. 1970. Humidity and weight loss in cold stored pecans. ASHRAEJ. 12:49-51.

- Heaton, E.K., A.L. Shewfelt, A.E. Badenhop, and L.R. Beuchat. 1977. Pecan: Handling, storage, processing and utilization. Univ. Georgia. Athens, Georgia, USA. Agric. Res. Bull. 197:pp.77.
- King, A.D. Jr., M.L. Miller, and L.C. Eldridge. 1970. Almond harvesting, processing, and microbial flora. Appl. microbiol. 20:208-214.
- King, A.D.Jr., W.U. Halbrook, G. Fuller, and L.C. Whitehand. 1983. Almond nutmeat moisture and water activity and its influence on fungi, flora, and seed composition. J. Food Sci. 48:615-617.
- King, A.D. Jr. and J.E. Schade. 1986. Influence of almond harvest, processing, and storage on fungal populations and flora. J. Food Sci. 51:202-205.
- Lagerstedt, H.B. 1977. The occurrence of blank in the filbert Corylus avellana and possible causes. Botany. 31:153-159.
- Lillard, H.S., R.T. Hanlin, and D.A. Lillard. 1970. Aflatoxigenic isolate of Aspergillus flavus from pecan. Appl. Microbiol. 19:128-131.
- Mehlenbacher, S.A. and D.C. Smith. 1988. Heritability of ease of hazelnut pedicel removal. HortScience. 23:1053-1054.
- Mehlenbacher, S.A. 1991. Genetic resources of temperate fruit and nut crops (hazelnuts) 290. Ch.17 pp.809-810. Acta. Hort.
- Notermans, S., J. Dufrenne, and P.S. Soentoro. 1988. Detection of molds in nuts and spices: The mold colony count versus the enzyme linked immunosorbent assay (ELISA). J. Food Sci. 53:1831-1834.
- Phillips, D.J., M. Uota, D. Monticelli, and C. Curtis. 1976. Colonization of almond by Aspergillus flavus. J. Amer. Soc. Hort. Sci. 101:19-23.
- Preston, C.M. and B.G. Sayer. 1992. What's in a nutshell: An investigation of structure by carbon-13 cross-polarization magic-angle spinning nuclear magnetic resonance. J. Agr. Food Chem. 40:206-210.

- Purcell, S.L., D.J. Phillips, and B.E. Mackey. 1980. Distribution of Aspergillus flavus and other fungi in several almond growing areas of California. *Phytopathology*. 70:926-929.
- Richardson, D.G. 1988. Hazelnut quality. Nut growers society of Oregon, Washington, and British Columbia. 83-86.
- Sanchis, V., S. Sala, A. Palomes, P. Santamarina, and P.A. Burdaspal. 1986. Occurrence of aflatoxin and aflatoxigenic molds in foods and feed in Spain. *J. Food Prot.* 49:445-447.
- Schade, J.E., K. McGreevey, A.D. King, B.Mackey, and G. Fuller. 1975. Incidence of aflatoxin in California almond. *Appl. Microbiol.* 29:48-51.
- Schade, J.E. and A.D. King, Jr. 1984. Fluorescence and aflatoxin content of individual almond kernels naturally contaminated with aflatoxin. *J. Food Sci.* 49:493-497.
- Wehner, F.C. and C.J. Rabic. 1970. The micro-organisms in nuts and dried fruits. *Phytophylactica.* 2:165-168.

Table 3.1. Percent of main species of fungi isolated from inside the nut shells from hazelnuts growing at the horticulture farm, 1988.

		G-10	E-10	H-7	D-9	E-11
May	R*	5	8	16	0	0
	O*	6	0	2	0	0
June	R	64	100	50	84	94
	O	8	0	7	15	0
June	R	66	70	74	42	45
	O	0	9	13	0	11
July	R	57	100	100	100	100
	O	0	0	0	0	0
August	R	85	57	79	0	75
	O	0	0	5	0	0
September	R	60	63	0	2	17
	O	0	0	0	0	0
September	R	44	24	80	0	20
	O	11	0	7	50	5

\*R= Ramularia

\*O= Other fungi (Cladosporium, Ulocladium, Alternaria, Epicoccum, Chaetomium, and Aspergillus)

G-10= OSU 23.006 (Barcelona x Tombul)

E-10= OSU 17.028 (Barcelona x Tombul Ghiaghli)

H-07= OSU 23.010 (Barcelona x Tombul)

D-09= GH 130.33 (Negret x Daviana)

E-11= OSU 17.028 (Barcelona x Tombul Ghiaghli)

Table 3.2. Percentage of mold on three major varieties of Oregon hazelnuts over three consecutive years.

Year	Variety	% Mold*	Mean
1986	Barcelona	8.3 a	7.6 a
	Ennis	7.5 b	
	Daviana	7.2 b	
1987	Barcelona	3.3 c	2.6 d
	Ennis	1.9 e	
	Daviana	2.6 d	
1988	Barcelona	1.8 e	1.8 e
	Ennis	1.6 e	
	Daviana	1.9 e	

\*Each value represents a mean of 348 replicates.

Four ways sampling

Four farms

9600 Nuts

Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 3.3. Percentage of mold on hazelnuts kernel sampled from tree and on the ground for 1986, 1987, and 1988.

Year	Variety	Position	% Mold*
1986	Barcelona	Tree	9.4 a
		Ground	7.2 b
	Ennis	Tree	7.8 b
		Ground	7.1 b
	Daviana	Tree	8.2 a b
		Ground	6.2 c
1987	Barcelona	Tree	3.6 d
		Ground	3.1 d
	Ennis	Tree	2.1 e
		Ground	1.7 f
	Daviana	Tree	3.1 d
		Ground	2.2 e
1988	Barcelona	Tree	2.1 e
		Ground	1.5 f
	Ennis	Tree	1.5 f
		Ground	1.7 f
	Daviana	Tree	1.9 e f
		Ground	1.9 e f

\*Each tree sample represents 240 replicates, 60,000 nuts. Each ground sample represents 144 replicates, 36,000 nuts. Four farms. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 3.4. Comparison of hazelnut kernel mold incidence relative to two sampling methods.

Year	Farm	P	Varieties			
			Barcelona		Ennis	
			pre-harvest	Post-harvest	Pre-harvest	Post-harvest
1986	A		6.6 b	5.6 c		
	B		7.2 b	7.3 b		
	C		6.5 b	6.3 b c		
	D		9.2 a	8.8 a	8.5 a	8.1 a
1987	A		2.6 e	2.8 e		
	B		3.5 d	3.5 d		
	C		3.9 d	4.0 d		
	D		2.0 e	2.2 e	2.3 e	2.6 e
1988	A		2.2 e	2.0 e		
	B		2.3 e	2.8 e		
	C		2.6 e	3.1 d e		
	D		2.4 e	2.3 e	2.2 e	2.1 e

Each value represents a mean of 5 replicates.  
 1250 nuts. Examined individually.  
 Means followed by the same letter in each year are not significantly different,  $p=0.05$ .

Table 3.5. Hazelnuts per cluster and the incidence of kernel mold. (Barcelona)

Nuts/Cluster	1987	1988*
1	3.8 a	2.8 b
2	3.8 a	2.6 b
3	4.1 a	2.8 b
4	4.1 a	2.8 b
5	3.9 a	2.9 b

\*Each value represents a mean of 6 replicates.

From two different farms.

From trees only

Means followed by the same letter are not significantly different,  $p=0.05$ . Values are the mean of 1500 nuts.

Table 3.6. Percentage of kernel mold on two selected genotypes of hazelnuts from the horticulture farm.

Year	Group	% Mold*	% Mean
1987	susceptible	9.1 a	5.2 a
	non-susceptible	1.3 b	
1988	susceptible	9.3 a	5.3 a
	non-susceptible	1.3 b	
1989	susceptible	8.7 a	5.2 a
	non-susceptible	1.6 b	

\*Each value represents a mean of 48 replicates.

3 varieties

One way sampling

4800 nuts

Res=D-9, E-11, J-7

Sus=E-10, G-10, H-11

Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 3.7. Percentage of different quality defects associated with hazelnuts .\*

	1986	1987	1988
Blank	13.8 a	13.6 a	13.4 a
Undeveloped	2.5 c	2.7 c	2.7 c
Shriveled	4.7 b	4.2 b	4.6 b
Black tip	0.1 e	0.1 e	0.1 e
Rotten	0.09 e	0.08 e	0.1 e
Worm	0.1 e	0.08 e	0.1 e
Split	0.1 e	0.1 e	0.1 e
Double	0.5 d	0.5 d	0.4 d
Brown tip	0.07 e	0.06 e	0.05 e

\*Each value represents a mean of 48 replicates.

Four farms

Two way Tree + Ground

Two varieties (Barcelona and Ennis) pooled.

Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 3.8. Effect of storage time and drying temperature on white mold of two varieties of hazelnuts, 1986.

		Barcelona			Ennis		
		temperature			temperature		
tmt	time, months	0°C	10°C	15°C	0°C	10°C	15°C
Farm	0	5.6 a	5.4 a	5.6 a	7.3 a	7.2 a	6.1 b
	3	5.3 a	5.1 a	5.8 a	7.1 a	6.9 a b	5.9 b c
	6	5.3 a	5.1 a	5.5 a	7.1 a	6.6 a b	5.9 b c
	9	4.7 a b	4.9 a b	5.4 a	7.0 a	6.9 a b	6.0 b
	12	5.1 a	4.8 a b	5.1 a	6.7 a b	6.4 b	5.8 b c
Farm, dried	0	5.1 a	4.9 a b	5.0 a	5.1 c	5.1 c	5.6 c
	3	4.8 a b	4.6 a b	4.8 a b	4.9 c	4.6 c	5.3 c
	6	4.8 a b	4.6 a b	4.9 a b	4.5 c	4.5 c	5.3 c
	9	4.6 a b	4.3 a b	4.6 a b	4.5 c	4.5 c	5.2 c
	12	4.5 b	4.3 b	4.6 a b	4.5 c	4.4 c	5.2 c
Wash	0	5.1 a	5.6 a	5.3 a	6.6 a b	6.7 a b	6.3 b
	3	5.2 a	5.3 a	5.3 a	6.6 a b	6.6 a b	6.2 b
	6	5.3 a	5.2 a	5.4 a	6.3 a b	6.6 a b	6.4 b
	9	5.1 a	5.4 a	5.3 a	6.1 b	6.5 b	6.1 b
	12	5.2 a	5.3 a	5.3 a	6.2 b	6.3 b	6.1 b
Washed, dried	0	5.0 a	4.9 a b	4.9 a b	5.1 c	4.9 c	4.8 c
	3	4.9 a b	4.3 b	4.6 a b	5.1 c	4.9 c	4.8 c
	6	4.9 a b	4.5 b	4.8 a b	4.6 c	4.1 d	4.6 c d
	9	4.6 a b	4.3 b	4.6 a b	4.6 c d	4.0 d	4.6 c d
	12	4.5 b	4.1 b	4.5 b	4.5 c	4.0 d	4.6 c d

\*Each value represents a mean of 3 replicates, 250 observations per replicate. Means followed by the same letter are not significantly different, p=0.05.

Table 3.9. Effect of storage time and drying temperature on white mold incidence of two varieties of hazelnuts, 1987.\*

		Barcelona			Ennis		
		temperature			temperature		
tmt	time, months	0°C	10°C	15°C	0°C	10°C	15°C
Farm	0	1.1 a b	0.9 b	1.5 a	0.8 b	0.9 b	1.3 a b
	3	1.0 a b	0.9 b	1.5 a	0.6 b	0.8 b	1.1 a b
	6	0.6 b	0.6 b	1.1 a b	0.6 b	0.8 b	1.2 a b
	9	0.6 b	0.7 b	1.1 a b	0.5 b	0.7 b	1.2 a b
	12	0.4 b	0.2 b	1.0 a b	0.4 b	0.6 b	0.9 b
Farm, Dried	0	1.3 a b	1.1 a b	0.9 b	1.0 a b	0.6 b	0.7 b
	3	0.8 b	0.5 b	0.8 b	0.3 b	0.5 b	0.6 b
	6	0.6 b	0.5 b	0.6 b	0.3 b	0.3 b	0.6 b
	9	0.4 b	0.6 b	0.6 b	0.0 c	0.3 b	0.5 b
	12	0.0 c	0.1 c	0.4 b	0.3 b	0.0 c	0.4 b
Wash	0	0.8 b	1.2 a b	1.4 a	1.2 a b	0.9 b	0.8 b
	3	0.8 b	1.1 a b	1.2 a b	1.1 a b	0.8 b	0.7 b
	6	0.8 b	0.9 b	1.1 a b	0.9 b	0.7 b	0.8 b
	9	0.6 b	0.8 b	1.1 a b	1.1 a b	0.7 b	0.5 b
	12	0.7 b	0.9 b	1.0 a b	1.2 a b	0.6 b	0.5 b
Wash, Dried	0	0.6 b	0.5 b	1.2 a b	0.5 b	0.6 b	0.9 b
	3	0.3 b	0.5 b	0.9 b	0.5 b	0.2 b c	0.6 b
	6	0.3 b	0.3 b c	0.8 b	0.0 c	0.1 c	0.4 b
	9	0.0 c	0.1 c	0.5 b	0.0 c	0.1 c	0.4 b
	12	0.1 c	0.0 c	0.8 b	0.1 c	0.2 b c	0.3 b c

\*Each value represents a mean of 3 replicates, 250 observations per replicate. Means followed by the same letter are not significantly different, p=0.05.

Fig. 3.1. "Barcelona" kernel seasonal mold incidence for 1986, 1987, and 1988.

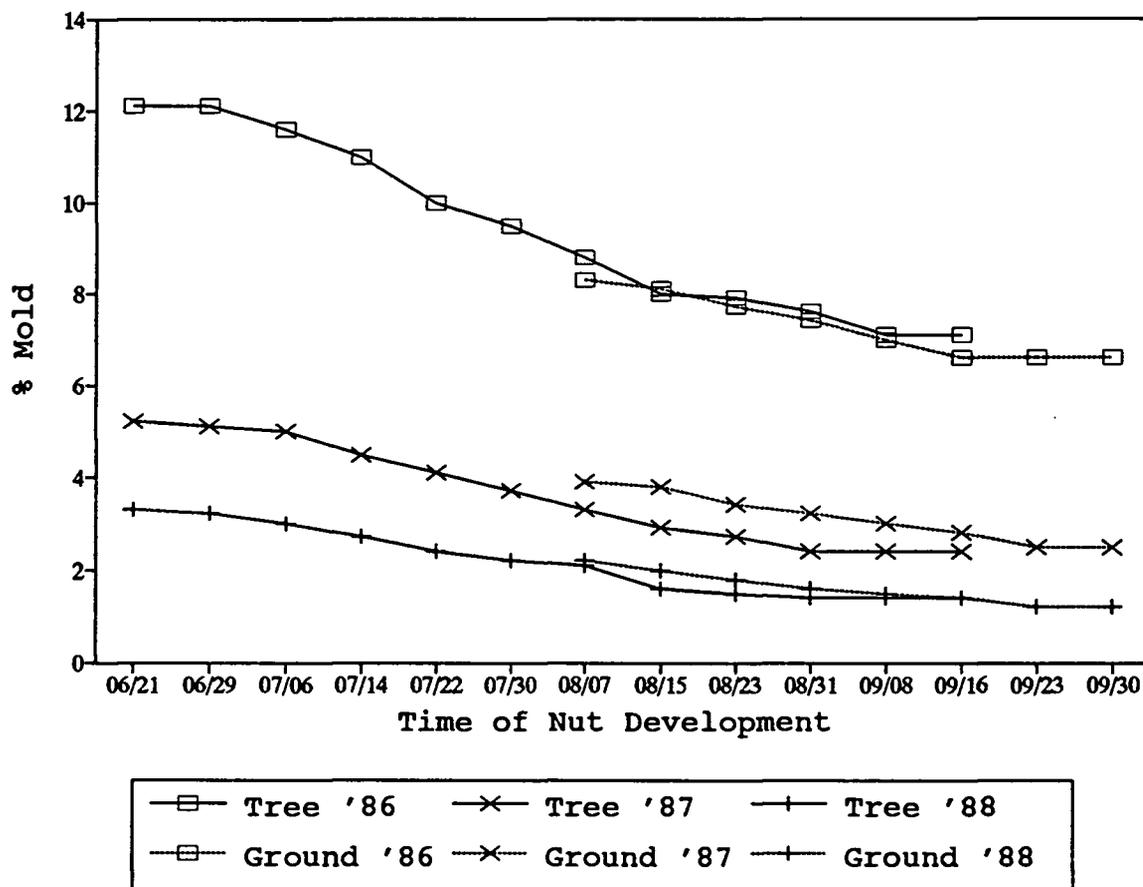


Fig. 3.2." Daviana" kernel seasonal mold incidence for 1986, 1987, and 1988.

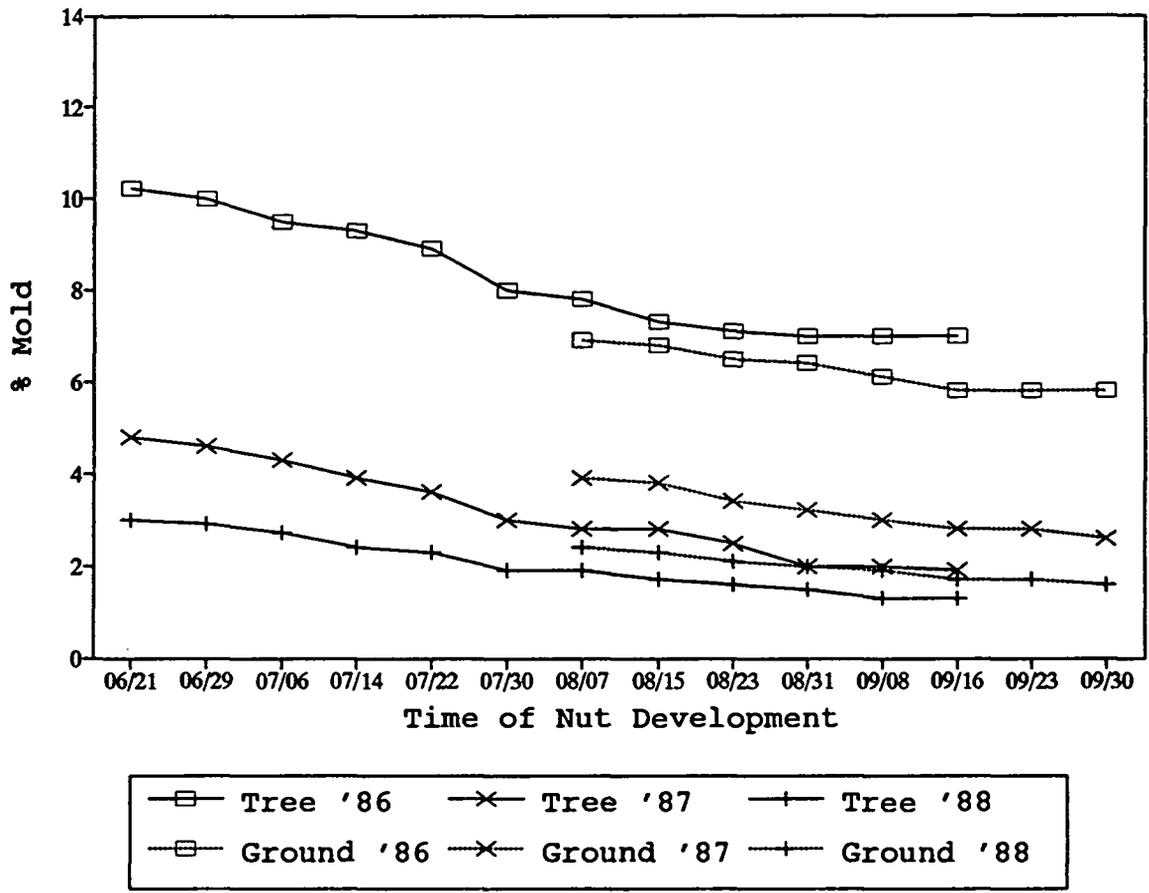


Fig. 3.3. " Ennis" kernel seasonal mold incidence for 1986, 1987, and 1988.

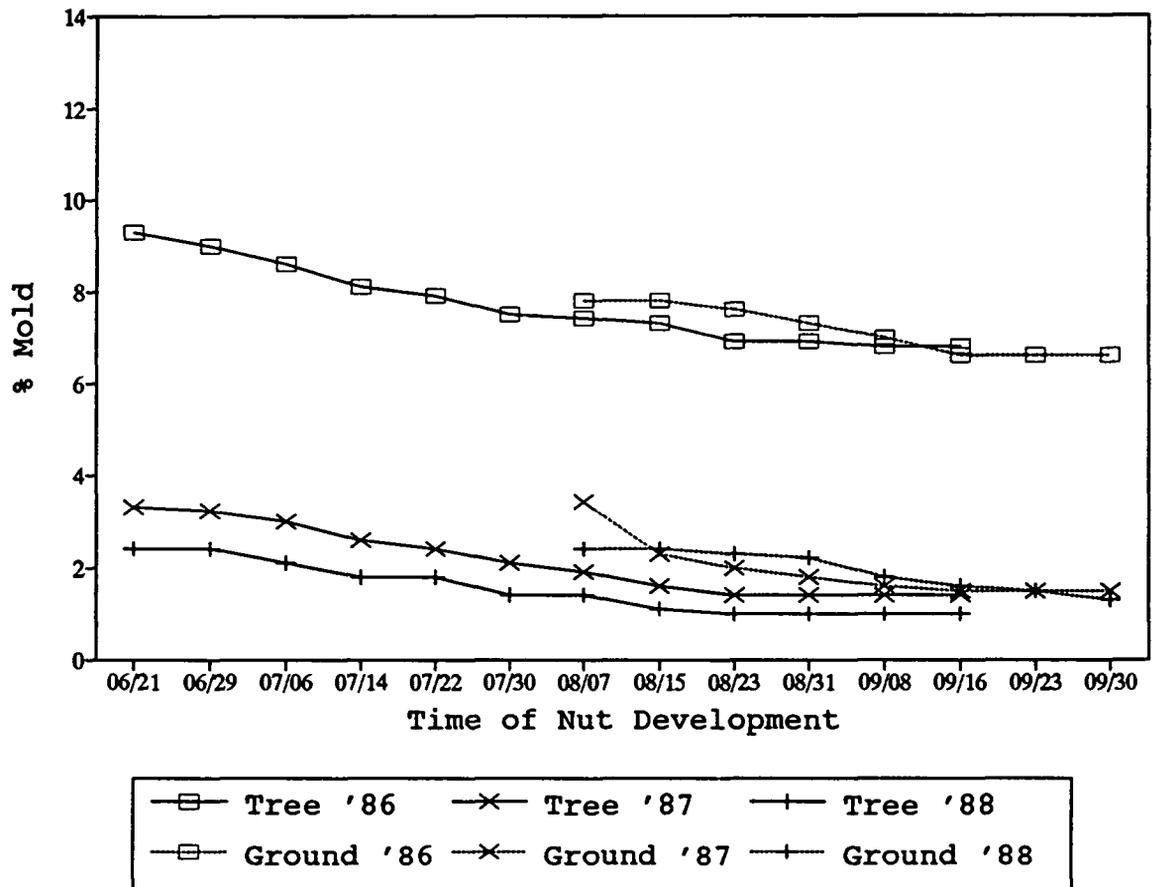


Fig. 3.4. Percent of mold during the growing season for Barcelona, Daviana, and Ennis, 1986.

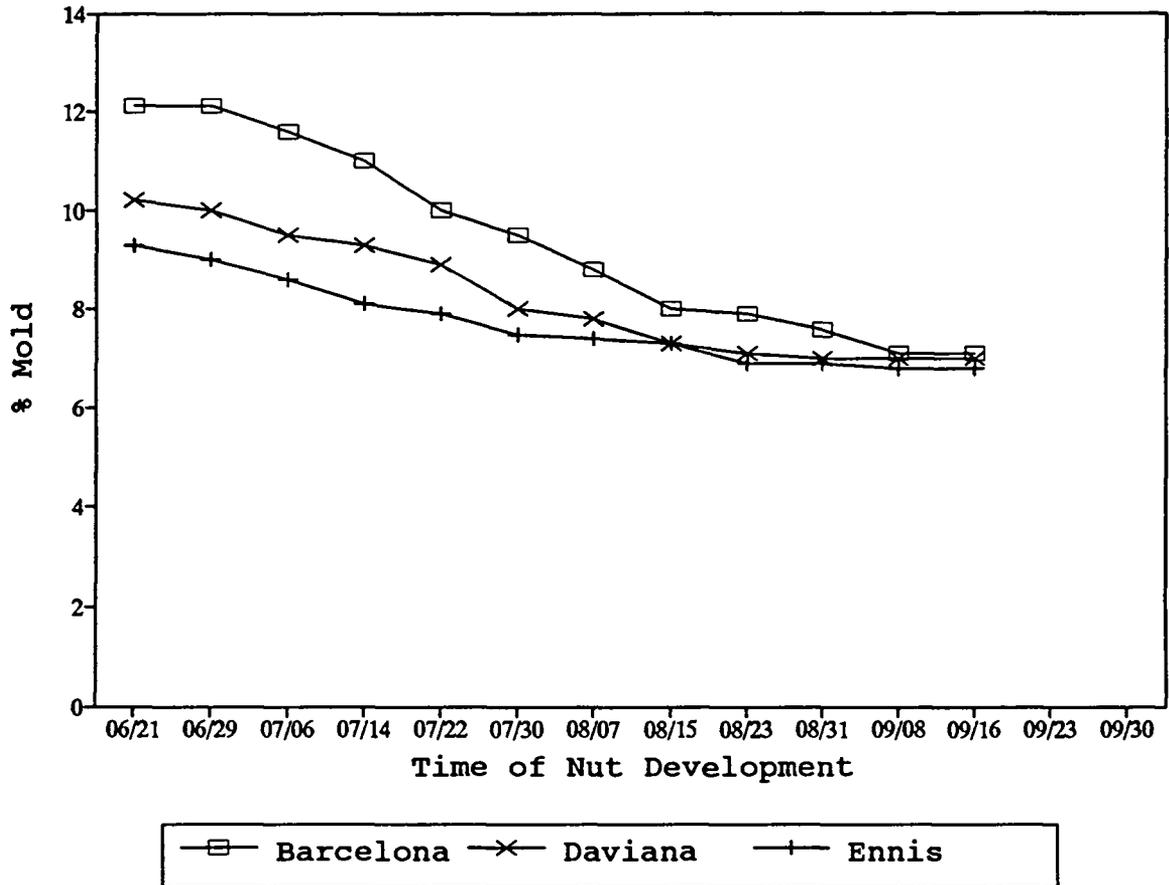


Fig. 3.5. Percent of mold during the growing season for Barcelona, Daviana, and Ennis, 1987.

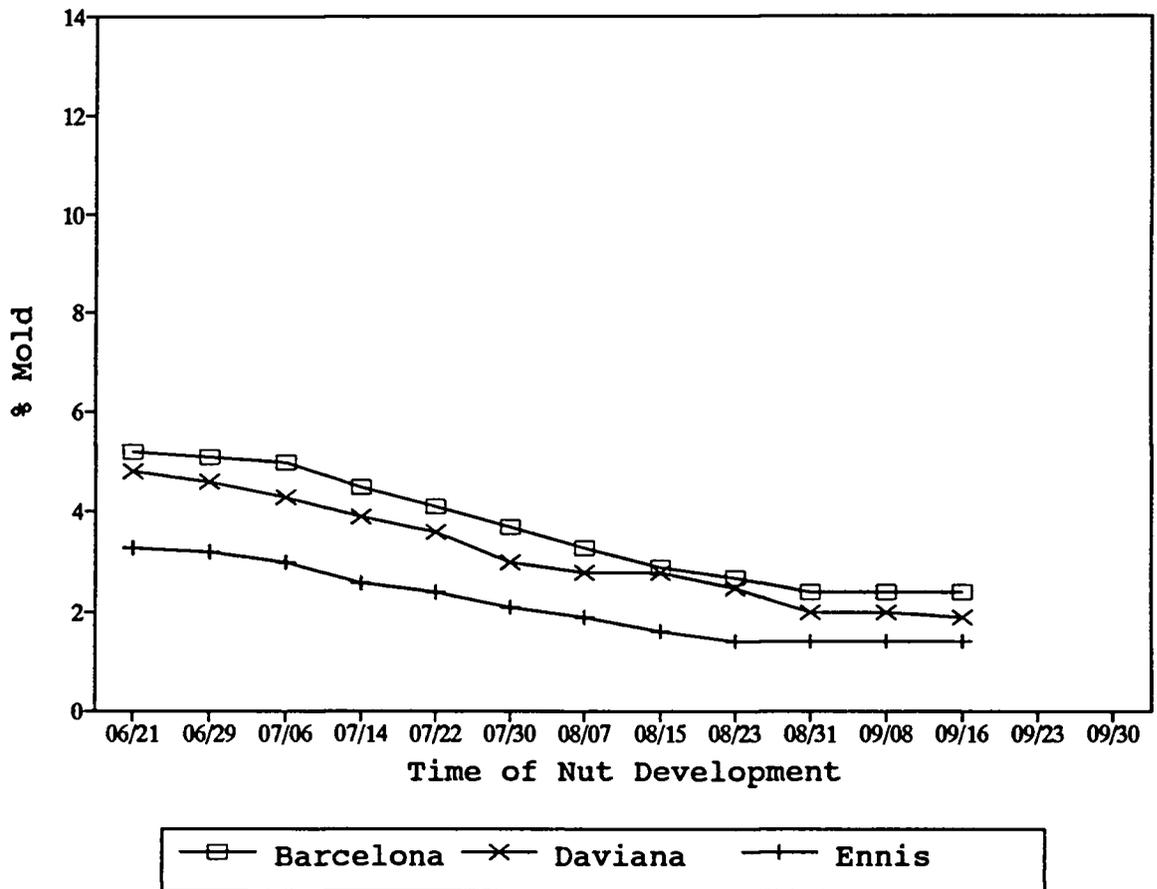
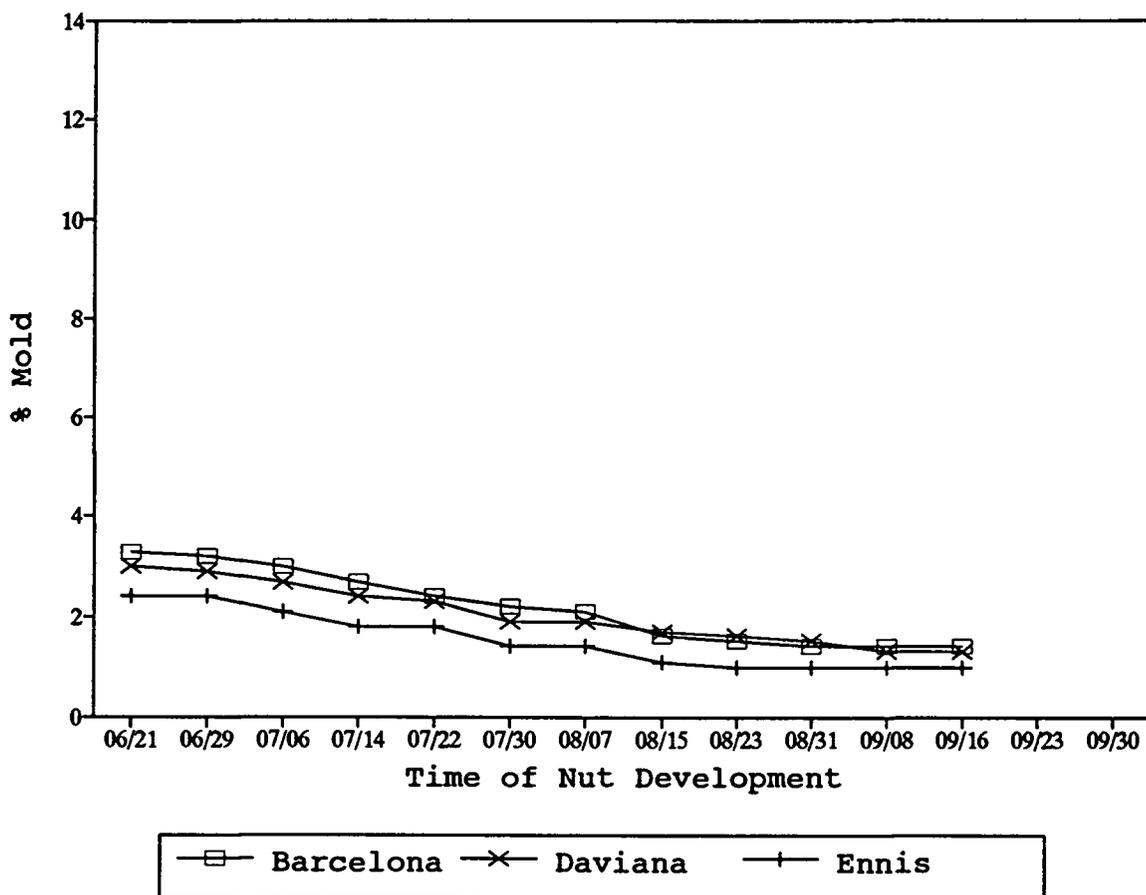


Fig. 3.6. Percent of mold during the growing season for Barcelona, Daviana, and Ennis, 1988.



**Chapter 4** Changes in oil content, fatty acid, and vitamin E composition in developing hazelnut kernels.

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Additional index words: Hazelnuts, Corylus avallana, fatty acids, oil content, tocopherol, vitamin E.

**Abstract**

Samples were collected from seven different hazelnut varieties: Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli. Hazelnuts exhibit a sigmoidal development pattern and there were two important periods in nut development. The period of growth and enlargement of the shell and the period of filling of the nut by the kernel which begins at the time of shell hardening.

Kernel oil content increased while moisture content decreased during development. Oil concentration was between 59.6% and 67%, at harvest and the major lipid class was triglycerides. The fatty acids comprising the triglycerides showed some interesting seasonal patterns. Oleic acid increased from 10% to become the most abundant fatty acid at harvest (74%). Linolenic acid content was high (up to 40%) at the beginning of growth but then decreased to about 1% by the end of the season. Linoleic increased from about 4% to around 30% early in the season but then decreased although it finally represented a high proportion of total fatty acids (between 19-22%).

Total vitamin E increased as oil content increased.  $\alpha$ -tocopherol was the major form of vitamin E and its concentration increased to around  $400\mu\text{g/g}$  oil throughout the season and was almost 95% of total vitamin E.  $\delta$ -tocopherol was high at the beginning and decreased until there was none.  $\beta$ -tocopherol was only a minor constituent and decreased from the beginning to around  $10\text{-}20\ \mu\text{g/gm}$  of oil at the end.  $\Gamma$ -tocopherol increased during the first stage of growth and then decreased during the second and third stages. The amount of  $\Gamma$ -tocopherol differed among the cultivars. The pattern of  $\alpha$ -tocopherol synthesis implies progressive methylation during development.

## Introduction

There have been studies on the seasonal formation of oil in pecans (Finch and Van horn, 1936; Thor and Smith, 1935; Boone, 1924), macadamias (Cheel and Morrison, 1935; Jones and Shaw, 1943; Jones, 1937,1939; Hartung and Storey, 1939), almonds (Munshi et al., 1983; Munshi and Sukhija, 1984; Soler et al., 1988) walnuts (Greve et al., 1992), and chestnuts (Berry, 1982).

While information has been published concerning the fatty acid composition of most tree nuts, it is sometimes difficult to compare data from various sources because of a lack of uniformity of analytical techniques used for quantitation. Information about vitamin E content is available only for some tree nuts.

Changes in agronomic practices and the introduction of new cultivars in recent years have been shown to affect tree nut composition. For example, Tkhayushev et al (1971), demonstrated that irrigation retarded oleic acid synthesis in hazelnuts and reduced its proportion at all stages of ripening. Heaton et al (1966) showed that nitrogen application to pecan trees caused oleic acid to decrease and linoleic acid to increase in the kernels. Heaton et al (1977) reported that variations in fatty acid composition of pecan nuts were mainly associated with cultivar and year of production while Shokraii (1977) showed that fatty acid composition of pistachio nuts was cultivar dependent. Fatty

acid profiles in macadamia nuts vary according to species (Salaeb, et al, 1973). These variations in fatty acid composition may influence the nutritional value and storage stability of tree nuts. The geographic locations where hazelnuts are grown and environmental factors such as temperature and season have significant influences on fatty acid and vitamin E composition. Low environmental temperatures stimulate desaturation activity and consequently increase the linoleic and linolenic acid content.

Variety, climate, and maturity stages are cited as factors affecting the relative fatty acid composition. Extensive investigations on complete chemical composition of ripe almonds including oil, were previously carried out by Saura et al (1985). The vitamin E content of cereal grains is also affected by such factors as the time of harvest, the weather, drying, handling, storage methods, and the length of storage (Kivimae, 1973). The moisture content of stored grain appears to be one of the most critical factors affecting the level of vitamin E in the grain.

The concentration of alpha-tocopherol in grasses generally decreases as development approaches seed maturity. The level in alfalfa and timothy falls some 20 to 65% depending on whether the crop is harvested at the grass stage or at the full-flowering stage. Decreases from 79 to 90% have been reported in different grasses covering the early to late maturity stages (Brown, 1952, 1953, Booth, 1963, 1964, and

Buck, 1968). Much rain and humidity during harvest causes substantial damage to the grain. This results in reduced germination and is associated with increased peroxide content and lowered tocopherol content.

Plant genetics variably influences the tocopherol level of plants. With different cultivars of white, red, and yellow corn, Combs and Combs, Jr (1985) showed that the total tocopherol varied about 10% within the cultivars and about 30% overall. Hazelnut breeders are working to produce new varieties which have eastern filbert blight resistance, increased yields, and shorter maturation times. Introduced with some of these improvements may be other genetic changes which effect the nutrient value of the hazelnut in positive or negative ways.

No research has been undertaken on the biochemical changes occurring during kernel development of hazelnuts. The objective of this work was to examine the changes in moisture content, size, oil content, fatty acid composition, vitamin E content, and vitamin E composition of seven cultivars of hazelnut during development and maturity.

### Material and Methods

Hazelnut trees of Barcelona, Daviana, and Ennis were sampled to represent American varieties. Tombul and Tombul Ghiaghli represented Turkish varieties. Tonda Romana and Tonda Gentile delle Langhe are Italian varieties. These varieties were selected for normal health and dense foliage from the hazelnut orchard of the Horticulture Department, Oregon State University, Corvallis, Oregon. The developing fruits were collected in 1987 and 1988 from the beginning of season in May until the nuts started dropping on the ground. The fruits were collected in the morning every week in polyethylene bags placed in an ice box and immediately brought to the laboratory. The date of fruit set (time 0) was considered to be the point when the fruits weighed 0.013 gm.

The first four weeks (May 22 to June 20), the measurements were done only on the whole nuts because the kernels had not started to develop. After that, the measurements were done on both whole nuts and kernels.

The physical characters measured included weight, length, width from both sides, and color changes. The whole nuts (husk and nut), nuts alone and the kernels were weighed separately. The dimensional characters of the nuts and the kernels were also recorded by direct measurement. Kernels were cut into slices 0.2 to 0.3 mm thick and each sample was divided into three parts for dry matter estimation, general lipid analysis and vitamin E analysis. Each sample comprised

three replicates.

## Lipid Extraction and Analysis

### Oil Content

#### Hexane Extraction Method

##### Procedure

Three grams of the ground sample were put into a test tube and blended at high speed in a Brinkmann Polytron tissue homogenizer with ten ml of hexane. The test tube was kept in a beaker with ice to keep the solution cool while the homogenizer was running. Then the material was centrifuged, the hexane drawn off and saved, and another ten ml of hexane was added and the procedure was repeated twice. The three extracts were combined and transferred to a tared 50-100 ml round-bottom boiling flask. The solvent was removed under vacuum in a rotary evaporator (40°C, 100 mm Hg), the weight was determined, and the oil was dissolved in a small volume of hexane, transferred to a screw cap glass vial, sealed under N<sub>2</sub> and stored at -5°C until analyzed for fatty acids.

wt of lipid (g)

percent oil content =  $\frac{\text{wt of lipid (g)}}{\text{wt of nut sample (g)}} \times 100$  (100)

wt of nut sample (g)

#### Chloroform-Methanol Method

The lipids in the hazelnut kernels were extracted and quantitated by the procedures of Folch et al (1957). Duplicate 10 gm kernel samples were blended at high speed in a Brinkmann

Polytron tissue homogenizer with chloroform methanol (2:1 V\|V) in a solvent to kernel ratio of 20:1 (w/v). Each macerate was quantitatively transferred to a Buchner funnel and vacuum filtered through #2 Whatman filter paper. The residue was washed with two 20 ml portions of solvent. The filtered volume was determined, and an aqueous solution of 0.88% KCl was added equal to one quarter of the extract volume. After thorough mixing and separation of the two phases, the top aqueous phase was removed by aspiration and discarded. The bottom phase (chloroform) was washed twice with two 20 ml portions of chloroform-methanol water (3:47:48 V/V), and the top phases were removed with aspiration. The solvent was removed under vacuum in a rotary evaporator (40°C, 100 mm Hg), the weight was determined, and the oil was transferred to a screw cap glass vial and stored under nitrogen at -5 C until the samples were analyzed for fatty acids.

#### Fatty Acids

For the fatty acid analysis the sample tubes were brought to a volume of 10 ml under nitrogen. Four ml of the total lipid extract were evaporated in a nitrogen stream to dryness, dissolved in 2 ml hexane and then 2 ml 14% BF<sub>3</sub>/ methanol (Pierce Chem. Co.) and 1 ml of internal fatty acid standard (21:0) was added to the tubes which were then tightly capped and gently refluxed in a heater block for 30 min. After cooling, 2 ml of deionized water was added to stop the reaction. The fatty acid methyl esters were recovered in the

hexane phase, transferred to a test tube, then evaporated to dryness under a nitrogen stream and dissolved in 0.5 ml of methylene chloride. Three  $\mu$ l of this extract were injected into a F&M model 810 gas chromatograph equipped with FID detector and a 2 meter x 4mm O.D. stainless steel column packed with 3% SP 2310 / 2% SP 2300 on 100/200 mesh chromosorb WAW (Supelco), run isothermally at 190 C and N<sub>2</sub> carrier flow rate of 30 ml/min. The individual fatty acid methyl esters were identified by their retention times compared to authentic standards (Supelco).

An aliquot of lipids extracted in hexane were evaporated to determine the oil content (%), while another aliquot was subjected to fatty acid analysis by converting fatty acids into their methyl esters (Metcalf and Schmitz, 1961). The esters were analyzed using gas chromatography. The peaks were identified by comparison of their retention time with those of standard fatty acyl esters. Another aliquot was subjected to vitamin E analysis by HPLC.

#### Methanolic-KOH

Formation of fatty acid methyl esters from hazelnut oil.

#### Reagents:

0.1 M KOH (0.56 grams in anhydrous methanol), diethyl ether, hexane, and 0.15 M HCl.

#### Procedure:

1. Place 10 - 100 mg lipid sample added to screw cap vials
2. Add 3.0 ml diethyl ether

3. Add 3.0 ml basic methanol
4. Place screw cap on tightly
5. Heat 50°C for 5 min
6. Cool
7. Add 3.0 ml 0.15 N HCl
8. Add 3.0 ml hexane
9. Remove epiphase to a clean tube
10. Re-extract lower phase with 3.0 ml 1:1 hexane:ether
11. Remove epiphase and pool with other hexane extract
12. Evaporate hexane under N<sub>2</sub> to concentrate fatty acid methylesters.
13. Take up in solvent for injection
- 14, Add 1 ml methylene chloride CH<sub>2</sub>Cl<sub>2</sub>

Note: One drop hazelnut oil is about 15 mg (from Pasteur pipette)

Take up to 2.0 ml with CH<sub>2</sub>Cl<sub>2</sub>, inject 3 micromiliter.

#### Tocopherol Analysis

Tocopherol determination was done on hazelnut kernel samples which were ground in a coffee grinder. Approximately three grams of ground material was put in a test tube and blended at high speed in a Brinkmann polytron tissue homogenizer with ten ml of hexane. The test tube was kept in a beaker with ice to keep the solution cool while the homogenizer was running. Then the material was centrifuged, the hexane drawn off, and another 10 ml of hexane was added and the procedure was repeated twice. The three X 10mL

extracts were then combined and transferred to a small round-bottom flask. The solvent was removed under vacuum in a rotary evaporator (40°C). The sample preparation for the analysis by HPLC was achieved simply by dissolving the sample in hexane (0.1 gm lipid in 10 ml hexane). The direct analysis of unsaponified oils avoids the destruction of tocopherols and tocotrienols that has been reported by other researchers (Shen and Sheppard, 1980, Speek et al., 1985, Rammell and Hogenboom, 1985, Piironen et al., 1986, Hadansson et al., 1987, Ball, 1988, and Guzman and Murphy, 1986).

DL-alpha-tocopherol acetate was obtained from Sigma (St. Louis, Mo). Samples were separated on a Beckman model 334 HPLC equipped with a Beckman model 110A pump. The HPLC column was a Lichrosorb Si-60 (250 x 4.6 mm), eluted isocratically with degassed hexane/isopropyl alcohol (99:1, V/V) at a flow rate 1 ml/min (Hadanson, et al, 1987). A Hot Bath model Haake FE and water jacket were used to maintain HPLC column temperature at 40°C, and with a 20mL sample injection  $\mu$ L loop. Detection was achieved with Hitachi model (100-10) spectrophotometer. Absorbance was measured at 295 nm and the Chromatogram recorded with a Shimadzu chromatopac C-R3A integrator.

The quantities of the various tocopherols and tocotrienols were calculated from peak areas using  $\mu$ g standards of DL-alpha- tocopherol acetate. The standards were obtained from Sigma, St. Louis, Mo. Alpha and  $\beta$ - tocotrienol

were not available, but were quantified using the corresponding tocopherol standards, as these give the same molar response (Thompson and Hatina, 1979).  $\beta$ -tocotrienol was tentatively identified in the samples by reference to published data on its natural occurrence (McLaughlin and Weihrauch, 1979; Piironen et al, 1986).

At the end of each day, methanol was pumped through the HPLC column for two hours, in order to remove triglycerides and any other absorbed components. After this washing step, pumping the mobile phase through the column for one hour was found adequate for re-equilibration before resuming injection of samples.

#### Standard Curve of D-Alpha-Tocopherol

1. 20.8 mg of 67% D-alpha-tocopherol was diluted in 13.95 ml hexane = 1 mg/ml. This dilution in hexane was diluted to give 1.0, 0.9, ... 0.01 mg/ of  $\alpha$ -tocopherol per ml.

Standard Curve  $y = 106.95 + 124519.59x$

Standard curve is shown in Appendix fig. A.4.

#### Moisture Content

##### 1. AOAC Method

Moisture content of hazelnuts was determined by the official methods of analysis of the Association of Official Chemists (A.O.A.C., 1975).

##### Procedure

The sample was ground in a coffee grinder, and approximately five grams of ground material was put into a

pre-weighed bottle and dried to a constant weight at 90-100°C in a vacuum oven, with the vacuum not exceeding 100 mm Hg (approximately ten hours) and then cooled in a desiccator and weighed. The moisture content was determined with the following calculations:

$$\text{percent moisture} = \frac{\text{loss in weight}}{\text{weight of sample}} \times (100)$$

## Results

### Development of nuts

Hazelnuts exhibit a sigmoidal growth pattern and three different periods of development can be observed in whole nut and kernel development. Fig. 4.1 shows the development of whole nuts and kernels for two years, 1987 and 1988. Each one of these curves is a mean of the seven varieties (Ennis, Barcelona, Daviana, Tombul Ghiaghli, Tombul, Tonda Romana, and TGDL). The first period (stage 1) was from May 22 to June 20, 0-5 weeks after nut development (WAND), the second period was from June 20 to August 22, 5-12 WAND (stage 2), the third period was from August 22 to the end of the season, 14-18 WAND (stage 3).

Fig. 4.1 and Appendix Fig. A.2 show the average kernel growth curves for 1987 and 1988. Again, these curves are the mean of seven varieties. The first period is for the first three weeks from June 20 to July 7, 0-7 weeks after nut development (WAND) (stage 1). The second period is from July 7 to August 29, 8-14 WAND (stage 2), and the third period is from August 29 to the end of the season, 15-18 WAND (stage 3). The first and third periods are slow growing compared to the second period which is fast growing. It is during this second period that most of the accumulation and changes in composition takes place.

Fig. 4.2 shows varieties from Turkey (Tombul and Tombul Ghiaghli), Italy (Tonda Romana and Tonda Gentile delle

Langhe), and America (Barcelona, Ennis, and Daviana). These varieties show somewhat different periods of development in whole nuts. The Turkish variety curve is the mean of two cultivars, Tombul and Tombul Ghiaghli. The Italian variety curve is also the mean of two cultivars, Tonda Romana and TGDL. The American variety curve is the mean of three cultivars, Ennis, Barcelona, and Daviana.

Fig. 4.3 shows kernel development in the same cultivars as Appendix Fig. A.2. In both developing nuts and kernels, American varieties are the biggest and Turkish varieties are the smallest. American varieties, whole nuts reach 8 grams and kernels 2.9 grams fresh weight.

#### Moisture Content

Fig. 4.4 shows the moisture content of whole nuts, husks, and kernels and are the means of different varieties for 1987 and 1988. The percent of moisture decreased from 90% for the whole nut at the beginning of the season to 50% at the end of the season followed by further drying once nuts fall to the ground. Whole nuts included the kernel, nut shell, and the husk. For the kernel only, the moisture dropped from 88% to 36% and for the husk from 80% to 44%. These changes were essentially the same in both years.

Fig. 4.5 shows the changes in moisture content, oil content, and residue and it will be noted that moisture content decreased as oil content and residue (to a lesser extent) increased.

### Physical characteristics

There were two main stages of development during this study, which began in May 1987 and 1988 to the end of the season, which varied between varieties.

The first stage was devoted to developing the shell, husk, and the spongy material inside the shell, forming almost 85% of the final size and weight of the hazelnut. During this period the husk began growing and covering the shell, and the color was green at the beginning. Before the kernel developed, the shell began to harden which parallels what happens in the stone fruits. The color of the shell was green at the beginning of growth and progressively became yellowish. During the first five weeks of development (before kernel development) the shell was very soft and easy to cut or break.

The kernel began developing during the second period. At the beginning of development the kernel was very small and creamy white in color and was embedded in the spongy material. The size of the kernel increased rapidly and by eight weeks into the second period had reached its final size, which filled the whole space of the shell. The spongy material started to disappear and the kernel began to harden, and a space developed between the shell and the kernel. But before the kernel hardened, it was soft and the pellicle was easy to separate. As the season progressed the pellicle became more firmly attached to the kernel. The color of the shell changed to brown and the shell began to harden. For most varieties,

the husk was completely separated from the nut when nuts started to drop to the ground, but in some varieties such as Tombul and Tombul Ghiaghli the nut did not fall free of the husk.

Fig. 4.6 shows general length to width ratio (L/W) for 1987 and 1988, for whole nuts. In both years the pattern was the same with only small differences. L/W increased at the beginning and then was steady after the middle of the season.

Fig 4.4 shows the L/W ratio for kernels only for 1987 and 1988. Each data point (whole nut and kernel) is the mean of seven varieties. It was almost the same pattern as in whole nut development. Kernel L/W increased at the beginning of the season and then was steady during the remainder of the season.

Kernel fresh weight increased from 0.06 gm to 3.8 gm and whole nuts from 0.02 gm to 8.16 gm. The width increased from 0.22 to 1.4 cm and the length increased from 0.22 to 1.6 cm.

#### Kernel Oil Concentration and Fatty Acid Composition

The changes in oil concentration (percent fresh weight) of developing hazelnut kernels were consistent over the two years studied, as shown in Fig. 4.5. Oil was only 3.5% at the beginning of development in the kernels (the third week of June) and rose to 57.3% at harvest (the beginning of October). The final values were similar for both years (1987, 1988). The rate of accumulation was also similar, although some differences were observed during 1987, probably due to the exceptional climatic conditions.

There were varietal differences in oil percent at the end of the season. Table 4.1 shows percent oil for seven varieties. The highest oil contents were found in the Turkish varieties such as Tombul Ghiaghli (61.9%) and the lowest was found in Daviana (54.5%).

### Fatty Acids

At the beginning of the growing season unsaturated fatty acids were high, especially essential fatty acids such as linolenic acid (18:3). 18:3 was high (about 40%) during the first three weeks and then decreased steadily to about 1% at harvest. The decrease in 18:3 paralleled the loss of chlorophyll tissues as has been reported several times before. Linoleic acid (18:2) increased during the first period of kernel development and peaked at about 30% in the second period and then decreased to a constant 25% in the third period (Figs. 4.7 and 4.8). The percent of linoleic acid was high compared to linolenic acid (18:3). Oleic acid (18:1) steadily increased from 10% in the first period and almost levelled at 75% in the third period, with most of the oleic acid accumulating during the second period. Palmitoleic acid (16:1) was detected only in the beginning of the season and then disappeared at the second stage of development.

Saturated fatty acids were lauric, myristic, palmitic, stearic, and arachidic acid. Some of these, such as lauric, myristic, and arachidic, disappeared a few weeks into the growing season. Palmitic decreased from initially 20% to 5.3%

at the end of the third stage.

Figs. 4.9 and 4.10 show changes in fatty acid composition in American varieties, for 1987 and 1988. Oleic acid increased more during the second stage in 1987 than in 1988. However, at the end of the season the percentages were very close. Linoleic was higher in 1987 than in 1988. All other fatty acids were similar. Figs. 4.11 and 4.12 show changes in fatty acid composition for Italian varieties for 1987 and 1988. Oleic acid was higher in 1988 than in 1987. Linoleic was higher in 1987 and began decreasing after the sixth week, but in 1988 it began decreasing after the fifth week. Figs. 4.13 and 4.14 show changes in fatty acid composition for Turkish varieties for 1987 and 1988. Oleic acid was the same in both years. Linoleic acid was higher in 1987 during the first stage of growth and began decreasing after the sixth week.

Fig. 4.15 plots the ratio of unsaturated/saturated fatty acid  $[(18:1 + 18:2 + 18:3) \div (14:0 + 16:0 + 18:0)]$  for 1987 and 1988. The unsat/sat ratio increased from the beginning to the end of the season. Appendix Fig. A.3 shows oleic acid (18:1) increasing for three groups for two years (1987 and 1988). American varieties have high percentages of oleic acid, especially in 1987 which was higher than 1988. Italian and Turkish varieties were similar to each other.

### Vitamin E

Figs. 4.16 and 4.17 shows total vitamin E (tocopherol)

concentration during the growing season for 1987 and 1988. Vitamin E increased in the same pattern as oil (and 18:1) increased. It slowly increased in the first period of kernel growth, and there were some small changes during the third period. Most of the increases and accumulations took place during the second stage. Total tocopherol differed among varieties (Table 4.1). The highest concentration was found in Tombul (498  $\mu\text{g}/\text{gm}$  oil) and the lowest was Daviana (359  $\mu\text{g}/\text{g}$  oil).

$\alpha$ -tocopherol was the main form (95%) of vitamin E in hazelnuts and was the only one increasing during the growing season.  $\sigma$ -tocopherol was high in the beginning of the season and then started decreasing and disappeared during the third stage.  $\beta$ -tocopherol decreased during the growing season, but at the end was measurable in all varieties at different concentrations.  $\Gamma$ -tocopherol increased in the first stage of development until the fifth week and then it started decreasing, but in most varieties the concentrations were higher than  $\beta$ -tocopherol.

Figs. 4.18 - 4.23 show changes in vitamin E concentrations and vitamin E composition during 1987 and 1988 for American, Italian, and Turkish varieties. Turkish varieties started with high concentrations and remained at high concentrations. There are individual figures for each variety in the appendix, chapter IX.

### Extraction Methods

Table 4.2 shows oil percent, vitamin E composition, and total vitamin E for two methods of extraction. From the data there were no significant differences between the methods. Hexane extraction was easier, less hazardous, faster, and just as efficient as the chloroform-methanol extraction method.

### Weather

Appendix Figs. A.5 - A.12 show the mean (low and high) temperatures for June through September, 1987 and 1988. There were no big differences between the two years during most days. Low temperatures during the night may have resulted in increases of unsaturated fatty acids. The average June temperatures in 1987 were higher than June of 1988. August temperatures were about the same in 1987 and 1988. Average September temperatures were a little warmer in 1987 than in 1988.

## Discussion

Fig. 4.6 shows that there is an inverse relationship between moisture content and oil percent. The moisture content decreased as the oil content increased, most of this took place during the second stage of development. Dry residue was slow during the first stage and then accelerated to a fairly constant rate during the second stage and then slowed in the third stage. A similar trend was found in almonds (Munshi and Sukhija, 1984; Soler et al., 1988), Black walnut, McLeanahan, 1959, corn (Leng, 1967; Curtis et al., 1988; Doehlert and Lambert, 1991; Vereshagin, 1991), soybeans (Rubel, 1972) and oats (Brown et al., 1970).

It is known that in oil seeds, phospholipids and glycolipids are biosynthesized first. Later at an intermediate stage, the triacylglycerides begin to accumulate, a lipid class that represents about 95% of oil in mature fruits (seeds), (Munshi et al, 1983; Privett, 1973), and the same was found in avocados (Gaydou et al., 1987; Lozano et al., 1992).

Oil composition changes during the three stages of hazelnut development. The first stage is characterized by higher concentrations of saturated and essential fatty acids, especially linolenic. During the second stage, the percentage of these fatty acids decreased, whereas oleic acid increased. At the end of stage three, linolenic and arachidic acids practically disappear, coinciding with the time when complete

physical growth of the kernel has taken place (maximum weight and size). The same thing has been reported with almonds (Prunus amygdalus) (Munshi et al., 1983; Munshi and Sukhija, 1984).

High initial concentrations of palmitic, linoleic, and linolenic acids may be related to their incorporation into polar lipids, the main constituents at the beginning, and with the formation of cell membranes. Later, phospholipid and glycolipid content progressively decreases and triacylglyceride accumulation becomes the dominant feature of lipid synthesis.

After the first stage, oleic acid is the main constituent of triglycerides, and it increases continuously until harvest. The inverse relationship of oleic and linoleic acids observed from the third week (WAND) seems to indicate that the oleic acid content generally increases without conversion to linoleic acid.

During the growth of the kernels the contents of saturated fatty acids decrease, final values being one-third of the initial values, whereas, the unsaturated fatty acids accumulate so that the proportion of unsaturated/saturated fatty acids increases considerably. At the end, oleic acid and linoleic acid make up 90% or more of total fatty acids which is expected in most higher plant tissues, such as safflower seeds and olives (Fedeli, 1977; Harwood 1980, 1983, and 1988).

The ratio of these acids to one another is important to the economic value of the nut. Low linoleic and linolenic acid content might improve the shelf life, but a higher linoleic acid content might be nutritionally desirable. It is not known how these might affect flavor compared to other constituents of nuts such as pyrazines.

Three factors were found to influence the final oil content and fatty acid distribution of the oil in nuts. The first was the duration of synthesis for oil and fatty acids. The time from start to finish of active synthesis of oil and fatty acids varied from one variety to another. For example 'Ennis' continued linoleic accumulation longer than did the other two American varieties (Barcelona and Daviana).

Second, some fatty acids that had accumulated early in development were apparently metabolized later. Also, it is possible that conversion to other fatty acids might occur and thus contribute to selective decreases in some oil components.

Third, the rates of accumulation should be influenced primarily by types of enzymes and activities catalyzing the various synthetic processes. Enzymes for fatty acid synthesis have been affected by temperature in soybean (Thompson, 1986; Cheesbrough, 1989).

Palmitic and stearic acids, on the basis of chemical structures, are intermediates in the synthesis of oleic acid. Oleic acid normally would then be converted to linoleic acid, then to linolenic acid via desaturase enzymes. In 1987

hazelnuts had slightly more 18:2 and slightly less 18:1 than in 1988. The differences in 18:2 seemed to be induced during the month of July, when oil content began to increase. The cooler temperature in July 1987 vs. July 1988 may have had important initiation effects. Some recent research by Sanchez and Mancha (Instituto de la Grasa, Seville) on olive fatty acid synthetase and oleate desaturase, shows that from the time of oil synthesis there are quite strong temperature influences on fatty acid composition (Garces et al., 1992).

Studies show that the growth and development of soybean seeds is dependent upon the translocation of photosynthate from leaves to the developing seeds. The primary form of translocated photosynthate is sucrose. Sucrose metabolism by the developing soybean seed plays a major role in the synthesis of protein and oil, the major storage components (Smith et al, 1989).

The mode of control of the relative proportions of oleic, linoleic, and linolenic acids in oilseeds differs among species and is influenced by temperature. In safflower, the oleic and linoleic acid percentages are entirely under genetic control of the seed embryo. However, in soybeans the level of oleic, linoleic, and linolenic acids are essentially controlled by the genotype of the maternal plant with minor contribution from the genotype of the embryo (Appelquist et al, 1975, 1980; Robertson et al, 1985). Lajarae et al (1990) reported that oil quality of sunflower seeds was under

genetic control and that breeding for different levels of oleic and linoleic acid is a practical objective. However, evidence indicates that the unsaturation of sunflower oil depends largely upon the environmental temperature during maturation of the seed (Lajara et al., 1990). Harris and James (1968) concluded that an increase in the level of linoleic acid in sunflower seed at low temperatures was due to increased availability of  $O_2$  for the desaturation steps. Since then, other studies have shown that low temperature by itself has direct effects on fatty acid composition.

From the data on hazelnut kernel vitamin E (Figs. 4.20 - 4.27) we can see that  $\alpha$ -tocopherol (the dominant form) increases during the growing season and all other forms of vitamin E decreased. This is likely due to conversion of other forms to  $\alpha$ -tocopherol by stepwise methylation.  $\delta$ -tocopherol (the least methylated form) was converted to the  $\Gamma$ -form by extra methylation and that was perhaps the reason for the increase in  $\Gamma$ -concentration during the first five weeks. It has been shown that lettuce chloroplasts are able to synthesize  $\alpha$ - and  $\Gamma$ - tocopherols by methylation (Marshall et al., 1985). Then  $\Gamma$ -concentration decreased in the same way that other forms decreased. This may be due to the conversion of  $\Gamma$ -tocopherol to  $\alpha$ -tocopherol, as was found in other plants (Zea mays L.) by Whistance and Threlfall, (1967 and 1968), Whistance et al., (1967), and Soll and Schultz (1980). We did not detect any tocotrienol and it may be that hazelnuts lack

this pathway to tocotrienol vitamin E using the Phytyl PP pathway (Pennock, 1976). Similar results were found in corn and Phaseolus (Pennock, et al., 1964).

The high initial concentration and subsequent decrease of  $\beta$ -tocopherol is consistent with the fact that  $\beta$ -tocopherol is a precursor of  $\alpha$ -tocopherol. This was shown to be the case for other plants such as Zea mays, Phaseolus aureus, and Picea abies (Wellburn, 1969, 1970; Franzen and Haab et al., 1991; Franzen et al., 1991).

An increase in the  $\alpha$ - form may be coupled with an increase in the oil concentration. It may be that there is a relationship between either the total amount of oil or some specific fatty acid components and the amount of vitamin E. There could also be a relationship between oil, dry matter and vitamin E content since all of them increase together. The total tocopherol concentration increased when the corn or soybean seed total oil content increased. Gutfinger and Letan (1975) studied the concentration and distribution of tocopherols in soybean, cottonseed, olive, avocado, and coconut oil. They found a direct positive correlation between total oil content and tocopherol concentration. It is hypothesized that seeds which synthesize higher amounts of oil also synthesize higher amounts of tocopherols to protect their lipids from oxidation (Brook and Sallany, 1978).

The patterns of tocopherols show variation among species. The balance between methylation and hydrogenation logically

must be under genetic regulation although no genetic analysis of tocopherol pattern has yet been presented. The relative importance of each may be important taxonomically. The non- $\alpha$ -tocopherols may be biosynthetic precursors of  $\alpha$ -tocopherol and may be synthesized outside the chloroplast and transported there only for the final methylation steps (Newton and Pennock, 1971).

The data for L/W shows that in American varieties the length of the nut is 1.3 cm larger than the width (.96 cm), and that this ratio can be observed as early as the fifth week of development. Turkish and Italian varieties have the same pattern but the L/W in Turkish was higher than in the Italian cultivars. The length in Turkish and Italian varieties were .79 cm and .83 cm width and .74 cm and .89 cm, respectively. Thus American varieties are generally longer in shape than Italian and Turkish.

During the development of nuts we saw that the first stage of growth of the whole nut was devoted to external parameters, such as the shell, husk, and spongy materials inside. This could be to provide enough protection for the kernel from environmental factors. The spongy material provides a bed for the developing kernel. The green color of the husk and shell may be used in photosynthesis for the kernel. The same thing was observed with pecans (Shuhart, 1927; Woodroof and Woodroof, 1927; Crane and Hardy, 1934; Thor and Smith, 1935; Finch and Vanhorn, 1936)

**Literature Cited**

- A.O.A.C. 1975. Twelfth Edition. W. Horwitz, ed. Washington DC:Assoc. Off. Anal. Chem.
- Applequist, L.A. 1975. Biochemical and structural aspects of storage and membrane lipids in developing oil seeds. In: Recent Advances in the Chemistry and Biochemistry of Plant Lipids, Galliard, T. and E.I. Mercer, Eds., Academic Press, London. pp.247.
- Applequist, L.A. 1986. Metabolism and control of lipid structure modification. Biochem Cell Biol. 64:66-69.
- Ball, G.F.M. 1988. Applications of HPLC to the determination of fat-soluble vitamins in foods and animal feeds. Micronutrient. 4:255-283.
- Berry, S. K. 1982. Fatty acid composition and cyclopropane fatty acid content of china-chestnuts. J. Amer. Oil Chem. Soc. 59: 57-58.
- Boone, P.D. 1924. Chemical constituents of pecan oil. J. Ind. and Eng. Chem. 16:54-55.
- Booth, V. H. 1963. Alpha-tocopherol, Its occurrence with chlorophyll. Phytochemistry. 2: 421-429.
- Booth, V. H. 1964. The Alpha-tocopherol content of forage crop. J. Sci. Fd. Agric. 15: 342-344.
- Brooks, R. I. and A. S. Csallany. 1978. Effect of air, ozone, and nitrogen dioxide exposure on the oxidation of corn and soybean lipids. J. Agric. Food Chem. 26:1203-1209.
- Brown, C.M., E.J. Weber, and C.M. Wilson. 1970. Lipid and amino acid composition of developing oats. Crop Science. 10:488-491.
- Brown, F.J. 1953. The tocopherol content of farm feed-stuffs. J. Sci. Food Agric. 4:161-165.
- Bucke, C. 1968. The distribution and stability of alpha-tocopherol in subcellular fractions of broad bean leaves. Phytochemistry 7: 693-700.
- Cheel, E. and F.R. Morrison. 1935. The cultivation and exploitation of the Australian nut (Macadamia ternifolia). Technol. Museum, Sydney, Australia, Bull. 20.

- Cheesbrough, T.M. 1989. Changes in the enzymes for fatty acid synthesis and desaturation during acclimation of developing soybean seeds to altered growth temperature. *Plant Physiology*. 90:760-764.
- Combs, S. B. and G. F. Combs, Jr. 1985. Varietal difference in the vitamin E content of corn. *J. Agric. Food Chem.* 33:815-817.
- Crane, H.L. and M.B. Hardy. 1934. Interrelations between cultural treatment of pecan trees, the size and degree of filling of the nuts, and the composition of kernels. *J. Agric. Res.* 49:643-661.
- Curtis, P.E., E.R. Leng, and R.H. Hageman. 1988. Developmental changes in oil and fatty acid content of maize strains varying in oil content. *Crop Science*. 8:689-693.
- Doehlert, D.C. and R.J. Lambert. 1991. Metabolic characteristics associated with starch, protein, and oil deposition in developing maize kernels. *Crop Science*. 31:151-157.
- Fedeli, E. 1977. Lipids of olives. *Prog. Chem. Fats and Other Lipids*. 15:57-74.
- Finch, A.H. and C.W. Van Horn. 1936. The physiology and control of pecan nut fulling and maturity. *Arizona Agric. Exp. Stat. Tech. Bull.* 62.
- Folch, J., M. Lees, and G.H. Sloane-Stanley. 1957. A simple method for the isolation and purification of total lipids from animal tissues. *J. Biol. Chem.* 226:497-509.
- Franzen, J. and M.M. Haab. 1991. Vitamin E content during development of some seedlings. *Hytochemistry*. 30:2911-2913.
- Franzen, J., J. Bausch, D. Glatzle, and E. Wagner. 1991. Distribution of vitamin E in spruce seedling and mature tree organs, and with the genus. *Phytochemistry*. 30:147-151.
- Garces, R., C. Sarmiento, and M. Mancha. 1992. Temperature regulatons of oleate desaturase in sunflower (*Helianthus annuus* L.) seeds. *Planta*. 11:461-465.
- Gaydou, E.M., Y. Lozano, and J. Ratovohery. 1987. Triglyceride and fatty acid compositions in the mesocarp of *Persea americana* during fruit development. *Phytochemistry*. 26:1595-1597.

- Greve, L.C., C. McGranahan, J. Hasey, R. Snyder, K. Kelly, D. Goldhamer, and J.M. Labavitch. 1992. Variation in polyunsaturated fatty acids composition of persian walnut. *J. Amer. Soc. Hort. Sci.* 117:518-522.
- Guzman, G.J., and P.A. Murphy. 1986. Tocopherol of soybean seeds and soybean curd (tofu). *J. Agric. Food Chem.* 34:791-795.
- Hadansson, B., M. Jagerstad, and R. Oste. 1987. Determination of vitamin E in wheat products by HPLC. *J. Micronutr. Anal.* 3:301-318.
- Harris R.V., A.T. James, and P. Harris. 1967. The effect of temperature on fatty acid synthesis in sunflower seeds. *Biochem. Chloroplast Proc.* 2:241-253.
- Hartung, M.E. and W.B. Storey. 1939. The development of the fruit of Macadamia ternifolia. *J. Agr. Res.* 59:397-406.
- Harwood, J.L. 1980. Fatty acid synthesis. In: *Biogenesis and Function of Plant Lipids*. Ed. P. Mazliak, P. Benveniste, C. Costes, R. Douce. Elsevier, Amsterdam. pp.143-152.
- Harwood, J.L. 1983. Adaptive changes in the lipids of higher plant membranes. *Biochem. Soc. Trans.* 11:343-346.
- Harwood, K.P. and H.J. Teede. 1988. Fatty acid metabolism. *Annu. Rev. Plant Physiol.* 39:101-103.
- Heaton, E.K., J.E. Marion, and J.G. Woodroof. 1966. Pecan oil is highly unsaturated. *Peanut J. Nutworld.* 45:36-38.
- Heaton, E.K., A.L. Shewfelt, A.E. Badenhop, and L.R. Beauchat. 1977. Pecan: Handling, storage, processing, and utilization. Univ. Georgia, Athens, Georgia, USA. *Agric. Res. Bull.* 197:77.
- Jones, W.W. 1937. The physiology of oil production in the macadamia. *Proc. Amer. Soc. Hort. Sci.* 35:239-245.
- Jones, W.W. 1939. A study of developmental changes in composition of the macadamia. *Plant Physiology.* 14:755-768.
- Jones, W.W. and L. Shaw. 1943. The process of oil formation and accumulation in the macadamia. *Plant Physiol.* 18:1-6.

- Kashani, G.G. and L.R.G. Valaden. 1983. Effect of salting and roasting on the lipids of Iranian pistachio kernels. *J. Food Technol.* 18: 461-467.
- Kiviamae, A. and C. Carpena. 1973. The level of vitamin E content is some conventional feeding stuffs and the effects of genetic variety, harvesting, processing, and storage. *Acta Agric. Scand. Suppl.* 19:161-168.
- Lajara, J.R., U. Diaz, and R.D. Quidiello. 1990. Definite influence of location and climatic conditions on the fatty acid composition of sunflower seed oil. *J. Amer. Oil Chem. Soc.* 67:618-623.
- Leng, E.R. 1967. Changes in weight, germ ratio, and oil content during kernel development in high oil corn. *Crop Sci.* 7:333-334.
- Lozano, Y.F., J.V. Ratovohery, and E.M. Gaydou. 1991. Compositional changes in triglycerides of avocado mesocarps associated with fruit development. *Lebensm. Wiss. U. Technol.* 24:46-52.
- Marshall, P.S., S.R. Morris, and D.R. Threlfall. 1985. Biosynthesis of tocopherol: A re-examination of the biosynthesis and metabolism of 2-methyl-6-phytyl-1, 4-benzoquinol. *Phytochemistry.* 24:1705-1711.
- McLaughlin, P.J. and J.L. Weihrauch. 1979. Vitamin E contents of foods. *J. Amer. Diet. Assoc.* 75:647-781.
- McLeanahan, F.M. 1959. The development of fat in the black walnut. *J. Amer. Oil Chem. Soc.* 31:1093-1098.
- Metcalf, L.D. and A.A. Schmitz. 1961. The rapid preparation of fatty acid esters for gas chromatography. *Anal. Chem.* 33:363-364.
- Munshi, S.K., P.S. Sukhija, and I.S. Bhatia. 1983. Lipid biosynthesis in developing kernels of almond, Prunus amygdalus. *Phytochemistry.* 22:79-83.
- Munshi, S.K. and P.S. Sukhija. 1984. Compositional and biosynthesis of lipids in the developing kernels of almonds (prunus amygdalus) *J. Sci. Food Agric.* 35:689-697.
- Newton, R.P. and J.F. Pennock. 1971. The intracellular distribution of tocopherol in plants. *Phytochemistry.* 10:2323-2328.

- Pennock, J. F., F. W. Flemming and J. D. Kerr. 1964. A reassessment of tocopherol chemistry. *Bioch. Biophys. Res. Comm.* 17:542-546.
- Piironen, V., E.L. Syvaaja, P. Varo, K. Salminen, and P. Koivistoinen. 1986. Tocopherols and tocotrienols in Finnish foods: Vegetables, fruits, and berries. *J. Agric. Food Chem.* 34:742-746.
- Privett, O.S., K.A. Dougherty, W.L. Erdahyl, and A. Stolyhwo. 1973. Studies on the lipid composition of developing soybeans. *J. Amer. Oil Chem. Soc.* 50:516-520.
- Rammell, C.G. and J.J.L. Hoogenboom. 1985. Separation of tocols by HPLC on an amino-cyano polar phase column. *Micro. Nutrient.* 8:707-717.
- Robertson, J.A., R.G. Roberts, and G.W. Chapman, Jr. 1985. Changes in oil type sunflower seed stored at 20°C at three moisture levels. *J. Amer. Oil Chem. Soc.* 62:1335-1339.
- Rubel, A., R.W. Rinne, and D.T. Canvin. 1972. Protein, oil, and fatty acid developing soybean seeds. *Crop Science.* 12:739-741.
- Saleeb, W.F., D.M. Yermanos, C.K. Huszar, W.B. Storey, and C.K. Labanauskas. 1973. The oil and protein in nuts of Macadamia tetraphylla L. Johnson, Macadamia integrifolia Maiden and Betche, and their F<sub>1</sub> hybrid. *J. Amer. Soc. Hort. Sci.* 98:453-456.
- Saura-Calixto, F., J. Canellas, and A. Garcia-Raso. 1985. Characteristics and fatty acid composition of almond tegument oil. Comparison with almond kernel oil. *Fette, Seifen, Anstrichm.* 87:4-6.
- Shen, C.S.J. and A.J. Sheppard. 1980. A rapid high-performance liquid chromatographic method of separating tocopherols. *J. of Micronutrient Anal.* 2:43-53.
- Shokraii, E.H. 1977. Chemical composition of the pistachio nuts of kerman, Iran. *J. Food Sci.* 43:244-246.
- Shuhart, E.V. 1927. Morphology and anatomy of the fruit of pecan. *Bot. Gaz.* 93:1-20.
- Smith, A.J., R.W. Rinne, and R.D. Seif. 1989. Phosphoenolpyruvate carboxylase and pyruvate kinase involvement in protein and oil biosynthesis during soybean seed development. *Crop Sci.* 29:349-353.

- Soler, L., J. Canellas, and F. Saura-Calixto. 1988. Oil content and fatty acid composition of developing almond seeds. *J. Agric. Food Chem.* 36:695-697.
- Soll, J. and G. Schultz. 1980. 2-methyl 6-phytylquinol and 2,3-dimethyl 5-phytylquinol as precursors of tocopherol synthesis in spinach chloroplast. 1980. *Phytochemistry.* 19:215-229.
- Speek, A.J., J. Schrijver, and W.H.P. Schreurs. 1985. Vitamin E composition of some seed oils as determined by high-performance liquid chromatography with fluorometric detection. *J. of Food Sci.* 50:121-124.
- Thompson, G.A. 1986. Metabolism and control of lipid structure modification. *Biochem. Cell Biol.* 64:66-69.
- Thompson, J.N. and G. Hatina. 1979. Determination of tocopherol and tocotrienols in foods and tissues by high performance liquid chromatography. *J. Liq. Chromatog.* 2:327-344.
- Thor, C.J.B. and C.L. Smith. 1935. A physiological study of seasonal changes in the composition of the pecan during fruit development. *J. Agr. Res.* 50:99-121.
- Tkhagushev, N.A., V.V. Grinenko, and Y.A. Merzhanian. 1971. *Izvestiy Vysshikh Uchebnykh Zavedenii Pishchevay Tekhnologiya.* 2:39-42.
- Vereshagin, A.G. 1991. Comparative kinetic analysis of oil accumulation in maturing seeds. *Plant Physiol. Biochem.* 29:385-393.
- Wellburn, A.R. 1969. The stereochemistry of hydrogen transfer during the reduction of G20 isoprenoid in higher plants. *Phytochemistry.* 7:1523-1528.
- Wellburn, A.R. 1970. Studies on the biosynthesis of the tocopherols in higher plants. *Phytochemistry.* 9:743-748.
- Whistance, G.R. and D.R. Threlfall. 1967. Biosynthesis of phytoquinones: An outline of the biosynthetic sequences involved in terpenoid quinone and chromanol formation by higher plants. *Biochem. Biophys. Res. Commun.* 28:295-302.
- Whistance, G.R., D.R. Threlfall, and T.W. Goodwin. 1967. Observation on the biosynthesis of phytoterpenoid Quinone and chromanol nuclei. *Biochem. J.* 105:145-153.

Whistance, G.R. and D.R. Threlfall. 1968. Biosynthesis of phytoquinones: utilization of homogentisic acid by maize shoots for the biosynthesis of plastoquinone. *Biochem. J.* 109:482-483.

Woodroof, J.C. and N.C. Woodroof. 1927. The development of the pecan nut from flower to maturity. *J. Agr. Res.* 34:1049-1063.

Fig. 4.1. Growth of the whole nut and kernel of seven hazelnut varieties, 1987 and 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

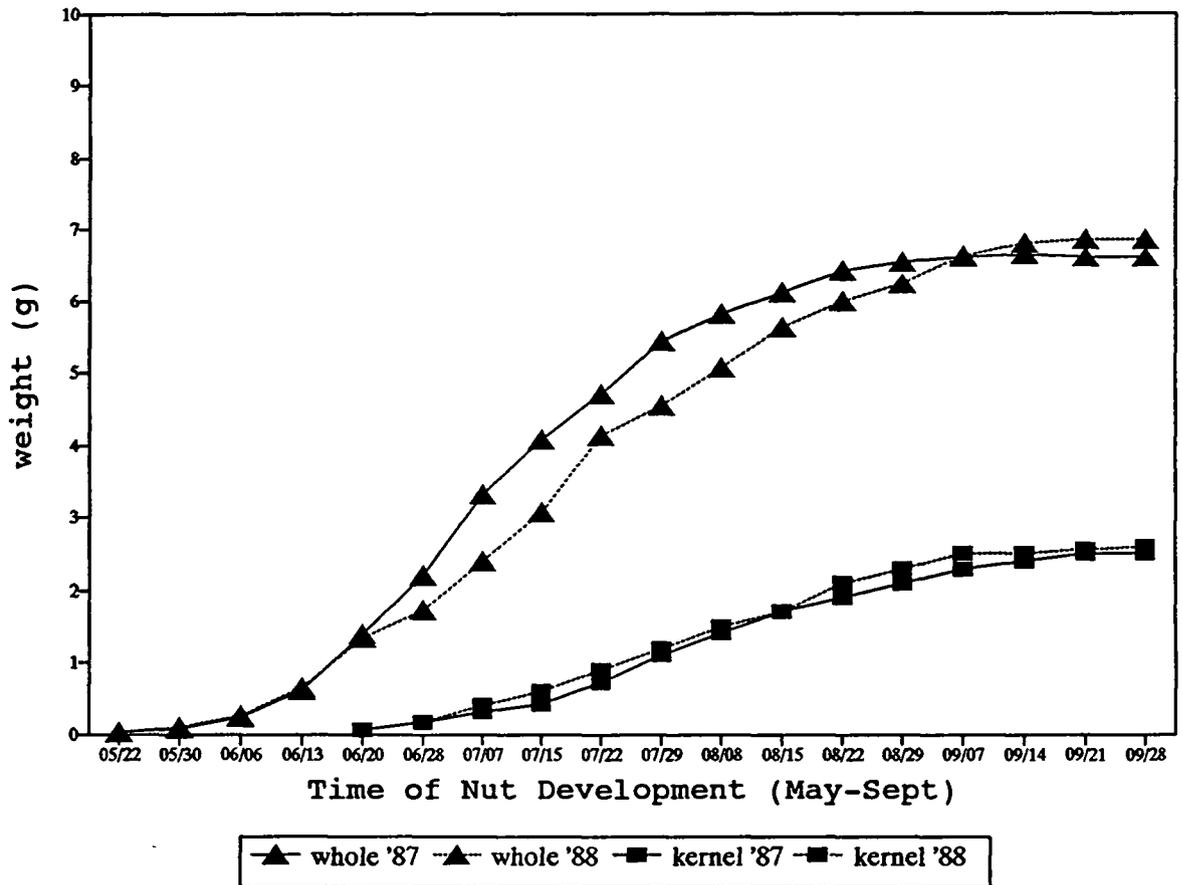


Fig. 4.2. Growth of the whole nut of seven hazelnut varieties, 1987 and 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiagli)

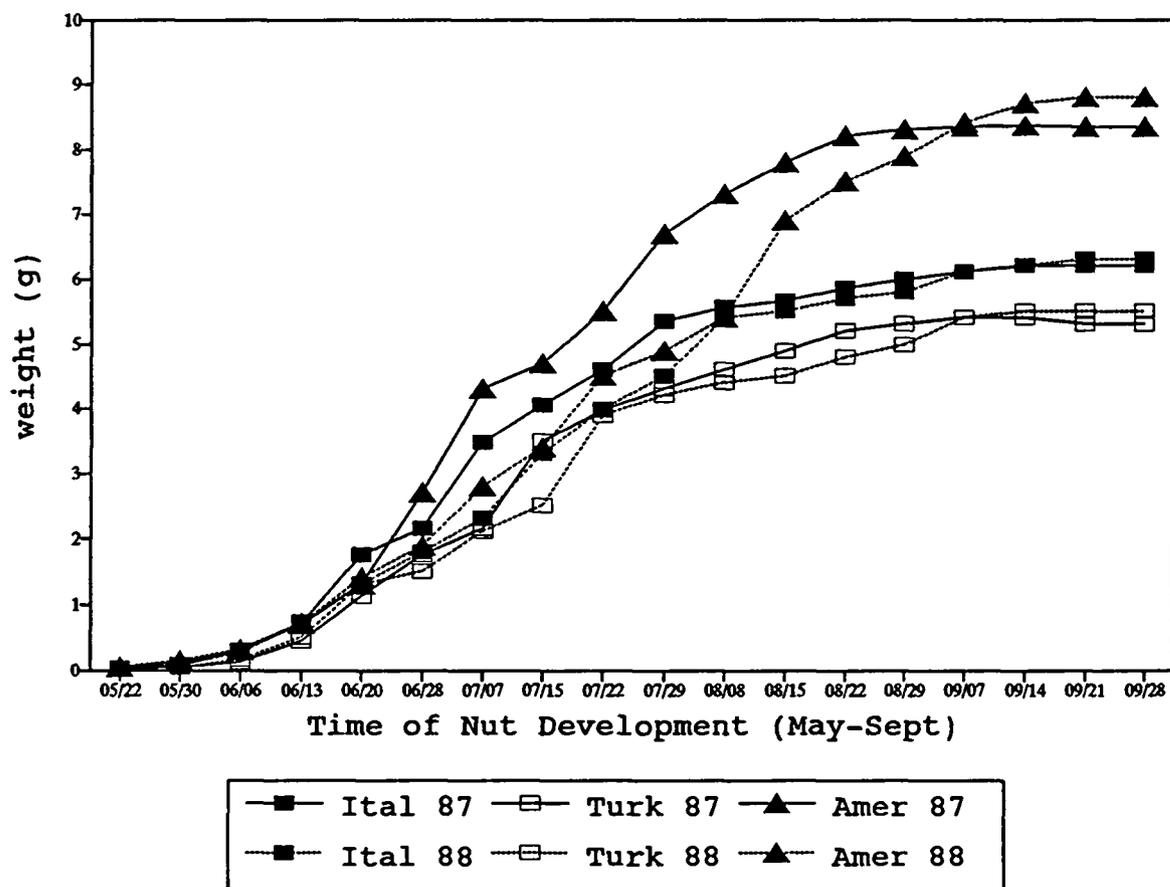


Fig. 4.3. Growth of the kernel of seven hazelnut varieties, 1987 and 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

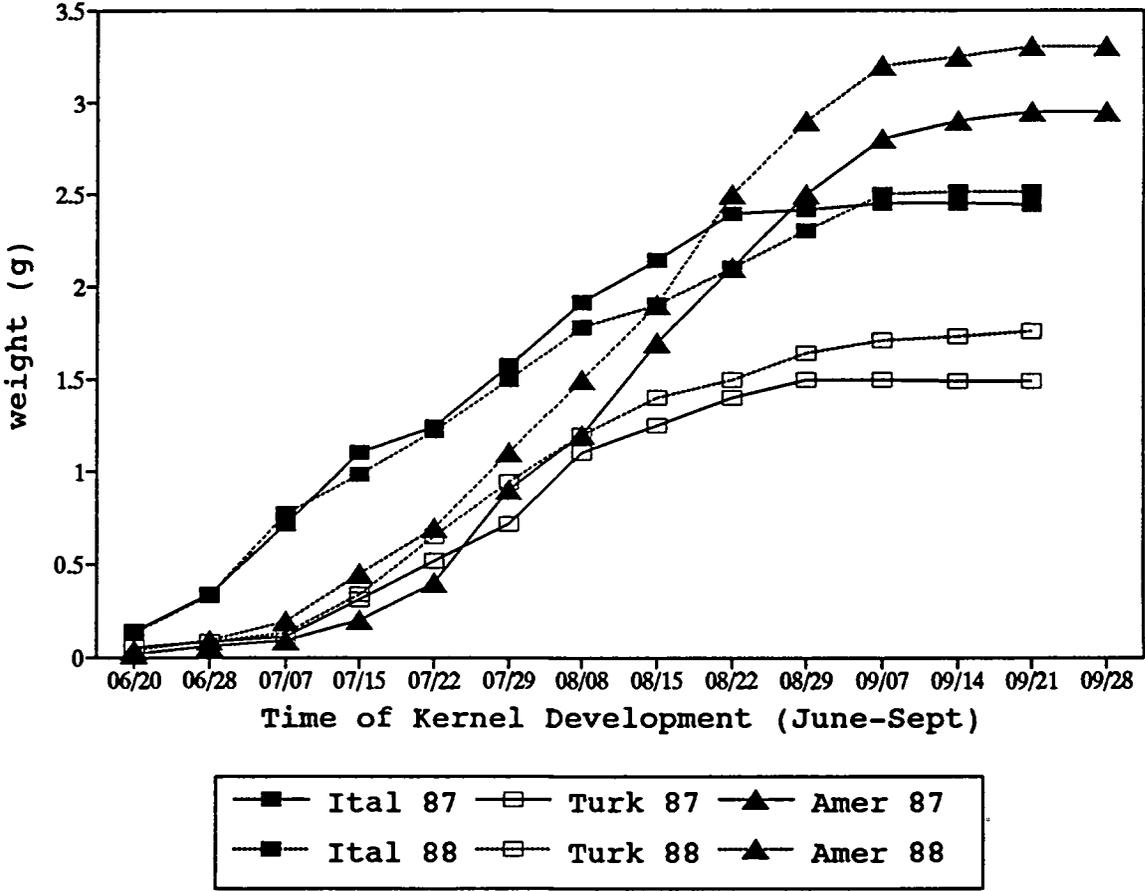


Fig. 4.4. Moisture content of seven hazelnut varieties. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiagli)

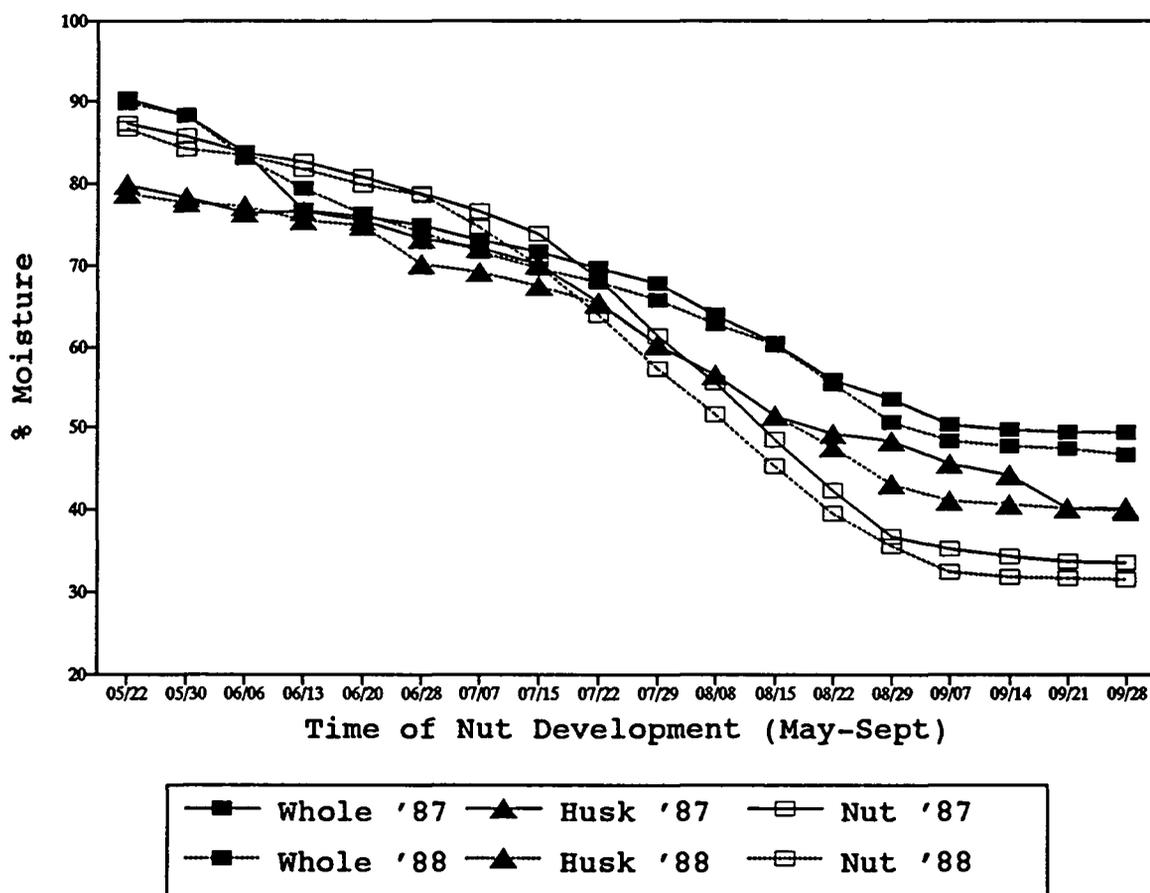


Fig. 4.5. Changes in % oil, moisture, and residue in seven varieties of hazelnut kernels, 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

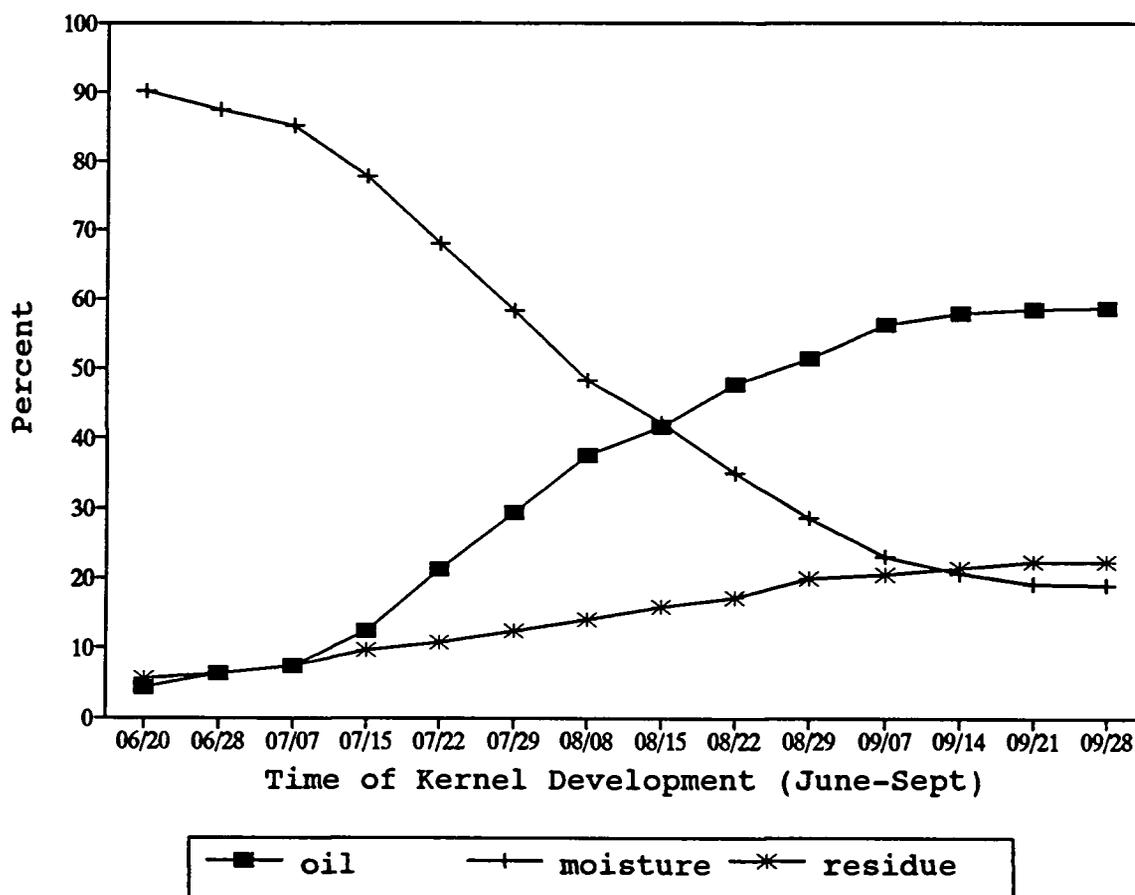


Fig. 4.6. Length to width ratio of seven hazelnut varieties, 1987 and 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

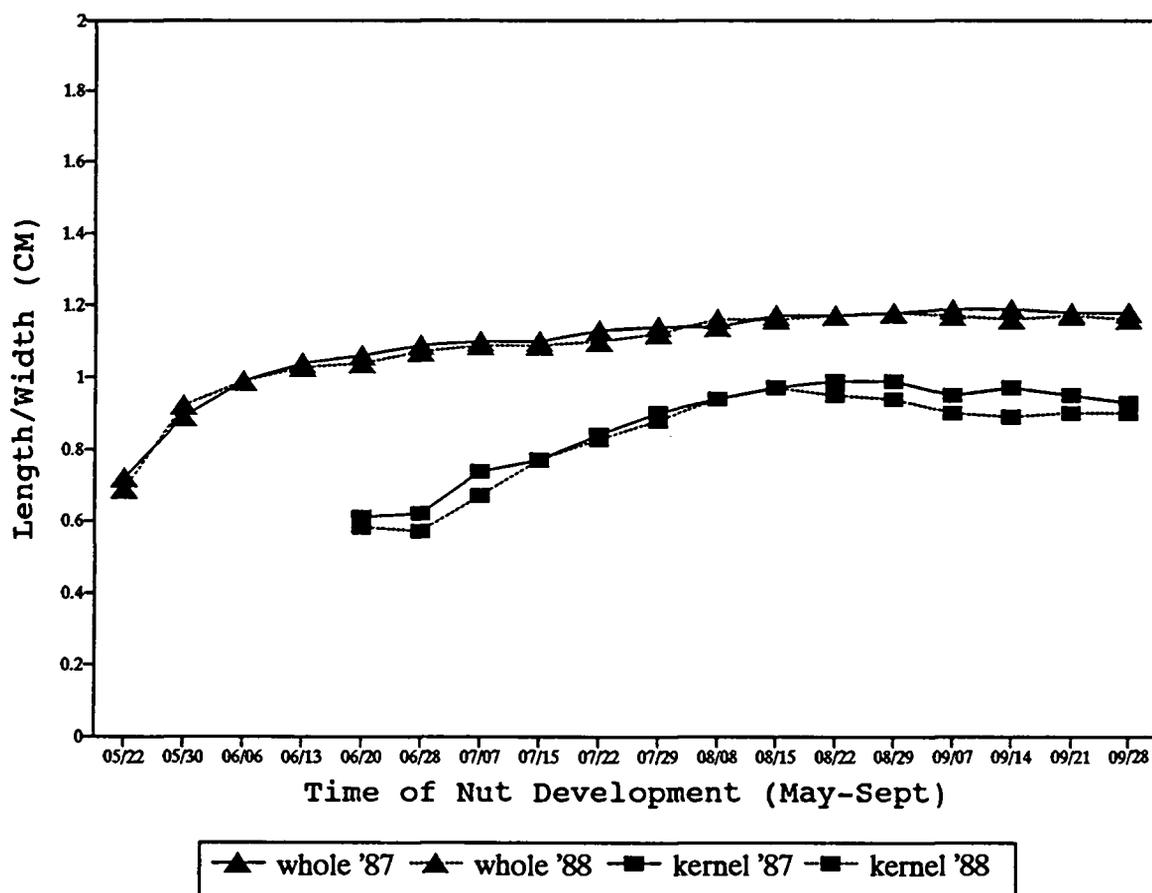


Fig. 4.7. Fatty acid development of seven hazelnut varieties, 1987. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiagli)

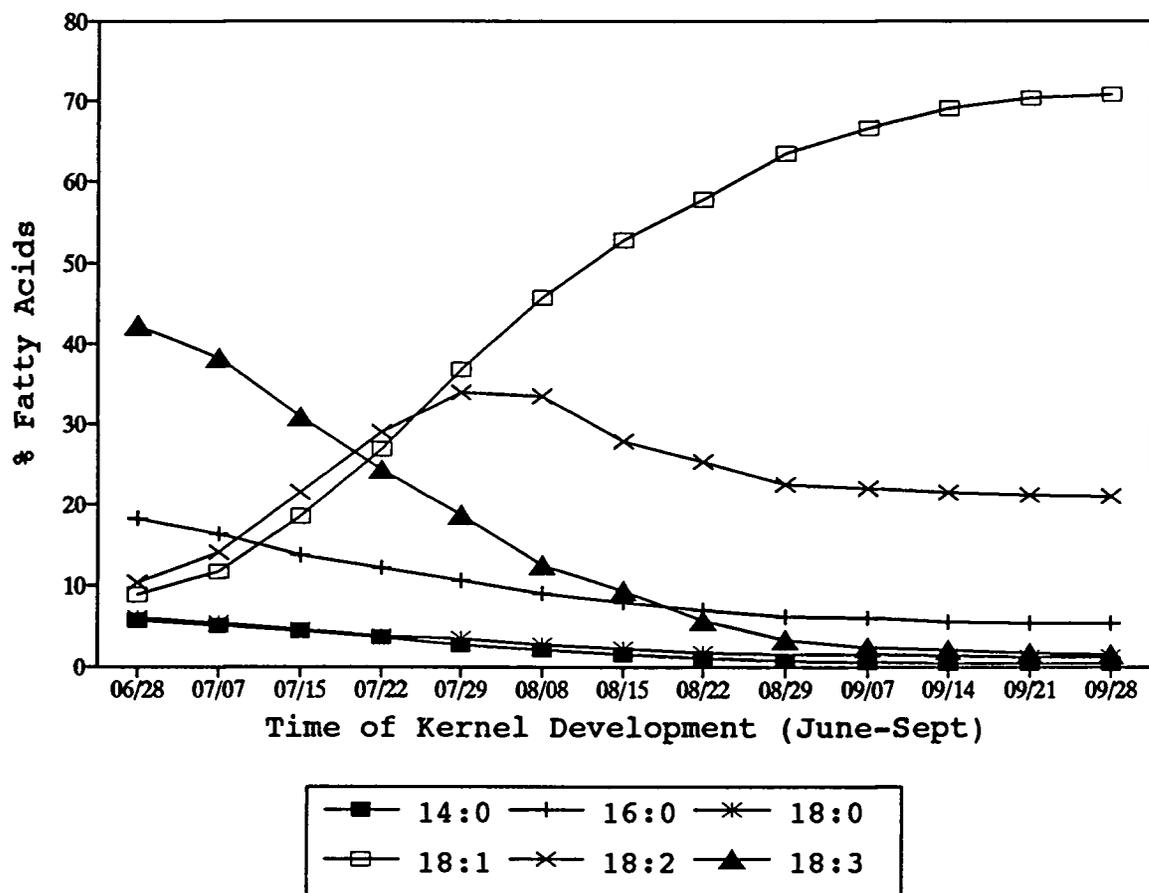


Fig. 4.8. Fatty acid development of seven hazelnut varieties, 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiagli)

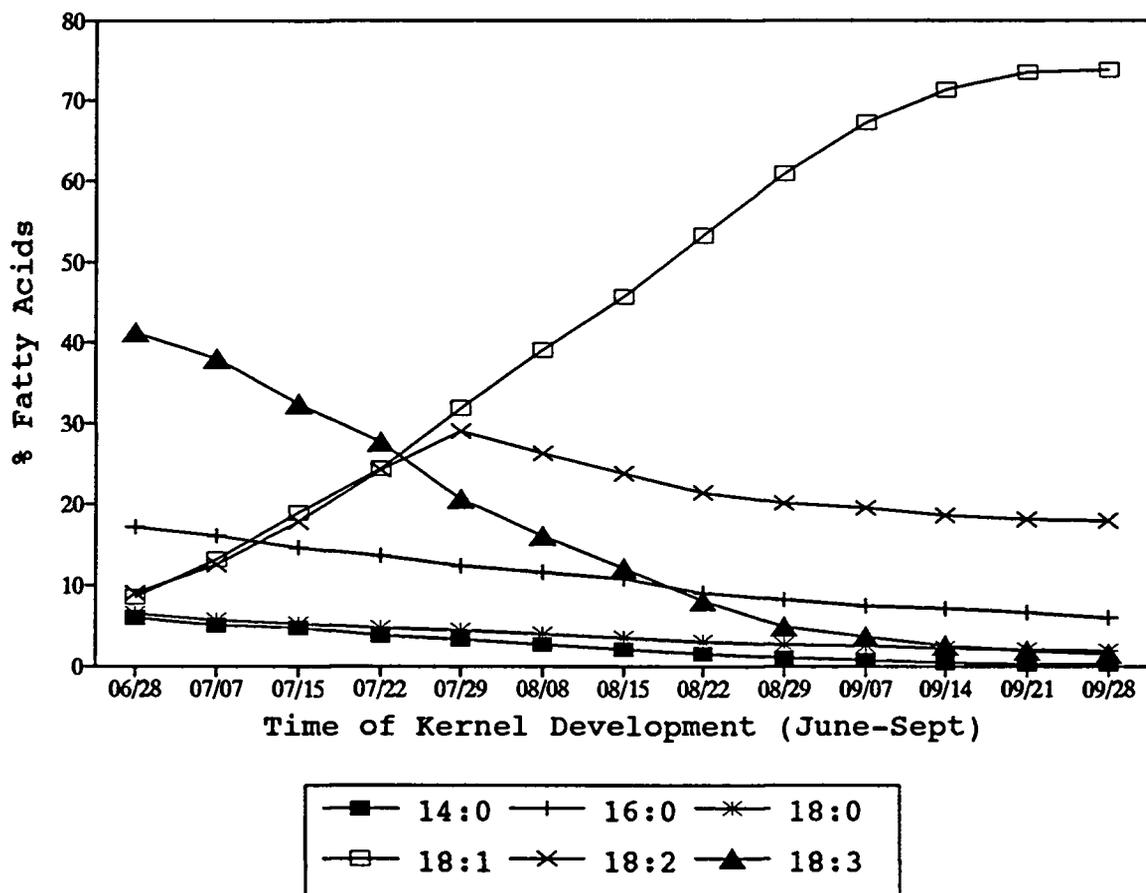


Fig. 4.9. Fatty acid development of three hazelnut varieties, 1987. (Barcelona, Ennis, and Daviana)

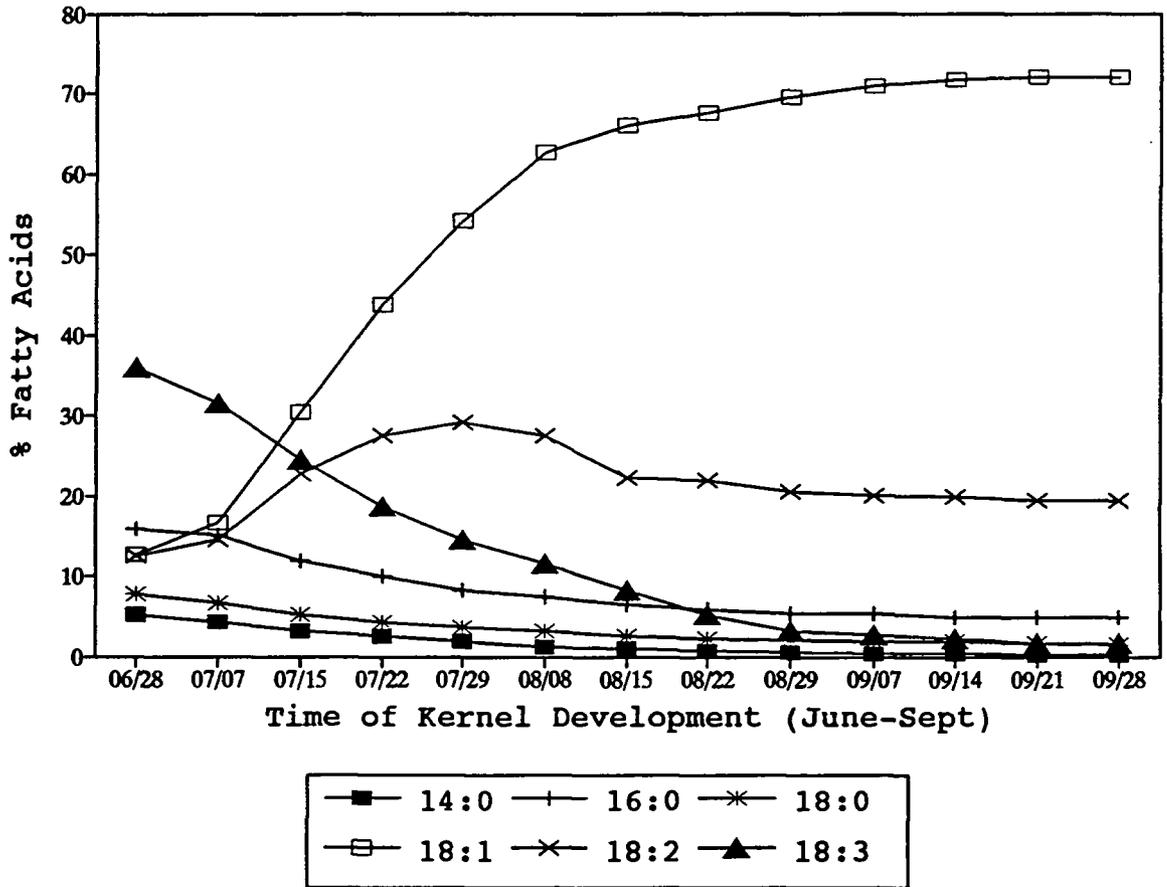


Fig. 4.10. Fatty acid development of three hazelnut varieties, 1988. (Barcelona, Ennis, and Daviana)

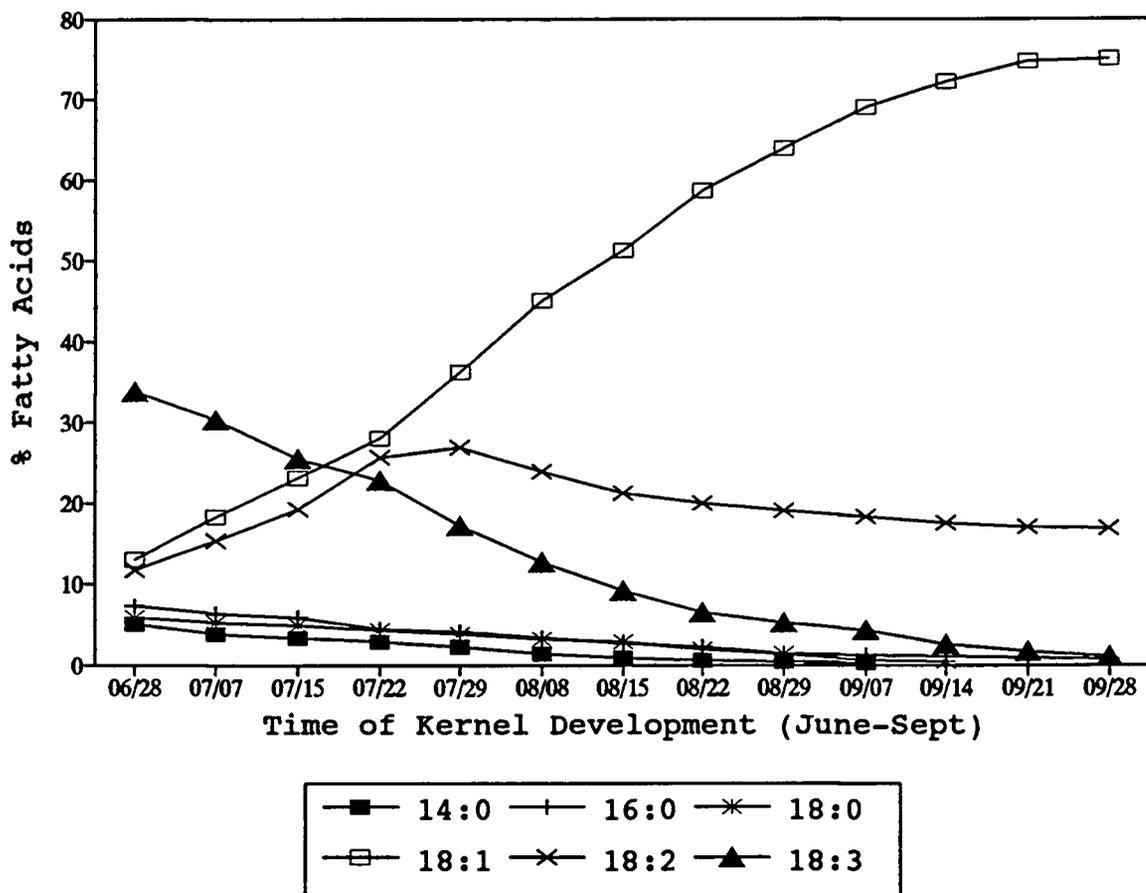


Fig. 4.11. Fatty acid development of two hazelnut varieties, 1987. (Tonda Romana and Tonda Gentile delle Langhe)

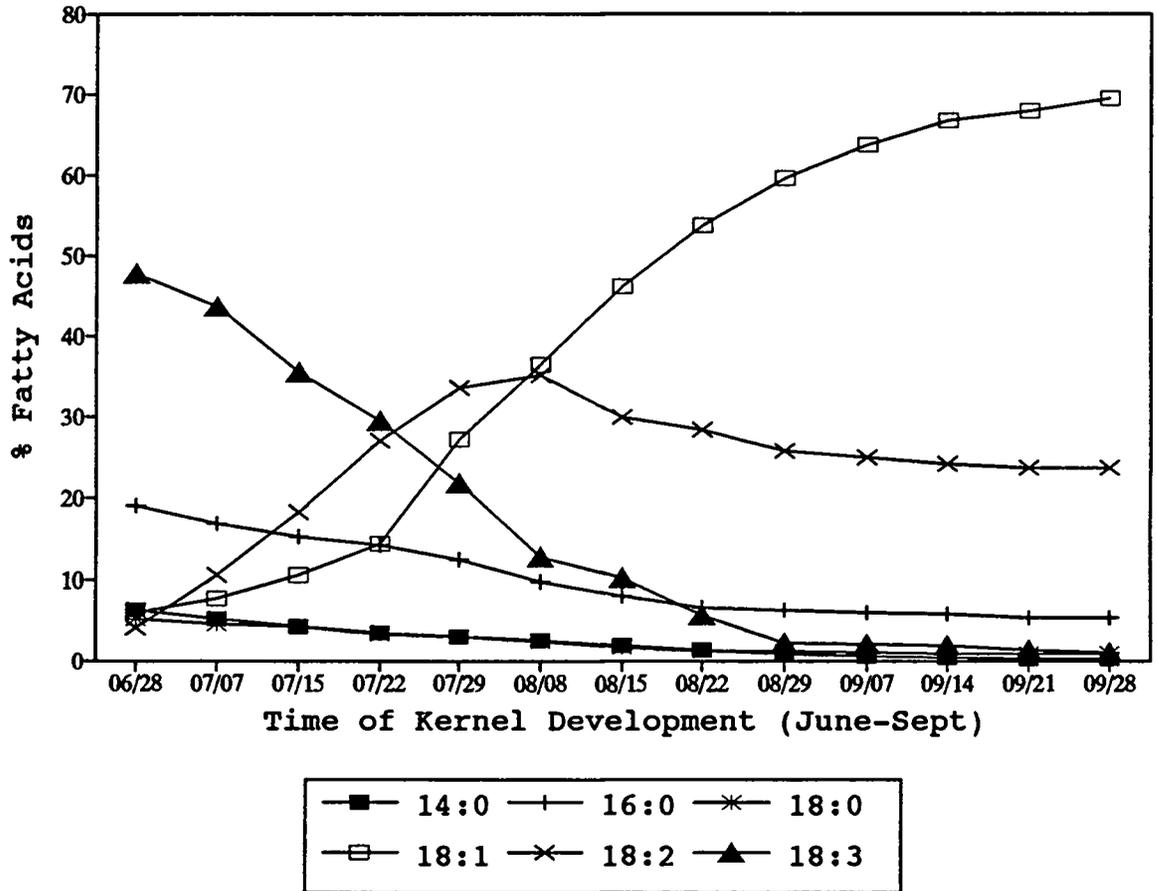


Fig. 4.12. Fatty acid development of two hazelnut varieties, 1988. (Tonda Romana and Tonda Gentile delle Langhe)

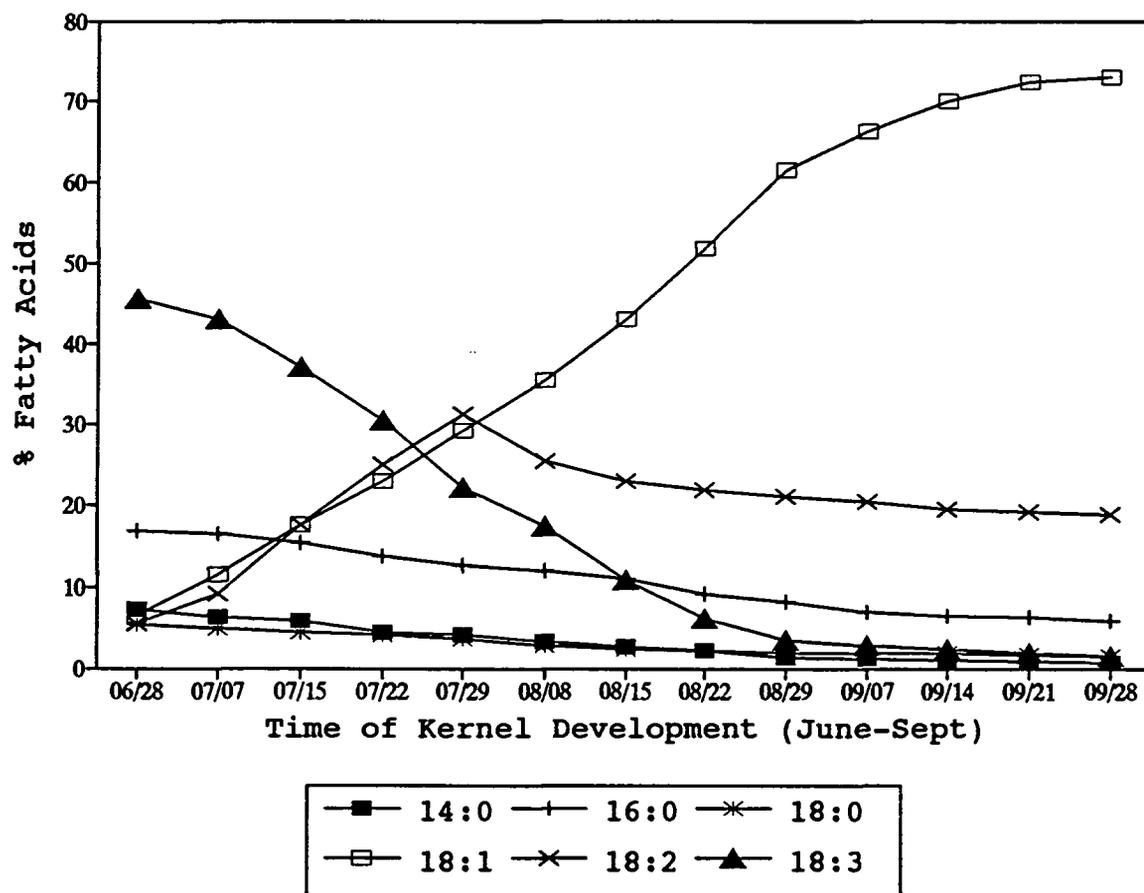


Fig. 4.13. Fatty acid development of two hazelnut varieties, 1987. (Tombul and Tombul Ghiaghli)

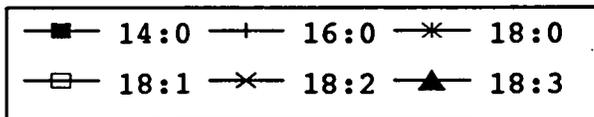
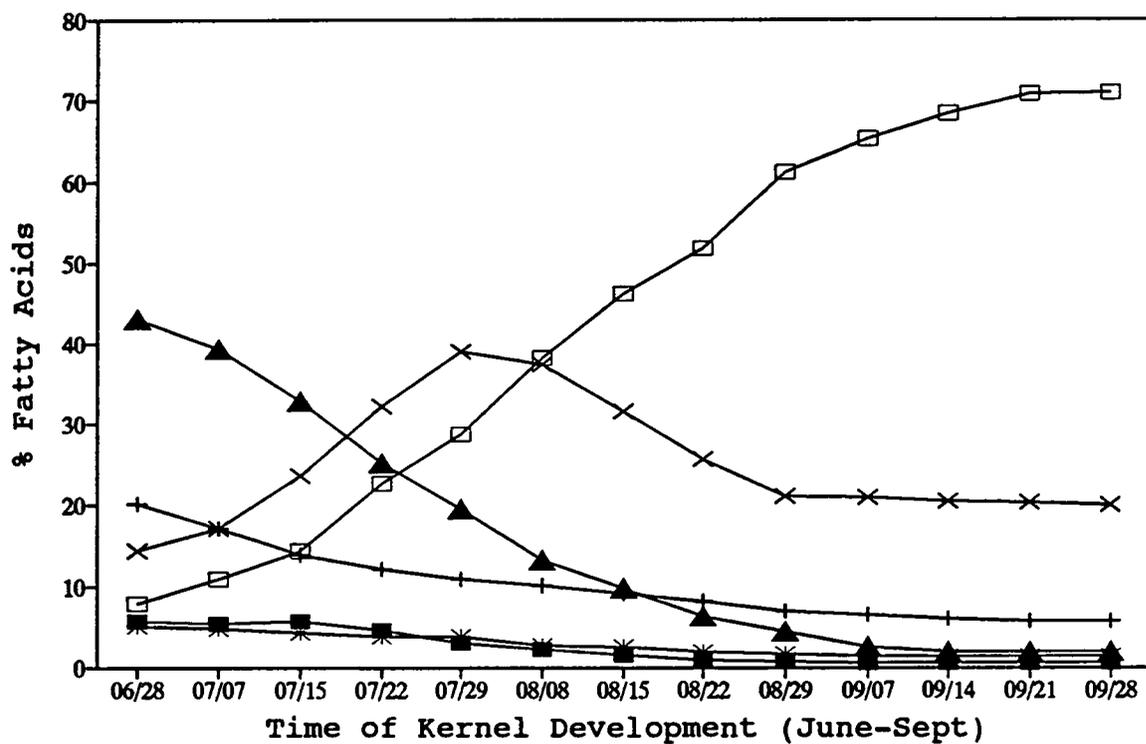


Fig. 4.14. Fatty acid development of two hazelnut varieties, 1988. (Tombul and Tombul Ghiaghli)

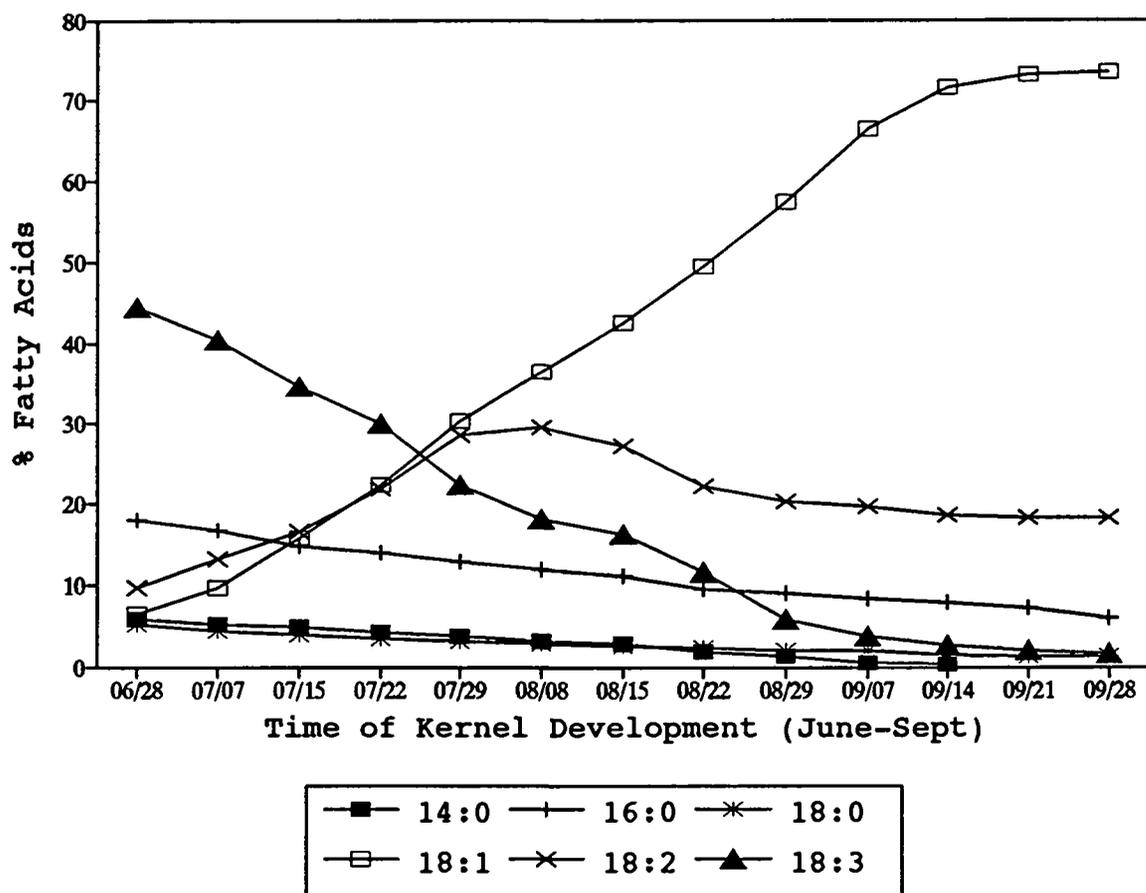


Fig. 4.15. Ratio of unsaturated to saturated fatty acids in kernels of seven hazelnut varieties. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiagli)

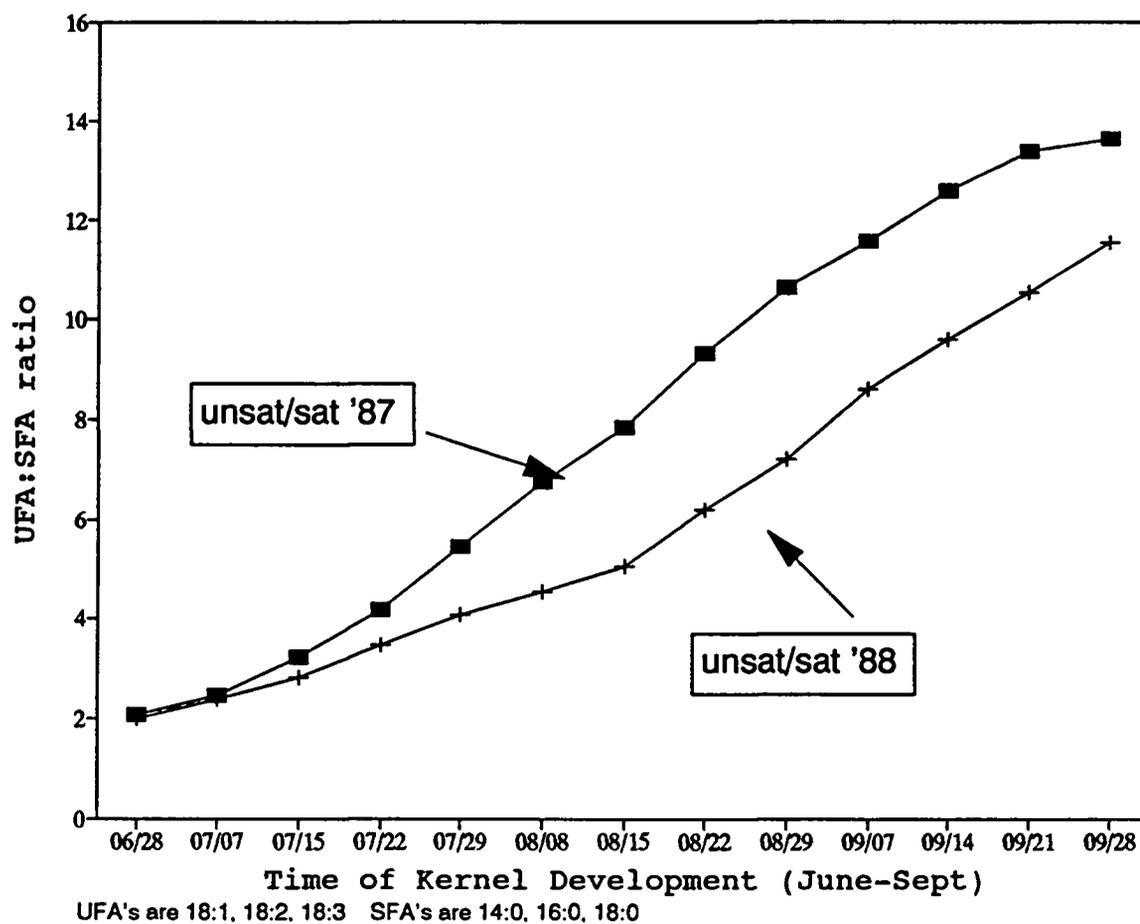


Fig. 4.16. Vitamin E development in seven hazelnut varieties, during the growing season, 1987. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

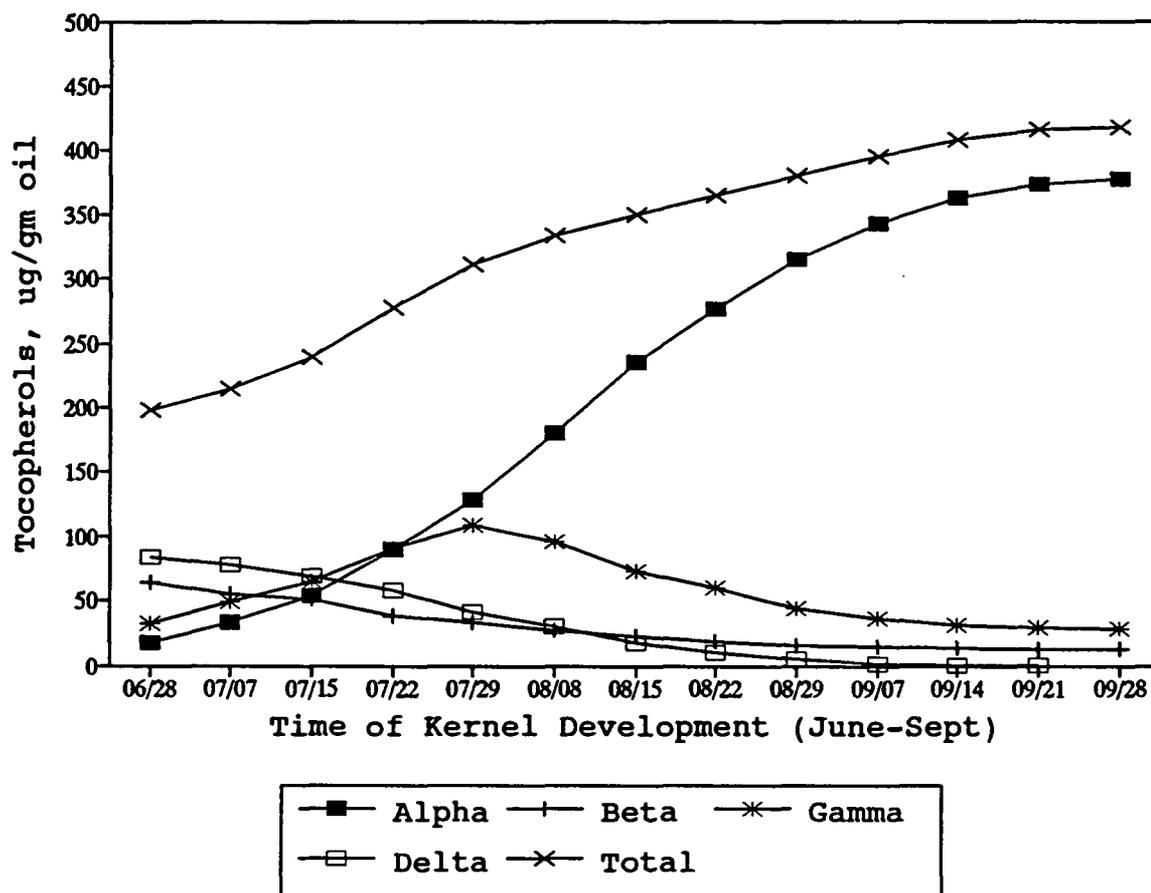


Fig. 4.17. Vitamin E development in seven hazelnut varieties, during the growing season, 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

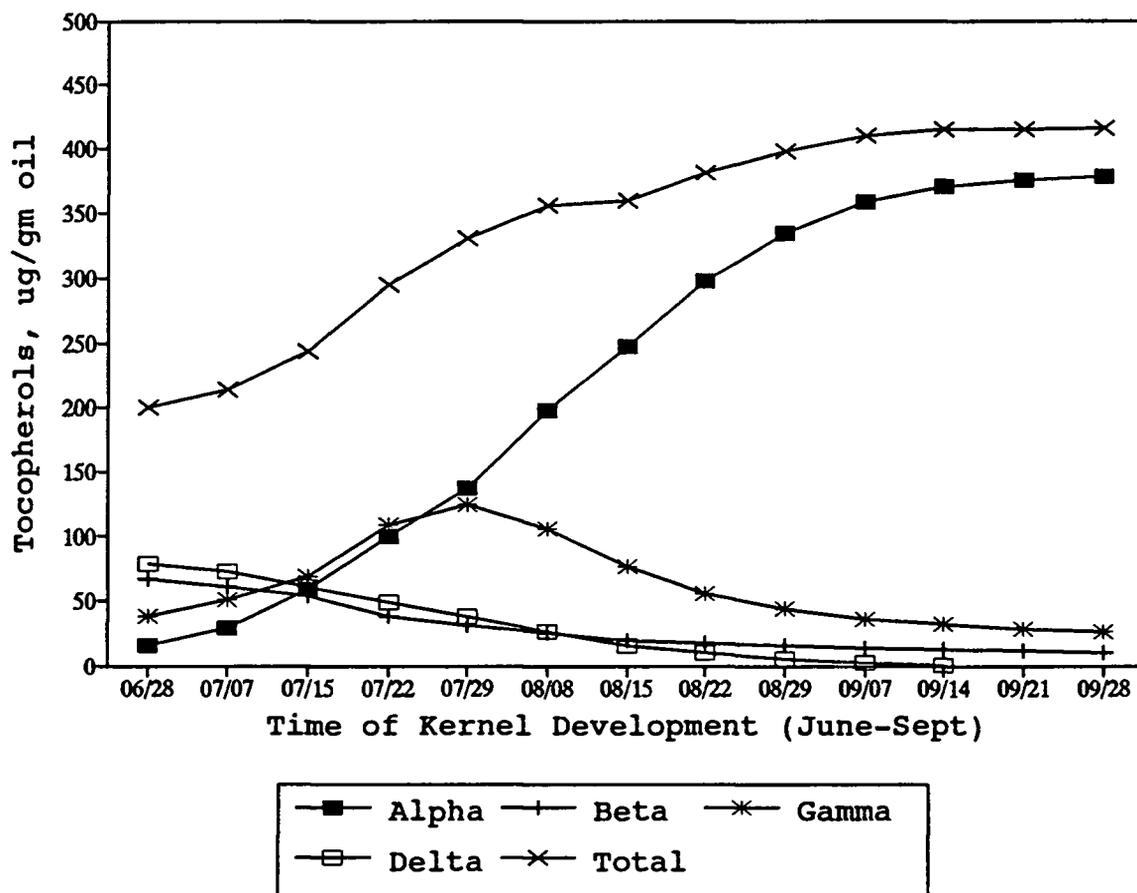


Fig. 4.18. Vitamin E development in three hazelnut varieties, during the growing season, 1987. (Barcelona, Ennis, and Daviana)

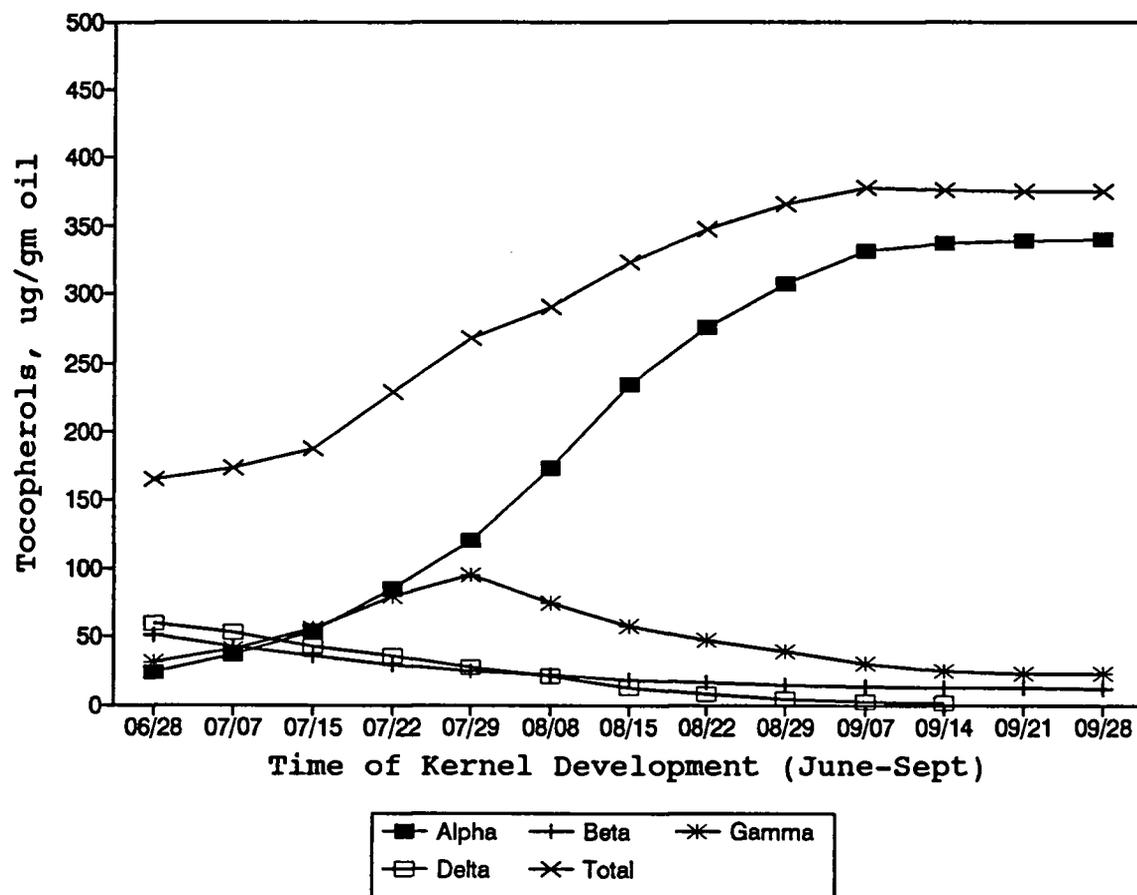


Fig. 4.19. Vitamin E development in three hazelnut varieties, during the growing season, 1988. (Barcelona, Ennis, and Daviana)

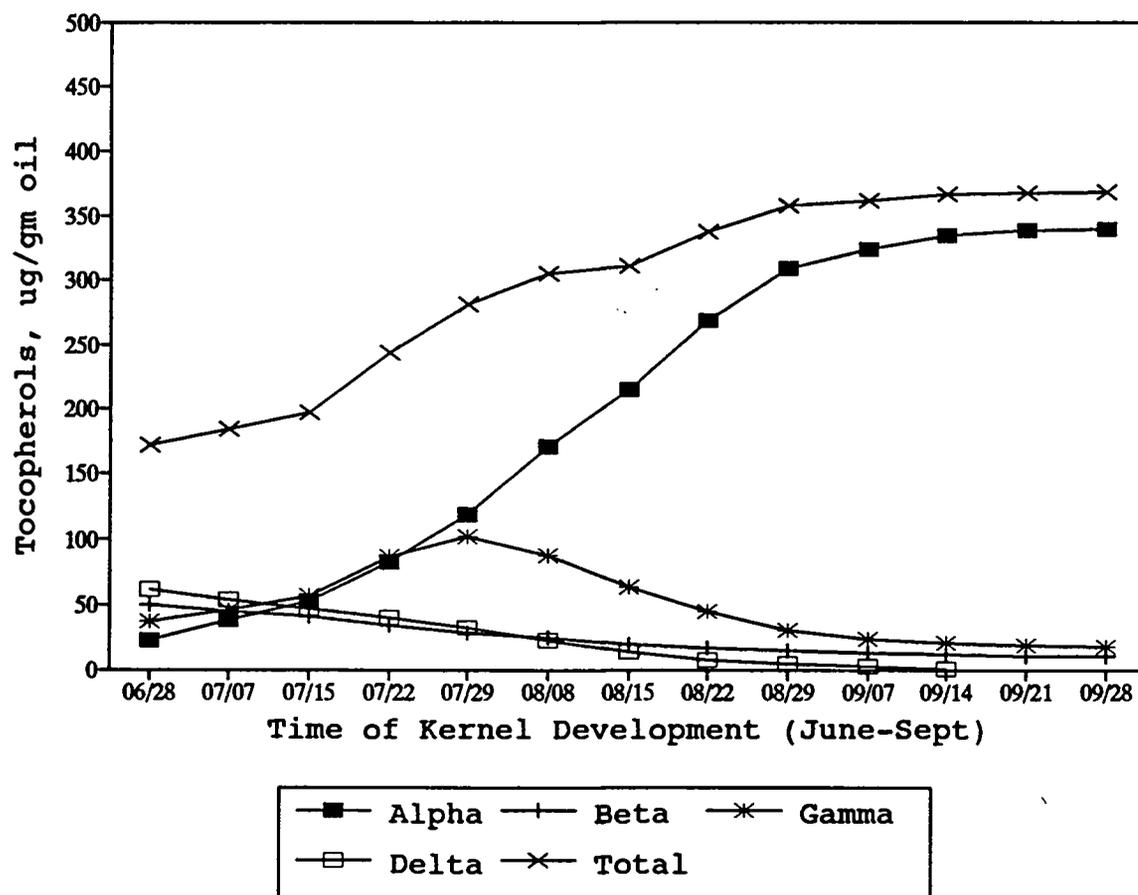


Fig. 4.20. Vitamin E development in two hazelnut varieties, during the growing season, 1987. (Tonda Romana and Tonda Gentile delle Langhe)

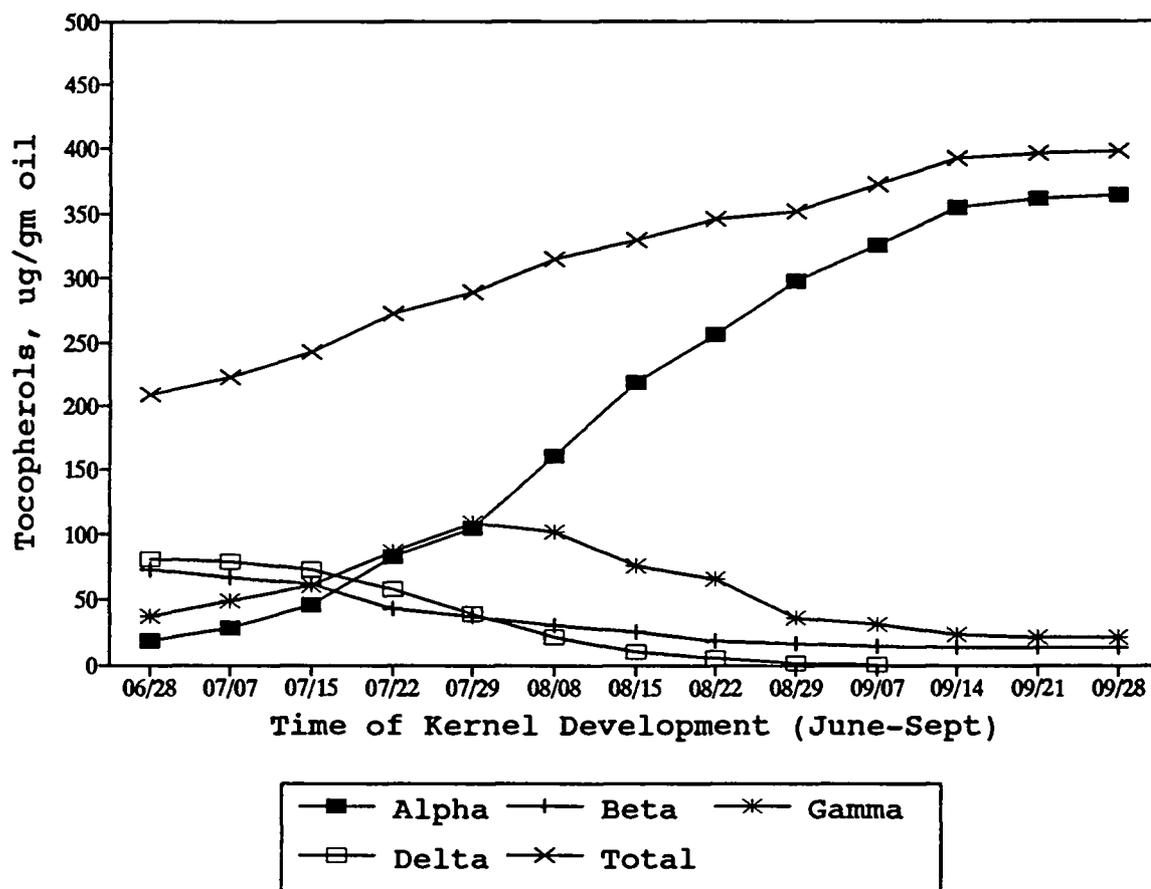


Fig. 4.21. Vitamin E development in two hazelnut varieties, during the growing season, 1988. (Tonda Romana and Tonda Gentile delle Langhe)

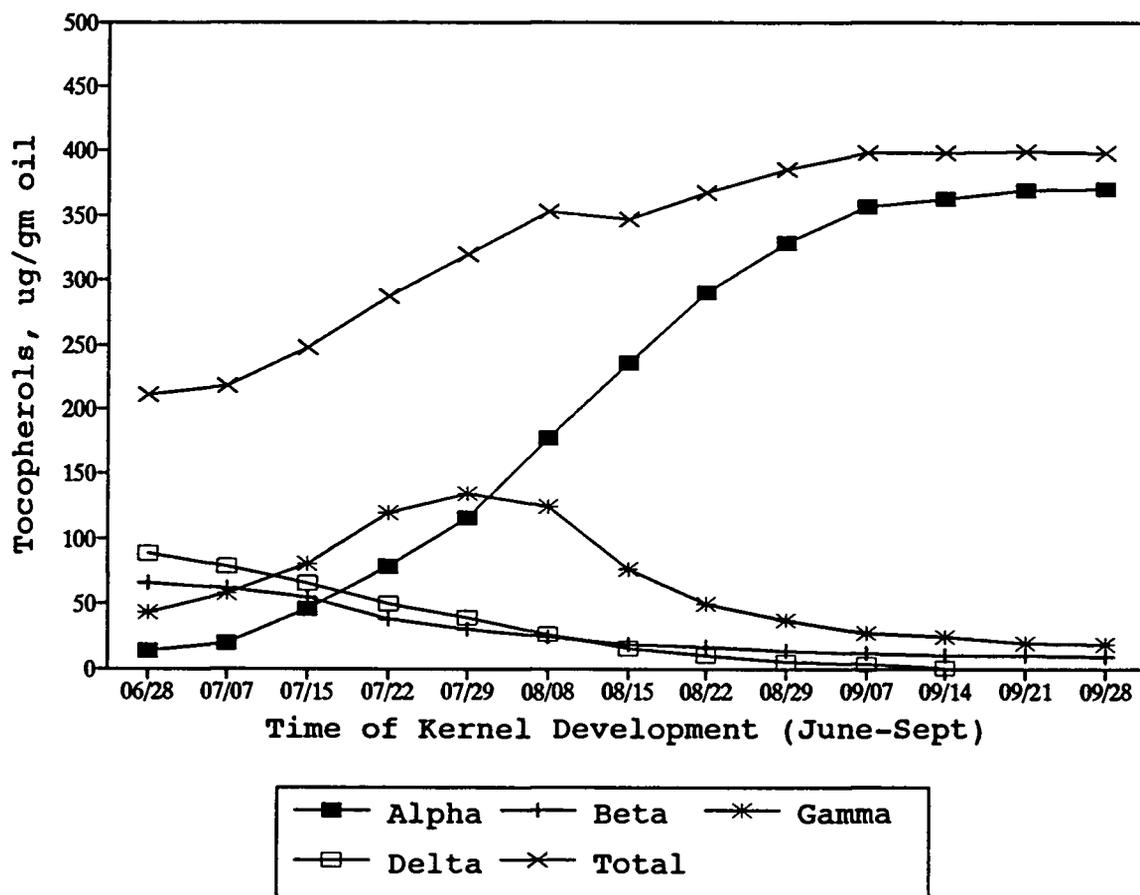


Fig. 4.22. Vitamin E development in two hazelnut varieties, during the growing season, 1987. (Tombul and Tombul Ghiagli)

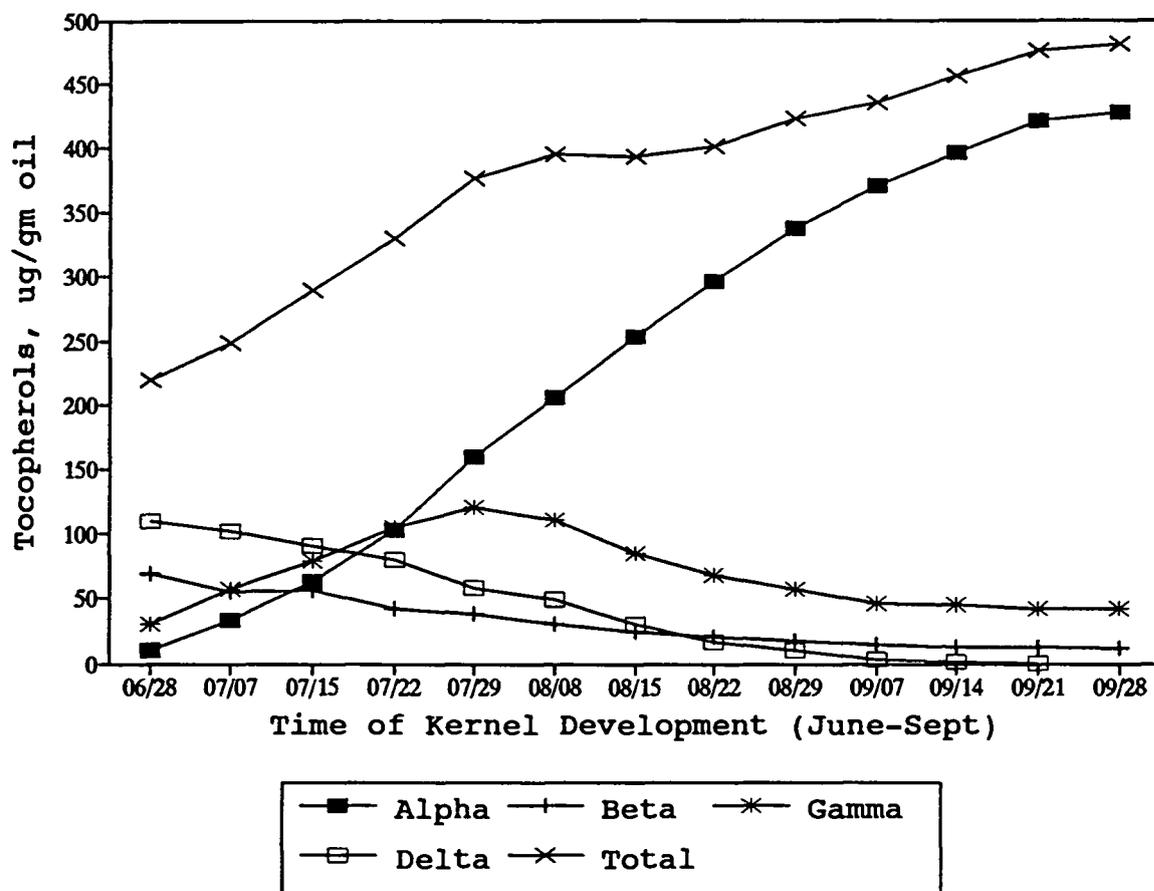


Fig. 4.23. Vitamin E development in two hazelnut varieties, during the growing season, 1988. (Tombul and Tombul Ghiaghli)

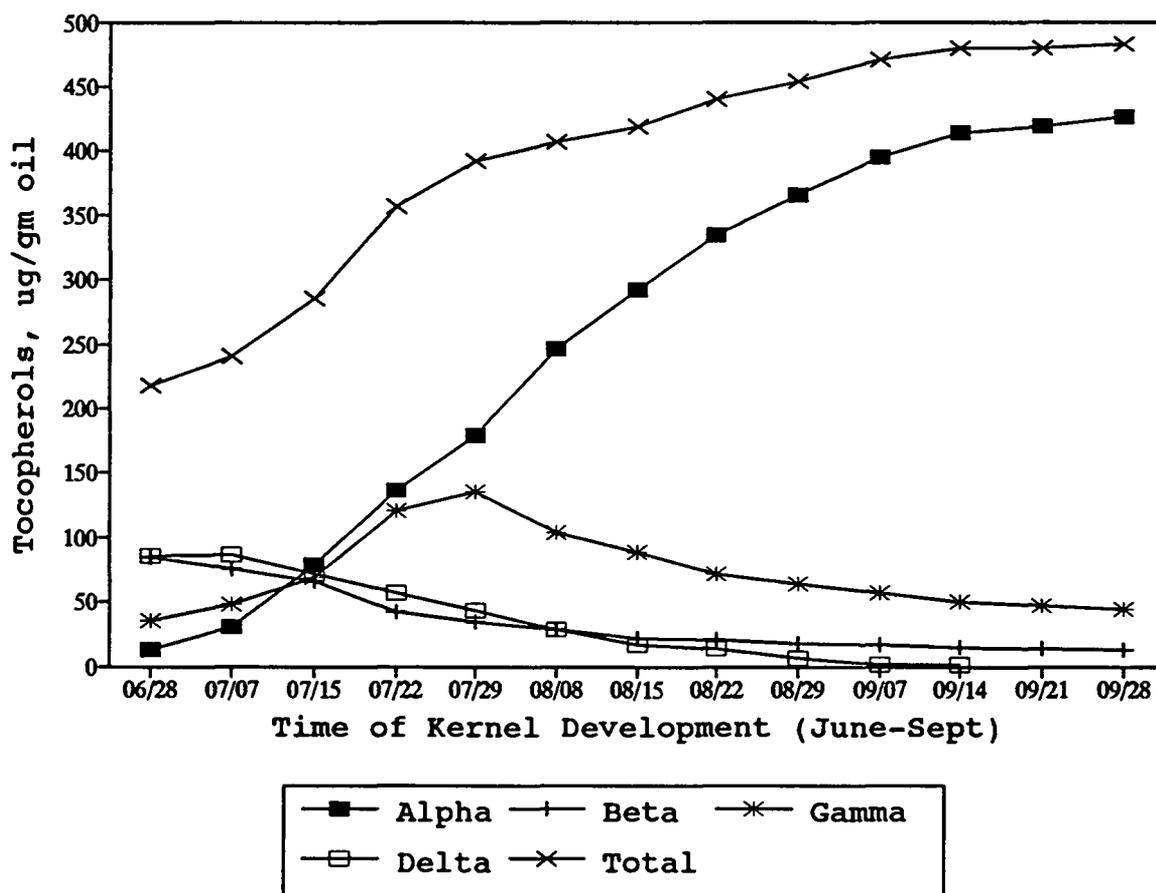


Table 4.1. Oil percent and vitamin E concentration for different varieties of hazelnuts, for 1987 and 1988.\*

Variety	Oil %		Vitamin E ( $\mu\text{g/g}$ oil)	
	87	88	87	88
Barcelona	57.4b	58.8c	384d	387d
Daviana	54.5d	55.1e	388d	359e
Ennis	56.5c	56.7d	354e	360e
TGDL	59.9a	60.7a	395c	412c
Tonda Romana	60.7a	59.8b	403c	386d
Tombul	59.8a	61.7a	494a	498a
Tombul Ghiaghli	60.5a	60.9a	468b	471b

\*Each value represents a mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 4.2. Effect of different extraction methods on oil % and vitamin E.\*

Extraction methods	Oil %	Vitamin E ( $\mu\text{g/g}$ oil)			
		$\alpha$	$\beta$	$\Gamma$	Total
Hexane	61.8a	345.7a	10.4a	13.8a	370a
CH <sub>3</sub> -MeOH	62.4a	349.5a	10.7a	14.1a	374a

\*Each value represents a mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

**Chapter 5** Oil content, fatty acid composition, and vitamin E concentration of seventeen varieties of hazelnuts, compared to other nuts and oil seeds. Storage studies of hazelnut oil composition.

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Additional index words: Corylus avellana, tocopherol, autoxidation, peroxide value, and rancidity.

### Abstract

Oil content, fatty acid and vitamin E composition of seventeen varieties of hazelnuts, thirteen types of nuts, and seven different oil seeds were determined as part of a larger study on Hazelnut kernel quality. Tocopherols and tocotrienols were analyzed by HPLC, fatty acids by GLC. Alpha-tocopherol was the predominant (90%) tocopherol in all hazelnut varieties. Beta- and  $\Gamma$ -tocopherol were found in small amounts. In other nuts  $\alpha$ - and  $\Gamma$ -tocopherols were predominant. Delta-tocopherol was found in some kinds of nuts but it was not found in hazelnuts. All four kinds of tocopherols were found in oil seeds and tocotrienols were found in some. Hazelnuts are a rich source of  $\alpha$ -tocopherol.

Oil concentration varied among hazelnut cultivars and ranged from a low of 57.9% in Hall's Giant to 65.7% in Tombul. Macadamias were the highest in oil content (76.9%) and chestnuts were the lowest (2.8%). In oil seeds, oil content ranged from 4.5% in corn to 49.9% in sesame seed. Oleic acid and linoleic acid comprised more than 90% of the fatty acid

composition in all nuts. Oleic, linoleic, and linolenic acids were the major fatty acids found in oil seeds.

Hazelnut varieties were stable during storage for up to two years. Although some loss in vitamin E and an increase in peroxide values were detected during the third year, even then they were not perceived as rancid.

## Introduction

The kernel of hazelnuts develops from an ovule fertilized by pollen from the pollenizer variety and consequently is composed of hybrid tissue. Hazelnut cultivars are self-incompatible so pollenizers are required in hazelnut orchards (Miller, 1991). Therefore, one might expect to recognize a genetic contribution to the kernel from the pollen parent as well as from the maternal tree bearing the nut. While one might think it important to select a pollenizer variety which would make the most favorable contribution to the kernels of the main variety, as it turns out there is very little influence of the male parent on hazelnut kernel quality. This is because the endosperm is the major part of the kernel, and thus is dominated by the maternal parent (Thompson and Richardson, 1978). Comparison of pollen effects on the development of nuts of four pistachio varieties showed that pollen of pistachio species other than P. vera tended to retard nut development. The greatest delay in ripening of nuts occurred when P. chinensis and P. integerrina pollen were used. In general, large kernels and increased shell splitting resulted from the use of P. vera pollen (Whitehouse et al, 1964). Hazelnut varieties vary in size, shell characteristics and composition. However, in contrast to pistachios, hazelnut kernels are almost all endosperm entirely derived from maternal tissue, thus pollenizer effects on kernel quality are largely limited to the small embryo. Each variety tends to

have its own unique shell structure, which ranges from extremely thick and hard to thin and soft. The oil content may also vary, from as low as 50% to above 67%. However, differences in oil content of hazelnut also depends slightly upon the degree of maturity when harvested.

New varieties will likely be important to future markets. In 1968, Oregon had 16,000 acres of hazelnuts and an average of 92 trees per acre. The state's acreage had increased to 22,000 acres with an average of 115 trees per acre in 1982 producing 18,000 field tons. New varieties that can increase the Northwest production to 20,000 to 25,000 tons annually are needed. Almost 99% of the hazelnut trees in the United States are located in Oregon and over one-third of these trees have been planted since 1981. Oregon has 989 commercial hazelnut operations (Williamson, 1991).

Among the more important characteristics needed in new hazelnut varieties are high percentage of kernel, well formed nuts, good texture and good flavor. Careful attention must also be given to nut shape and to such factors as yield, disease resistance, hardness, and bearing habits.

Exported nuts are 23% as in-shell products and 61% as kernels. The future growth will be in the kernel market as this market becomes better defined and production meets its needs. More than one variety is needed, one that blanches well to remove the pellicle, is high in oil for the paste market, and one low in oil for the chocolate market. A single

variety will not do all these things, but it will be necessary to grow enough of each to supply the various markets. Foreign countries already produce a wide number of high quality varieties and Oregon needs to do the same. We need to increase yield per acre from the varieties that now yield 800 pounds of shelled kernels per acre.

Almonds and hazelnuts are very tightly intertwined on the world market. However walnuts, pecans, peanuts, cashews, brazil nuts, and others, are not really related as closely in the eyes of the world's buyers as are almonds and hazelnuts (Eustace, 1989).

There is every indication that in the future hazelnut growers will be subject to even greater competition from growers of other kinds of nuts. With the rapidly increasing tonnage of almonds, English walnuts, and pecans in the United States and a steadily increasing importation of cheaply produced brazil nuts and cashew nuts from abroad, it appears likely that the consumer will be looking for bargains.

Vitamin E is an antioxidant with potential activity as a chemopreventive agent for cancer. During the last decade, increasing interest has been focused on the question of whether ample intake of vitamin E may reduce the risk of cancer. Animal experiments and in vitro studies have shown that vitamin E can block the formation of carcinogenic nitrosamines (Chen et al., 1988; Knekt et al., 1991). There is a growing body of evidence that vitamin E is important in

the mediation of immune response. For example, vitamin E deficiency is associated with depressed humoral and cell-mediated immunity in laboratory animals (Anon, 1992). Very recently, vitamin E and nuts in the diet have increased as important for precution of coronary heart disease in the study (Fraser etal., 1992).

The current interest in the human demand for vitamin E as well as the trend toward preferred consumption of highly unsaturated fats, has emphasized the need for surveys of the tocopherol content of foods. Earlier, Horwitt (1961) had claimed an increased need for  $\alpha$ -tocopherol when the consumption of polyunsaturated fat was increased. For the RDA (Recommended Daily Allowance) figure to be of use, the tocopherol content and form of food stuffs must be known, and total vitamin E or  $\alpha$ -tocopherol equivalent value added to food composition tables.

Lipid oxidation is one of the primary mechanisms of quality deterioration in stored foods regardless of whether oil content is high or low. The changes in quality can be manifested by deterioration in flavor, color, texture, and nutritive value and the production of toxic compounds (Kanner et al., 1988; Ladikos and Lougovois, 1990). During the past 35 years, a great deal of experimental evidence has accumulated suggesting that lipid peroxidation in cellular membranes is implicated in a variety of pathological conditions (Pompella et al., 1987).

Many methods are available to measure the extent of lipid peroxidation. These methods include thiobarbituric acid (TBA), detection of the UV absorption characteristic of conjugated dienes, fluorescent analysis of ethane and pentane formation, detection of chemiluminescence, measurement of oxygen uptake, measurement of the loss of polyunsaturated fatty acids in membrane phospholipids, the detection of lipid hydroperoxides, and measurement of specific aldehydes such as alkenal (Pompella et al., 1987).

Thiobarbituric acid (TBA) is the most widely used test for measuring the extent of oxidative deterioration of lipids in muscle foods, particularly of fish (Gray, 1978; Rhee, 1978). This test, which expresses lipid oxidation in mg of malonaldehyde per kg of sample, or TBA number, initially was reported to measure only malonaldehyde (Sinnhuber et al., 1958 and 1977). Malonaldehyde was shown to be a secondary oxidation product of polyunsaturated fatty acids containing three or more double bonds (Dale et al., 1962; Pryor et al., 1976). For this reason it is not very useful for hazelnuts, because 18:3 (linolenic acid) accounts for less than 1% in most varieties.

Hydroperoxides, commonly called peroxides, are primary products of lipid oxidation which may break down to secondary products such as aldehydes (Gray, 1978) or react with protein (Gardner, 1986). We used peroxide value to measure rancidity for three reasons. First, because the major fatty acid in

hazelnut kernels is oleic acid (18:1) for which this method is suitable. Secondly, because hazelnut kernels are stable for a long period of time, due to the presence of vitamin E (a natural antioxidant). Finally, the peroxide value is a simple efficient procedure and suitable for use with a large number of samples. Peroxide value measurements have been used in pecans (Forbes et al., 1980 and 1983), soybeans (Hara and Totani, 1988; Jung and Min, 1990), peanuts (Adan, 1980), and olives (Kiritsakis and Dugon, 1984; Kim et al., 1988).

Because of the increasing interest in growing different varieties of hazelnuts in Oregon and the demand for nutritional information for marketing, we felt that a current survey of the chemical constituents of recently introduced varieties would be helpful.

Oils, vitamin E, moisture concentration, and storage behavior of the kernel are of fundamental importance for the evaluation and understanding of these varieties.

The first part of the present study was conducted to further elucidate the chemical composition of nutmeats, and to compare the lipids and vitamin E of well established standard cultivars, newly developed hazelnut cultivars, different types of nuts, and oil seeds. The second part was to study the effects of long duration storage, and the effect of light in the tree canopy on oil content, fatty acid composition, and vitamin E concentration.

### Material and Methods

All seventeen varieties of hazelnuts were supplied for 1986, 1987, and 1988 by Dr. Shawn Mehlenbacher, director of hazelnut breeding program at Oregon State University. The trees were grown on similar soil types and received similar levels of fertilization and sprays for insect and disease control. Nuts of almonds, brazil nuts, cashews, chestnuts, macadamia, pecans, pine nuts, pistachio, and walnuts and seeds of sunflower, corn, soybean, sesame, pumpkin, and watermelon were obtained from local markets, farmers, and from other universities. To study the effects of light in the tree canopy, hazelnuts were sampled from two farms, where the trees are close to each other so lower parts of the trees are always shaded. Samples were collected both from lower shaded branches and branches at the top, which were exposed to sunlight.

Oil concentration, fatty acids, and vitamin E analyses were performed on total lipids extracted by hexane using the same procedures cited in chapter IV, page 131. The samples of hazelnuts were divided into two groups. One group was analyzed to compare with other nuts and oil seeds. The other group was stored for different times. The 1986 crop was stored for up to three years, the 1987 crop was stored for up to two years, and the 1988 for up to one year, in polyethylene bags at 5 °C with relative humidity 68-70%. At each sampling period twenty- five nuts were randomly selected from each

variety and were manually shelled and further inspected to assure selection of nuts with fully developed nutmeats that were free from defects including rots. The nutmeats from each cultivar were combined and chopped to small particle size with a coffee grinder. Moisture and oil determinations were made in triplicate on 10 gm samples from each cultivar.

The quality parameters which were measured included weight, oil concentration, fatty acid composition, vitamin E concentration, and vitamin E composition. Alpha-tocopherol equivalents were calculated based on published factor values of 1.0 for  $\alpha$ -, 0.1 for  $\Gamma$ -, and 0.05 for  $\beta$ -tocopherol (Hjarde et al., 1973).

#### Peroxide value Determination

Measurement of peroxide value (PV) has been one of the most satisfactory means to follow the autoxidation of lipids. The two most widely used methods for PV determination, the Iodometric and the ferric thiocyanate method, are based on the oxidation of iodide and ferrous ion by peroxides, respectively. The ferric thiocyanate method was employed in this study because it uses a very small sample (as little as 1 drop of oil) and it is sensitive accurate and simple method.

#### Ferric Thiocyanate Method using Benzene-Methanol

The ferric thiocyanate method with benzene-methanol (B-M) is based on the method of Hill and Thiel, (1946) which was modified by Chapman and Mackey (1949).

### Reagents

1. Benzene-methanol- The solvent is a mixture of 70 volumes of benzene, A.R. (Fisher scientific company, Fair Lawn, New Jersey) and 30 volumes of absolute methanol, A.R. (Mallinckrodt, Inc., St. Louis, Missouri).

2. Ferrous chloride solution- 0.4 grams hydrated barium chloride A.R. dissolved in 50 ml of distilled deionized water was added slowly while stirring to 0.5 ml of ferrous sulfate, (reagent grade) dissolved in 50 ml of distilled deionized water. Two ml of 10 N hydrochloric acid was then added. The precipitate of barium sulfate was allowed to settle. The clear solution was filtered through Whatman number 1 filter paper into a bottle protected from light. The solution remained stable for approximately one week.

3. Ammonium thiocyanate solution- The solution was made by dissolving 30 grams of ammonium thiocyanate, A.R. in distilled, deionized water and diluted to a volume of 100 ml.

4. Standard ferric ion solution- 0.25 g of bright iron wire, analytical reagent was dissolved in 25 ml of 10 N HCl and oxidized with 2 ml of 30% hydrogen peroxide, analytical reagent. The excess peroxide was removed by boiling and the solution was diluted to 250 ml and used as stock standard solution.

### Procedure

A. PV determination of the sample.

1. 10 mg of oil was weighed into a screw-cap test

tube and dissolved in 10 ml benzene-methanol (7:3) solvent. If dilution was required, the sample was weighed in a volumetric flask and an aliquot was taken for proper dilution.

2. A drop of both ammonium thiocyanate solution and ferrous chloride solution was added.

3. The tube was shaken and placed in a water bath at 50 C for two minutes and then cooled to about 25 C.

4. The developed red color was read at 520 nm in a Bausch and Lomb Spectronic 20 spectrophotometer against a blank reagent.

5. The blank contained all reagents except the oil and was subjected to the same treatment as the sample.

6. The PV was calculated as milliequivalent O<sub>2</sub> per kg of oil as follows:

(A) (B)

PV=-----

(C) (55.84)

where A= net micrograms of iron per 10 ml

B= volume of original dilution

C=weight of the sample

55.84 =molecular weight of iron

#### B. Standard Curve

1. 0.5 ml of the stock standard solution was pipetted into a 100 ml volumetric flask and dissolved in B-M to make a standard solution.

2. 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the

standard solution was then pipetted into test tubes and diluted to 10 ml.

3. One drop of ammonium thio-cyanate solution and then one drop of ferrous chloride solution was added to each test tube and then the test tubes were shaken.

4. The color was developed and the intensities of the standard solutions were measured using the same procedure as for the test sample.

Peroxide values were expressed as milliequivalent of oxygen per kilogram of oil (meq O<sub>2</sub>/kg). Values were determined from standard curves (Fig A.13) of optical density (x) vs μg of Fe (y), and from the corresponding regression equation:

$$y = 0.2242 + 0.389x$$

$$r^2 = 0.99$$

## **Results**

### **Moisture Concentration**

Tables 5.1, 5.2, and 5.3 show moisture content for seventeen varieties of hazelnuts, for 1986, 1987, and 1988, respectively. Moisture content in 1986 ranged between 6.5% in Hall's Giant to 5.1% in many varieties. For 1987 moisture content was high in Daviana, 6.3% and low with 5.2% which was found in many varieties. For 1988 moisture content was high in Casina, 6.1% and low was found in Hall's Giant with 5.1% optimum moisture content was considered not higher than 6.5% and not lower than 4%.

### **Oil concentration**

Tables 5.1, 5.2, and 5.3 show oil percentage, moisture content, residue, different forms of vitamin E, and total vitamin E equivalents for seventeen varieties of hazelnuts for 1986, '87, and '88, respectively. Oil content ranged from 57.9% in Hall's Giant to 65.7% in Tombul, in 1986, and from 56.8% in Hall's Giant to 65.1% in negret in 1987. For 1988 Hall's Giant was the lowest with 56.4% and TGDL was the highest with 64.8%.

### **Residue Concentration**

Tables 5.1, 5.2, and 5.3 show residue percent (mostly cell wall material and protein). In 1986 residue concentration ranged from 38.6% in Tombul to 35.6% in Hall's Giant. There were very small differences from one year to another.

### Fatty Acids

Tables 5.4, 5.5, and 5.6 show total lipid fatty acid composition of seventeen varieties of hazelnuts for 1986, '87, and '88. There were five major fatty acids found in all varieties; palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), and linolenic (18:3) which collectively comprised 99% of all fatty acids. Palmitoleic (16:1) and arachidic (20:0), are fatty acids that were found, less commonly, and only in a few varieties and measured less than 1%. Typical composition of hazelnut oil is about 72% oleic, 20% linoleic, 6% palmitic, and 2% stearic. Oleic and linoleic composed nearly 90% of the total. Palmitic acid ranged from 3.8% in OSU 43-58 (Willamette) and Tombul to 6.6% in TGDL for 1986. 1987 and 1988 had very similar ranges, with only a few differences. Palmitoleic acid was found in some varieties, however it was very low (<1%). Mortarella was the highest in palmitoleic, and it measured 0.9% in 1988. Stearic ranged from 0.6% in Casina for 1986 to 2.6% in Tonda Romana for 1987. But in most varieties stearic was higher than 1.5%. Oleic was the major fatty acid in all varieties and reached a high of 77.1% in Montebello for 1988. In almost all varieties oleic was higher than 70%. Linoleic acid is the second major fatty acid and was 23.8% in Tombul. Linolenic was found in all varieties, at low levels, but was a bit higher in Mortarella in all three years (2.1, 2.4, and 2.9%). The low was 0.1% 18:3 in Butler for 1986. Arachidic (20:0) was found in some

varieties and always was < 1% in the three years.

### Different Types of Nuts

Table 5.7 shows composition of fatty acids for different nuts. There were eight kinds of fatty acids found in different nuts but two of them (oleic and linoleic) are main fatty acids found in all kinds of nuts. Palmitic acid was high in chestnuts (15.2%) and black walnuts (3.3%), but was found in all kinds of nuts. Palmitoleic was very high in macadamia (22.4%) and was low (<1% or not detected) in all others. Stearic was high in Brazil nuts (9.4%) and cashew (9.4%) but was low in almonds (1.4%), and was detected in all nuts. Oleic was found in all kinds of nuts and was high in hazelnuts (74.5%) and hickories (71.7%) and low in English walnuts (18.3%). Linoleic acid measured 57.6% and 58.3% in English and black walnuts, respectively. Macadamia had low levels of linoleic acid, 2.4%. Linolenic acid was high in english walnuts (14.1%) and low in pistachios (0.41%), hazelnuts, almonds, Brazil nuts, and cashews. Macadamia did not have any 18:3. Arachidic was found in some nuts and was high in macadamia (2.4%). Gadoleic (20:1) was found in pistachios, pecans, pinenuts, macadamia, and chestnuts, and was high in macadamia with 3.1% and low in pecans with 0.12%.

### Oil Seeds

Table 5.8 shows the fatty acid composition of some oil seeds. There were eight kinds of fatty acids. Oleic (18:1) and linoleic (18:2) were the two main fatty acids. Palmitic

(16:0) was highest in corn, oat, and pumpkin (12.6, 19.3, and 16.4% respectively), it was also found in all other seeds at <10%. Palmitoleic (16:1), arachidic (20:0), and gadoleic (20:1) were found in some types, however each was <1% in all cases. Stearic (18:0) was found in all kinds of oil seeds but was less abundant than palmitic. Stearic was high in pumpkin (7.7%) and low in corn (2.4%). Oleic is the major fatty acid in some seeds and linoleic is the major fatty acid in others. In sunflower, oleic is the major fatty acid (54.3%). Linoleic was high in watermelon seeds (64.8%), corn (58.5%), and soybean (54.1%). Linolenic was high in sunflower (12.8) and low in soybean seeds (8.1%).

#### Vitamin E

Tables 5.1, 5.2, and 5.3 show oil percent, different forms of vitamin E, and total vitamin E concentration for seventeen varieties of hazelnuts. There were three kinds ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -) of tocopherol in all hazelnut varieties. The predominant form (89% on average) was  $\alpha$ -tocopherol in all varieties. Tocotrienols were either absent or present in only trace amounts. The amount of  $\alpha$ -tocopherol was variety dependent. The lowest was 302  $\mu\text{g/gm}$  oil in Ennis and the highest was 434  $\mu\text{g/gm}$  oil in Tombul, Casina, and OSU 43-58 for 1986. For 1987 the lowest was Butler with 303  $\mu\text{g/gm}$  oil, and the highest was around 434  $\mu\text{g/gm}$  oil in Casina, Tombul, Tombul Ghiaghli, and OSU 43-58. In 1988 the lowest  $\alpha$ -tocopherol was in Ennis (317  $\mu\text{g/gm}$  oil) and the highest was Casina with (451

$\mu\text{g/gm}$  oil).

Generally  $\beta$ - and  $\Gamma$ -tocopherols paralleled  $\alpha$ -tocopherol patterns by variety. Those hazelnuts high in  $\alpha$ - were also high in  $\beta$ - and  $\Gamma$ -. Beta-tocopherol ranged from a low of about  $8 \mu\text{g/g}$  oil to about  $30 \mu\text{g/g}$  oil. Gamma-tocopherol was higher than  $\beta$ - by about 5-fold, although an exception was Barcelona.

Table 5.9 shows total vitamin E ( $\alpha$ - +  $\beta$ - +  $\Gamma$ -) for three years, mean of three years, and  $\alpha$ -tocopherol equivalent ( $\alpha$ -Teq). Tombul was the highest in 1986 and 1987 ( $529, 519 \mu\text{g/gm}$  oil, respectively). Casina was high in 1988 with  $510 \mu\text{g/gm}$  oil. However, OSU 43-58 was the second highest in all three years and the averages for the three years were very close between Casina, Tombul, and OSU 43-58. Ennis was the lowest in 1986 and 1988 ( $319, 346 \mu\text{g/gm}$  oil, respectively). OSU 49-73 was the lowest in 1987 and was  $331 \mu\text{g/gm}$  oil. The mean for all varieties were 411, 406, and  $415 \mu\text{g/gm}$  oil for 1986, 1987, and 1988 respectively.

Table 5.10 shows the results of our analyses of 14 types of nuts for oil concentration, different forms of vitamin E, and total vitamin E concentration. The table was arranged from high total tocopherol to low, the highest being pistachios with  $526 \mu\text{g/gm}$  oil and the lowest being coconut with  $3.72 \mu\text{g/gm}$  oil.

From this table the nuts can be divided into three groups. The first group includes pistachios, hazelnuts, walnuts, and pecans, which are the highest in vitamin E

concentration (ie., greater than 300  $\mu\text{g}/\text{gm}$  oil). The second group is almonds, hickories, pine nuts, and Brazil nuts. These are intermediate (200 to 300  $\mu\text{g}/\text{gm}$  oil) in vitamin E concentration. The third group is peanuts, cashews, macadamia, chestnuts, and coconuts, which are lowest (less than 150  $\mu\text{g}/\text{gm}$  oil) in vitamin E concentration.

Oil concentration ranged from 76.9% in macadamia to 2.8% in chestnuts. Among the most economically (tonnage and value) important nuts which are almonds, pecans, walnuts, hazelnuts, and pistachios, the oil concentration ranges from 50.9% in pistachios to 67.2% in walnuts.

Alpha-tocopherol was high in hazelnuts, almonds, and hickories, at 366, 232, and 226  $\mu\text{g}/\text{gm}$  oil, respectively.  $\beta$ -tocopherol was low and was detected in pistachios, hazelnuts, hickories, and Brazil nuts.  $\Gamma$ -tocopherol was high in pistachios (456), English walnuts (343), pecans (331), black walnuts (305), pinenuts (222), and Brazil nuts (188).  $\delta$ -tocopherol was also detected in pistachios, English walnuts, and peanuts, the levels were 31.2, 23.3, and 6.23  $\mu\text{g}/\text{gm}$ , respectively.  $\delta$ -Tocotrienol was found in some nuts. Two kinds ( $\beta$ - and  $\Gamma$ -) of tocotrienol were found.  $\beta$ -tocotrienol was found in macadamia only, and  $\Gamma$ -tocotrienol was found in peanuts and cashews.

Pistachios were the only nuts which contained all four types of tocopherols. All others contained either two or three types.

There is a new ranking in nuts according to  $\alpha$ -Teq. Hazelnuts are highest and are way above the second highest, which are almonds. The value of  $\alpha$ -Teq for hazelnuts is 375  $\mu\text{g/gm}$  oil and almonds are 234  $\mu\text{g/gm}$  oil. Pistachios which were first in total vitamin E, now rank fifth in  $\alpha$ -Teq with 83  $\mu\text{g/gm}$  oil.

According to  $\alpha$ -Teq we can divide nuts into three groups again. The first group consists of hazelnuts with 375  $\mu\text{g/gm}$  oil. The second group consists of almonds and hickories at about 230  $\mu\text{g/gm}$  oil. The third group is all other nuts, which are below 100  $\mu\text{g/gm}$  oil.

### Oil Seeds

Table 5.11 shows the oil, different forms of vitamin E, and total vitamin E content for some oil seeds. Oil concentration ranged from 41.4% in sunflower seeds to 4.5% in corn. All forms of tocopherol were measured in oil seeds. Sunflower, corn, and sesame seeds had all four forms.  $\Gamma$ -tocopherol was highest in soybeans (704  $\mu\text{g/gm}$  oil), corn (464), and sesame seeds (416). Soybeans were higher in  $\delta$ -tocopherol (242  $\mu\text{g/gm}$  oil) than all hazelnut varieties and all other kinds of nuts.  $\alpha$ -tocopherol was highest in sunflower seeds (726  $\mu\text{g/gm}$  oil). Pumpkin and watermelon seeds were high in  $\Gamma$ -tocopherol, 281, 201  $\mu\text{g/gm}$  oil, respectively. Oats are the only seeds to contain tocotrienol, and they had 222.1  $\mu\text{g/gm}$  oil of  $\alpha$ -tocotrienol. Sunflower seeds were high in  $\alpha$ -

Teq (740  $\mu\text{g/gm}$  oil) followed by corn (242  $\mu\text{g/gm}$  oil). Watermelon seeds were low (21  $\mu\text{g/gm}$  oil).

### Storage Studies

Tables 5.12, 5.13, and 5.14 show the changes in total vitamin E content for seventeen hazelnut varieties in 1986, 1987, and 1988 crops. The hazelnuts were stored for three years, two years, and one year, respectively. From these three tables it can be seen that none of the varieties in any of the seasons lost any significant amount of vitamin E. After two years of storage for 1987 and 1988, there was only a slight decrease in the amount of total vitamin E; these amounts varied between the different varieties. OSU 43-58 and Tombul decreased from 502 and 529  $\mu\text{g/gm}$  oil to 481  $\mu\text{g/gm}$  oil after one year, after two years they decreased to 425 and 430  $\mu\text{g/gm}$  oil. However, in all varieties there was not a big decrease in total vitamin E. For nuts stored for three years there was an average decrease of 25 to 35% in vitamin E for all seventeen varieties. For example total vitamin E in Casina went from 490  $\mu\text{g/gm}$  oil at the beginning of storage to 339  $\mu\text{g/gm}$  oil after three years of storage.

Tables 5.15, 5.16, 5.17 and Tables Appendixes A.8, A.9, A.10, A.11, A.12, and A.13 show the losses of different forms of vitamin E ( $\alpha$ -tocopherol,  $\beta$ -tocopherol, and  $\Gamma$ -tocopherol) for 1986, 1987, and 1988 in all varieties. In all forms, there were no significant losses up to 18 months storage in both 1986 and 1987 crops. After that there were decreases in

amounts of  $\beta$ - and  $\Gamma$ -tocopherols. For example, in Barcelona  $\beta$ -tocopherol went from 9.7  $\mu\text{g/gm}$  oil at zero storage time to 5.8  $\mu\text{g/gm}$  oil after 3 years of storage. Tombul  $\beta$ -tocopherol went from 35.7  $\mu\text{g/gm}$  oil at beginning storage to 10.6  $\mu\text{g/gm}$  oil after 3 years storage.  $\Gamma$ -tocopherol in Tombul and OSU 45-58 decreased significantly from 41.5  $\mu\text{g/gm}$  oil at beginning storage to 17.8 and 6.3  $\mu\text{g/gm}$  oil, respectively at three years storage. Losses of vitamin E were similar for 1987 and 1988, with some small differences.

#### Moisture Content

Table Appendixes A.2, A.3, and A.4 show that moisture content did not change during the first 18 months of storage, but then moisture began to show a slight decrease, although was not statistically significant. For 1986 crops, moisture content was high in Hall's Giant (6.51%) and then decreased to 5.59%. Mortarella went from 5.1% to 4.95%. This was the same in 1987 and 1988, water content losses were not significant, and did not exceed 1%.

Table Appendixes A.5, A.6, and A.7 show percent oil of seventeen varieties for three years, 1986, 1987, and 1988, again stored for different durations. There were some increases and decreases in oil percent, but the changes were possibly related to moisture loss and were not significant. For example oil percent in Casina at the beginning of storage was 65.3% and after three years storage was 65.5% Barcelona was 62.8% at the beginning of storage as was 63.7% after three

years of storage.

### **Fatty Acid Changes**

Tables 5.18, 5.19, 5.20, 5.21, 5.22, and 5.23 show changes in fatty acids (oleic and linoleic) which are the main kinds of fatty acids. Both of these fatty acids have double bonds and are susceptible to oxidation. Oleic was much more stable than linoleic. Both of them were stable after more than a year of storage but after that time linoleic decreased faster than oleic. The decrease in linoleic acid was slow until there was a substantial loss in vitamin E, especially in  $\alpha$ -tocopherol. Linolenic acid which has three double bonds is considered more susceptible to loss and was very low in all varieties.

### **Peroxide Values**

Peroxide value was very low at the time of harvesting and was zero in some varieties. However, after six months of storage the values began to increase, but still were very low (less than 2 meq of  $O_2$ /kg oil) and were the same after one year. For 1986, varieties were stored for three years and the peroxide value increased slightly to about 25 throughout the storage time, however the hazelnuts were still not rancid. It is generally observed in the industry that PV=35 is about the incipient value to begin to taste rancidity while PV rancidity is readily tasted.

Tables 5.24, 5.25, and 5.26 show peroxide values for all seventeen varieties for 1986, 1987, and 1988 which were stored

for different periods of time. We chose some at low, medium, and high peroxide value. We can see Tombul Ghiaghli was somewhat higher in initial peroxide value (0.5 meq of O<sub>2</sub>/kg oil) and had increased after three years of storage (26.7 meq of O<sub>2</sub>/kg oil). OSU 43-58 had a low peroxide value after 3 years storage (13.5 meq of O<sub>2</sub>/kg oil).

Figs. 5.1, 5.2, and 5.3 show peroxide value for some varieties which have high vitamin E contents (OSU 43-58, Tombul, Casina) and three low in vitamin E content and peroxide value. Fig 5-1 also shows two varieties (OSU 43-58 and Barcelona) for three years 1986, 1987, and 1988. Both varieties follow the same pattern in peroxide values. During the first year there was little increase in peroxide values.

The fact that so little peroxidation had occurred in these samples is very likely due to the fact that these nuts were not subjected to high drying temperatures that often occurs under mechanically heated dryer conditions. The other study (Ch. 6) which shows the effect of high roasting temperatures on accelerated peroxide development is a case in point.

#### Farm Study

Table 5.27 shows the effect of shade and direct sun on hazelnut composition. Samples from the top of trees which were exposed to sun were high in oil content, residue, vitamin E, and lower in moisture, than those in the shade.

Total vitamin E content was higher in samples that

received direct sunlight and even individual forms of vitamin E were high.  $\alpha$ -tocopherol was significantly higher in sun than in shade.  $\Gamma$ -tocopherol was higher in direct sunlight than in shade.  $\beta$ -tocopherol was slightly higher in the shade.

Fatty acid composition for both sun and shade locations can be seen in table 5.28. They are similar in fatty acid composition. Oleic and linoleic acid are the major fatty acids. Oleic acid was higher in direct sunlight than in the shade, and stearic was higher in the shade, suggesting that stearic desaturase may be influenced by sunlight.

## Discussion

Listed in table 5.7 and 5.10 are the total oil concentration, fatty acid composition, and composition and total vitamin E of thirteen types of tree nut kernels. Data for oil concentration for some nuts agree closely with those reported by Adams (1975), Beuchat and Worthington (1978), USDA (1984), and Beuchat (1978).

For example we found almond oil concentration to be 50.8% and there have been other studies showing almonds at 52.1% (Beuchat, 1978; Mehran and Filsoof, 1974), 51.6% (Pominski et al., 1985), and 51.7 to 59.3% (Nassar et al., 1977). Unlike most other tree nuts, chestnuts are low in protein and fat, but high in carbohydrates (McCarthy and Meredith, 1988). Chestnuts in our study contained 2.8% oil. It is higher than that reported by FAO (1972) and Berry, (1982) which showed values and 1.5% and 1.6%, respectively. Another study by Payne et al (1983) found the levels of oil content at 8.4%. Our data was in good agreement with McCarthy and Meredith (1988), and Duke (1989). Macadamia nuts were 76.9% oil in our study, which was a little higher than 73.2% that reported by Beuchat (1978). Our data was in agreement with Saleeb et al (1973, Kadman and Slor (1983), and Rosenthal (1984), who all had values between 76 and 77.3%. The pistachio oil concentration values that we had were also close to other studies that have been done (Kashania, 1982; Labavitch et al., 1982; Kashania and Valadon, 1983, 1984; Dyszel and Pettit,

1990). Cashew oil values were also similar to other studies done on cashews (Barrosa, 1973; Maia et al., 1973, ; and Lecker and Pallota, 1984). We reported 43.4% and they reported 43.8%. Samant and Rege (1989) reported higher values (53.5%). Brazil nut percent oil was also in agreement with Assuncnao, et al (1984). Black walnut oil percent was 58.4% in our study and Senter and Horvat (1976) and Senter et al (1982) found values between 56.5 and 59.2%. Our English walnut percent oil values were close to those reported by Rockland et al (1961), Labavitch et al. (1984), Greve and Labavitch, (1985), Duke (1986), Greve et al. (1986), and Jan et al (1988). Pecan oil percent that we found was similar to a study done by Senter and Lorvat (1976). Peanut oil percent was in agreement with Singleton and Patte (1987), Wallerstein and Rosenthal (1989) and Branch et al. (1990).

Levels of fatty acids in several tree nuts differ somewhat from reports by other researchers. For example, Garcia (1971) reported that hazelnut oil contained 12% linoleic (18:2) and 39.1% oleic (18:1) acids as compared to 15.3% and 74.5%, respectively, which were the values we found.

Senter et al (1982) reported that black walnut oil contained 18.5% oleic and 32.6% linoleic, compared to 30.5% and 58.3%, respectively, which we reported. Greve et al. (1992) reported linoleic acid was between 57.3% and 72%. In our study linoleic acid was 58.3%. Oleic (18:1) and linoleic (18:2) in peanuts were in close agreement with studies

reported by Pearce et al (1980) and Wallerstein and Rosenthal (1980). Fatty acid composition of pistachios was similar to a study done by Kashani and Valadon (1983). Macadamia nuts had oleic acid at 58.3% in our study, while another study had a value of 66.3% (Rosenthal et al., 1984, 1989). However the level of linoleic acid was similar in both studies (2.4%). Brazil nut oleic and linoleic acids were in agreement with Assuncao et al (1984). Almond fatty acid composition is similar to a study done by Mehran and Filsoof (1974). We reported a high percent of oleic in pecans (58.6%) and linoleic (31.3%) compared to Senter and Horvat (1976 and 1979) who found values of 40.4% and 21.5%, respectively.

Oil seeds were similar to nuts in that our values were sometimes similar to and sometimes varied from other studies. Pumpkin and watermelon seed oil content were closely in agreement with that reported by Kamel et al (1982). In sunflower seeds we found oleic acid was 21.7% and linoleic was 54.3%. However, other studies have reported them at different levels. Oleic acid was found at 24.5% and linoleic at 52.7% (Warner, 1988; and Lajara et al., 1990). Keharo and Fernandez (1991) found oleic at 38.6% and linoleic at 52.7%. Oleic (53.4%) was higher in Robertson's (1978) sunflower work than in our work (41.4%). Corn oil percent was 4.5% which was less than the 5.5% reported by Brown et al (1970). Soybean oil percent was 18.2% in our study and was found at 20.5% by Rubel et al (1972). Fatty acid composition of oleic and linoleic was

close. However, linoleic (12.8%) was higher than Rubel et al (1972) and in agreement with Warner et al (1989) in all fatty acid composition. Oil content in sesame seeds was 50% in our study which was in agreement with Fukuda and Namiki, 1988; and Tashiro et al. (1990). These differences from other published values could be due to different varieties, or the same variety grown under different environmental conditions, especially temperature.

Unsaturation/saturation ratio, which gives an indication of potential susceptibility of tree nut kernels to oxidation and consequential flavor deterioration, English walnut with a ratio of 12:1 should be the least stable and Brazil nuts with a ratio of 5:1 should be among the most stable during prolonged storage.

In addition to the effects of cultivars and agronomic practices on oil content and fatty acid composition of tree nuts, the stage of maturity may have an influence. Mature pecan kernels contain a higher percentage of oil accompanied by a higher degree of saturation than do immature nuts. (Heaton et al., 1977). Oil from mature cashews also has been noted to be more saturated than that from immature fruits (Maia et al., 1975). Pecan trees having a heavy crop are likely to yield nuts that are smaller in size, lower in oil content, and higher in unsaturated/saturated fatty acid ratio (Heaton et al., 1977). Barroso et al. (1973), reported that there were some differences in the fatty acid values of two

kernel sizes of Brazil nuts and cashews.

Many factors are playing important roles in the relative composition of the fatty acids, especially oleic and linoleic. Those factors are related to local climatic conditions such as temperature at time of planting, blooming and maturing, and geographical latitude (Lajara et al., 1990). Fatty acid composition of mature sunflower seed oil is more a function of the geographical location and climatic conditions than anything else. The relative proportions of oleic and linoleic acids which are highly negatively correlated (Canvin, 1965) to high temperature increases the concentration of oleic acid and decreases that of linoleic acid, while low temperatures increase linoleic concentration. Oleic and linoleic acid percentages are entirely under genetic control of the seed embryo of safflower (Applequist, 1974). Whereas in soybean the levels of oleic, linoleic, and linolenic acids are essentially controlled by the genotype of the maternal plant with minor contributions from the genotype of the embryo (Applequist, 1974).

Many reports give only total vitamin E or  $\alpha$ -tocopherol for different nuts and oil seeds. In our data we reported all homologues of vitamin E. McLaughlin and Weihrauch (1979) reported total vitamin E as mg/100gm of dry matter. Fukuba and Murota (1985) reported vitamin E as  $\mu$ g/gm of oil. Total vitamin E content of cashews in our study was in agreement with Fukuba and Murota (1985). Total vitamin E concentration

in macadamia nuts was 29.6  $\mu\text{g}/\text{gm}$  oil. However, Fukuba and Murota reported zero vitamin E in macadamia nuts. Ironically tins of macadamia nuts have been advertized as being rich sources of vitamin E. Apparently no one bothered to make the analysis. We found a total vitamin E concentration in pistachio of 526  $\mu\text{g}/\text{gm}$  oil which we found was higher than the value reported by Fukuba and Murota (1985) (339  $\mu\text{g}/\text{gm}$  oil). Pecan total vitamin E was 339  $\mu\text{g}/\text{gm}$  oil was different than results reported by McLaughlin and Weihrauch (1979) (19.8 gm/100 gm weight of kernel).

Reports on the concentration of individual tocopherols in peanut oils are contradictory. In some studies, the  $\alpha$ -tocopherol was higher than  $\Gamma$ -tocopherol (Carpenter et al., 1976), while in others the reverse was true (Lambertsen et al., 1962; Rao et al., 1965; and Strum et al., 1966). In our study, the  $\Gamma$ -tocopherol was high, 222  $\mu\text{g}/\text{gm}$  oil.

Different forms of vitamin E in different nuts may be due to genetic variations. Each one has a dominant form of vitamin E. Fatty acid composition may have an influence on the type of vitamin E. It may be that synthesis of vitamin E is closely linked to synthesis of certain of the unsaturated fatty acids.

Hazelnuts rank first in  $\alpha$ -tocopherol equivalent. The major form of vitamin E in hazelnuts is  $\alpha$ -tocopherol and according to the biological activity of each one. If  $\alpha$ -tocopherol is made equal to 1.0, the typical activity factors

are  $\beta$ -tocopherol 0.05,  $\Gamma$ -tocopherol 0.1,  $\delta$ -tocopherol 0.01,  $\alpha$ -tocotrienol 0.3,  $\beta$ -tocotrienol 0.05, and  $\Gamma$ -tocotrienol 0.01 (Bieri and Evarts, 1973, 1975; and Hjarde et al., 1973; Bieri and Farrell, 1976; McLaughlin and Welhrauch, 1979). Hazelnut  $\alpha$ -Teq is 375 and pistachio which was the first in the table according to total vitamin E content became fifth in  $\alpha$ -Teq because the major form of pistachio vitamin E is  $\Gamma$ -tocopherol and biological activity of  $\Gamma$ -tocopherol is 0.1.

The data on hazelnut varieties is presented for the first time. We found some varieties higher in vitamin E concentration and others low, this is clearly due to genetic differences since these were all grown under the same conditions. For example Tombul was high in vitamin E content and Barcelona was low and they were both growing on the same farm and experienced the same field conditions. For fatty acids there were differences between the varieties and these differences are apparently related to a difference in vitamin E concentration. For example  $\alpha$ -tocopherol was high and that seemed to relate to high levels of oleic acid. It may be that during the time of synthesis of oleic acid there is another closely linked pathway to synthesize  $\alpha$ -tocopherol.

Storage studies show that hazelnuts are stable in storage under low temperatures (5°C) for long periods of time, up to two years. Hazelnuts can be kept for long periods when the temperature is reduced, moisture content of kernels is 5-6%, and relative humidity is suitable for storage. The protective

shell of the hazelnut and the polyphenolic compounds in the pellicle are other factors in long stability.

The main thing which stabilized hazelnuts in storage was vitamin E content. Vitamin E is a major antioxidant that keeps fatty acids from rancidity. Another reason is that there may be a relationship between fatty acid synthesis and vitamin E synthesis. From other studies on oil seeds, the optimum concentration of tocopherol for oxidative stability of soybean oil seems related to the oxidative stability of each individual tocopherol. The oxidative stability of the tocopherol was  $\alpha$ ,  $\Gamma$ , and  $\sigma$ -tocopherol (Ikeda and Fukuzumi, 1977). Perhaps there is something to be gained with respect to kernel longevity in hazelnuts by breeding for tocopherol levels, because the same was found in wheat (Fielding and Goldsworthy, 1980). Vitamin E acts as a biological lipid antioxidant by reacting with free radicals (Tappel, 1962; Burton and Ingold, 1983; Mitsumoto et al., 1991).

There have been reports which associate declining tocopherol levels with storage or aging of seed materials. Wheat germ lost 5.1% of tocopherol during 6 months storage. In several oil seeds tocopherols declined with storage time and aging (Sharma, 1977).

Moisture concentration was low and is another reason that hazelnuts in our study did not go rancid quickly. Peroxide values slowly increased after different storage times, but even after more than two years the hazelnuts were good for

consumption. It is well known that the residual water content of dried products is of great importance for the rate of oxidative deterioration. The humidities of all the cereals were found to be well within the range of 8-10% of residual water content (Percheron and Loliger, 1990). The high stability of hazelnuts may be due to the inactivity of some enzymes such as lipase and lipoxygenase, as a result of the drying process. Studies on English walnuts (Rockland et al., 1961), soybean (Hammond and Fehr, 1984; Davis et al., 1987; Dahmer et al., 1989), and fish oil (Karahadian and Lindsay, 1989) showed similar results.

Oleic and linoleic acids were higher in direct sunlight than in the shade and this was in agreement with other studies done on walnuts (Greve et al., 1992), sunflower seeds (Lajara et al., 1990b) and soybean (Rennie and Tanner, 1989).

**Literature Cited**

- Adams, C.F. 1975. "Nutritive value of American foods" ARS, USDA. Agriculture handbook No. 456, Washington, DC.
- Adnan, M. 1980. Lipid properties and stability of partially defatted peanuts. Ph.D. thesis. Urbana, Illinois.
- Anon. 1992. Vitamin E supplementation enhances immune response in the elderly. Nutrition Reviews. 50:85-87.
- Appelquist, L.A. 1974. Metabolism and control of lipid structure modification. Biochem. Cell Biol. 64:66-69.
- Assuncao, F.P., M.H.S. Bentes, and H. Serraya. 1984. A comparison of the stability of oils from brazil nut, Para rubber and passion fruit seeds. J. Amer. Oil Chem. Soc.. 61: 1031-1035.
- Barroso, M.A.T., F.M. Whiting, W.H. Brown, and J.W. Stull. 1973. Fatty acids of Brazilian cashew kernels. Hortscience 8:99-101.
- Berry, S.K. 1982. Fatty acid composition and cyclopropene fatty acid content of china-chestnuts (Sterculia monosperma, Venenat). J. Amer. Oil Chem. Soc. 59:57-58.
- Beuchat, L.R. 1978. Relationship of water activity to moisture content in tree nuts. J. Food Sci. 43:754-755.
- Beuchat, L.R., and R.E. Worthington. 1978. Technical note: Fatty acid composition of tree nut oils. J. Food Tech. 13:355-358.
- Bieri, J.G. and R.P. Everts. 1973. Tocopherols and fatty acids in American diet. The recommended allowance for vitamin E. J. Am. Diet Assoc. 62: 147-152.
- Bieri, J. C. and R. P. Everts. 1975. Effect of dietary polyunsaturated fatty acids on tissue vitamin E status. U. Nutr. 108: 392-398.
- Bieri, J. C. and P. M. Farrell. 1976. Vitamin E. Vitamins Hormones. 34: 31-75.
- Branch, W.D., T. Nakayama, and M. Chinnon. 1990. Fatty acid variation among U.S. runner type peanut cultivars. J. Amer. Oil Chem. Soc. 67:591-593.

- Brown, C.M., E.J. Wever, and C.M. Wilson. 1970. Lipid and amino acid composition of developing oats. *Crop Sci.* 10:488-491.
- Burton, G.W., and K.U. Ingold. 1983. Autoxidation of biological molecules. 1. The antioxidant activity of vitamin E and related chain breaking phenolic antioxidants in vitro. *J. Amer. Oil Chem. Soc.* 103:6472-6477.
- Canvin, D.T. 1965. The effect of temperature on the oil content and fatty acid composition of the oil from several oil seed crops. *Canadian J. Bot.* 43:63-69.
- Carpenter, D. L., J. Lehman, B. S. Mason and H. T. Slover. 1976. Lipid composition of select vegetable oils. *J. Amer. Oil Chem. Soc.* 53: 714-716.
- Chapman, R.A., and K. Mackey. 1949. The estimation of peroxides in fats and oils by the ferric thiocyanate method. *J. Amer. Oil Chem. Soc.* 26: 360-364.
- Chen, L.H., G.A. Boissonneault, and H.P. Glauert. 1988. Vitamin C, vitamin E and cancer. *Anticancer Res.* 8:739-748.
- Dahmer, M., P. Fleming, G. Collings, and D. Hildebrand. 1989. A rapid screening method for the determination of the lipid composition of soybean seeds. *J. Amer. Oil Chem. Soc.* 66:543-548.
- Dale, L.K, E.G. Hill, and R.T. Holman. 1962. The thiobarbituric acid reaction and the autoxidations of polyunsaturated fatty acid methyl esters. *Arch. Biochem. Biophys.* 98:253.
- Davies, C.S., S.S. Nielson, and N.C. Nielson. 1987. Flavor improvement of soybean preparations by genetic removal of lipoxygenase 2. *J. Amer. Oil Chem. Soc.* 61:1428-1433.
- Duke, J.A. 1985. Medicinal plants (letter), *Science.* 229: 1036.
- Duke, J.A. and A.A. Atchley. 1986. Handbook of proximate analysis tables of higher plants. CRC press, Inc. Boca Raton, Florida. p.389.
- Dyszal, S.M. and C.P. Bruce. 1990. Determination of the country of origin of pistachio nuts by DSC and HPLC. *J. Amer. Oil Chem. Soc.* 67:947-951.

- Eustace, H.J. 1989. There is only one way. Nut Grower Society of Oreg., Wash., and Brit. Col. 74th Annual meeting. pp. 113-120.
- FAO. 1972. Food composition table for use in East Asia. Food and Agric. Organ. of United Nations, Rome.
- Feilding, J.L. and A. Goldsworthy. 1980. Tocopherol levels and aging in wheat grains. J. Food Sci. 46:453-456.
- Forbes, W.R. Jr., S.D. Senter, B.G. Lyon, and H.P. Dupey. 1980. Correlation of objective and subjective measurements of pecan kernel quality. J. food Sci. 45: 1378-1379.
- Forbes, W.R. Jr., S.D. Senter, and R.L. Wilson. 1983. Cultivar, processing, and storage effects on pecan kernel color. J. Food Sci. 48: 1646-1649.
- Fraser, G. E., F. J. Sabat, W. L. Beeson, and M. Strahan. 1992. A possible protective effect of nut consumption on risk of coronary heart disease. Arch Intern Med. 152:1416-1424.
- Fukuda, Y., and M. Namiki. 1988. Recent studies on sesame seed and oil. Nippon Shokutin Kogyo Gakkaishi. 35: 552-555.
- Garcia-Olmedo and M.A. Marcos-Garcia. 1971. Contribucion al Estudio de los Aceites de Frutos Secos Espanoles. Composicion Acidica. Anal. Bromatol. 23:253-258.
- Gardner, H.W. 1986. Preparative isolation of monogalactosyl and digalactosyl diglycerides by thin-layer chromatography. Lipid. 9:139-141.
- Gray, J.I. 1978. Measurement of lipid oxidation. J. Amer. Oil Chem. Soc. 55:539-543.
- Greve, L.C. and J.M. Labavitch. 1985. Development of rancidity in walnuts. Walnut research reports. pp.235-243.
- Greve, L.C., R. Darnell, and J.M. Labavitch. 1986. Development of rancidity in walnuts. Walnut research reports. pp.102-106.
- Greve, L.C., G. McGranahan, J. Hasey, R. Snyder, K. Kelly, D. Goldhamer, and J.M. Labavitch. 1992. Variation in polyunsaturated fatty acids composition of Persian walnut. J. Amer. Soc. Hort. Sci. 117(3):518-522.

- Hammond, E.G. and W.R. Fehr. 1984. Improving the fatty acid composition of soybean oil. *J. Amer. Oil Chem. Soc.* 61:1713-1716.
- Hara, S. and Y. Totani. 1968. A highly sensitive method for the micro-determination of lipid hydroperoxides by potentiometry. *J. Amer. Oil Chem. Soc.* 65:1948-1950.
- Heaton, E.K., A.L. Shewfelt, A.E. Badenhop, and L.R. Beuchat. 1977. Pecan: Handling, storage, processing, and utilization. Univ. Georgia. Athens, Georgia, USA. *Agric. Res. Bull.* 197:pp.77.
- Hills, G.L. and C.C. Thiel. 1946. The ferric thiocyanate method of estimating peroxide in the fat of butter, milk and dried milk. *J. Dairy Res.* 14: 340-344.
- Hjarde, W., E. Leerbeck, and T. Leth. 1973. The chemistry of vitamin E including its chemical determination. *Acta Agri. Scand. Suppl.* 19: 87-92.
- Horwitt, M.K. 1961. Vitamin E in human nutrition. *Bordens Rev. of Nutr. Res. Handl.* 22: 1-5.
- Ikeda, N., and K. Fukuzumi. 1977. Quantitative analysis of tocopherol in autoxidized methyl linoleate. *J. Japan Oil Chem. Soc.* 26:343-346. In: *Food Sci. Tech. Abstr.* (1978). 10:2A133.
- Jan, M., D.I. Langerak, T.G. Wolters, J. Farkas, H.J.V.D. Kamp, and B.G. Muuse. 1988. The effect of packaging and storage conditions of the keeping quality of walnuts treated with disinfestation doses of gamma rays. *Acta Alimentaria.* 17:13-31.
- Jung, M.Y. and D.B. Min. 1990. Effect of  $\alpha$ -,  $\Gamma$ -,  $\delta$ -tocopherol on oxidative stability of soybean oil. *J. Food Sci.* 55:1464-1464.
- Kadman, A. and E. Slor. 1983. "Yonik" macadamia. *Hort. Sci.* 17:991.
- Kanner, J., I. Shegalovich, S. Harel, and B. Hazan. 1988. Muscle lipid peroxidation dependent on oxygen and free metal ions. *J. Agric. Food Chem.* 36:409-412.
- Karahadian, C. and R.C. Lindsay. 1989. Action of tocopherol type compounds in directing reactions forming flavor compounds in auto-oxidizing fish oils. *J. Amer. Oil Chem. Soc.* 66:1302-1308.

- Kashani, G.G.. 1982. The effect of roasting and of gamma irradiation on various chemical constituents of six varieties of Iranian pistachio nuts. PhD thesis. University of London.
- Kashani, G.G. and L.R.G. Valaden. 1983. Effect of salting and roasting on the lipids of Iranian pistachio kernels. *J. Food Technol.* 18: 461-467.
- Kashani, C.G. and L.R.G. Valadon. 1984. Effect of gamma irradiation on the lipids, carbohydrates, and proteins of Iranian pistachio kernel. *J. Food Tech.* 19:631-638.
- Kim, M.A., T. Matoba, and K. Hasegawa. 1988. Thermal oxidation stability of interesterified oils under continuous heating conditions. *Agric. Biol. Chem.* 52:1239-1244.
- Kiritsakis, A.K. and L.R. Dugan. 1984. Effect of selected storage conditions and packaging materials on olive oil quality. *J. Food Sci.* 49: 334-336.
- Knekt, P., A. Aromaa, J. Maatela, R. Aaran, M. Hadama, and L. Tepp. 1991. Vitamin E and cancer prevention. *Am. J. Clin. Nutr.* 53:2835-2865.
- Labavitch, J.M., C.M. Heintz, H.L. Rae, and A. Kader. 1982. Physiological and compositional changes associated with maturation in 'Kerman' pistachio nuts. *J. Amer. Soc. Hort. Sci.* 107:688-692.
- Labavitch, J.M., L.C. Greve, and A.A. Kader. 1984. Factors affecting rancidity of walnuts. *Walnut research reports.* pp.184-185.
- Ladiko, D. and V. Lougovois. 1990. Lipid oxidation in muscle foods. *Food Chem.* 35:295-314.
- Lajara, J.R., U. Diaz, and R.A. Quidiello. 1990. Definite influence of location and climatic conditions on the fatty acid conditions of sunflower oil. *J. Amer. Oil Chem. Soc.* 67:618-623.
- Lambertsen, G., H. Myklestad, and O.R. Brekkan. 1962. Tocopherol in nuts. *J. Sci. Food Agric.* 13: 617-620.
- Lercker and Pallotta. 1984. Cashew seed and oil composition. In: *Cashew research and development.* Ed. Bhaskara E.V. and Khan H.H. pp.184-195. Published by Indian Soc. for plantation Crops

- Maia, G.A., W.H. Brown, F.M. Whiting, and J.W. Stull. 1975. Cashew fatty acids. *HortScience*. 10:233-234.
- McCarthy, M.A. and F.I. Meredith. 1988. Nutrient data on chestnuts consumed in the United States. *Econ. Bot.* 42:29-36.
- McLaughlin, P.J. and J.L. Weihrauch. 1979. Vitamin E contents of foods. *J. Amer. Diet. Assoc.* 75: 647-781.
- Mehran, M. and M. Filsoof. 1974. Characteristics of Iranian almond nuts and oil. *J. Amer. Oil Chem. Soc.* 51:433-434.
- Miller, A. 1991. Pollinizer selection and spacing. Nut grower society of Oregon, Washington, and British Columbia. pp.74-79.
- Mitsumoto, M.C., R.G. Faustman, R.N. Cassen, and K.K. Scheller. 1991. Vitamin E and C improve pigment and lipid stability in ground beef. *J. Food Sci.* 56:194-197.
- Nassar, A.R., B.S. El-Tahawi, and A.S. El-Deen. 1977. Chromatographic identification of oil and amino acid constituents in kernels of some almond varieties. *J. Amer. Oil Chem. Soc.* 54:553-556.
- Payne, J.A., R.A. Jaynes, and S.J. Kays. 1983. Chinese chestnut production in the United States: practice, problems, and possible solutions. *Econ. Bot.* 37(2):187-200.
- Pearce, R.S. and I.M.A. Samual. 1980. Change in fatty acid content of polar lipids during aging of seeds of peanut. *J. Exp. Bot.* 31:1283-1290.
- Percheron, E. and J. Loliger. 1990. Influence of drying technology on pre-cooked cereal autoxidation. *Lebensm. Wiss. U. Tech.* 23:400-403.
- Pominski, J., H.M. Pearce Jr., and R.E. Ritter. 1985. Development of partially defatted almonds: Laboratory evaluations. *J. Food Sci.* 50:716-718.
- Pompella, A., E. Maellaro, A.F. Casini, M. Ferrali, and M. Comporti. 1987. Measurement of lipid peroxidation in vivo: A comparison of different procedures. *Lipids* 22:206-211.

- Pryor, W.A., J.P. Stanley, and E. Blair. 1976. Autoxidation of polyunsaturated fatty acids. 2. A suggested mechanism for the formation of TBA-reactive materials from prostaglandin-like endoperoxids. *Lipids* 11:370.
- Rao, M. K. G., and K. T. Achaya. 1967. Role of tocopherol as an antioxidant in safflower oil. *Fette, Seifen, Anstrich Mittel*. 67: 711. in: *Biol. Abstr.* (1986) 49: 44310.
- Rennie, B.D. and J.W. Tanner. 1989. Fatty acid composition of oil from soybeans grown at extreme temperatures. *J. Amer. Oil Chem. Soc.* 66:1622-1624.
- Rhee, C.O. and Z.U. Kim. 1982. Analysis of the lipid components in chestnut (*Castanea crenata*). Part 1. Composition of lipid fraction of inner and outer part of chestnut. *J. Korean Agric. Chem. Soc.* 25(4):239-247.
- Robertson, J.A., G.W. Chapman, and R.L. Wilson. 1978. Relation of days after flowering to chemical composition and physiological maturity of sunflower seed. *J. Amer. Oil Chem. Soc.* 55:266-269.
- Rockland, L.B., K.M. Swarthout, and R.A. Johnson. 1961. Studies on English walnuts, *Juglans regia* III. *Food Technol.* 15:112-116.
- Rosenthal, I., U. Merin, D. Basker, and A. Kadman. 1984. A study of macadamia nuts of the "Yonik" variety. *J. Food Qual.* 7:67-73.
- Rosenthal, I., U. Merin, and A. Kadman. 1986. Comparison of some properties of macadamia nuts of the "Yonik" and "Beaumont" cultivars. *Lebensm. Wiss. U. Technol.* 19:53-55.
- Rubel, A., R.W. Rinne, and D.T. Canvin. 1972. Protein, oil, and fatty acids in developing soybean seeds. *Crop Sci.* 12:739-741.
- Saleeb, W.F., D.M. Yermanos, C.K. Huszar, W.B. Storey, and C.K. Labanauskas. 1973. The oil and protein in nuts of *Macadamia tetraphylla* L. Johnson, *Macadamia integrifolia* Maiden and Betche, and their F<sub>1</sub> hybrid. *J. Amer. Soc. Hort. Sci.* 98:453-456.
- Samant, S.K. and D.V. Rege. 1988. Carbohydrate composition of cashew nut and charoli. *Lebensm. Wiss. U. Technol.* 21:164-168.
- Senter, S.D. and R.J. Horvat. 1976. Lipids of pecan nut meats. *J. Food Sci.* 41:1201-1203.

- Senter, S.D. and R.J. Horvat. 1979. Lipid constituents of black walnut kernels. *J. Food Sci.* 44:266-268.
- Senter, S.D., R.J. Horvat, and W.R. Forbus. 1982. GLC-MS analysis of fatty acids from five black walnut cultivars. *J. Food Sci.* 47:1753-1755.
- Sharma, K.D. 1977. Biochemical changes in stored oil seeds. *Indian J. Agric. Res.* 11:137-141.
- Singleton, J.A. and H.E. Pattee. 1987. Characterization of peanut oil triacylglycerols by HPLC, GLC, and EIMS. *J. Amer. Oil Chem. Soc.* 64:534-538.
- Sinnhuber, R.O. and T.C. Yu. 1958. 2-Thiobarbituric acid method for the measurement of rancidity in fishery products. 2. The quantitative determination of malonaldehyde. *Food Tech.* 12:9.
- Sinnhuber, R.O. and T.C. Yu. 1977. 2-Thiobarbituric acid reaction an objective measure of the oxidative deterioration occurring in fats and oils. *J. Japan Oil Chem. Soc.* 26:259.
- Sturm, P.A., R.M. Parkhurst, and W.A. Skinner. 1966. Quantitative determination of individual tocopherol by thin layer chromatographic separation and spectrophotometry. *Anal. Chem.* 38: 1245-1248.
- Tappel, A.L. 1962. Vitamin E as the biological lipid antioxidant. *Vitamin Horm.* 20:493-496.
- Tashiro, T., Y. Fukuda, T. Owasa, and N. Namiki. 1990. Oil and minor components of sesame strains. *J. Amer. Oil Chem. Soc.* 67:508-511.
- Thompson, M.M. and D.G. Richardson. 1978. Is there an effect of pollenizers on filbert kernel quality? Nut growers society of Oregon, Washington, and British Columbia. pp.52-58.
- USDA. 1984. Composition of foods: nut and seed products; raw, processed, prepared. USDA. *J. Agric. Handbook.* 8-1.
- Wallerstein, I.S., U. Merin, and I. Rosenthal. 1989. Comparison of kernels of three Virginia-type peanut cultivars. *Lebensm. Wiss. U. Technol.* 22:179-181.
- Warner, K., E.N. Frankel, and T.L. Mount. 1988. Flavor evaluation of crude oil to predict the quality of soybean oil. *J. Amer. Oil Chem. Soc.* 65:386-391.

Whitehouse, W.E., E.J. Koch, L.E. Jones, J.C. Long, and C.L. Stone. 1964. Influence of pollen from diverse pistachio species on development of pistachio nuts. J. Amer. Soc. Hort. Sci. 84:224-229.

Williamson, P.M. 1991. The hazelnut industry measuring its growth. Nut grower society of Oregon, Washington, and British Columbia. pp.34-40.

Table 5.1. Oil content, moisture, residue, and vitamin E concentration of seventeen varieties of hazelnuts for 1986.\* Tocopherols are expressed as  $\mu\text{g/g}$  oil.

Variety	Oil %	H <sub>2</sub> O %	Res %	$\alpha$ -toc.	$\beta$ -toc.	$\Gamma$ -toc.	Total toc.	$\alpha$ -toc equiv
Tombul	65.7 a	5.7	28.6	433.7 a	35.7 a	41.9 a	529.3 a	453 a
OSU 43-58 Willamette	63.4 d	5.3	31.3	428.8 c	31.6 b	41.6 a	502.0 b	446 a
Casina	65.3 a, b	5.8	28.9	431.6 b	19.3 d	38.7 b	489.6 c	444 a, b
Tombul Ghiaghli	65.4 a, b	5.3	29.4	416.9 d	29.7 c	28.7 c	475.3 d	432 c
Imperial	61.8 g	5.9	32.4	416.1 d	14.0 e	16.7 f	446.8 e	423 d
Mortarella	63.4 d	5.1	31.5	401.5 e	12.3 k j	15.6 g	429.4 f	408 e
Tonda Romana	62.9 e	5.3	31.8	398.7 f	12.0 k	15.6 g	426.2 g	405 f
Negret	64.9 c	5.0	30.1	377.8 g	13.6 ihj	14.1 h	405.5 h	385 g
Tonda di Giffoni	62.9 e	5.3	31.8	376.7 h	9.9 l	11.7 j	398.3 i	382 h
Daviana	60.3 i	5.7	34.0	362.3 i	15.2 e	20.0 d	397.2 i	370 i
Hall's Giant	57.9 j	6.5	35.6	360.9 i	12.7 k	13.8 i	387.4 j	368 j
TGDL	63.0 e	5.7	31.3	355.6 j	12.8 ijk	17.8 e	386.3 j	368 j
OSU 49-73	62.9 e	5.3	31.9	325.7 k	13.7 ihj	11.2 j	350.5 k	363 k
Montebello	61.3 h	5.4	33.5	318.7 m	15.6 e	14.3 h	348.6 k	332 i
Butler	61.4 h	5.8	32.8	323.2 l	14.6 efg	11.2 j	349.0 k, l	326 m
Barcelona	62.8 e	5.3	31.9	317.4 m	9.7 l	10.8 k	337.9 m	324 n
Ennis	61.4 h	5.2	33.4	302.2 n	8.1 m	9.1 i	319.4 n	322 o

\* Each value represents the mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.2. Oil content, moisture, residue, and vitamin E concentration of seventeen varieties of hazelnuts for 1987.\* Tocopherols are expressed as  $\mu\text{g/g}$  oil.

Variety	Oil	H <sub>2</sub> O	Res	$\alpha$	$\beta$	$\Gamma$	Total	$\alpha\text{Teq}$
Tombul	64.1 d	5.5	30.4	433.5 b	19.4 a	65.8 a	518.7 a	448 b
OSU 43-58 Willamette	63.5 e	5.2	31.3	455.2 a	11.2 e	38.5 b	505.8 b	464 a
Casina	63.9 d	5.8	30.3	435.7 b	15.8 c	39.7 b	491.2 c	446 b
Tombul Ghiaghli	64.3 c	5.6	30.1	433.5 b	17.8 b	27.9 c	479.2 d	445 b
Imperial	60.7 i, j	5.3	34.1	418.8 c	12.5 d	17.9 e	449.2 e	426 c
Mortarella	62.1 h	5.2	31.8	414.9 d	13.5 d	17.9 e	446.2 e	422 c
Montebello	62.5 g	5.2	32.4	325.6 j	8.3 g h	10.2 j	344.2 e	329 h
Negret	65.1 a	5.8	29.1	380.6 e	12.6 d	11.4 h	404.6 f	386 d
TGDL	62.6 g	6.0	31.4	364.4 g	8.5 g f	25.4 d	398.4 f	370 e
Hall's Giant	56.8 n	5.9	37.3	370.4 f	10.9 e f	6.2 l	387.5 g f	375 e
Tonda di Giffoni	62.9 f	5.5	31.6	365.4 g	7.0 h	8.6 k	381.0 g	368 f, e
Tonda Romana	64.5 b	5.5	30.0	347.1 i	9.1 g f	13.9 g	370.1 h	352 g
Daviana	59.9 m	6.3	33.8	355.6 h	11.7 e	16.7 f	384.0 g f	362 f
Barcelona	60.5 j k	6.1	33.5	348.4 i	11.2 e	9.4 k j	369.0 h	354 j
Butler	60.8 i	6.0	33.2	303.4 l	12.9 d	10.5 i j	353.8 i	310 j
Ennis	60.1 l	5.5	34.1	312.2 k	11.6 e	14.1 g	337.9 j	319 i
OSU 49-73	63.4 e	5.3	31.2	313.3 k	7.8 g h	9.8 k j	330.9 k	317 i

\*Each value represents a mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.3. Oil content, moisture, residue, and vitamin E concentration of seventeen varieties of hazelnuts for 1988.\* Tocopherols are expressed as  $\mu\text{g/g}$  oil.

Variety	Oil %	H <sub>2</sub> O %	Res %	$\alpha$ -toc.	$\beta$ -toc.	$\gamma$ -toc.	Total toc.	$\alpha$ toc equi
Casina	64.5 b	6.0	29.5	450.5 a	17.9 b	41.9 c	510.3 a	462 a
OSU 43-58 Willamette	63.4 c	5.6	31.1	415.4 b	20.8 a	51.0 b	487.3 b	429 b
Tombul	64.5 b	5.6	30.0	401.8 d	9.5 i	59.3 a	470.6 c	412 c, b
Imperial	63.3 c	5.9	30.8	412.5 c	13.7 f	20.6 d	446.8 d	420 b
Mortarella	60.1 g	6.4	31.4	415.5 b	10.8 h	13.4 h i	439.7 d	421 b
Tombul Ghiaghli	64.5 b	5.4	30.1	409.5 d	11.4 g	15.4 g	436.3 d	416 c
Hall's Giant	56.4 h	5.1	35.5	386.1 e	14.1 e	17.2 f	417.4 e	393 d
Negret	63.6 c	5.5	30.9	381.9 f	16.8 c b	14.3 h	413.0 e	390 e d
Tonda di Giffoni	63.5 c	5.8	30.8	388.3 e	11.6 g	12.5 j	412.4 e	394 d
TGDL	64.8 a	6.0	29.2	377.9 g	13.8 f e	18.9 e	410.6 e	385 e
Tonda Romana	63.4 c	5.6	31.1	368.9 h	13.3 f	16.9 f	399.1 e	376 f e
Montebello	60.5 f	5.2	33.4	364.7 h	17.3 b	12.0 j k	393.9 f	372 f
OSU 49-73	62.0 d	5.8	32.1	355.2 i	16.3 d	13.0 j i	384.5 f	363 g
Daviana	61.6 e	6.0	33.3	357.2 i	10.4 h i	11.6 l k	379.2 f	362 g
Butler	61.9 e	6.0	32.2	331.6 j	13.9 e	13.7 h i	359.2 g	339 h
Barcelona	62.0 e, d	5.5	32.6	324.9 k	11.0 g	11.7 l k	347.5 g	331 h
Ennis	60.8 g	5.7	35.1	316.9 l	14.5 e	14.8 h g	346.2 g	324 i

Each value represents the mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.4. Fatty acid composition of seventeen varieties of hazelnuts for 1986.\* Fatty acids are expressed as percentage of total.

Variety	16:0	16:1	18:0	18:1	18:2	18:3	20:0
Tombul	3.8	---	1.1	72.4 e	21.6 a	1.1	---
OSU 43-58 Willamette	3.8	0.4	1.0	74.2 b	19.3 d	1.3	---
Casina	4.3	0.1	0.8	73.2 d	20.7 b	0.9	---
Tombul Ghiaghli	5.8	0.4	1.9	70.2 h	19.4 e	1.9	0.4
Imperial	5.8	0.3	2.1	71.9 f	18.1 g	1.8	---
Mortarella	4.6	0.9	1.5	73.7 c	16.1 i	2.9	0.3
Tonda Romana	5.1	0.3	1.5	73.9 c	18.3 g	0.9	---
Negret	5.1	0.6	2.1	72.6 e	18.9 f	0.7	---
Tonda di Giffoni	5.3	0.8	2.3	66.3 i	16.6 h	1.3	0.2
Daviana	5.1	---	1.4	72.8 c	20.2 c d	0.5	---
Hall's Giant	5.9	0.8	1.9	71.3 g	19.9 d	0.2	---
TGDL	6.6	---	1.9	71.7 f	18.3 g	1.3	0.2
OSU 49-73	6.2	---	2.2	71.9 f	18.8 f	0.9	---
Montebello	5.1	0.4	2.3	77.1 a	12.8 j	1.7	0.6
Butler	6.5	0.6	2.6	68.9 i	20.5 c b	0.4	0.3
Barcelona	5.9	0.3	1.4	71.7 f	19.9 d	0.8	---
Ennis	6.2	---	1.8	71.2 g	20.4 c b	0.4	---

\*Each value represents the mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.5. Fatty acid composition of seventeen varieties of hazelnuts for 1987.\* Fatty acids are expressed as percentage of total.

Variety	16:0	16:1	18:0	18:1	18:2	18:3	20:0
Tombul	4.5	---	1.3	69.6 h	23.8 a	0.8	---
OSU 43-58 Willamette	3.3	0.3	1.4	73.8 d	20.4 c	0.8	---
Casina	3.6	---	0.6	73.5 e d	21.9 b	0.4	---
Tombul Ghiaghli	5.3	0.6	2.0	73.8 d	17.6 e	0.5	0.2
Imperial	5.5	---	1.5	75.6 a	16.5 f	0.9	---
Mortarella	4.8	0.5	1.9	74.5 e b	15.3 g	2.1	---
Montebello	6.1	---	1.9	75.4 a	16.3 f	0.3	---
Negret	6.1	0.4	1.6	75.2 a	15.6 g	1.1	---
TGDL	5.8	---	1.3	74.0 c d	17.8 e	0.8	0.3
Hall's Giant	4.9	0.4	1.2	70.2 h	21.5 b	1.8	---
Tonda di Giffoni	6.3	0.4	2.2	74.5 e b	14.8 h	1.5	0.3
Tonda Romana	5.4	---	1.6	70.1 h	21.8 b	1.1	---
Daviana	4.9	---	1.9	73.5 e d	18.7 d	1.0	---
Barcelona	6.1	0.5	1.6	72.6 f	18.8 d	0.4	---
Butler	6.1	0.3	1.6	73.2 e d	18.7 d	0.1	---
Ennis	5.9	---	1.9	70.9 g	20.5 c	0.8	---
OSU 49-73	6.4	---	1.8	74.7 b	16.5 f	0.6	---

\*Each value represents the mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.6. Fatty acid composition of seventeen varieties of hazelnuts for 1988.\* Fatty acids are expressed as percentage of total.

Variety	16:0	16:1	18:0	18:1	18:2	18:3	20:0
Casina	4.5	0.2	1.1	73.3 d c	20.3 d c	0.6	---
OSU 43-58 Willamette	4.9	---	1.7	74.5 b	17.8 h	1.1	---
Tombul	4.8	---	1.4	72.3 d e	20.4 c	1.1	---
Imperial	6.9	0.2	2.2	73.8 c	15.3 k	1.6	---
Mortarella	5.8	0.6	1.9	72.0 g f	17.1 i	2.4	0.2
Tombul Ghiaghli	5.9	0.4	1.7	71.8 g	18.7 g	1.2	0.3
Hall's Giant	5.1	---	1.1	70.1 h	22.2 a	1.5	---
Negret	5.6	0.3	1.8	73.6 d c	17.5 i h	1.2	---
Tonda di Giffoni	6.3	0.5	2.4	73.0 e	15.7 k j	1.8	0.3
TGDL	6.8	---	2.4	70.0 h	18.3 g	1.3	0.3
Tonda Romana	6.9	0.4	2.6	69.0 i	19.8 d e	1.3	---
Montebello	6.7	0.3	2.1	73.5 d c	15.9 j	1.1	0.4
OSU 49-73	6.6	---	2.4	75.3 a	14.8 l	0.9	---
Daviana	5.8	---	2.5	75.2 a	15.9 j	0.6	---
Butler	5.8	0.4	1.6	72.1 g f	19.7 f e	0.2	0.2
Barcelona	5.3	0.5	1.1	72.9 e	19.3 f	0.9	---
Ennis	5.8	---	2.1	70.4 h	21.1 b	0.6	---

\* Each value represents a mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.7 . Fatty acid composition of different nuts.\*

Nuts	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1
Hazelnut, Barcelona	6.1 e	---	2.2 c	74.5 a	15.3 j	2.0 d	---	---
Hickory	7.8 dc	---	3.1 b	71.7 b	14.5 j	2.9 k	---	---
Almond	6.6 e	0.5 b	1.4 d	68.1 c	23.4 g	---	---	---
Peanut	10.8 b	---	2.8 c	47.7 e	36.2 d	1.1 e	1.3 b	---
Pistachio	8.9 c	0.6 b	2.6 c	67.9 c	18.6 i	0.4 f	0.3 cd	0.6 bc
Brazilnut	15.4 a	0.5 b	9.4 a	31.5 g	42.9 c	---	0.3 cd	---
English Walnut	7.5 d	0.2 cb	2.4 c	18.3 h	57.6 a	14.1 a	---	---
Pecan	6.1 e	0.1 c	2.2 c	58.6 d	31.6 e	1.3 de	0.2 cd	0.1 d
Pinenut	6.2 e	0.3 b	3.4 b	39.4 f	48.2 b	0.9 f	0.6 c	0.9 b
Black Walnut	3.3 f	---	2.8 bc	30.5 g	58.3 a	5.1 b	---	---
Macadamia	8.4 c	22.4 a	2.1 c	58.3 d	2.4 k	---	2.4 a	3.1 a
Cashew	11.4 b	0.5 b	9.4 a	67.4 c	19.1 h	---	0.7 c	---
Chestnut	15.2 a	0.8 b	1.5 d	52.9 e	25.6 f	2.8	---	1.2 b

Each value represents a mean of 3 replicates. Mean followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.8 . Fatty acid composition in oil seeds.\*

Seeds	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1
Sunflower	7.8 e	0.4 a	2.5 c	54.3 a	21.7 g	12.8 b	0.5 a	---
Corn	12.6 c	0.2 a	2.4 c	24.7 e	58.5 b	1.0 d	0.4 a	0.2 a
Oat	19.3 a	---	2.1 d	39.3 b	37.2 f	2.1 c	---	---
Soybean	9.8 d	0.4 a	3.9 c	23.7 e	54.1 c	8.1 a	---	---
Pumpkin	16.4 b	---	7.7 a	33.8 d	42.0 e	---	---	---
Seasame	9.6 d	0.2 a	6.4 b	34.2 c	48.9 d	0.32 e	0.4 e	---
Watermelon	12.4 c	---	6.4 b	16.4 f	64.8 a	---	---	---

Each value represents a mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.9. Total vitamin E of hazelnut varieties at harvest, for three consecutive years.\* Tocopherol is expressed as  $\mu\text{g/g}$  oil.

Variety	1986	1987	1988	Mean	$\alpha$ -Teq
OSU 43-58 Willamette	502 b	506 b	488 b	499 b	447 a
Tombul	529 a	519 a	471 c	507 a	438 b
Casina	490 c	492 c	511 a	498 b	451 a
Tombul Ghiaghli	475 d	480 d	437 d	464 c	431 b c
Imperial	446 e	450 e	447 d	448 d	423 d
Mortarella	430 f	447 e	440 d	439 e	417 e
Montebello	349 k	345 e	394 f	363 j	366 h
Negret	406 h	405 f	413 e	408 f	387 f
TGDL	387 j	340 f	411 e	379 h i	374 g
Hall's Giant	388 j	388 g f	418 e	398 g	379 g
Tonda di Giffoni	340 i	382 g	412 e	378 h i	381 f
Tonda Romana	427 g	371 h	400 e	399 g	378 g
Daviana	398 i	384 g f	379 f	387 h	365 h
Barcelona	338 m	369 h	348 g	351 k	336 j
Butler	349 k l	353 i	360 g	354 k	325 k
Ennis	320 n	338 j	347 g	335 l	322 k
OSU 49-73	351 k	331 k	385 f	356 k	348 i

\*Each value represents a mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.10. Oil and, different vitamin E concentration, and total vitamin E in different nuts.\* Tocopherols are expressed as  $\mu\text{g/g}$  oil.

Nuts	Oil %	$\alpha$ -toc.	$\beta$ -toc.	$\Gamma$ -toc.	$\delta$ -toc.	$\beta$ -T <sub>3</sub>	$\Gamma$ -T <sub>3</sub>	Total toc.	$\alpha$ -toc. equiv
Hazelnut	61.8 g	366 a	15.9 a	19 h	---	---	---	401.2 b	369 a
Hickory	65.7 e	225 b	6.7 c	15 i	---	---	---	246.8 g	227 c
Almond	50.8 j	231 c	---	23 g	---	---	---	253.8 f	233 b
Peanut	56.4 i	86 d	2.9 d	1 l	6.2 c	---	48.2 b	143.9 j	87 d
Pistachio	50.9 j	30 f	9.6 b	456 a	31.2 a	---	---	526.2 a	77 e
Brazilnut	66.1 d	42 e	1.0 e	188 f	---	---	---	231.7 i	62 f
Walnut, E.*	67.2 c	6 j	---	342 b	23.3 b	---	---	372.4 c	41 g
Pecan	65.9 d	7 i	---	331 c	---	---	---	339.0 d	40 g
Pinenut	65.5 e	17 g	---	221 e	---	---	---	238.9 h	41 g
Walnut, B.^	58.4 h	3 k	---	305 d	---	---	---	308.6 e	34 h
Macadamia	76.9 a	15 h	---	---	---	14.0	---	29.6 l	17 i
Cashew	43.8 k	1 l	---	---	0.9 d	---	116.0 a	118.2 k	2 k
Chestnut	2.8 l	7 i	---	5.1 j	0.7 d	---	---	13.6 m	9 j
Coconut	68.8 b	---	---	3.72 k	---	---	---	3.7 n	1 l

Each value represents a mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

\*English walnut

^Black walnut

Table 5.11. Oil, different vitamin E, and total vitamin E concentration in oil seeds.\*  
Tocopherols are expressed as  $\mu\text{g/g}$  oil.

Seeds	Oil %	$\alpha$ -toc.	$\beta$ -toc.	$\Gamma$ -toc.	$\delta$ -toc.	$\alpha$ -T <sub>3</sub>	Total	$\alpha$ -toc equiv
Sunflower	41.4 b	725.7 a	33.5 a	7.4 f	10.0 c	---	776.6 b	727 a
Corn	4.5 g	189.2 b	8.9 c	463.8 b	24.1 b	---	686.0 c	236 b
Oat	6.7 f	154.1 c	20.7 b	5.3 g	---	222.1	402.3 e	158 c
Soybean	18.2 e	45.3 d	---	703.8 a	241.9 a	---	990.9 a	118 d
Pumpkin	39.0 c	12.0 f	---	281.0 d	---	---	293.0 f	40 f
Sesame	49.9 a	13.5 e	3.8 d	415.8 c	8.7 d	---	441.8 d	57 e
Watermelon	25.0 d	7.0 g	---	201.0 e	---	---	208.0 g	27 g

\*Each value represents mean of 3 replicates. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.12. Change in total vitamin E (tocopherol) concentration for different storage times, (months) 1986. Tocopherol is expressed as  $\mu\text{g/g}$  oil.

Variety	0	6	12	18	24	30	36
Tombul	529	520	468	437	400	376	339
OSU 43-58 Willamette	502	494	460	443	404	379	368
Casina	489	486	450	412	404	372	338
Tombul Ghiaghli	475	473	437	407	383	338	312
Imperial	446	440	426	410	322	297	243
Mortarella	429	43	417	416	389	342	316
Tonda Romana	426	423	401	396	364	343	330
Negret	405	403	378	328	305	256	244
Tonda di Giffoni	398	392	368	361	327	300	219
Daviana	397	395	391	372	322	243	217
Hall's Giant	387	383	362	339	309	257	226
TGDL	386	382	353	345	322	297	243
OSU 49-73	350	347	344	314	269	257	234
Montebello	348	345	333	318	289	233	208
Butler	349	338	334	329	264	228	216
Barcelona	337	336	326	325	311	275	253
Ennis	319	318	318	309	296	270	228

Each value represents a mean of 3 replicates.

Table 5.13. Change in vitamin E (tocopherol) concentration for different storage times, (months) 1987.\* Tocopherol is expressed as  $\mu\text{g/g}$  oil.

Variety	0	6	12	18	24
Tombul	518	511	499	485	454
OSU 43-58 Willamette	450	446	437	416	402
Casina	491	486	482	467	443
Tombul Ghiaghli	479	468	451	415	367
Imperial	449	443	436	398	342
Mortarella	446	441	433	405	362
Montebello	344	336	327	316	261
Negret	404	401	395	380	315
TGDL	398	392	380	366	321
Hall's Giant	387	382	379	341	275
Tonda di Giffoni	381	375	367	319	270
Tonda Romana	370	368	362	348	294
Daviana	384	377	350	326	319
Barcelona	369	364	359	348	328
Butler	353	350	345	329	309
Ennis	337	336	327	320	300
OSU 49-73	330	327	326	317	280

\*Each value represents the mean of 3 replicates.

Table 5.14. Change in total vitamin E (tocopherol) concentration for different storage times, (months) 1988.\*  
Tocopherol is expressed as  $\mu\text{g/g}$  oil.

Variety	0	6	12
Casina	510	508	487
OSU 43-58 Willamette	487	484	471
Tombul	470	460	437
Imperial	446	430	408
Mortarella	439	429	414
Tombul Ghiaghli	436	423	411
Hall's Giant	417	412	391
Negret	413	409	388
Tonda di Giffoni	412	406	389
TGDL	410	399	394
Tonda Romana	399	385	377
Montebello	385	377	349
OSU 49-73	384	381	361
Daviana	379	374	351
Butler	359	357	335
Barcelona	347	343	336
Ennis	346	343	325

\*Each value represents the mean of 3 replicates.

Table 5.15. Change in  $\alpha$ -tocopherol concentration for different storage times, (months) 1986.\* Tocopherol is expressed as  $\mu\text{g/g}$  oil.

Variety	0	6	12	18	24	30	36
Tombul	433	432	406	389	361	346	311
OSU 43-58 Willamette	429	422	402	398	363	343	335
Casina	432	430	401	385	365	341	312
Tombul Ghiaghli	417	416	406	388	365	322	298
Imperial	416	412	399	386	351	333	304
Mortarella	401	421	401	393	367	324	301
Tonda Romana	399	397	377	372	343	323	312
Negret	378	377	355	302	289	241	232
Tonda di Giffoni	377	372	352	347	316	290	211
Daviana	362	362	340	302	278	225	200
Hall's Giant	361	359	340	324	295	245	216
TGDL	356	351	333	326	305	281	231
OSU 49-73	326	322	312	268	255	241	222
Montebello	319	316	311	296	265	220	196
Butler	323	313	310	307	246	211	201
Barcelona	317	315	307	307	295	260	241
Ennis	302	302	302	294	298	260	218

\*Each value represents the mean of 3 replicates.

Table 5.16. Change in  $\alpha$ -tocopherol concentration for different storage times, (months) 1987.\* Tocopherol is expressed as  $\mu\text{g/g}$  oil.

Variety	0	6	12	18	24
Tombul	433	431	424	426	408
OSU 43-58 Willamette	401	400	395	384	375
Casina	435	433	432	422	404
Tombul Ghiaghli	433	425	415	382	341
Imperial	418	414	407	372	320
Mortarella	414	410	407	388	345
Montebello	325	318	312	302	250
Negret	380	378	375	362	301
TGDL	364	359	349	338	298
Hall's Giant	370	366	365	327	266
Tonda di Giffoni	365	359	353	305	261
Tonda Romana	347	346	345	330	281
Daviana	355	349	325	306	301
Barcelona	348	344	341	330	311
Butler	330	328	326	311	294
Ennis	312	311	303	302	283
OSU 49-73	313	310	310	301	266

\*Each value represents a mean of 3 replicates.

Table 5.17. Change in  $\alpha$ -tocopherol concentration for different storage times, (months) 1988.\* Tocopherol is expressed as  $\mu\text{g/g}$  oil.

Variety	0	6	12
Casina	450	450	436
OSU 43-58 Willamette	415	412	408
Tombul	401	393	385
Imperial	412	404	385
Mortarella	415	408	393
Tombul Ghiaghli	409	398	388
Hall's Giant	386	386	366
Negret	381	379	359
Tonda di Giffoni	388	384	368
TGDL	377	374	366
Tonda Romana	368	366	361
Montebello	364	363	327
OSU 49-73	355	352	342
Daviana	357	354	333
Butler	331	329	310
Barcelona	324	322	316
Ennis	316	316	301

Each value represents the mean of 3 replicates.

Table 5.18. Change in oleic acid of different varieties of hazelnuts during storage, months for 1986.\* Fatty acid is expressed as percentage of total.

Variety	0	6	12	18	24	30	36
Tombul	72.4	72.4	72.3	71.9	70.1	68.4	64.5
OSU 43-58 Willamette	74.2	74.1	73.6	71.4	69.9	68.1	65.8
Casina	73.2	72.9	72.7	71.5	70.3	66.5	64.3
Tombul Ghiaghli	70.2	69.5	68.3	66.6	64.3	62.1	59.8
Imperial	71.9	71.8	71.1	69.5	67.3	65.3	63.1
Mortarella	73.7	73.5	72.8	71.5	70.4	68.4	66.3
Tonda Romana	73.9	73.3	73.1	72.6	71.5	68.5	64.3
Negret	72.6	72.1	71.5	69.7	67.5	64.6	63.1
Tonda di Giffoni	66.3	65.9	64.3	62.5	60.4	58.6	55.6
Daviana	72.8	72.1	71.3	69.5	68.4	65.3	61.1
Hall's Giant	71.3	70.9	69.5	68.4	66.3	62.2	57.8
TGDL	71.7	71.3	70.2	69.7	67.3	65.8	61.7
OSU 49-73	71.9	71.8	71.3	70.3	68.7	65.9	62.7
Montebello	77.1	76.5	74.3	72.2	70.3	67.7	62.1
Butler	68.9	68.3	67.5	65.4	62.2	57.1	54.3
Barcelona	71.7	71.5	70.6	68.7	65.4	63.2	60.8
Ennis	71.2	70.8	68.9	66.7	64.3	60.7	57.1

\*Each value represents a mean of 3 replicates.

Table 5.19. Change in linoleic acid of different varieties of hazelnuts during storage, months for 1986.\* Fatty acid is expressed as percentage of total.

Variety	0	6	12	18	24	30	36
Tombul	21.6	21.4	20.6	18.1	16.5	15.6	13.9
OSU 43-58 Willamette	19.3	18.8	18.1	16.7	14.3	12.5	11.7
Casina	20.7	20.5	19.7	17.8	15.1	13.2	11.8
Tombul Ghiaghli	19.4	18.6	17.3	15.8	13.1	11.5	9.7
Imperial	18.1	17.7	16.5	14.3	13.2	11.5	10.2
Mortarella	16.1	15.8	15.1	14.3	11.5	9.7	7.3
Tonda Romana	18.3	18.1	17.3	15.4	14.1	12.3	10.2
Negret	18.9	18.1	17.2	16.3	13.3	11.2	9.7
Tonda di Giffoni	16.6	16.1	15.2	13.2	11.5	9.7	7.1
Daviana	20.2	19.6	18.3	16.5	14.3	13.5	11.5
Hall's Giant	19.9	19.4	18.3	17.2	15.2	11.7	9.8
TGDL	18.3	17.7	16.5	15.1	13.2	10.8	8.8
OSU 49-73	18.8	18.0	16.6	15.1	13.3	10.8	8.2
Montebello	12.8	12.1	11.6	9.3	7.3	6.1	4.9
Butler	20.5	20.1	19.5	18.2	15.3	13.5	12.2
Barcelona	19.9	19.7	18.1	16.5	13.2	10.5	8.6
Ennis	20.4	20.1	18.4	17.3	14.5	11.9	9.6

\*Each value represents a mean of 3 replicates.

Table 5.20. Change in oleic acid of different varieties of hazelnuts during storage, months for 1987.\* Fatty acid is expressed as percentage of total.

Variety	0	6	12	18	24
Tombul	69.6	69.2	68.4	67.5	67.1
OSU 43-58 Willamette	73.8	73.1	72.2	71.5	70.3
Casina	73.5	73.2	72.6	71.7	70.7
Tombul Ghiaghli	73.8	73.2	72.6	72.1	70.2
Imperial	75.6	75.1	74.3	72.2	71.7
Mortarella	74.5	74.1	73.2	72.5	71.6
Montebello	75.4	74.3	73.2	71.7	70.5
Negret	75.2	74.3	73.2	72.1	70.1
TGDL	74.0	73.2	72.5	71.1	70.5
Hall's Giant	70.2	69.8	68.5	67.5	66.8
Tonda di Giffoni	74.5	74.2	73.3	72.8	71.5
Tonda Romana	70.1	69.4	67.8	65.1	64.4
Daviana	73.5	72.8	72.1	70.3	68.1
Barcelona	72.6	71.1	70.3	68.1	66.5
Butler	73.2	72.6	71.5	69.5	67.6
Ennis	70.9	70.1	69.7	68.1	65.4
OSU 49-73	74.7	73.2	71.5	70.5	68.1

\*Each value represents a mean of 3 replicates.

Table 5.21. Change in linoleic acid of different varieties of hazelnuts during storage, months for 1987.\* Fatty acid is expressed as percentage of total.

Variety	0	6	12	18	24
Tombul	23.8	23.5	22.6	20.1	17.9
OSU 43-58 Willamette	20.4	20.1	19.7	17.5	16.8
Casina	21.9	21.5	20.5	18.7	16.3
Tombul Ghiaghli	17.6	16.9	14.3	13.2	12.9
Imperial	16.5	16.1	15.3	13.5	12.6
Mortarella	15.3	14.7	13.6	11.5	9.8
Montebello	16.3	15.8	15.1	14.2	11.5
Negret	15.6	15.1	13.8	11.5	9.7
TGDL	17.8	17.1	16.2	14.3	12.1
Hall's Giant	21.5	21.1	19.7	17.8	16.3
Tonda di Giffoni	14.8	14.1	13.6	11.5	10.1
Tonda Romana	21.8	21.1	19.7	17.6	15.4
Daviana	18.7	18.1	17.6	15.1	13.2
Barcelona	18.8	17.9	16.2	14.2	12.5
Butler	18.7	18.1	16.9	14.2	12.5
Ennis	20.5	20.1	19.5	17.9	15.3
OSU 49-73	16.5	16.1	15.8	13.2	11.1

\*Each value represents a mean of 3 replicates.

Table 5.22.

Change in linoleic acid of  
different varieties of hazelnuts  
during storage, months for 1988.\*  
Fatty acid is expressed as percentage  
of total.

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Variety	0	6	12
Casina	20.3	19.5	18.6
OSU 43-58 Willamette	17.8	17.6	16.2
Tombul	20.4	19.3	18.3
Imperial	15.3	14.5	12.5
Mortarella	17.1	16.2	15.5
Tombul Ghiaghli	18.7	18.1	16.8
Hall's Giant	22.2	21.5	20.1
Negret	17.5	17.1	15.2
Tonda di Giffoni	15.7	14.6	13.2
TGDL	18.3	17.2	16.1
Tonda Romana	19.8	18.6	16.1
Montebello	15.9	15.1	13.5
OSU 49-73	14.8	14.1	12.9
Daviana	15.9	15.1	14.2
Butler	19.7	18.1	17.8
Barcelona	19.3	18.7	17.9
Ennis	21.1	20.5	19.9

Each value represents a mean of 3 replicates.

Table 5.23. Change in oleic acid of different varieties of hazelnuts during storage, months for 1988.\* Fatty acid is expressed as percentage of total. 252

Variety	0	6	12
Casina	73.3	72.8	72.1
OSU 43-58 Willamette	74.5	74.1	73.2
Tombul	72.3	72.1	71.6
Imperial	73.8	73.1	72.5
Mortarella	72.0	71.5	70.8
Tombul Ghiaghli	71.8	71.3	70.5
Hall's Giant	70.1	69.2	68.3
Negret	73.6	72.9	71.5
Tonda di Giffoni	73.0	72.5	71.6
TGDL	70.0	69.2	68.6
Tonda Romana	69.0	68.4	66.5
Montebello	73.5	73.1	71.5
OSU 49-73	75.3	74.2	73.5
Daviana	75.2	74.6	73.2
Butler	72.1	71.6	70.1
Barcelona	72.9	72.1	71.5
Ennis	74.0	69.5	68.7

Each value represents a mean of 3 replicates.

Table 5.24. Change in peroxide value (meq of O<sub>2</sub>/kg of oil) for different storage times, (months) 1986.

Variety	0	6 mo.	12 mo.	18 mo.	24 mo.	30 mo.	36 mo.
Tombul	0.1	1.7	4.2	9.5	14.7	17.3	21.9
OSU 43-58 Willamette	0.1	1.5	3.1	5.3	8.9	13.5	14.5
Casina	0.3	1.9	3.1	7.9	8.6	12.5	15.3
Tombul Ghiaghli	0.5	1.6	6.3	12.1	20.3	23.9	26.7
Imperial	0.4	1.8	3.6	7.9	11.8	15.9	21.4
Mortarella	0.1	1.5	4.1	6.5	12.6	13.9	18.7
Tonda Romana	0.3	1.5	5.3	7.8	11.3	14.8	15.5
Negret	0.5	1.4	4.6	9.3	15.8	18.3	21.5
Tonda di Giffoni	0.4	1.5	6.2	9.8	15.8	17.3	19.9
Daviana	0.8	1.1	4.4	9.9	13.3	20.3	23.9
Hall's Giant	0.6	1.3	5.1	6.3	13.6	22.3	23.5
TGDL	0.4	1.8	5.3	9.3	14.4	17.7	21.5
OSU 49-73	0.3	1.8	3.4	7.8	12.9	16.3	18.4
Montebello	0.6	1.5	5.9	8.3	16.6	21.5	25.6
Butler	0.1	1.9	3.8	8.3	15.7	18.8	21.4
Barcelona	0.1	1.3	3.9	5.1	10.3	14.3	16.6
Ennis	0.3	1.6	3.4	7.3	11.5	13.9	18.2

Each value represents the mean of 3 replicates.

Table 5.25. Change in peroxide value (meq O<sub>2</sub>/kg oil) for different storage times, (months) 1987.\*

Variety	0	6	12	18	24
Tombul	0.1	1.3	2.9	6.6	8.8
OSU 43-58 Willamette	0.1	1.1	2.8	5.5	6.9
Casina	0.2	1.4	2.5	5.9	7.6
Tombul Ghiaghli	0.5	1.7	4.3	7.6	10.8
Imperial	0.1	1.7	3.3	8.6	13.1
Mortarella	0.2	1.9	3.3	7.6	11.1
Montebello	0.7	2.3	4.3	7.6	14.9
Negret	0.6	1.2	3.6	7.9	13.9
TGDL	0.2	1.5	3.7	7.3	12.8
Hall's Giant	0.3	1.2	4.4	9.3	15.4
Tonda di Giffoni	0.9	2.3	3.6	6.3	10.9
Tonda Romana	0.6	1.8	2.8	6.3	12.6
Daviana	0.5	1.4	3.6	8.9	14.6
Barcelona	0.4	1.6	3.4	8.8	11.6
Butler	0.2	1.6	3.3	7.5	13.8
Ennis	0.4	1.9	3.8	8.3	12.9
OSU 49-73	0.6	1.8	3.3	6.9	11.8

\*Each value represents the mean of 3 replicates.

Table 5.26. Change in peroxide value (meq O<sub>2</sub>/kg oil) for different storage times, (months) 1988.\*

Variety	0 mo.	6 mo.	12 mo.
Casina	0.1	1.3	3.4
OSU 43-58 Willamette	0.1	1.3	3.2
Tombul	0.3	1.4	3.3
Imperial	0.6	1.5	4.2
Mortarella	0.1	1.9	5.4
Tombul Ghiaghli	0.5	1.3	3.7
Hall's Giant	0.5	1.7	4.3
Negret	0.4	1.6	3.5
Tonda di Giffoni	0.3	1.3	3.7
TGDL	0.5	1.3	3.6
Tonda Romana	0.4	1.4	3.5
Montebello	0.3	1.8	4.9
OSU 49-73	0.3	1.4	4.1
Daviana	0.4	1.6	4.4
Butler	0.1	1.7	3.8
Barcelona	0.1	1.3	3.9
Ennis	0.3	1.9	4.1

\*Each value represents the mean of 3 replicates.

Table 5.27. The effect of nut position in the tree in light or shade on vitamin E, oil, residue, and moisture.\* Tocopherol expressed as  $\mu\text{g/g}$  oil.

Year	Position	Oil%	H <sub>2</sub> O%	Residue%	$\alpha$	$\beta$	$\Gamma$	Total
1987	Shade	58.9b	18.0a	23.1a	312.3b	15.0a	15.6c	342.8b
	Light	60.8a	16.8b	22.4b	328.7a	14.2b	21.0a	363.9a
1988	Shade	58.9b	17.4a,b	23.7a	325.1b	14.6a,b	16.4c	356.1b
	Light	60.4a	15.8b	23.8a	343.7a	15.3a	19.6b	378.6a

\*Each value represents a mean of 6 replicates, from 2 farms. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table 5.28. The effect of nut position in the tree in light or shade on fatty acid composition.\*

Fatty Acids	1986		1987	
	Sun	Shade	Sun	Shade
Stearic	1.6b	3.3a	1.8b	4.2a
Oleic	72.5a	69.6b	73.1a	70.2b
Linoleic	20.5a	18.6b	20.7a	19.1b

\*Each value represents the mean of 6 replicates from two farms. Means followed by the same letter are not significantly different,  $p=0.05$ .

Fig. 5.1. Peroxide value for seven hazelnut varieties, 1986. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

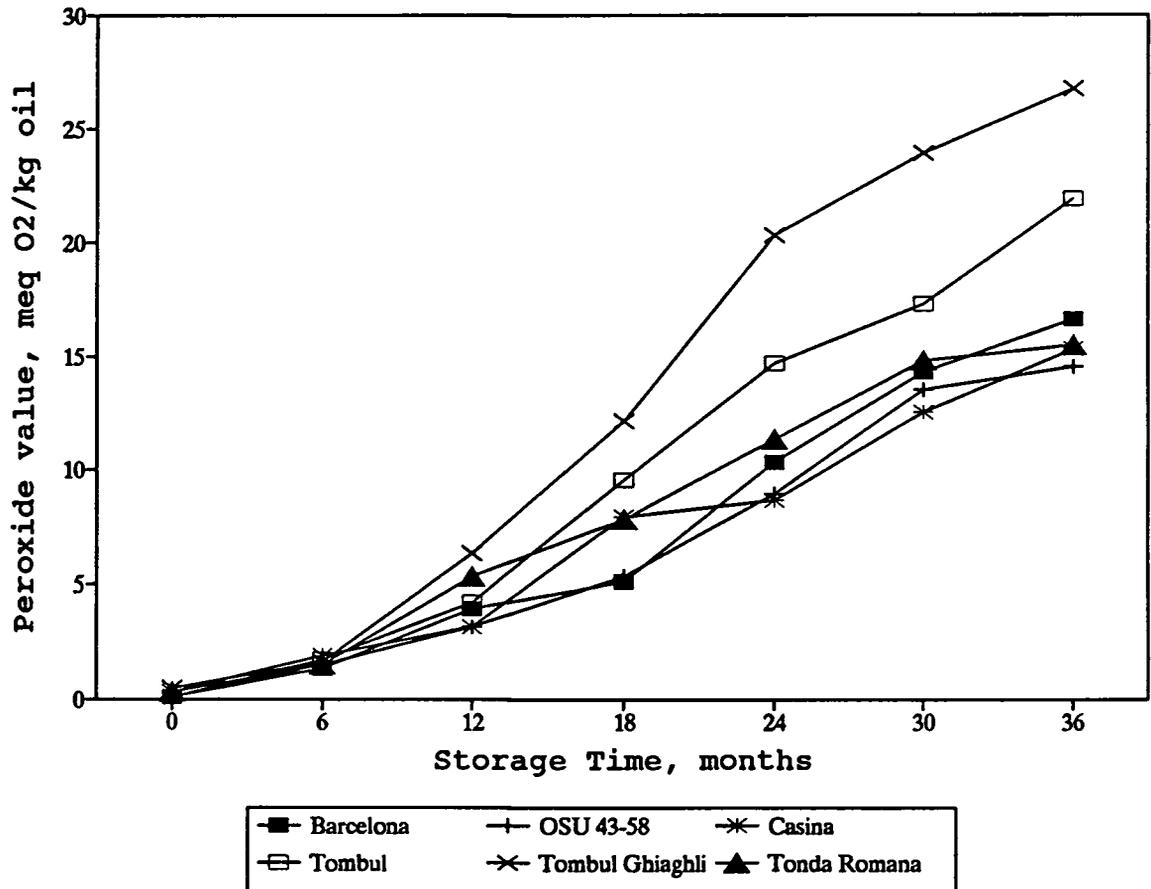


Fig. 5.2. Peroxide value for seven hazelnut varieties, 1987. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

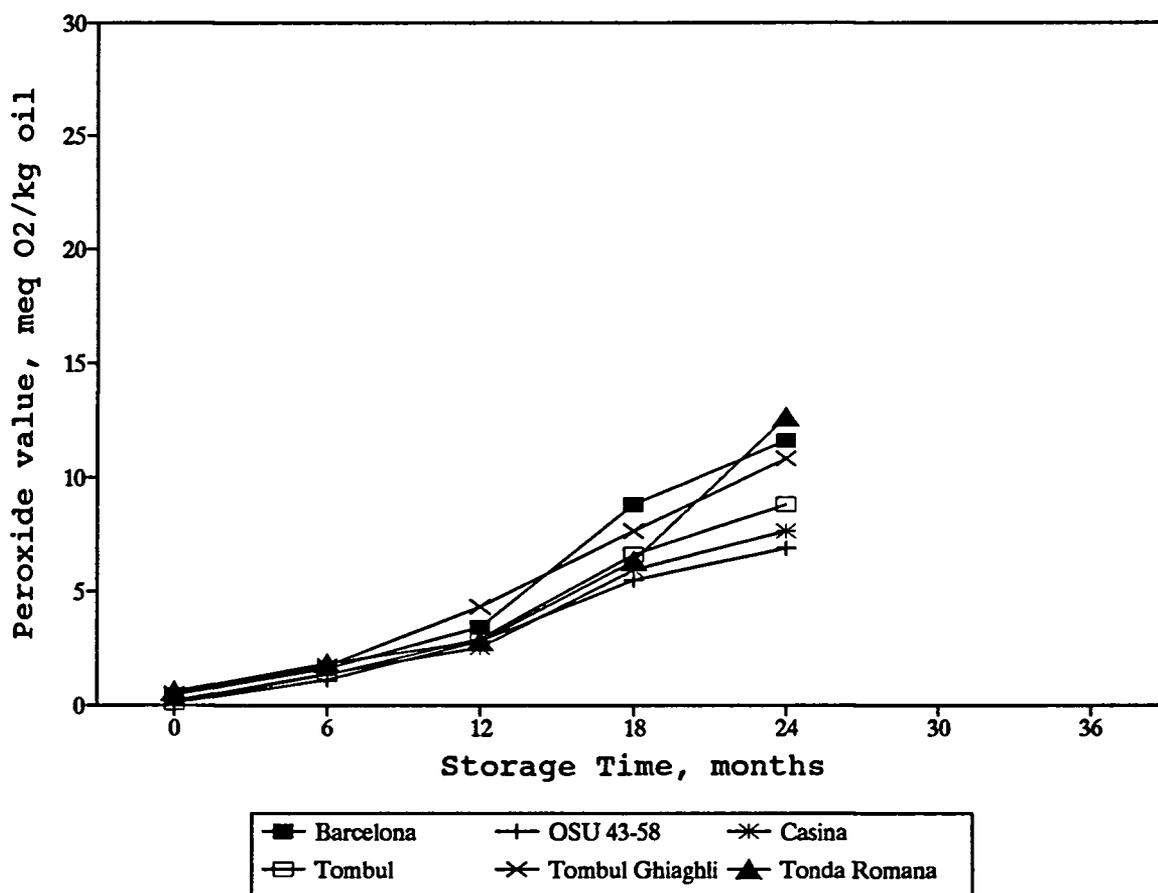
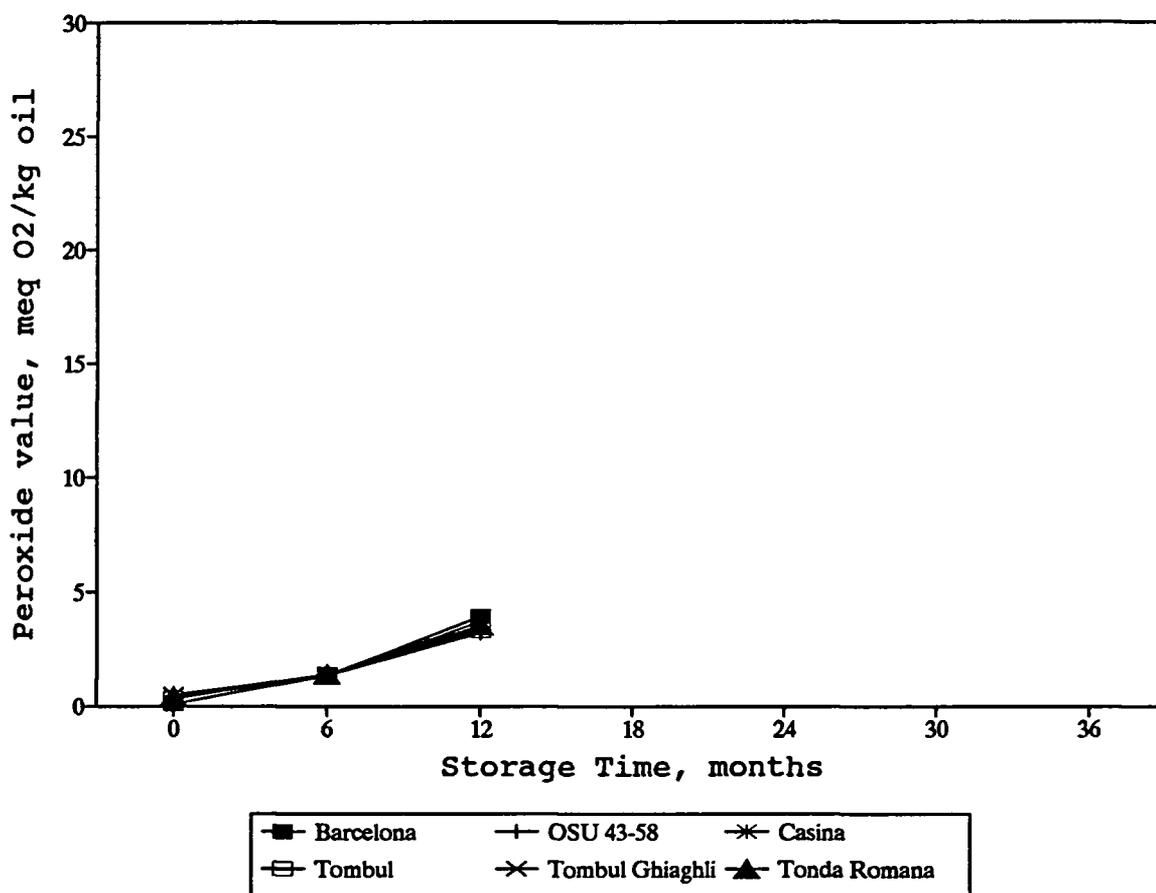


Fig. 5.3. Peroxide value for seven hazelnut varieties, 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)



**Chapter 6** Effects of storage temperature, kernel intactness, and roasting temperature on vitamin E, fatty acids and peroxide value of hazelnuts.

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**Abstract**

Kernels in the shell were compared to bare kernels with pellicles, half nuts, blanched nuts, finely chopped nuts, and roasted nuts. Whole nuts and whole kernels were stable for up to two years of storage provided they had not been exposed to high temperatures. Nuts stored at low temperatures (0 and 5°C) did not lose significant amounts of vitamin E. Increasing surface area by dividing nuts or finely chopping them, increased the loss of vitamin E. Samples that had lower surface areas (kernels in the shells or bare kernels with pellicles) did not lose much vitamin E and peroxide value was low. Higher roasting temperatures caused losses in vitamin E and increased peroxide values at the beginning and during storage, even when stored at 0°C. Intact nuts and low storage temperatures did not show changes in fatty acid composition. High temperature treatments changed fatty acid composition, mainly decreasing linoleic initially and finally oleic acids.

### Introduction

Nutritive products containing oils, when stored, may yield undesirable flavours as a result of oxidation reactions that produce hydroperoxides (RooH) as initial products. The presence of natural or synthetic antioxidants in the products may delay or diminish the oxidation rate. On the other hand, this reaction is known to be catalyzed by contaminant metals, particularly Fe, Cu, and Ni, which may be present at low concentrations. The autoxidation reaction of a given oil depends on the extent of contact with air (degree and kind of stirring) storage or processing temperatures. Additionally the decomposition of oil is influenced by environmental conditions eg., geographical origin, extraction method, and storage time (Assuncao et al., 1984).

The hazelnut is harvested in the fall, but sold throughout the year. The tree is susceptible to alternate bearing, which often results in a large crop every other season. In order to smooth out the supply, the nuts (usually in shell) are stored in warehouses from one season to the next. Since the hazelnut kernel has a low respiration rate it might be expected to be a relatively stable commodity. However, due to large amounts of unsaturated fatty acids, (mainly oleic), oxidative rancidity is a potential threat to the stability of the hazelnut kernel. Therefore, it is desirable to reduce the kernel moisture to about 6% and store at fairly low (5 to 10°C) temperatures in order to extend

hazelnut shelf life.

The hazelnut is in direct competition with other nuts, especially almonds, pecans, walnuts, and cashews, which are promoted extensively and are increasing in per capita consumption. Fig A.14 shows per capita consumption for five different nuts (walnuts, almonds, pecans, hazelnuts, and pistachios). They are aggressively marketed with funds coming from strong marketing orders. Almonds are now the dominant volume nut in the world (Eustace, 1989).

The industry is rapidly moving toward small scale packing in order to expand into the snack food and home baker markets. The industry also sells Oregon hazelnuts to Kellogg's, as an ingredient in its "Mueslix" breakfast cereal, and to "Planters" and "Pepperidge Farm", the latter produces hazelnut cookies. But the U.S. still has a long way to go before it catches up with Europe in terms of hazelnut consumption. "The per capita consumption of hazelnuts in West Germany, for example is in the neighborhood of six pounds a year. Here in the U.S., it's more like 0.06 pounds." (Stumbes, 1987).

There is a need for basic information concerning storage in order to enhance market potential for hazelnuts. Hazelnuts are sold in different forms, whole nuts (kernel in-shell), bare kernels with pellicles, half nuts, blanched (pellicles removed), ground, sliced, and roasted nuts. There are different factors that affect hazelnut quality during storage, such as the presence of shells, pellicles, heat treatments,

moisture content, surface area, and storage temperature.

Shells and pellicles protect the kernels from direct exposure to the atmosphere. The pellicles in pecans contain phenolic compounds such as protocatechuic acid (0.4  $\mu\text{g/g}$ ) (Senter et al., 1985), which act as antioxidants.

Drying may inactivate some enzymes (lipoxygenases). Steaming or wet heat at temperatures exceeding 82°C are needed to obtain 97% inactivation of lipoxygenase in soybean (Warner et al., 1988). High temperature drying is not appropriate because it damages the viability or physical properties of nuts. Drying can cause kernel breakage or decreased flavor.

When the surface area of the finely chopped nut is increased, more severe oxidation occurs due to the increased oxygen contact, which causes losses in different forms of vitamin E. The high exposure to oxygen could possibly be the explanation for their greater susceptibility to autoxidation.

The objectives of this research were to determine biochemical changes related to rancidity, such as fatty acids, vitamin E, and peroxide values with various time and temperature treatments.

### Materials and Methods

Hazelnuts from 1987 were harvested in Clackamas county, Oregon and were representative of a standard variety (Barcelona and Ennis). Samples (100 lb) were obtained from the ground and all the trees were grown on similar soil types and had received similar levels of fertilization and sprays for insect and disease control. After harvesting, the samples were taken to the laboratory, where all the processes of cleaning, grading, drying, and preparation for the experiments were performed. Half of the samples were manually shelled and inspected to assure selection of nuts with fully developed nutmeats and free from disease.

Samples were shelled manually and divided into five groups: intact kernels with skins, half kernels, blanched, finely chopped, and roasted kernels. In the sixth group the shells were left on. Kernels with skins were obtained by cracking the whole nuts and selection of those which were intact. Kernels were separated to make half kernels. Kernels without pellicles were preped by soaking kernel in water after which it was easy to remove the skin without using any chemical material which may affect rancidity. The purpose of this was to study the effect of the skin during storage then drying them to 5-6% moisture content. Hazelnut kernels were ground in a maulindex coffee mill and the purpose was to increase the surface area. The skin pellicle was mixed with the ground kernel. Nuts were roasted by placing the kernels

in an oven at 180°C for 25 minutes. All of the samples were further sub divided into three groups and stored at 0, 5, and 10°C and each of the three parts were divided into five additional groups and stored for 0, 6, 12, 18, and 24 months. Moisture content was 5-6% ± 0.5. The second part was to study the effect of roasting temperatures. Hazelnuts were roasted at 180, 210, 240, 270, and 300°C (± 5) for 25 minutes. Each of the treated samples were divided into five parts and stored for different periods of time (0, 3, 6, 9, and 12 months) at 0°C.

The samples were tested for chemical properties, peroxide value, fatty acids, and vitamin E concentration. The peroxide value was estimated according to the iron ( $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$ ) method described by Lea (1952).

## Results

### Vitamin E

Change in concentration of different forms of vitamin E and total content differed from one treatment to another and from one temperature to another. For in-shell whole nuts there were no significant changes in any form of vitamin E. Fig. 6.1 shows that  $\alpha$ -tocopherol decreased only slightly from 334 to 311  $\mu\text{g/g}$  oil after two years of storage at  $0^\circ\text{C}$ . In fig. 6.2  $\alpha$ -tocopherol in hazelnuts stored up to two years at  $5^\circ\text{C}$  decreased from 335 to 302  $\mu\text{g/g}$  oil. Fig. 6.3 shows that the  $\alpha$ -tocopherol went from 330 at the beginning of storage to 291  $\mu\text{g/g}$  oil after two years storage at  $10^\circ\text{C}$ . The percentage of loss was 7.1%, 10%, and 12% at storage temperatures 0, 5, and  $10^\circ\text{C}$ . Figs. 6.4, 6.5, and 6.6 show the effect of different treatments and different storage temperatures on  $\beta$ -tocopherol.  $\beta$ -tocopherol decreased from 12.1  $\mu\text{g/g}$  oil to 7.3  $\mu\text{g/g}$  oil after two years of storage at  $10^\circ\text{C}$ . Figs. 6.7, 6.8, and 6.9 show the effect of different treatments and different storage temperatures on  $\Gamma$ -tocopherol.  $\Gamma$ -tocopherol shows losses similar to  $\alpha$ -and  $\beta$ -tocopherol during storage and this loss increased as storage temperature increased.

For kernels there were slight changes in  $\alpha$ -tocopherol. Fig 6.2 shows that  $\alpha$ -tocopherol decline from 342 to 309  $\mu\text{g/g}$  oil after two years storage at  $0^\circ\text{C}$  temperature and the total 2 year loss was 10%. The losses increased as the storage temperature was increased, with the 16% loss at  $5^\circ\text{C}$  Fig.6.2

and 18% loss at 10°C (Fig. 6.3).

Half kernels lost more  $\alpha$ -tocopherol than whole nuts and kernels.  $\alpha$ -tocopherol went from 335 to 245  $\mu\text{g/g}$  oil after two years of storage at 10°C temperature.

The other three treatments (blanched, ground, and roasted) lost much more  $\alpha$ -tocopherol than the three previous treatments. The greatest loss was found in roasted nuts, followed by blanched, and the least loss in ground.  $\alpha$ -tocopherol in roasted nuts went from 296 to 151  $\mu\text{g/g}$  oil (49% loss) when stored at 0°C, and the loss was even greater (70%) when stored at 10°C.  $\alpha$ -tocopherol went from 324 to 131  $\mu\text{g/g}$  oil, after two years storage.

Figs. 6.10, 6.11, and 6.12 show the effect of different treatments and different storage temperatures on total vitamin E. In all three figures the greatest loss was found in roasted nuts and this loss increased as the roasting temperature increased. For example, whole nuts lost only 8% of total vitamin E when stored 2 years at 0°C, which is very small when compared to how much was lost when they were stored at 5°C (13%) and 10°C (15%) after two years of storage. Roasted nuts stored at 0°C lost about 58% of total vitamin E, they lost 70% when stored at 5°C and 73%, when stored at 10°C, for two years. When roasted nuts were compared to whole nuts or kernels at the beginning of storage we found roasted nuts had already lost almost 11% after only 25 minutes at 180°C.

Fig. 6.13 shows the effect of different temperatures on

total vitamin E concentration. For the control samples there were no significant changes after storage for one year. However, nuts roasted at 180°C had already reduced levels of vitamin E. They decreased 23% from 367  $\mu\text{g/g}$  oil at beginning of storage to 287  $\mu\text{g/g}$  oil after 12 months storage. The biggest losses were found in nuts roasted at 300°C. At the beginning of storage, total tocopherol was 320  $\mu\text{g/g}$  oil this is low when compared to the control which was 381  $\mu\text{g/g}$  oil. After 12 months storage the amount dropped to 53  $\mu\text{g/g}$  oil, which is almost 90% loss!

Figs. 6.15 and 6.16 show the effects of different roasting temperatures on  $\beta$ - and  $\Gamma$ -tocopherols.  $\beta$ - and  $\Gamma$ -tocopherols also decreased with increasing roasting temperatures. For example at 240, 270, and 300°C almost all  $\beta$ - and  $\Gamma$ -tocopherol were gone after 12 months of storage. The non-roasted control kernels had smaller amounts of losses, 5% for  $\beta$ -tocopherol and 7% for  $\Gamma$ -tocopherol. As the temperature of roasting increased and storage times increased there were increased losses in all forms of vitamin E.

In roasted nuts the color of the kernel changed after a short while in storage, it turned brown and the oil was seeping out. When nuts were placed on a paper it became greasy. Blanched nuts were initially bright white, but after storage they began to darken.

### Peroxide Value

Figs. 6.17, 6.18, and 6.19 show peroxide values of the

different treatments stored at the three temperatures for different times. Peroxide values were low in whole nuts and whole kernels, even after two years of storage. This was especially true when the temperatures were low (0 and 5°C). For example peroxide values were 7.4 and 8.6 meq of O<sub>2</sub>/kg of oil after 2 years at 0°C for whole nuts and whole kernels, respectively. At 10°C after the same storage time there was a slight increase, 14.8 and 18.7 meq of O<sub>2</sub>/kg of oil, respectively.

Peroxide values increased when the kernels were divided in half and were 14.4, 20.8, and 24.6 meq of O<sub>2</sub>/kg of oil at 0, 5, and 10°C after two years.

Peroxide values were high in all other treatments such as blanched, ground, and roasted nuts at all three storage temperatures. Peroxide values increased with increased storage times and temperatures. Peroxide values were 36.5, 55.7, and 63.3 meq of O<sub>2</sub>/kg of oil after two years in blanched nuts, which were stored at 0, 5, and 10°C. Roasted nuts were 39.5, 56.5, and 67.5 meq of O<sub>2</sub>/kg of oil after two years storage at the same three temperatures.

Fig. 6.20 shows that peroxide values were high for roasted nuts, no matter what temperature they were stored at. For example at 0°C after one year storage the peroxide value was 33.5 meq of O<sub>2</sub>/kg of oil compared to the control which was only 4.2 meq of O<sub>2</sub>/kg of oil. However, as roasting temperature increased so did the peroxide value. In

treatments with 240°C the peroxide value was 78.7 meq of O<sub>2</sub>/kg of oil after one year, and was 75.6 meq of O<sub>2</sub>/kg of oil after six months of storage when roasted at 300°C. Peroxide values then decreased at temperatures of 270 and 300°C after six months of storage and were 41.7 and 35.6 meq of O<sub>2</sub>/kg of oil after a year of storage. This decrease in peroxide value is explained by further breakdown of the peroxidized fatty acids to shorter aldehydes, ketones, and acids.

Figs. 6.21, 6.22, and 6.23 show the differences in peroxide values between control and roasted hazelnuts stored at 3 temperature. The control nuts showed a very slow increase in peroxide value, with rather effect of storage temperature. Roasted nuts, blanched, and ground up nuts however, showed a marked increase in peroxide value and were more influenced by temperatures.

Figs. 6.24, 6.25, and 6.26 show the changes in vitamin E concentration and in peroxide values during different storage times and temperatures. It is clear that when vitamin E was stable, peroxide value was very low. This occurred with whole nuts and with kernels. Fig. 6.26 shows that roasting caused large losses in vitamin E and increases in peroxide value.

#### Fatty Acids

Oleic and linoleic acids are two major fatty acids affected by storage times, temperatures, and treatments. For whole nuts, kernels, and half kernels there were only slight changes in those fatty acids, especially when stored at low

temperatures (0 and 5°C). Blanched, ground, and roasted nuts all had decreases in oleic and linoleic acid, and the greatest loss was found in roasted nuts.

Figs. 6.27 - 6.32 show changes in oleic and linoleic acid percentage for various treatments and different times of storage. Oleic and linoleic are stable without major losses in whole nuts and kernels. They began to decline in percentage of both acids in blanched, ground, and roasted nuts.

Fig. 6.32, 6.33, and 6.34 show the changes in fatty acid composition of hazelnut oils prepared at different roasting temperatures. There were small changes in fatty acid composition of hazelnut oils when prepared by roasting at temperatures less than 240°C. The fatty acid contents of oleic and linoleic acids were drastically reduced when roasted at 240°C or above. Although a taste panel of adequate size was not used, tasted nuts indicated that when peroxide values reach about 30 or more, that rancidity was be tasted.

## Discussion

Different forms of vitamin E and total vitamin E content decreased only slightly during long storage in whole nuts and kernels with testa (kernel coat). When other treatments such as blanching, or increasing surface area were used the amount of loss began to increase. When the surface area was increased such as in half kernels the tocopherols decreased more than in intact kernels. Samples of hazelnut halves had a 50% increase in total surface area ( $104 \text{ mm}^2/\text{g}$ ) compared to the whole intact kernel ( $50 \text{ mm}^2/\text{g}$ ) and this increase in total surface area also contributed to their increased (doubled) susceptibility to oxidation (surface area increased 2 times). The presence of the pellicle had a large protective effect on vitamin E content. When we blanched the kernels and exposed the whole kernel directly to the atmosphere, there were major changes in vitamin E content. This indicates that the pellicle serves to prevent oxidation, and acts as a barrier to prevent direct attack of oxygen. Chow and Draper (1974) reported that intact corn kernels were protected from oxidative damage when dried under different temperatures. Brooks and Csallany (1978), reported that seed coats in soybean and corn protected them from oxidation after exposing them to different temperatures, air, ozone, and nitrogen dioxide. Pellicle is important because it contains phenolic compounds such as protocatechuic acid ( $0.36 \mu\text{g}/\text{g}$ ) (Senter et al, 1985) which act as antioxidants. The  $\text{OH}^\circ$  groups on

protocatechuic acid have free radical scavenging capability and show good antioxidant activity. Diphenols such as caffeic acid, oleuropein, and hydroxy tyrosol have higher OH<sup>•</sup> capability than tyrosol, monophenol (Bores et al., 1984; Chimi et al., 1991; Papadopoulou and Boskou, 1991). This was further supported by work on pecans (Senter et al., 1985). The greatest antioxidant extracts were obtained with methanolic antioxidant extracts and were added to soybean oil (Duve and White, 1991). The high vitamin E concentration of some spices (oreganum and Laurel) prevents oxidation (Marero, 1986). Antioxidants can increase the shelf life of foods by 15-20% (Branen, 1973). When the surface area of the ground up hazelnuts was increased to 357 mm<sup>2</sup>/g, 7.2 times the total surface area of the whole intact kernels, more severe oxidation occurred due to the air, which caused losses in different forms of vitamin E. This resulted in destruction of tocopherols and unsaturated fatty acids. Drum-dried cereals are most easily oxidized even after the addition of antioxidants. This high exposure towards oxygen could possibly be the explanation for their greater susceptibility to autoxidation (Percheron and Loliger, 1990). Drying nuts to 5% moisture could be the best moisture content. Heaton and Beuchat (1980) found that reduced moisture content of pecan will keep them in good condition. Drying may inactivate some enzymes (lipoxygenases). Steaming or wet heat at temperatures exceeding 82°C are needed to obtain 97% inactivation of

lipoxygenase in soybean (Warner et al., 1988). hazelnuts roasted at 180°C for 25 minutes already had decreases in vitamin E. Amount of  $\alpha$ -tocopherol was 296  $\mu\text{g/g}$  of oil right after roasting which was 11% less than the was 333  $\mu\text{g/g}$  of oil for the control. Yoshida et al. (1991) reported losses of vitamin E from microwave heating. Heating whole peanuts for 60 minutes at 100°C reduced the vitamin E from 384 to 273  $\mu\text{g/g}$  oil (Adnan,1980).

Vitamin E decreased more as the roasting temperature increased, and the decrease continued on into storage. Tocopherol destruction in heat-treated samples occurred as the additive result of the following two reactions: the oxidation of tocopherols due to their direct reaction with the gaseous oxidants, and the oxidation of tocopherols resulting from their hydrogen donation as they served as anti-oxidants in inhibiting lipid oxidation within the seeds (Brooks and Csallany, 1978). High temperature drying is not appropriate because it damages the viability or physical properties of nuts such as kernel breakage or through decreased flavor. Many efforts have been made to establish alternative drying methods for maintaining the quality of fresh rice grain (Ohta et al., 1991).

In this study we found that peroxide values began increasing when vitamin E concentrations decreased more than 50%. The peroxide values were small in all cases until the vitamin E concentration dropped sharply. These findings were

similar to another study by Chow and Draper (1974). They found that vitamin E decreased when maize and soybean oils were heated in vitro. They noted that the peroxide value did not begin to rise until the vitamin E concentration had fallen to 683  $\mu\text{g/g}$  oil from its original value of 1635  $\mu\text{g/g}$  oil.

Increases in peroxide value right after roasting suggest that some degradation of the oil has rapidly taken place. The same was found with pistachios (Kashani and Valaden, 1983). Fleischman et al. (1963) and Yukil (1967), observed huge increases in free fatty acids in oils that were heated to 160°C or 180°C. Roasting peanuts causes changes in physicochemical properties, which might in turn alter the rate of oil oxidation (Chiou et al., 1991).

Peroxide value in nuts that we roasted at 270 and 300°C increased, then decreased after six months of storage and this was caused by the decomposition of peroxides. Our data agrees with data on pecans (Fourie and Basson, 1989). Leverington (1963) found that roasting increased peroxide value in macadamia nuts even though the iodine and acid values of oils showed no differences. Heating soybean oil at 180°C breaks down polyunsaturated fatty acids (Duve and White, 1991).

In other studies related to roasting they found a large degree of denaturation induced by roasting hazelnuts at 180°C (Garrone et al., 1988). They recommended 15-30 minutes at

150-170°C, which would develop a sample with full rich flavor from which protein can be extracted.

Using high temperatures in roasting caused decomposition of vitamin E, because at this temperature vitamin E can not protect oleic and linoleic acid from oxidation. Suarna and Southwell-Keely (1991), tested  $\alpha$ -tocopherol and 2,2,5,7,8-pentamethyl-6-chromanol initially at 60°C, but it was found that no compounds protected methyl linoleate successfully at this temperature. High temperatures may also damage the viability or physical properties of nuts, as was found with other seeds (Ohata et al., 1990). Using temperatures around 90-100°C may inactivate lipoxygenase enzyme and thus nut oils might stay in good condition without forming peroxidation. Senter et al. (1984) found that 90-100°C is best for pecans. The effect of low drying temperatures on oil content of sunflower, safflower, and flaxseed indicates that the oil content is not considerably affected by drying temperatures up to 104°C (Ghaly and Sutherland, 1984).

### Qualitative Relationship between Fatty Acids and Tocopherols

From the data in chapter IV and from tables in chapter V on different hazelnut varieties, different nut trees, and oil seeds, we have found that there is a relationship between certain polyunsaturated fatty acids and specific forms of vitamin E.

In chapter 4 we found that as in oleic acid increased in samples, this was associated with an increase in  $\alpha$ -tocopherol.  $\Gamma$ -tocopherol increased when linoleic acid increased and both of them started to decrease when stored for longer durations. Linolenic acid level was linked to  $\beta$ -tocopherol and both of them started to decrease from the beginning of growth. Fig. 6.35 shows a linear relationship between oleic acid and  $\alpha$ -tocopherol ( $r^2 = 0.977$ ;  $y = 28.78 + 1.51x$ ). Fig. A.15 plots the quadratic relationship between oleic acid and  $\alpha$ -tocopherol ( $r^2 = 0.993$ ;  $y = 5.253 + (-0.113 x1) + 0.016x^2$ ). Fig. 6.36 shows the linear relationship between linolenic acid and  $\beta$ -tocopherol ( $r^2 = 0.88$ ;  $y = -1.33 + 1.54x$ ). Fig. 6.37 shows the linear relationship between linoleic acid and  $\Gamma$ -tocopherol ( $r^2 = 0.77$ ;  $y = -9.82 + 1.716x$ ).

Data in chapter V show that in all varieties of hazelnuts  $\alpha$ -tocopherol is high and oleic acid is also high. Nut trees, for example English walnuts, black walnuts, Brazil nuts, and pinenuts were all high in linoleic acid and  $\Gamma$ -tocopherol. Almonds, hazelnuts, and hickory nuts were high in  $\alpha$ -tocopherol and oleic acid.

Data on oil seeds support this as well. For example, sunflower has high oleic content and a high  $\alpha$ -tocopherol content. Soybean is high in linoleic acid and this is associated with high levels of  $\Gamma$ -tocopherol. Corn has high levels of oleic and linoleic acid which is associated with high levels of  $\alpha$ - and  $\Gamma$ -tocopherol. Sesame seeds are high in linoleic acid content, associated with a high level of  $\Gamma$ -tocopherol.

There was no correlation between percent oil and total vitamin E content. For example, Tombul and OSU 43-58 have high vitamin E contents ( $> 500 \mu\text{g/g}$  oil) and percent of oil was above 64%; compared to Barcelona in which oil percent was 62.8% and vitamin E content was  $337 \mu\text{g/g}$  oil. From nut trees macadamia was high in oil content (76.9%), and had only  $29.6 \mu\text{g/g}$  oil of vitamin E. However, pistachios had 51% oil content and  $526 \mu\text{g/g}$  oil vitamin E content. Oil seeds showed the same as the nuts. Soybean has 18.2% oil and vitamin E content was  $990.9 \mu\text{g/g}$  oil, compared to sesame seeds which had 50% oil content and  $442 \mu\text{g/g}$  oil vitamin E content.

### Recommendation

Hazelnut (Barcelona) composition is 62.3% oil, 14.3% carbohydrate, 12.8% protein, and 10.6% ash, fibers, and minerals. Caloric content of food is 4.0, 4.0, and 8.9 kcal/g from carbohydrates, protein, and fats, respectively (Widdowson, 1987). The overriding concern about dietary fat as a source of excess calories for many segments of the population is saturated fatty acids and cholesterol. However, it should not be allowed to obfuscate the many important and critical functions of food lipids in maintaining a healthy, productive, and reproductive life.

The tocopherol requirement of humans has become of interest in recent years, because it is related to the intake of polyunsaturated fatty acids. Tocopherols are associated with the quality of the oils and they are of great nutritional significance in health and disease prevention (Andrikopoulous et al., 1989).

In this chapter we want to discuss the calories and advantages of eating hazelnuts in providing vitamin E as antioxidants. The daily consumption requirement of  $\alpha$ -tocopherol is 10-15 mg (NAS, 1980).

Calories from one hazelnut are:

#### Weight

Average weight of one kernel (Barcelona)= 1.3 g after drying.

$$1.3 \text{ g weight} \times \text{Oil content}\% 63.0 = 0.819 \text{ g oil}$$

1.3 g weight - Protein content% 13.0 = 0.169 g protein

1.3 g weight - Carbohydrate% 14.5 = 0.188 g  
carbohydrate

1.3 g weight - Others% 9.5 = 0.124 g others

### Calories

oil= (0.819) (8.9) = 7.28

protein= (0.169) (4) = 0.67

carbohydrate= (0.188) (4) = 0.75

other= (0.124) (4) = 0.49

**Total calories** = 9.19 kcal/one hazelnut (Barcelona)

100 g hazelnuts contain 76.9 nuts.

Calories per 100 g nuts is 707.5 kcal/100 g nuts.

Vitamin E content in hazelnuts is :  $\alpha$ - 366.4  $\mu\text{g/g}$

$\beta$ - 16.0  $\mu\text{g/g}$

$\Gamma$ - 19.0  $\mu\text{g/g}$

Requirements of vitamin E are 10 to 15 ET ( $\alpha$ -tocopherol equivalent).

To calculate  $\alpha\text{-T}_{\text{eq}} = \alpha\text{-T} + \beta\text{-T} (0.4) + \Gamma\text{-T} (0.1)$

$$= 366.4 + 6.4 + 1.9 = 375.5 \alpha\text{-T}_{\text{eq}}$$

To get 1 ET you must eat 2.6 nuts.

To get half of the daily requirement (7 ET) you must eat 2.6  
 $\times (7) = 18.2$  nuts.

The calories for half the daily requirement are: (18.2) (9.2)  
 $= 167.4$  kcal/18.2 nuts.

In this way we can get half our vitamin E requirement from a natural source, with very little calorie intake.

Weight of 18.2 nuts is  $(18.2) (1.3) = 23.7$  g

If eaten once a week then the weight is 23.7 g.

In one month  $(23.7) (4) = 94.8$  g.

In one year  $(94.8) (12) = 1137.6$  g.

$1137.6 \approx 1.2$  kg  $\approx 2.4$  lbs.

By this way we can increase the consumption of hazelnuts in America from 0.06 pounds to 2.4 pounds. But if we eat 18 hazelnuts twice a week we will increase the annual consumption from 0.06 pounds to 4.8 pounds ( $\approx 370$  times) and only take in 334 kcal each week which is less than the calories in one donut.

**Literature Cited**

- Adnan, M. 1980. Lipid properties and stability of partially defatted peanuts. Ph.D. thesis. Urbana, Illinois.
- Andrikopoulos, N.K., M.N. Hassapidou, and A.G. Manoukos. 1989. The tocopherol content of Greek olive oils. *J. Sci. Food Agric.* 46: 503-509.
- Anon. 1988. The surgeon general's report on nutrition and health. Washington D. C.: U. S. government printing office. DDHS publication (PHS) 88-50, 210.
- Assuncao, F.P., M.H.S. Bentes, and H. Serraya. 1984. A comparison of the stability of oils from Brazil nut, para rubber, and passion fruit seeds. *J. Amer. Oil Chem. Soc.* 62:1031-1035.
- Bors, W. C., M. M. Erben-Russ, B. Kreileder, D. Tait and M. Saran. 1984. Oxygen radicals in chemistry and biology, Edited by W. Bors, M. Saran and D. Tait. Walter De Gruyter, Berlin.
- Branen, J.J. 1973. Comparison of oxygen bomb method to other methods for measuring oxidative stability of peanuts. *J. Amer. Oil Chem Soc.* 50:59-63.
- Brooks, R.I. and A.S. Csallany. 1978. Effects of air, ozone, and nitrogen dioxide exposure on the oxidation of corn and soybean lipids. *J. Agric. Food Chem.* 26:1203-1209.
- Chimi, H.T., J. Cillard, P. Cillard, and M. Rahamni. 1991. Peroxyl and hydroxyl radical scavenging activity of some natural phenolic antioxidants. *J. Amer. Oil Chem. Soc.* 68:307-312.
- Chiou, R.Y.Y., Y.S. Chang, T.T. Tsai, and S. Ho. 1991. Variation of flavor related characteristics of peanuts during roasting as effected by initial moisture contents. *J. Agric. Food Chem.* 39:1155-1158.
- Chow, C.K. and H.H. Draper. 1974. Oxidative stability and antioxidant activity of the tocopherol in corn and soybean oils. *Int. J. Vit. Nutr. Res.* 44:369-371.
- Duve, K.J. and P.J. White. 1991. Extraction and identification of antioxidants in oats. *J. Amer. Oil Chem. Soc.* 68:365-370.
- Eustace, H.J. 1989. There is only one way. Nut grower society of Oregon, Washington, and British Columbia. 74th Annual meeting. 113-120.

- Fleischman, A.I., A. Florin, J. Fitzgerald, A.B. Caldwell, and G. Eastwood. 1963. Tocopherols and fatty acids in American diets. *J. Amer. Diet. Assoc.* 42:394.
- Fourie, P.C., and D.S. Basson. 1989. Changes in the tocopherol content of almond, pecan and macadamia kernels during storage. *J. Am. Oil Chem. Soc.* 66: 1113-1114.
- Garrone, W., M. Antonucci, U. Bona, and S. Clement. 1988. Determination of hazelnut content by means of their protein fraction in chocolate bars, chocolates, and milk containing spreads. *Lebensm. Wiss. U. Technol.* 2:76-82.
- Ghaly, T.F. and J.W. Sutherland. 1984. Heat damage to grain and seeds. *J. Agri. Engr. Res.* 30:337-345.
- Heaton, E.K. and L.R. Beuchat. 1980. Quality characteristics high-moisture pecans stored at refrigeration temperature. *J. Food Sci.* 45:255-261.
- Kashani, G.G. and L.R.G. Valadon. 1983. Effect of salting and roasting on the lipids of Iranian pistachio kernels. *J. Food Technol.* 18:461-467.
- Labavitch, J.M., L.C. Greve, and A.A. Kader. 1984. Factors affecting rancidity of walnuts. *Walnut research reports.* pp.184-185.
- Lea, C.H. 1952. Methods for determining peroxide in lipids. *J. Sci. Food Agric.* 3:386-389.
- Leverington, R.E. 1963. Evaluation of methods of roasting macadamia nut. *J. Agric. Sci.* 19:131-132.
- Marero, L.M., S. Homma, K. Aida, and M. Fujimaki. 1986. Changes in the tocopherol and unsaturated fatty acid constituents of spices after pasteurization with super heated steam. *J. Nutr. Sci. Vitaminol.* 32: 131-136.
- NAS-NRC. 1980. *Recommended Dietary Allowances, 9th ed;* National Academy of Sciences, National Research Council, Washington DC.
- Ohata, H., S. Aibara, H. Yamashita, F. Seklyama, and Y. Morita. 1990. Post-harvest drying of fresh rice grain and its effects on deterioration of lipids during storage. *Agri. Biol. Chem.* 54:1157-1164.
- Papadopoulous, G. and D. Boskou. 1991. Antioxidant effect of natural phenols on olive oil. *J. Amer. Oil Chem. Soc.* 68:669-671.

- Percheron, E. and J. Loliger. 1990. Influence of drying technology on precooked cereal autoxidation. *Lebensm. Wiss. U. Tech.* 4:400-403.
- Senter, S.D., W.R. Forbus Jr., S.O. Nelson, R.L. Wilson Jr., and R.J. Horvat. 1984. Effect of dielectric and steam heating treatments on the storage stability of pecan kernels. *J. Food Sci.* 49:893-895.
- Senter, S.D., R.J. Horvat, and W.R. Forbus. 1985. Comparative GLC-MS analysis of phenolic acids of selected tree nuts. *J. Food Sci.* 48:798-800.
- Sinnhuber, R.O., T.C. Yu, and Y.T. Chang. 2-Thiobarbituric acid method for the measurement of rancidity in fishery products. 1958. *Food Res.* 23:626.
- Stumbs, J. 1987. Hazelnut market heats up. *Sun-diamond grower.* Spring, 44-47.
- Suarna, C. and P.T. Southwill-Keely. 1991. Antioxidant activity of oxidation products of  $\alpha$ -tocopherol and of its model compound 2,2,5,7,8-penta methyl-6-chromanol. *Lipids.* 26:187-190.
- Warner, K., E.N. Frankel, and T.L. Mount. 1988. Flavor evaluation of crude oil to predict the quality of soybean oil. *J. Amer. Oil Chem. Soc.* 65:386-391.
- Widdowson, E. M. 1987. At water: A personal tribute from the U. K. *Am. J. Clin. Nutr.* 45:898-992.
- Yoshida, H., M. Tatsumi, and G. Kajimoto. 1991. Relationship between oxidative stability of vitamin E and production of fatty acids in oil during microwave heating. *J. Amer. Oil Chem. Soc.* 68:566-570.
- Yuki E. and Y. Ishikawa. 1976. Tocopherol contents of nine vegetable frying oils, and their changes under simulated deep fat frying condition. *J. Amer Oil Chem. Soc.* 53:673-678.

Fig. 6.1. Effect of storage duration on alpha-tocopherol concentration of treated hazelnuts, stored at 0°C. (Barcelona)

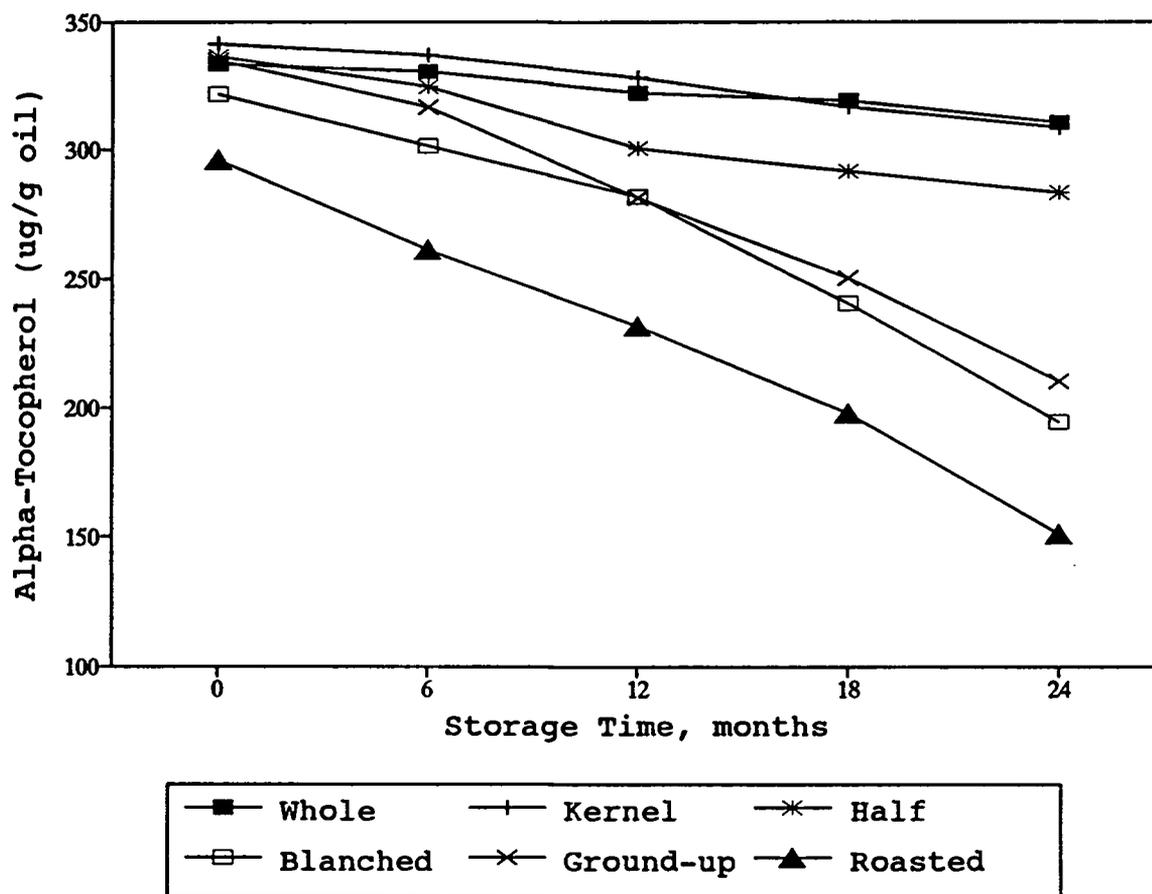


Fig. 6.2. Effect of storage duration on alpha-tocopherol concentration of treated hazelnuts, stored at 5°C. (Barcelona)

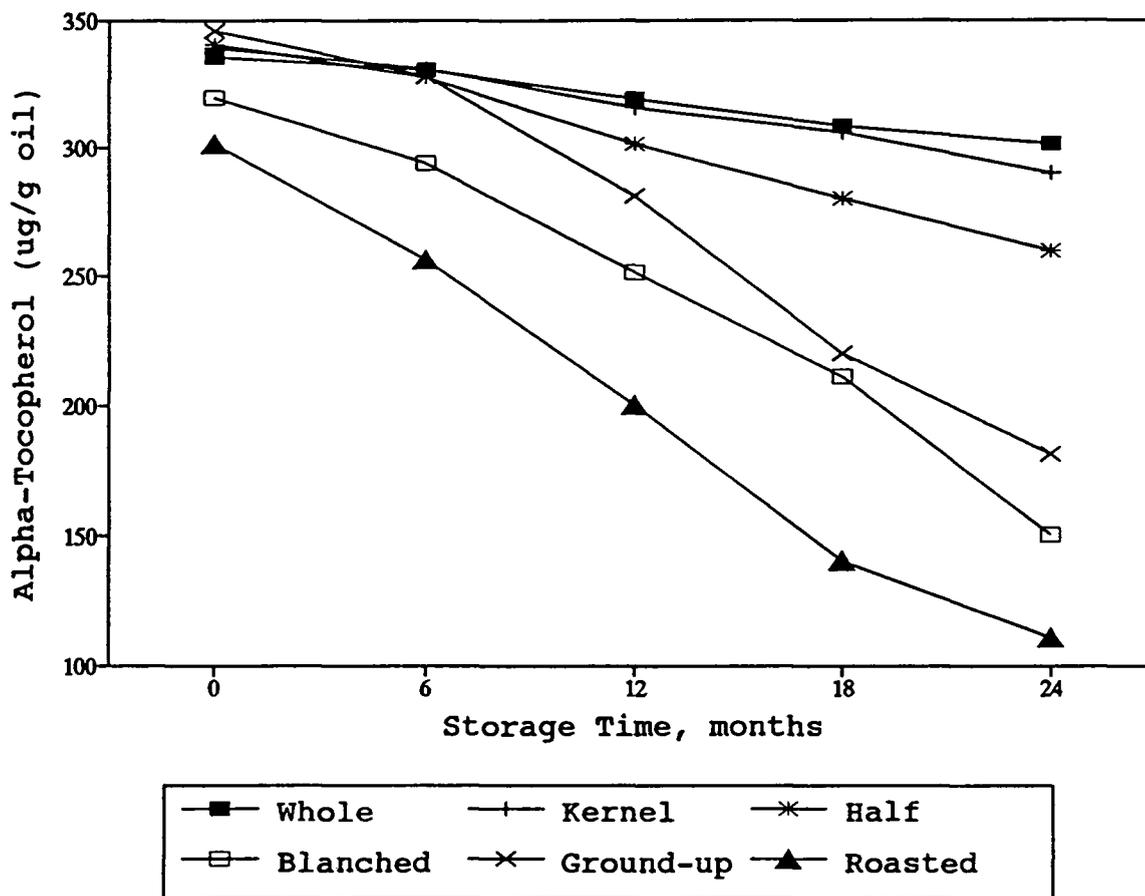


Fig. 6.3. Effect of storage duration on alpha-tocopherol concentration of treated hazelnuts, stored at 10°C.

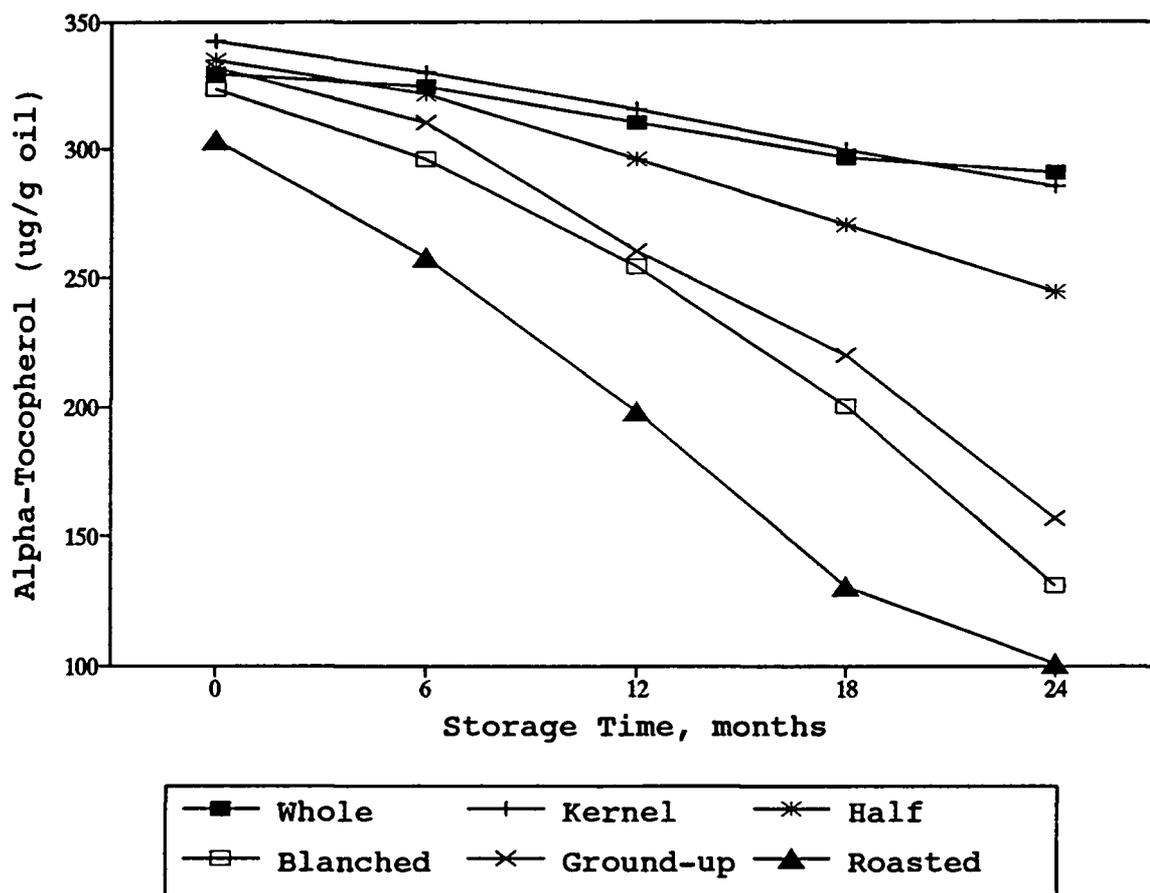


Fig. 6.4. Effect of storage duration on beta-tocopherol concentration of treated hazelnuts, stored at 0°C. (Barcelona)

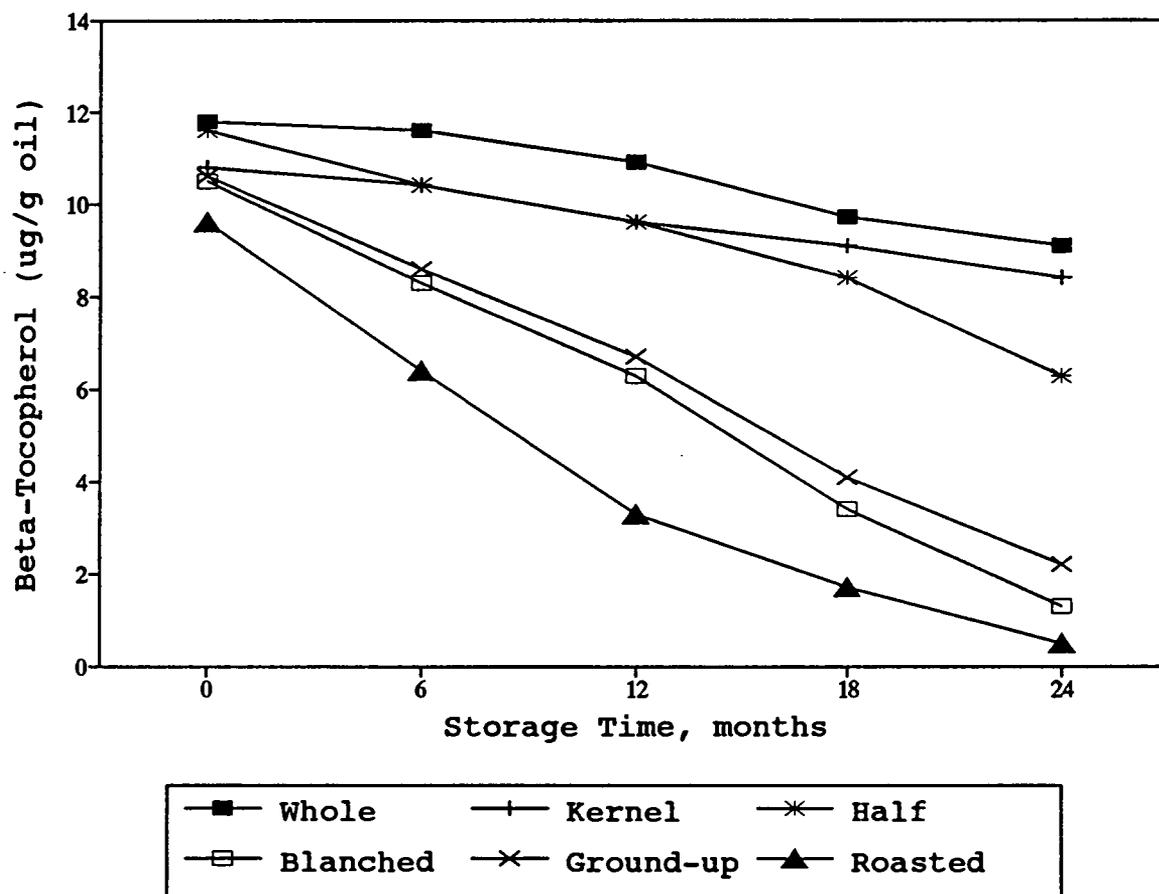


Fig. 6.5. Effect of storage duration on beta-tocopherol concentration of treated hazelnuts, stored at 5°C. (Barcelona)

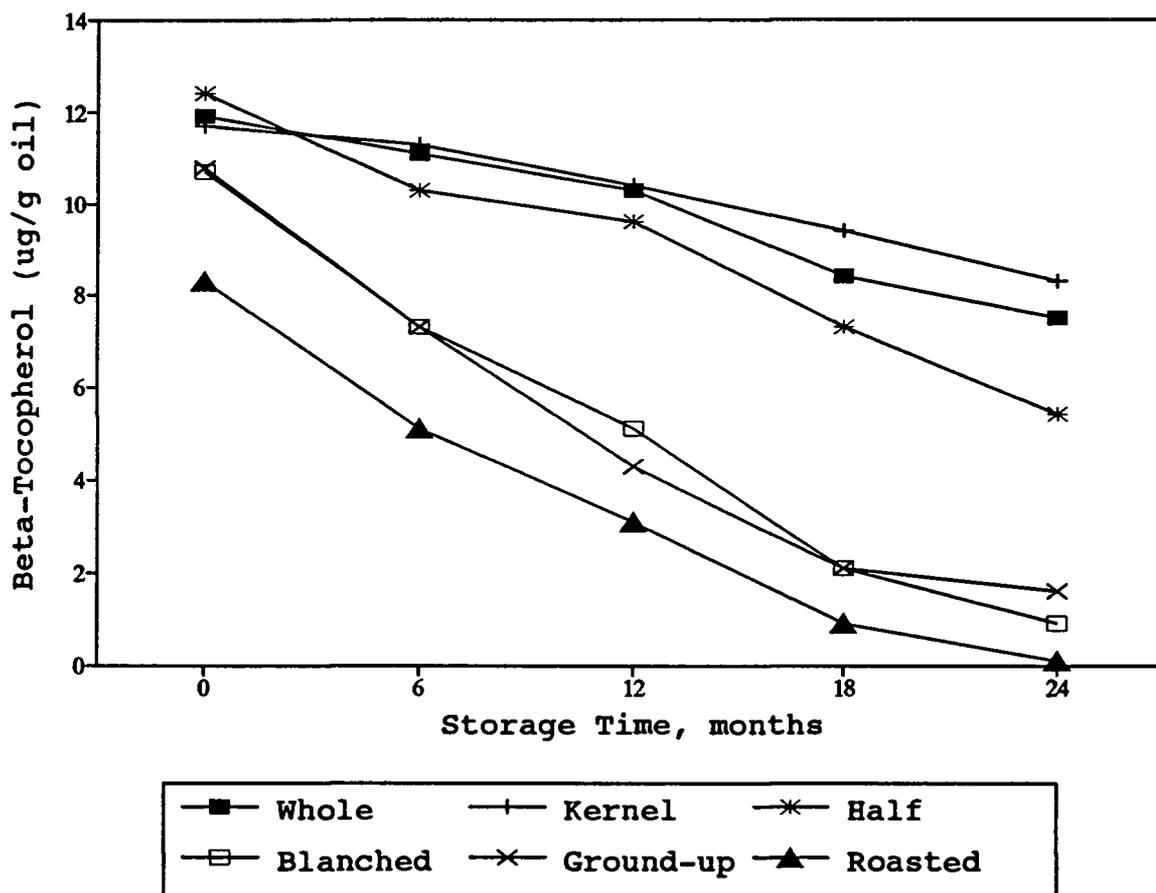


Fig. 6.6. Effect of storage duration on beta-tocopherol concentration of treated hazelnuts, stored at 10°C. (Barcelona)

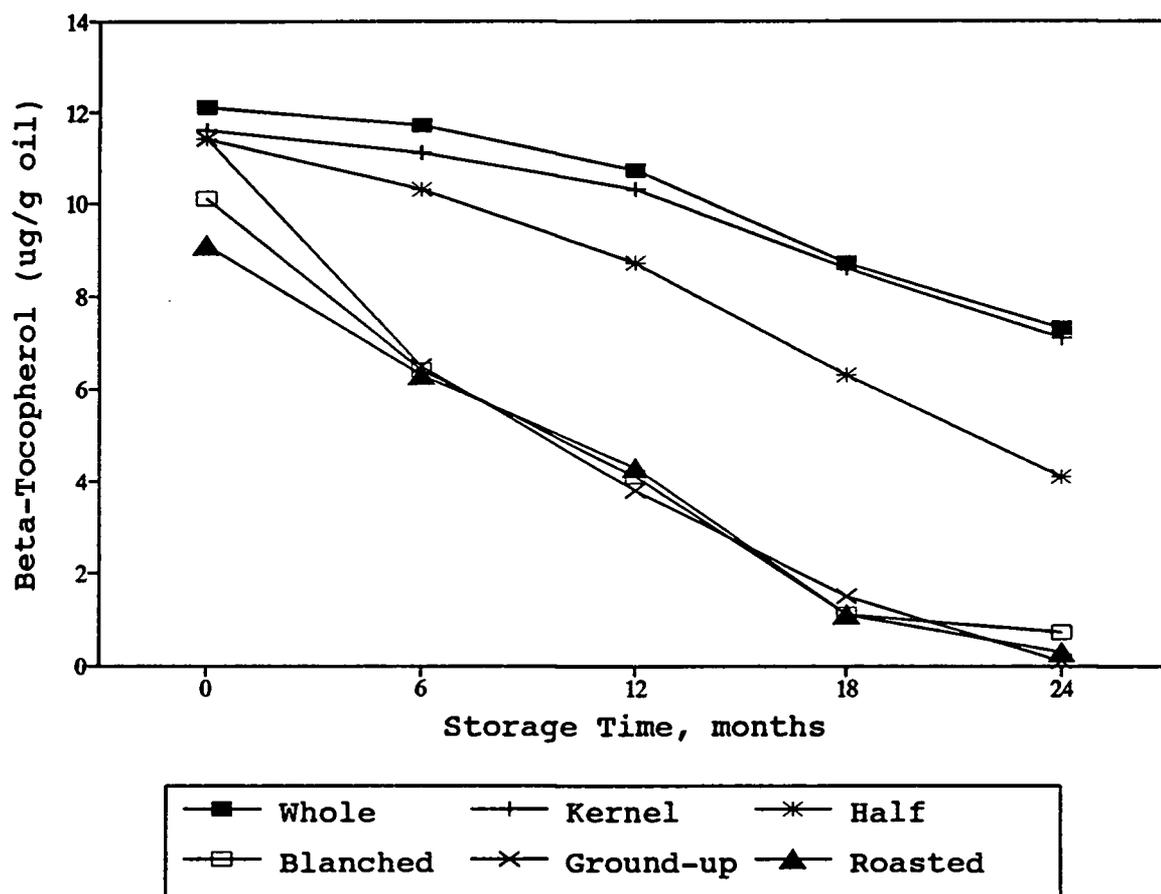


Fig. 6.7. Effect of storage duration on gamma-tocopherol concentration of treated hazelnuts, stored at 0°C. (Barcelona)

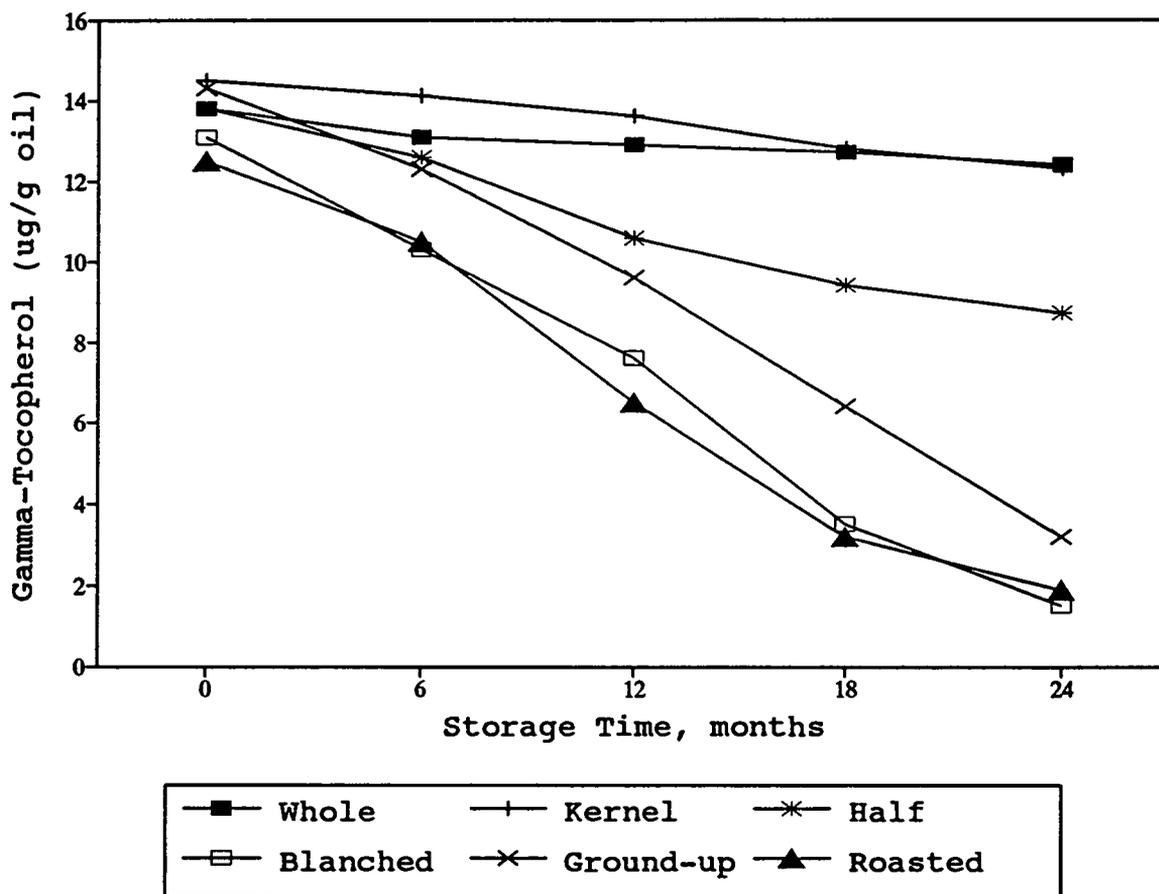


Fig. 6.8. Effect of storage duration on gamma-tocopherol concentration of treated hazelnuts, stored at 5°C. (Barcelona)

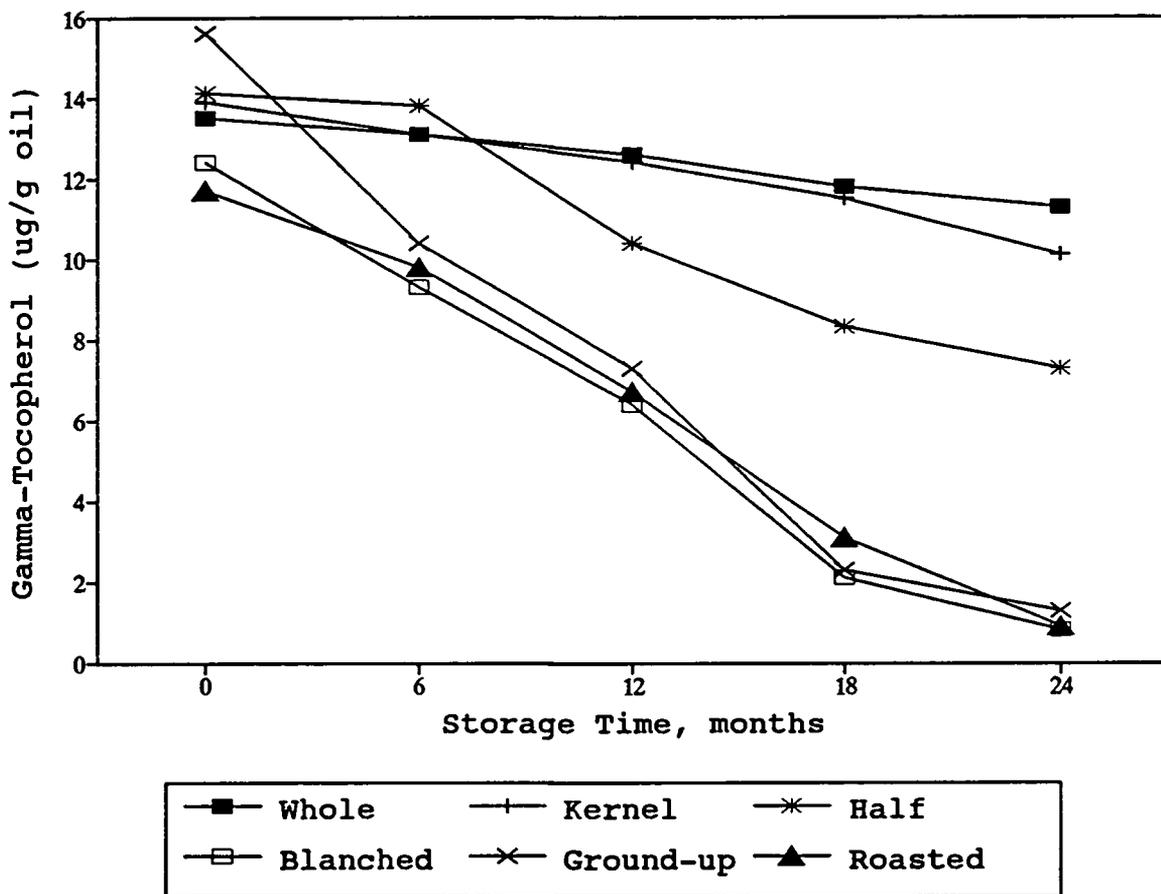


Fig. 6.9. Effect of storage duration on gamma-tocopherol concentration of treated hazelnuts, stored at 10°C. (Barcelona)

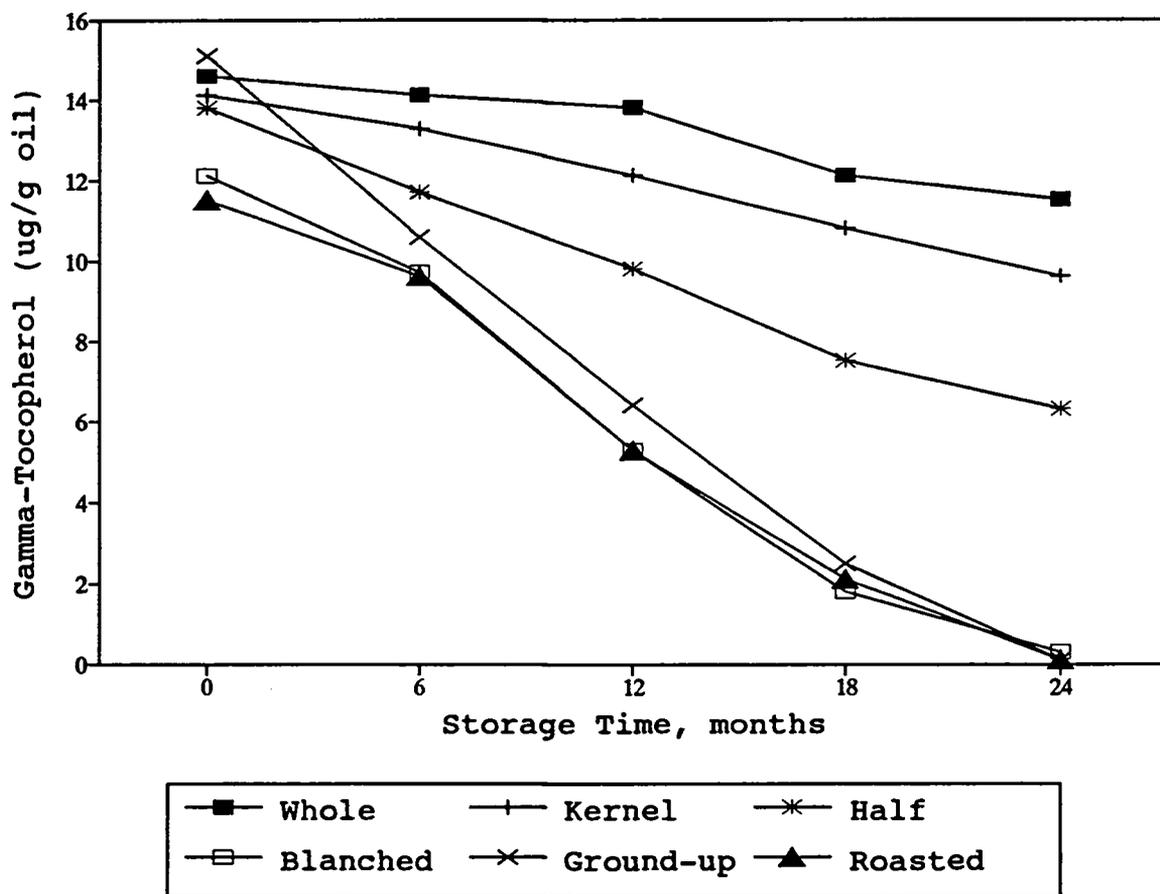


Fig. 6.10. Effect of storage duration on total vitamin E (tocopherol) concentration of treated hazelnuts, stored at 0°C. (Barcelona)

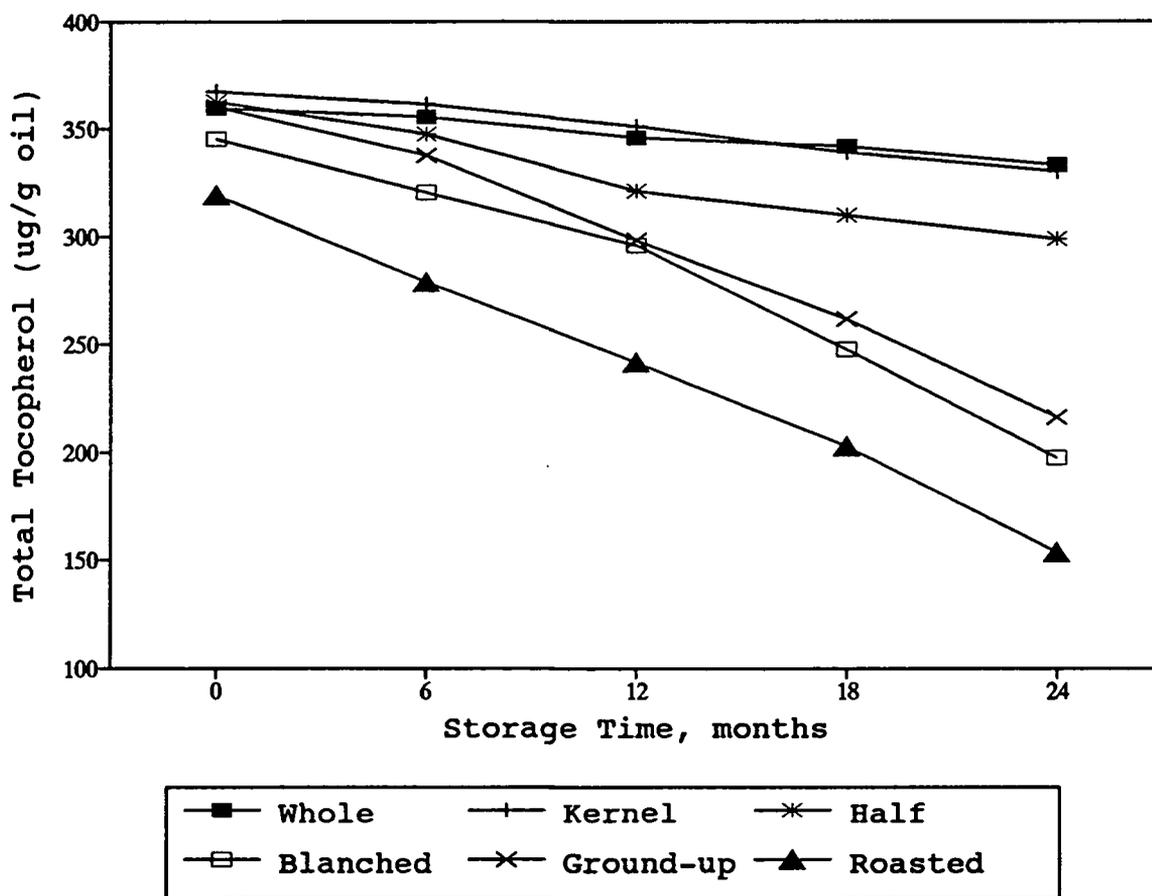


Fig. 6.11. Effect of storage duration on total vitamin E (tocopherol) concentration of treated hazelnuts, stored at 5°C. (Barcelona)

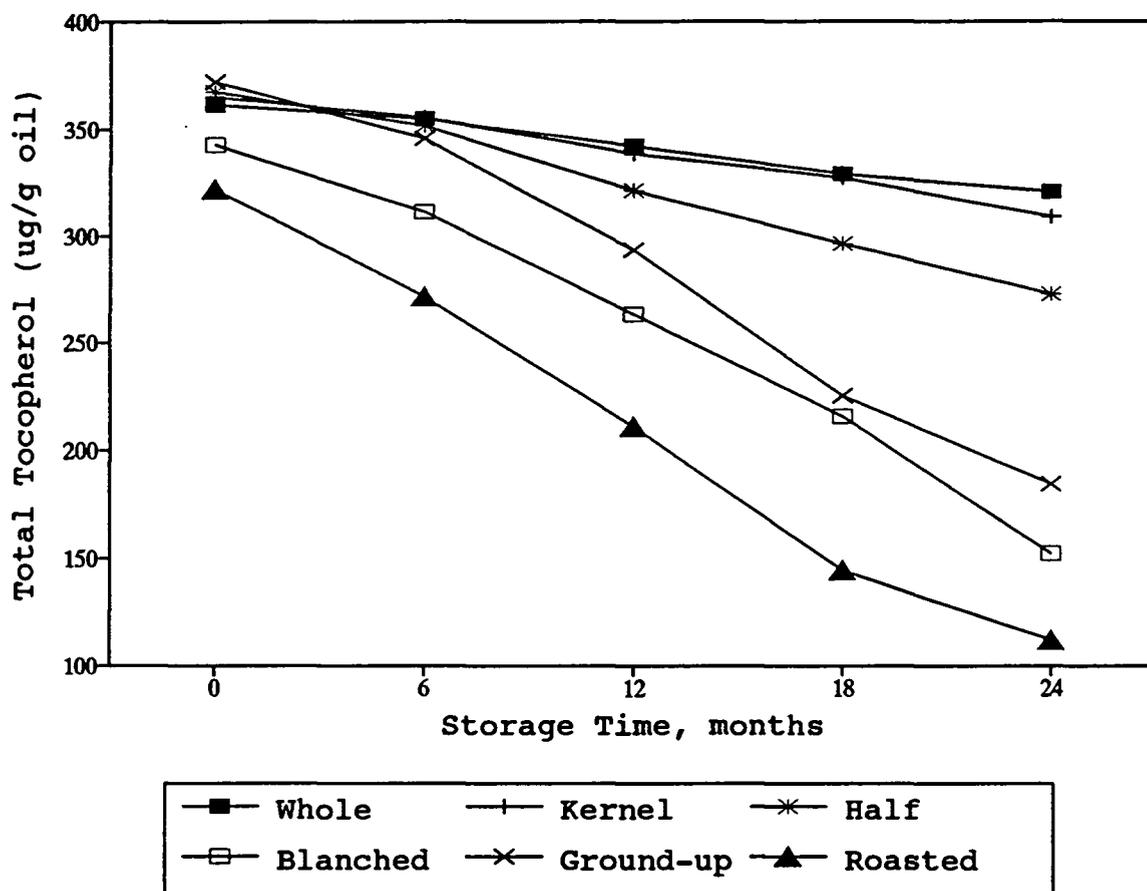


Fig. 6.12. Effect of storage duration on total vitamin E (tocopherol) concentration of treated hazelnuts, stored at 10°C. (Barcelona)

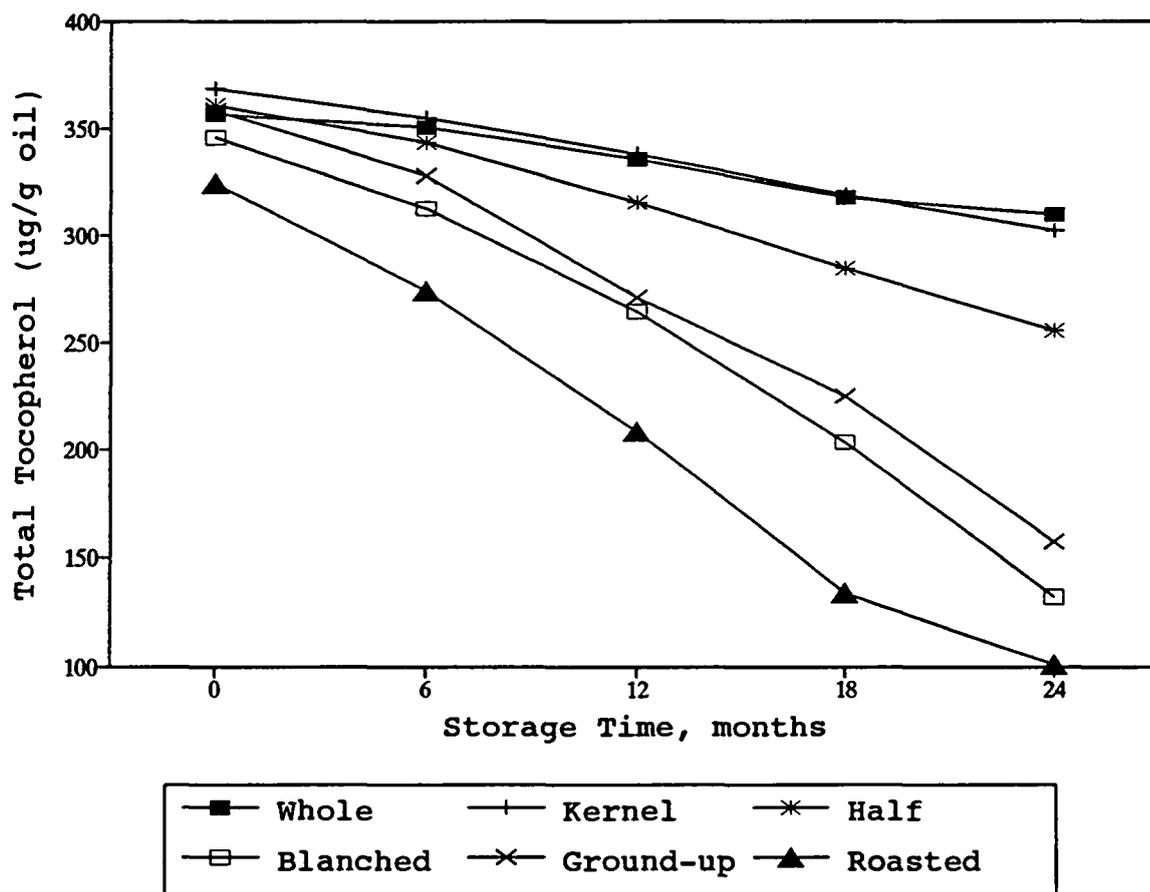


Fig. 6.13. Effect of different roasting temperatures on total vitamin E (tocopherol) concentration of hazelnuts. (Barcelona)

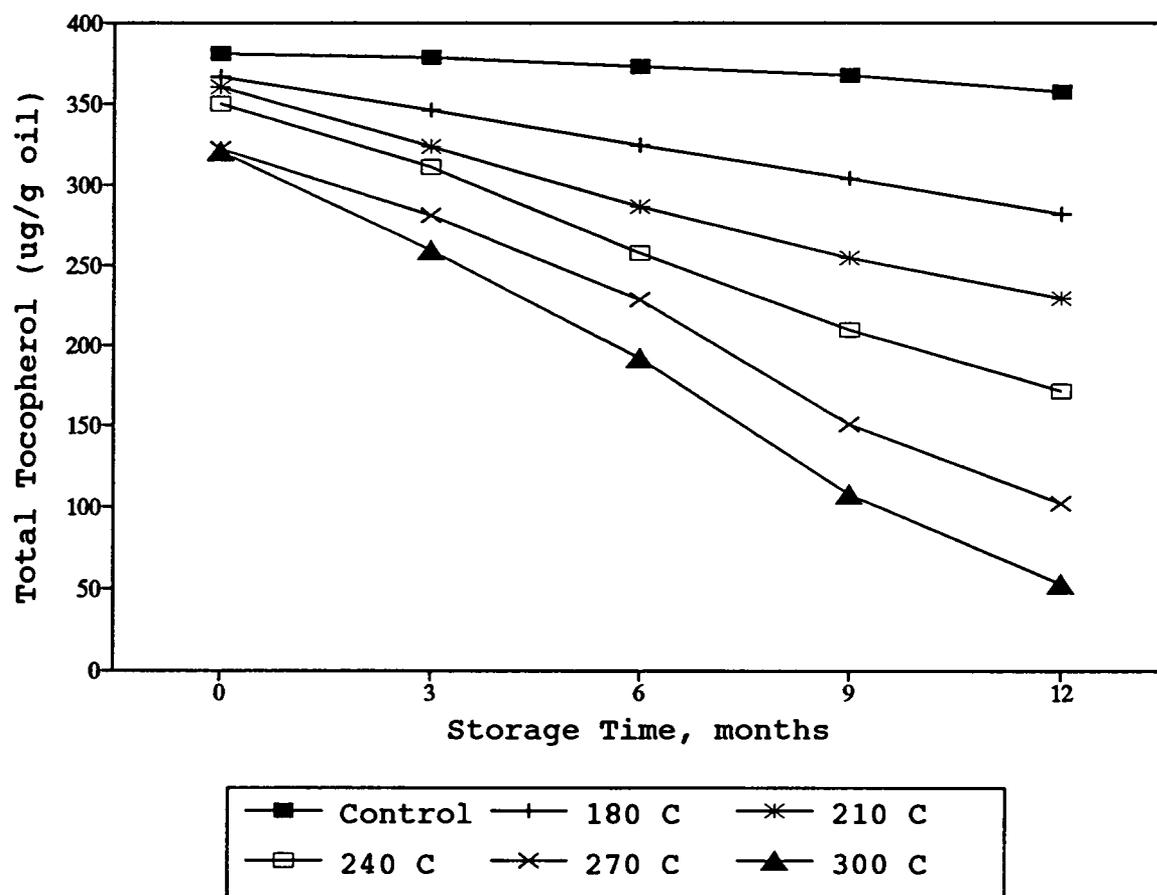


Fig. 6.14. Effect of different roasting temperatures on  $\alpha$ -tocopherol of hazelnuts. (Barcelona)

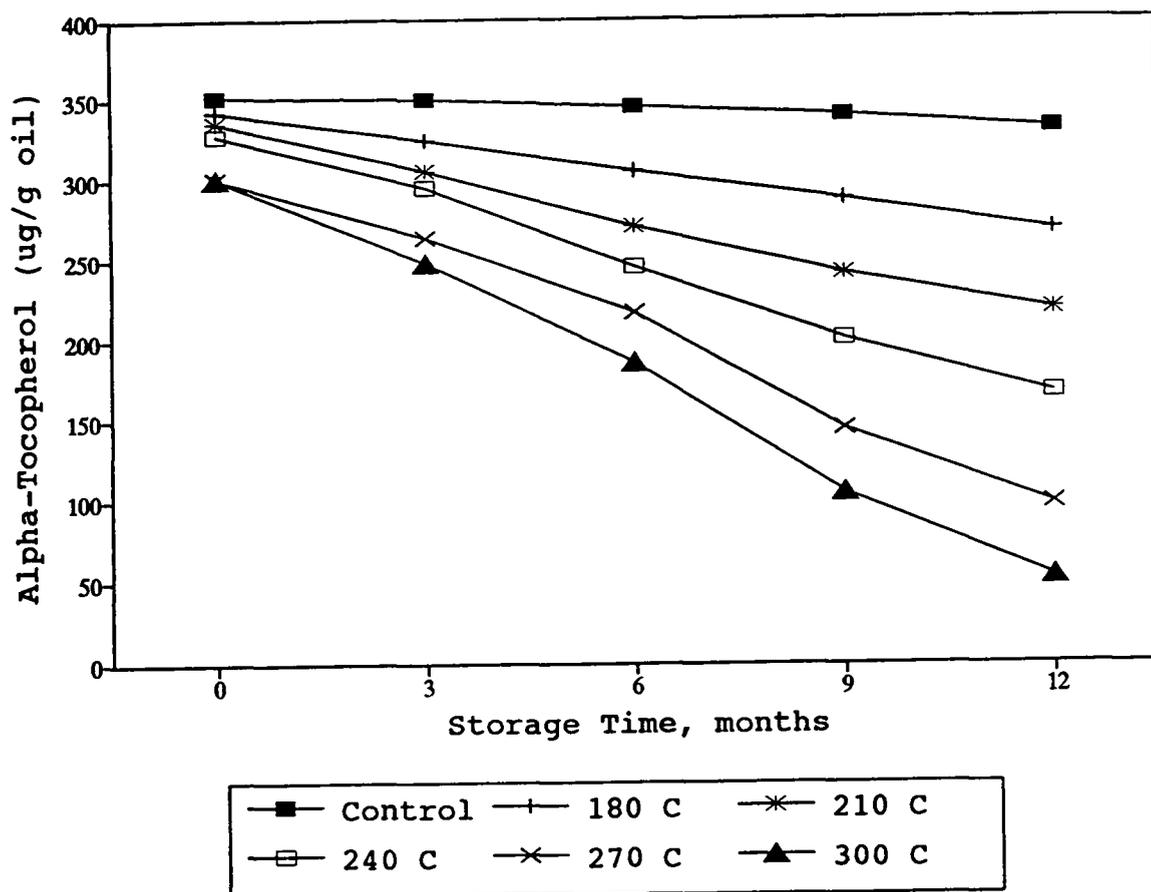


Fig. 6.15. Effect of different roasting temperatures on beta-tocopherol of hazelnuts. (Barcelona)

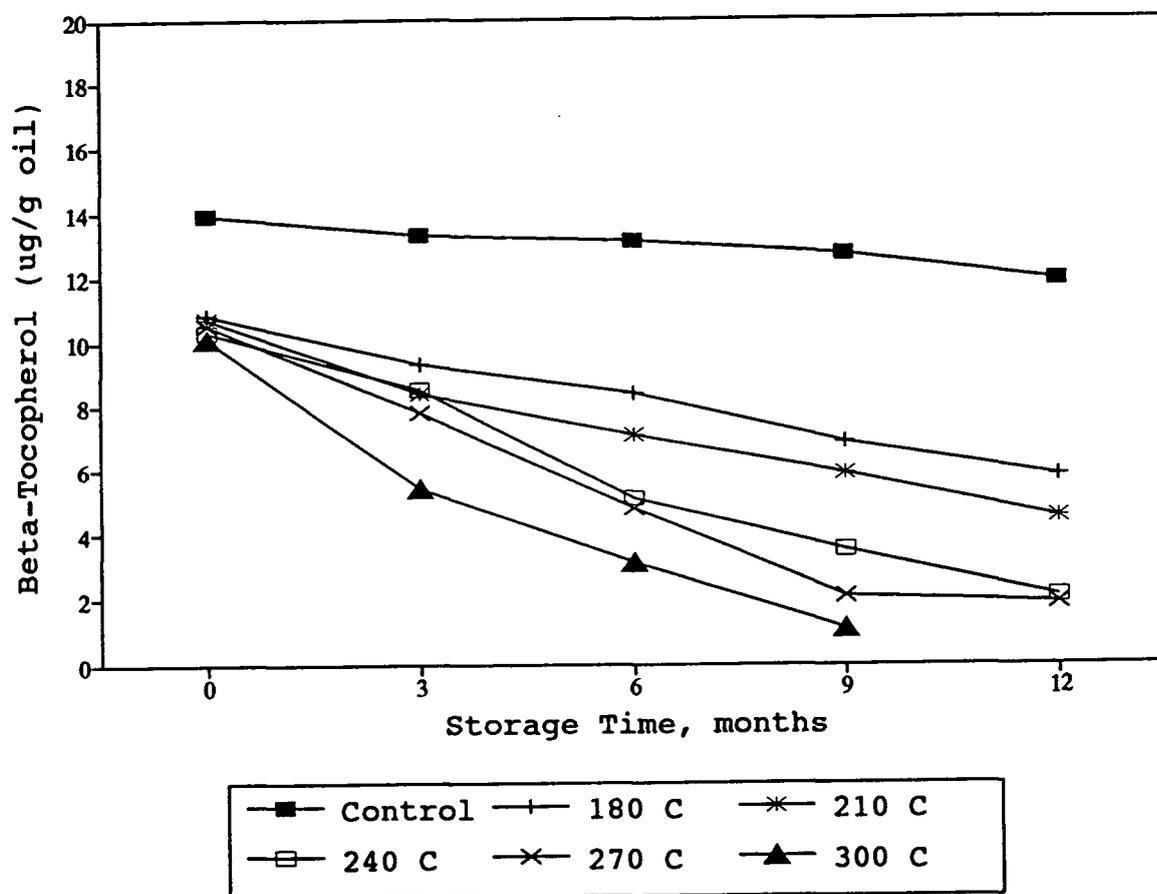


Fig. 6.16. Effect of different roasting temperatures on gamma-tocopherol of hazelnuts. (Barcelona)

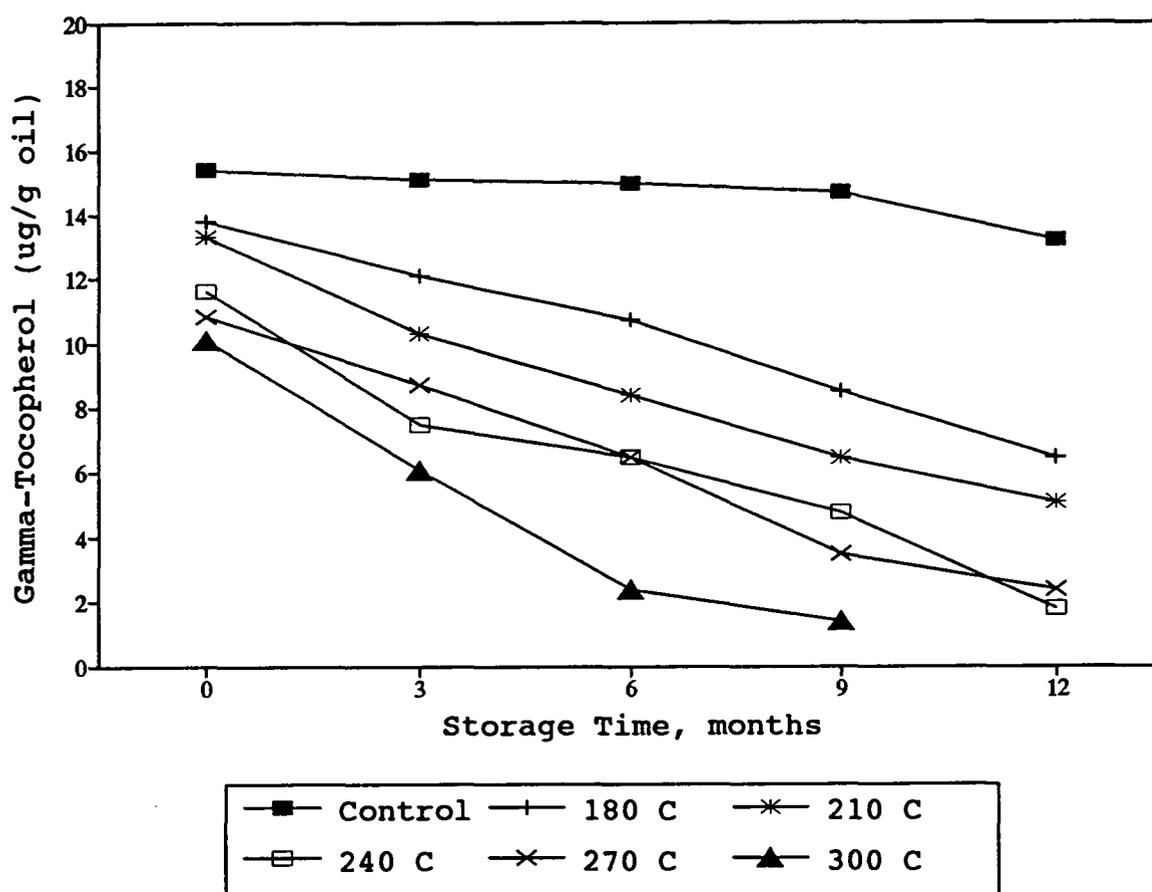


Fig. 6.17. Effect of storage duration on peroxide value of treated hazelnuts, stored at 0°C. (Barcelona)

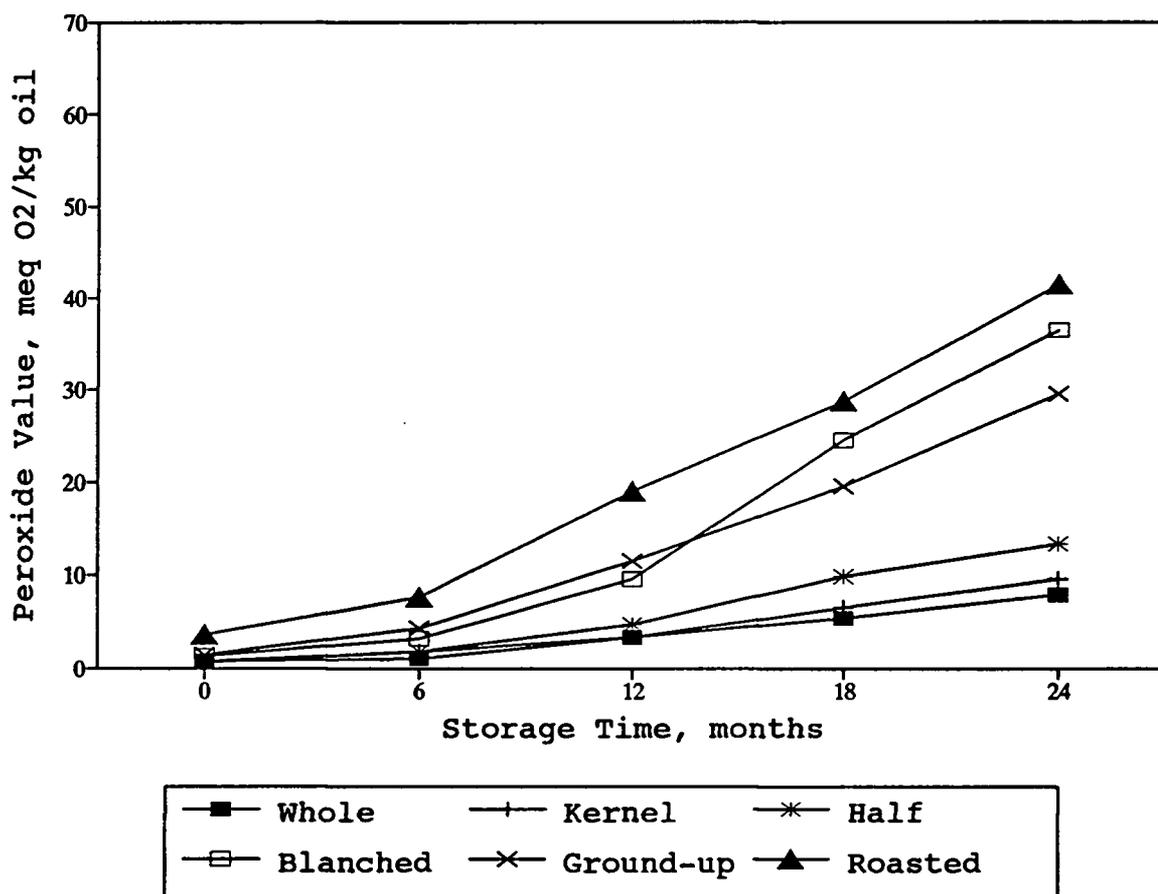


Fig. 6.18. Effect of storage duration on peroxide value of treated hazelnuts, stored at 5°C. (Barcelona)

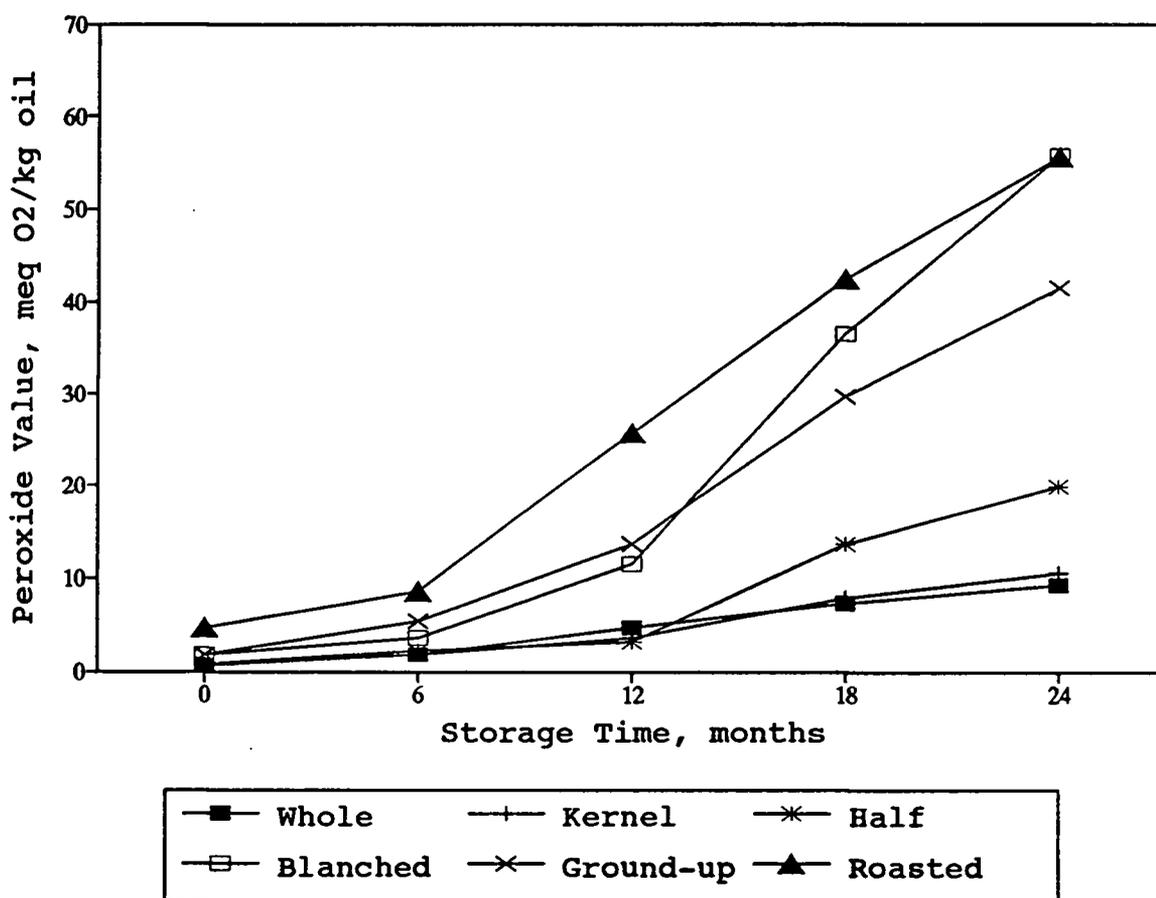


Fig. 6.19. Effect of storage duration on peroxide value of treated hazelnuts, stored at 10°C. (Barcelona)

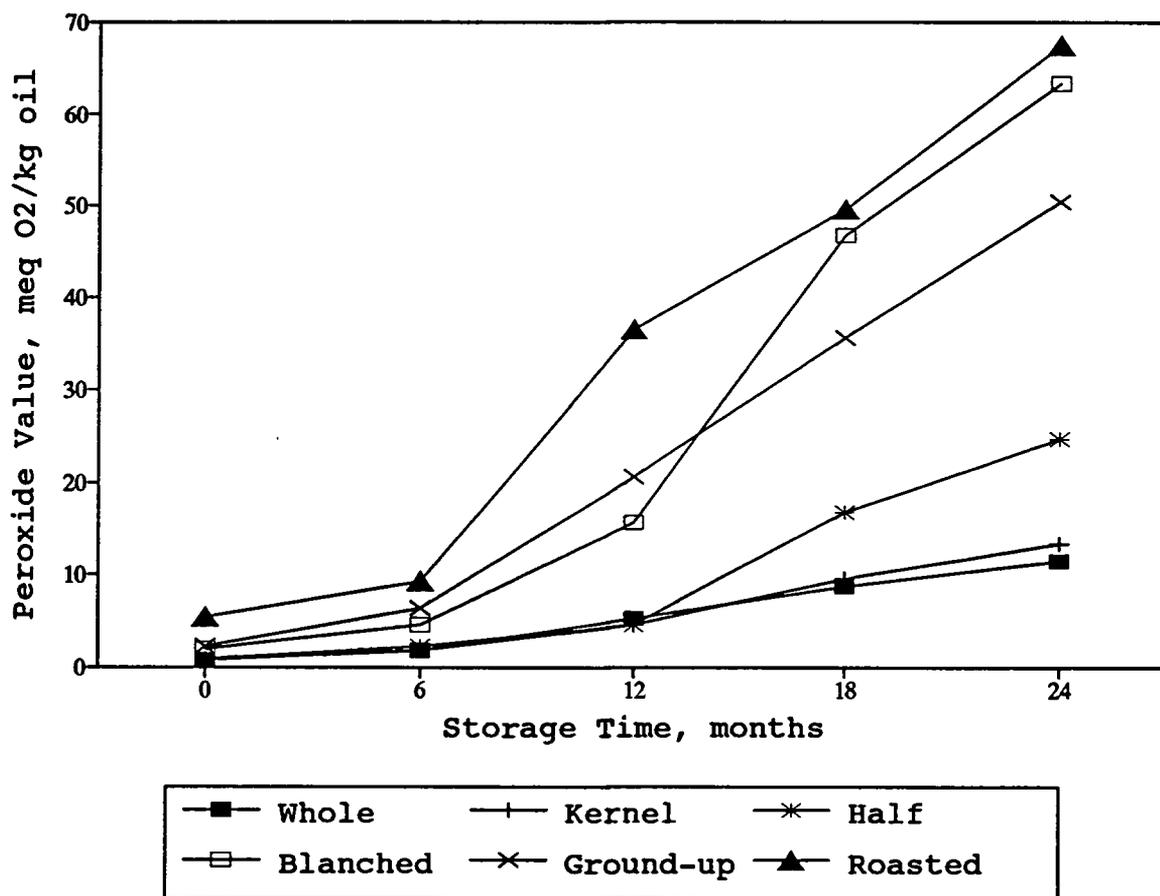


Fig. 6.20. Effect of different roasting temperatures on peroxide value of hazelnuts. (Barcelona)

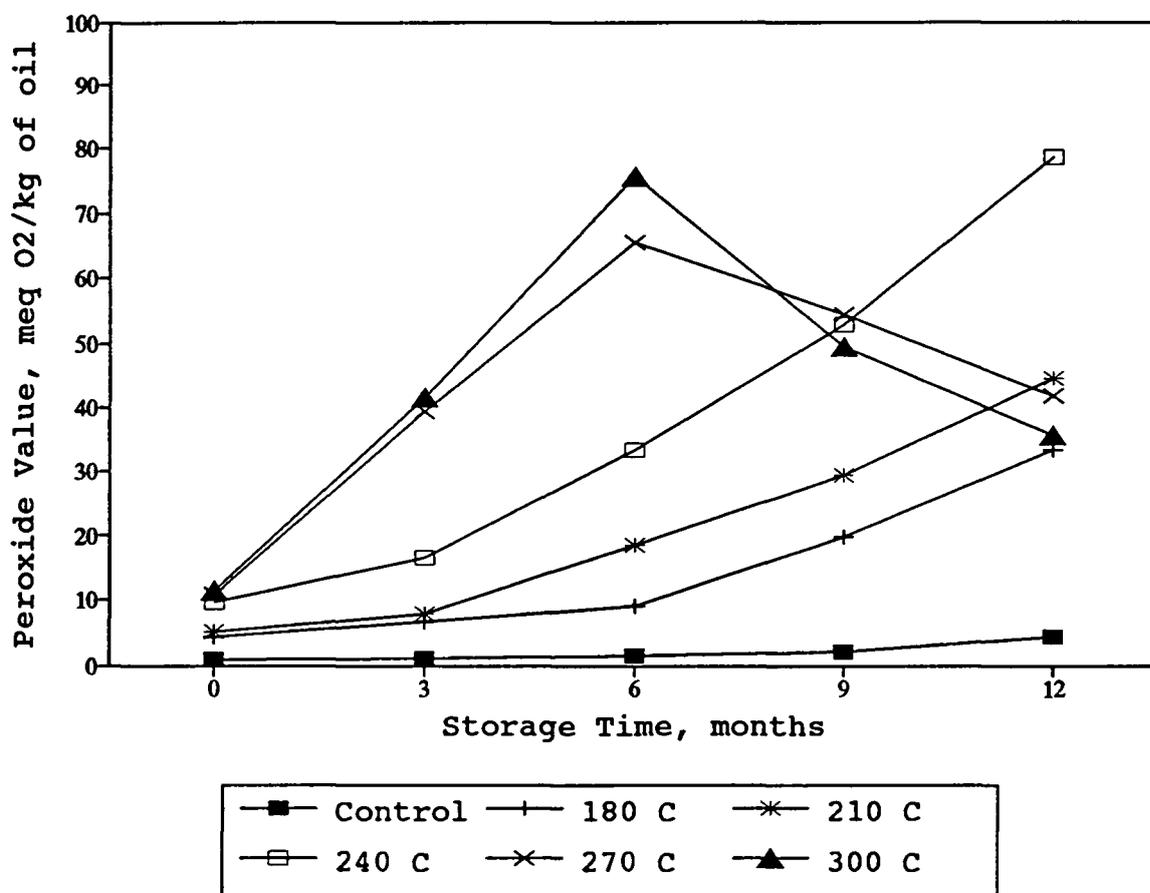


Fig. 6.21. Effect of different storage temperatures on peroxide value of roasted and unroasted hazelnuts. (Barcelona)

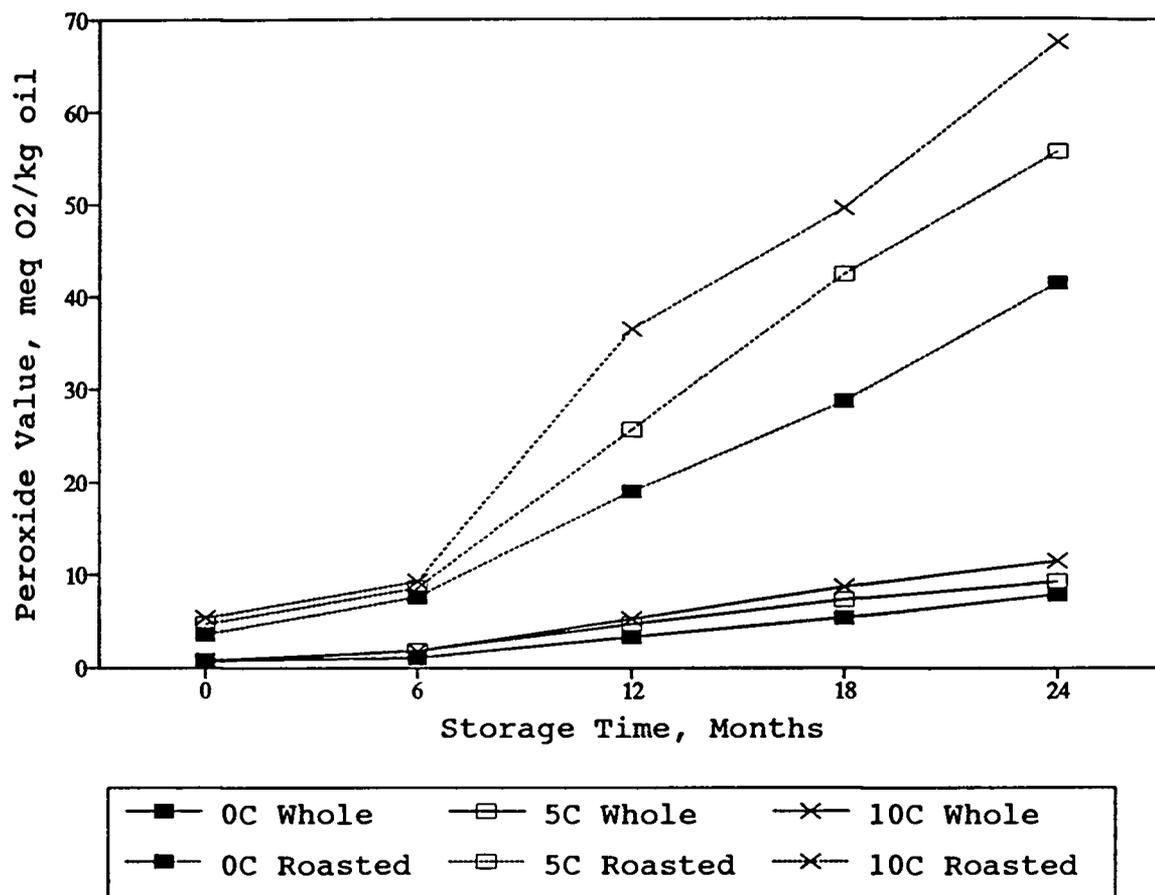


Fig. 6.22. Effect of different storage temperatures on peroxide value of intact vs ground up hazelnut kernels. (Barcelona)

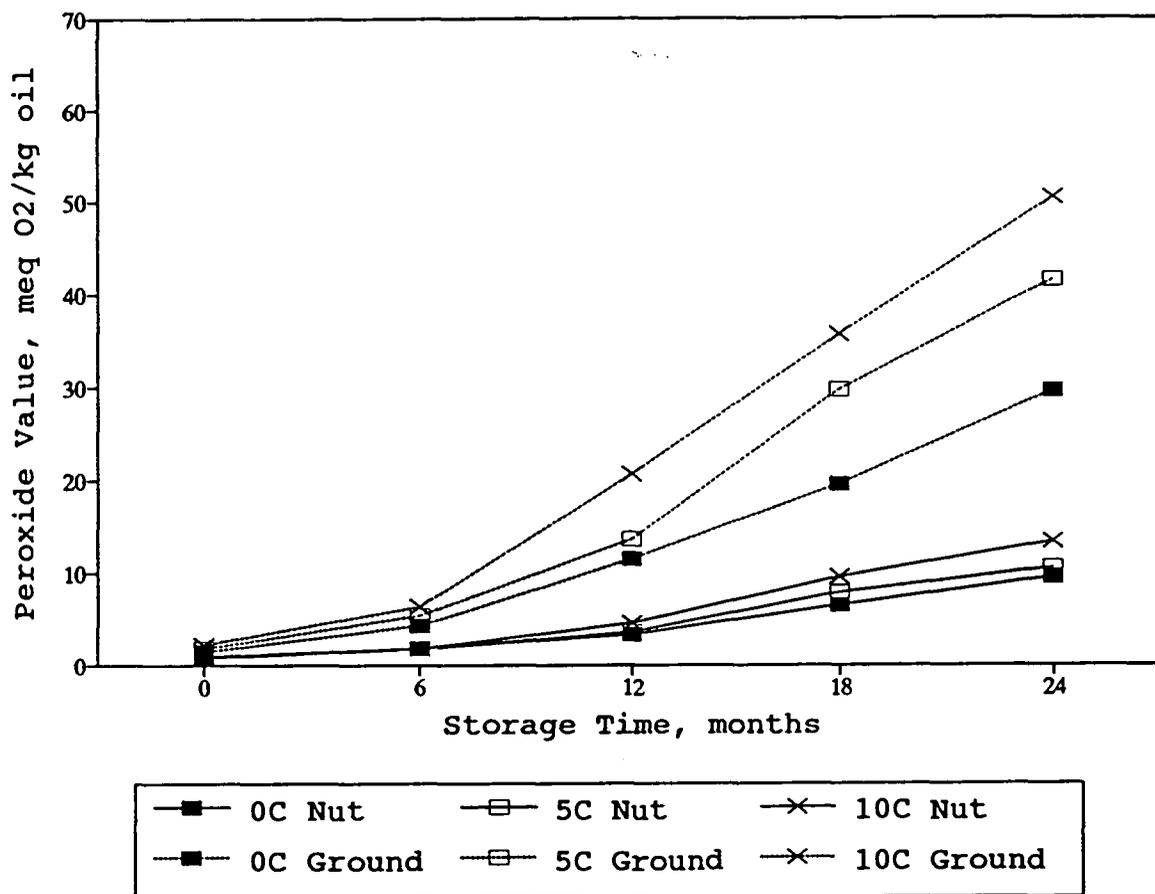


Fig. 6.23. Effect of different storage temperatures on peroxide value of blanched or halved hazelnut kernels. (Barcelona)

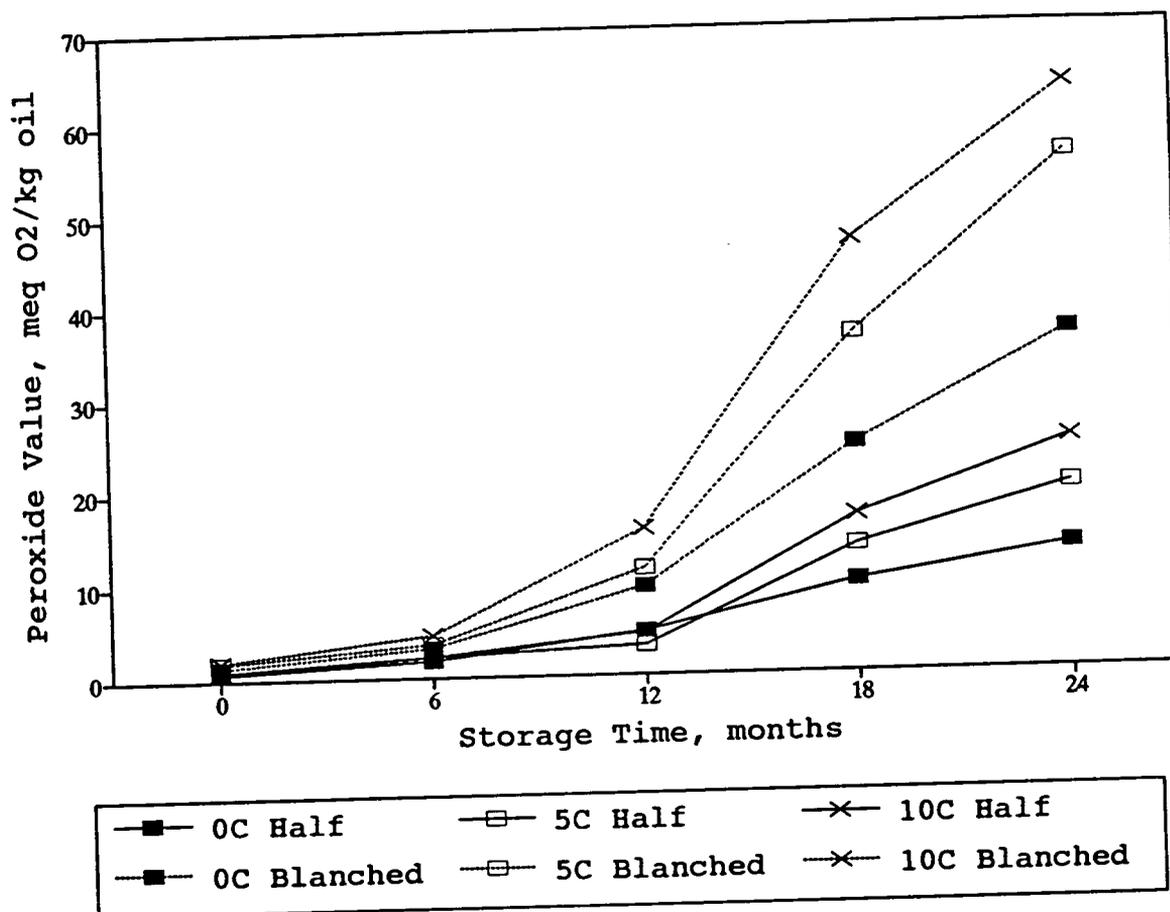


Fig. 6.24. Reciprocal relationship of total vitamin E (tocopherol) and peroxide value of whole hazelnuts at three storage temperatures. (Barcelona)

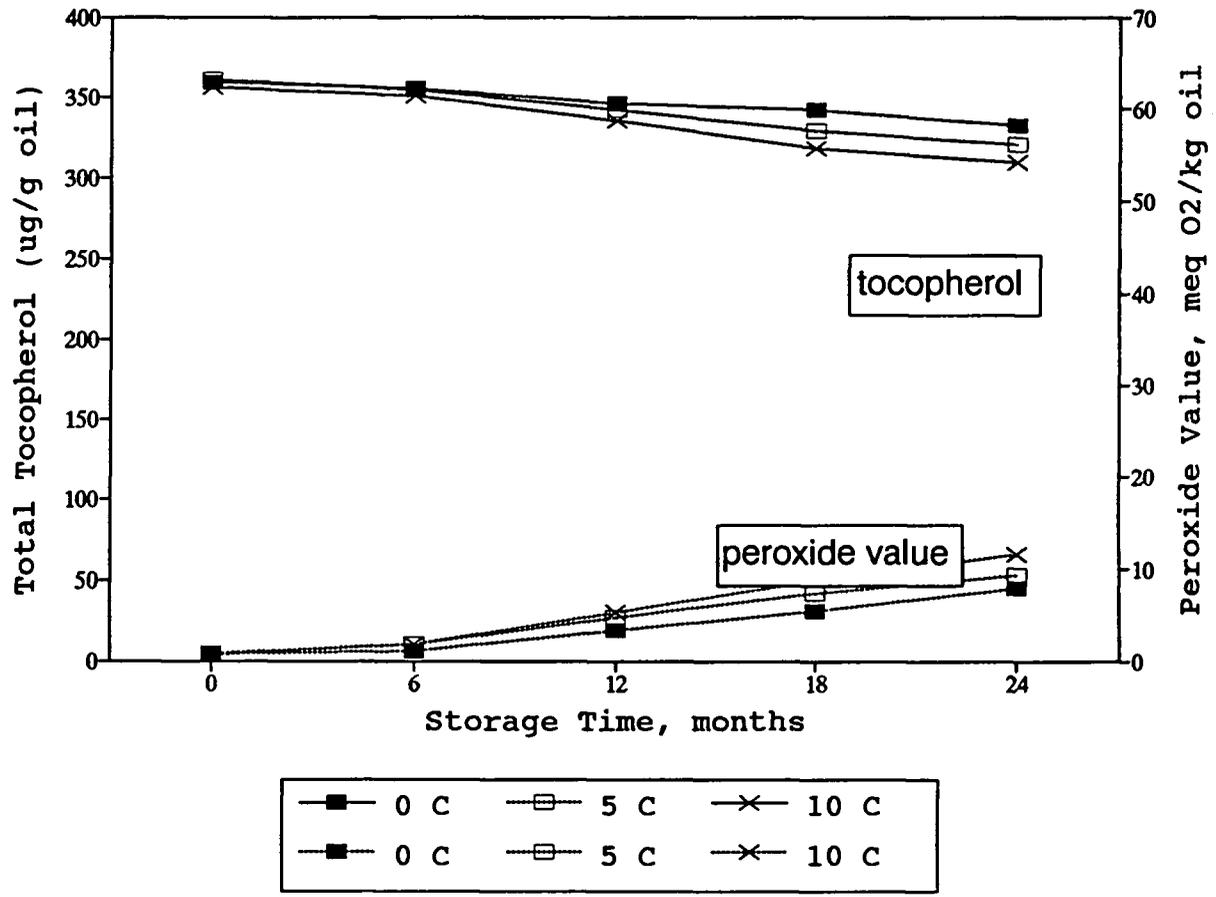


Fig. 6.25. Reciprocal relationship of total vitamin E (tocopherol) and peroxide value of ground hazelnuts at three storage temperatures. (Barcelona)

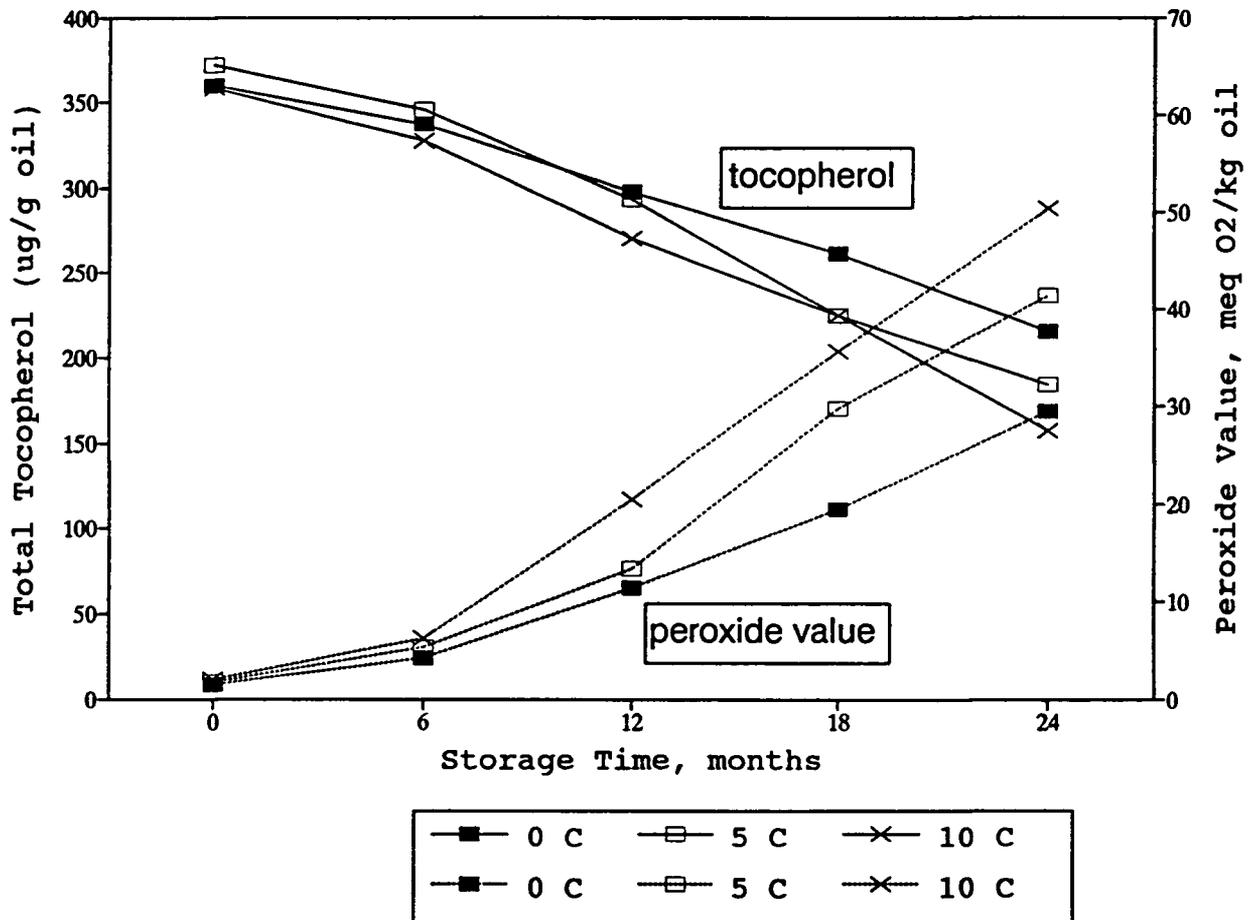


Fig. 6.26. Reciprocal relationship of total vitamin E (tocopherol) and peroxide value of 180 °C roasted hazelnuts at three storage temperatures. (Barcelona)

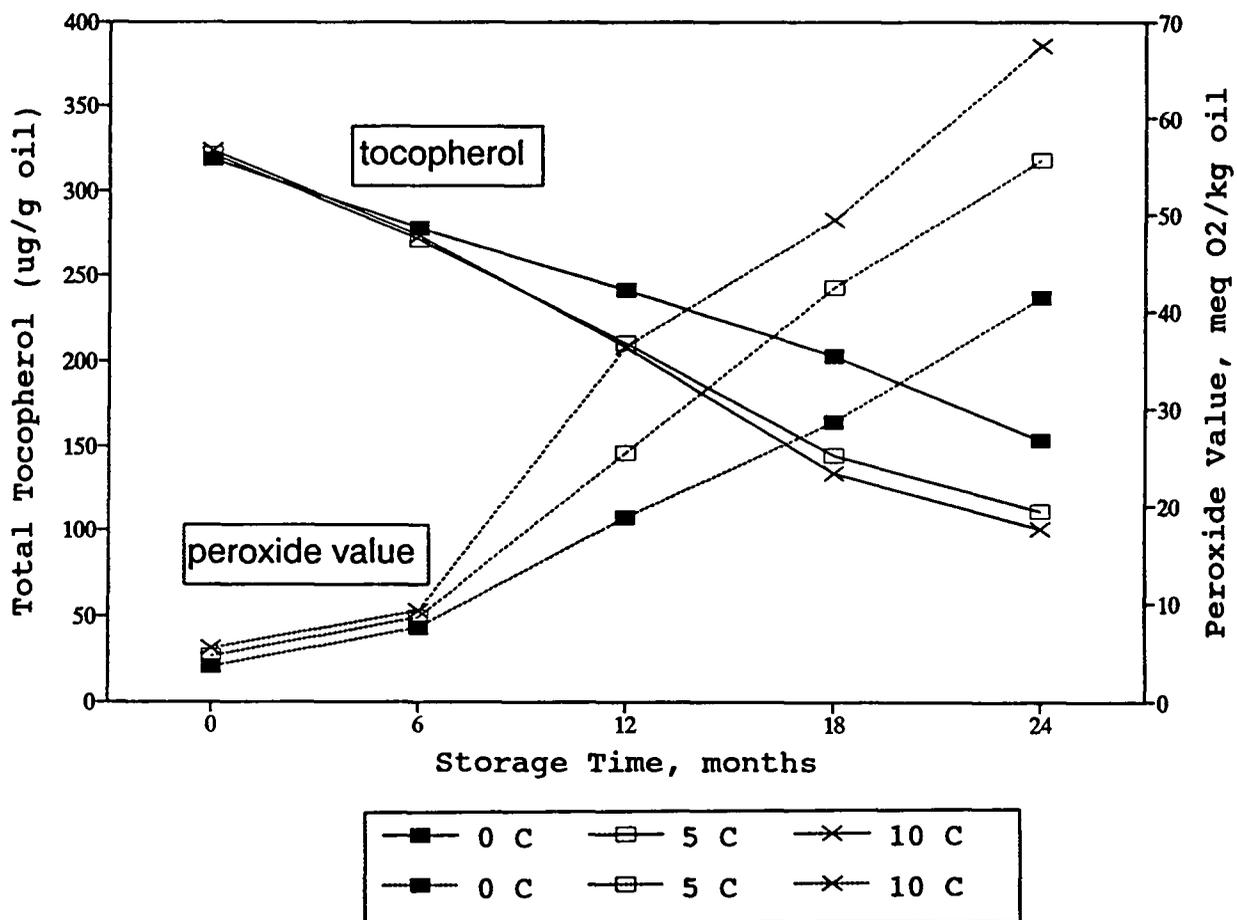


Fig. 6.27. Effect of storage duration on oleic acid of treated hazelnuts, stored at 0°C. (Barcelona)

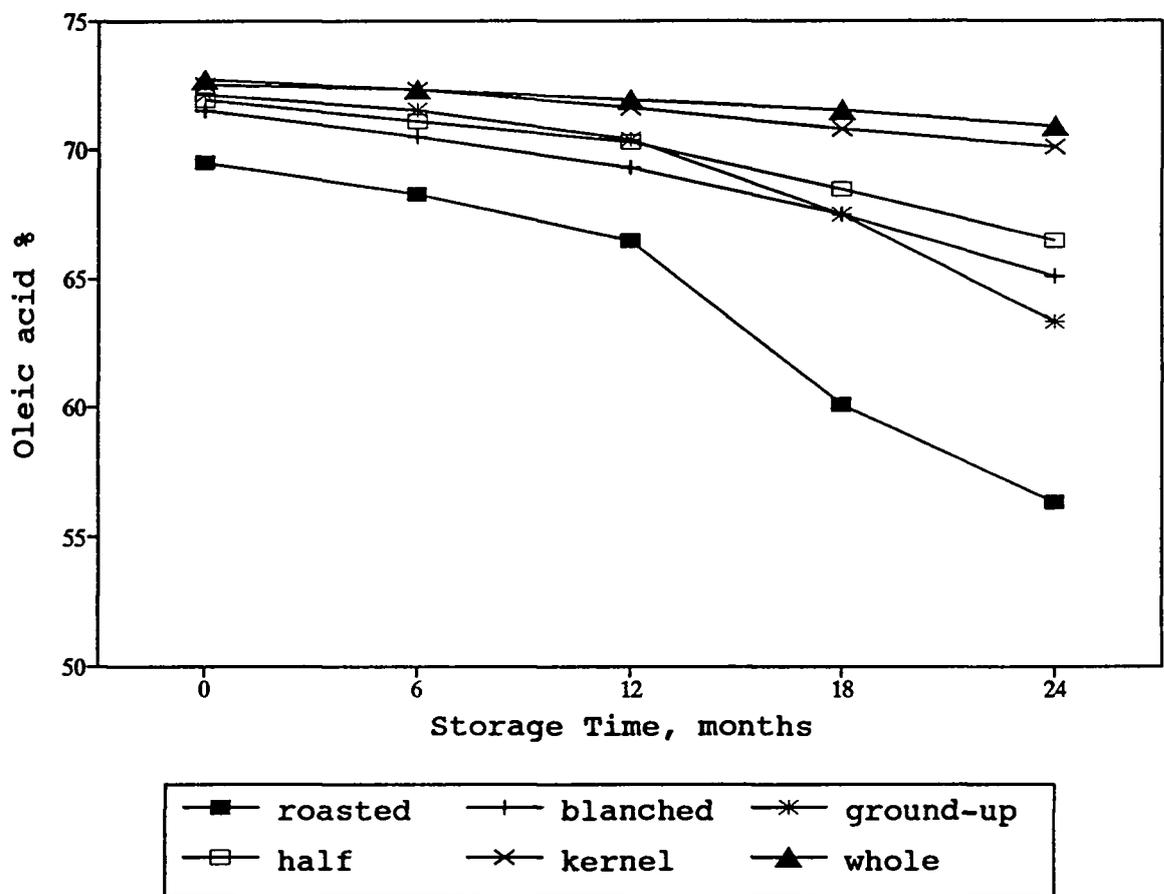


Fig. 6.28. Effect of storage duration on linoleic acid of treated hazelnuts, stored at 0°C. (Barcelona)

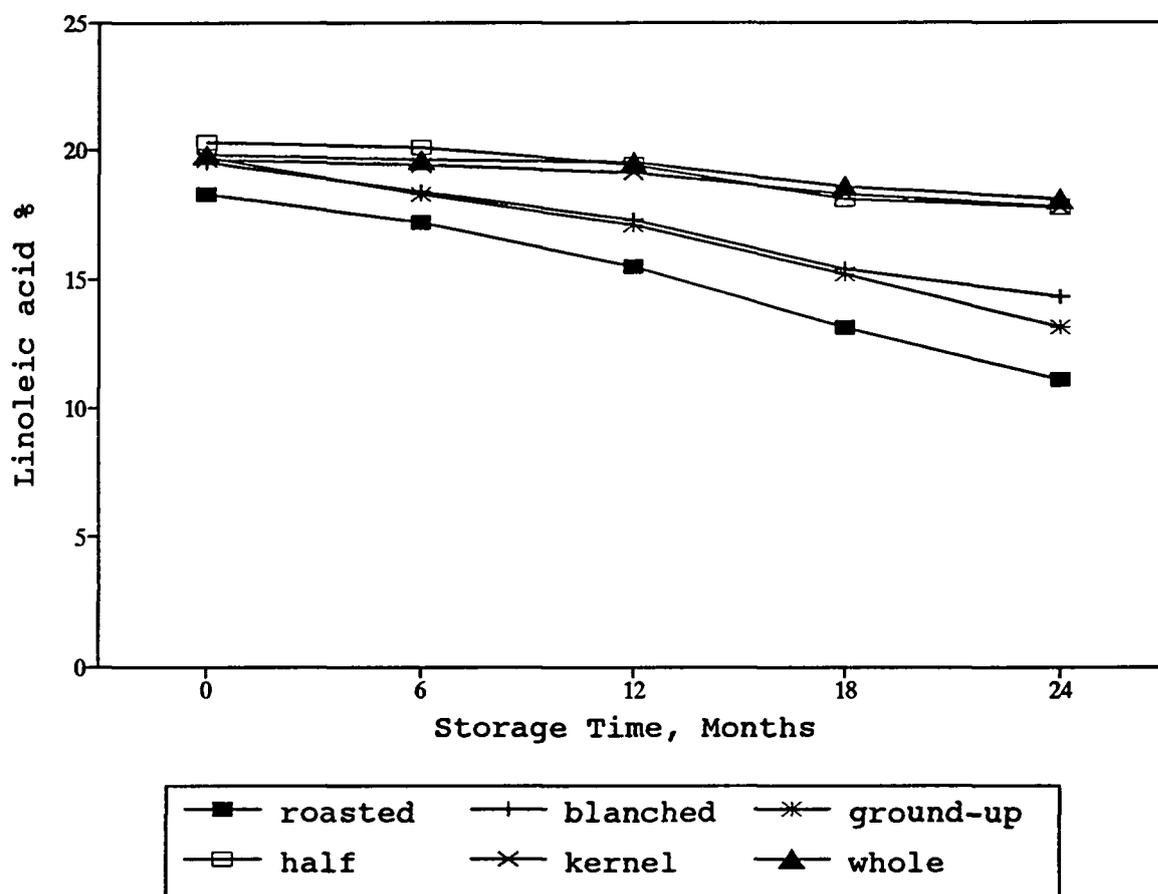


Fig. 6.29. Effect of storage duration on oleic acid of treated hazelnuts, stored at 5°C. (Barcelona)

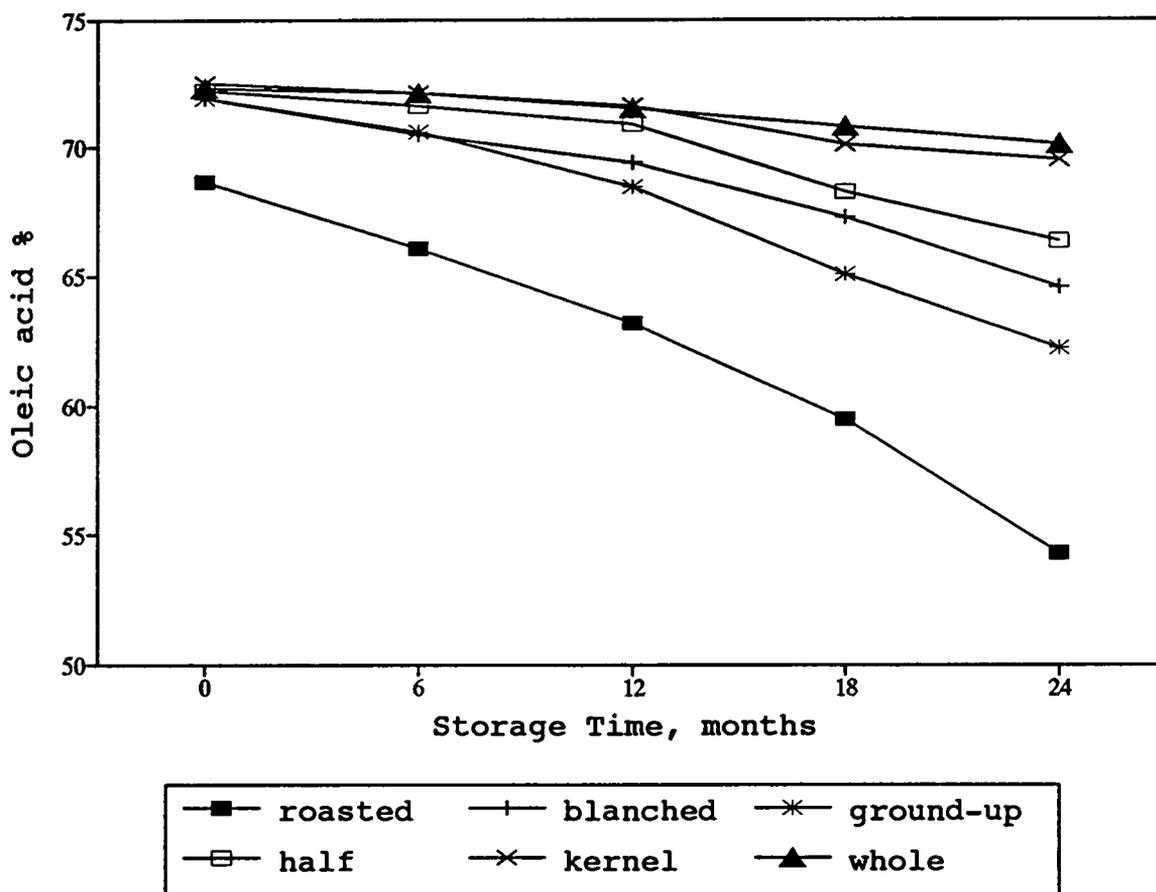


Fig. 6.30. Effect of storage duration on linoleic acid of treated hazelnuts, stored at 5°C. (Barcelona)

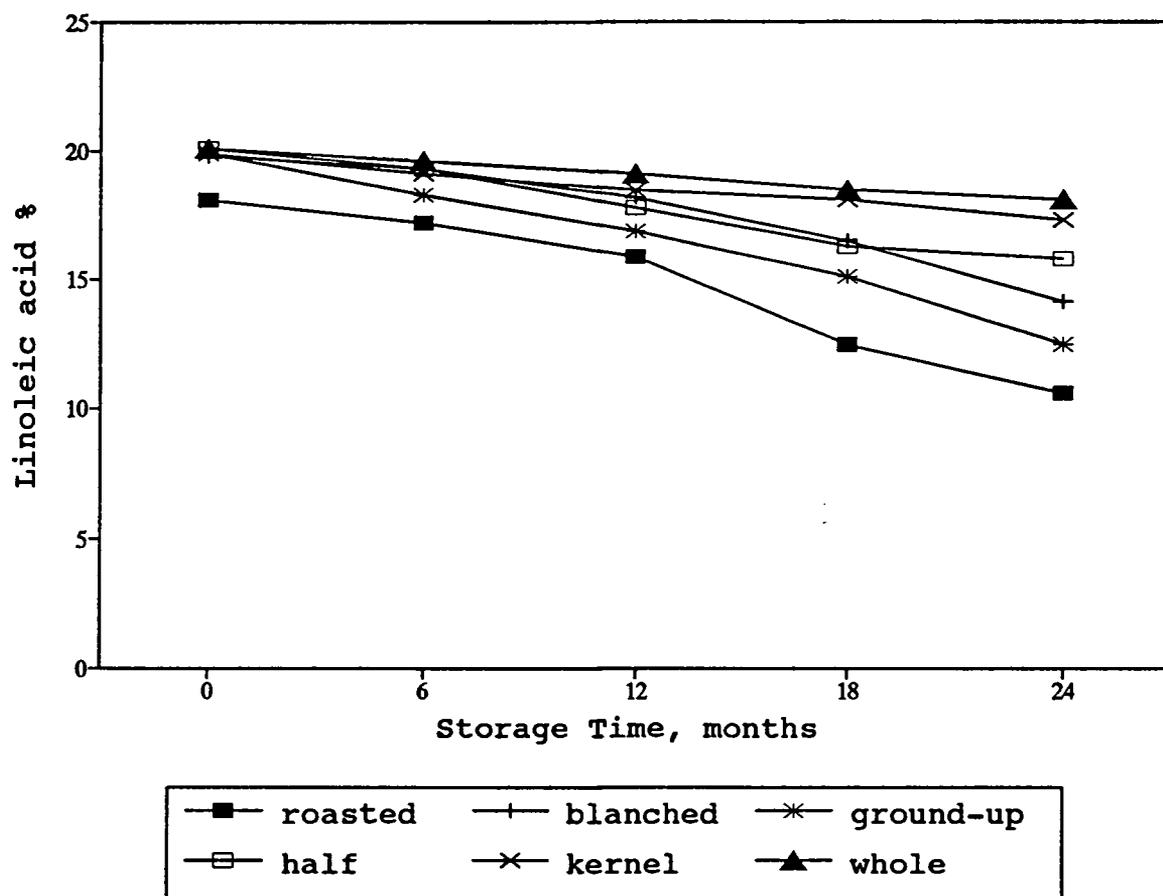


Fig. 6.31. Effect of storage duration on oleic acid of treated hazelnuts, stored at 10°C. (Barcelona)

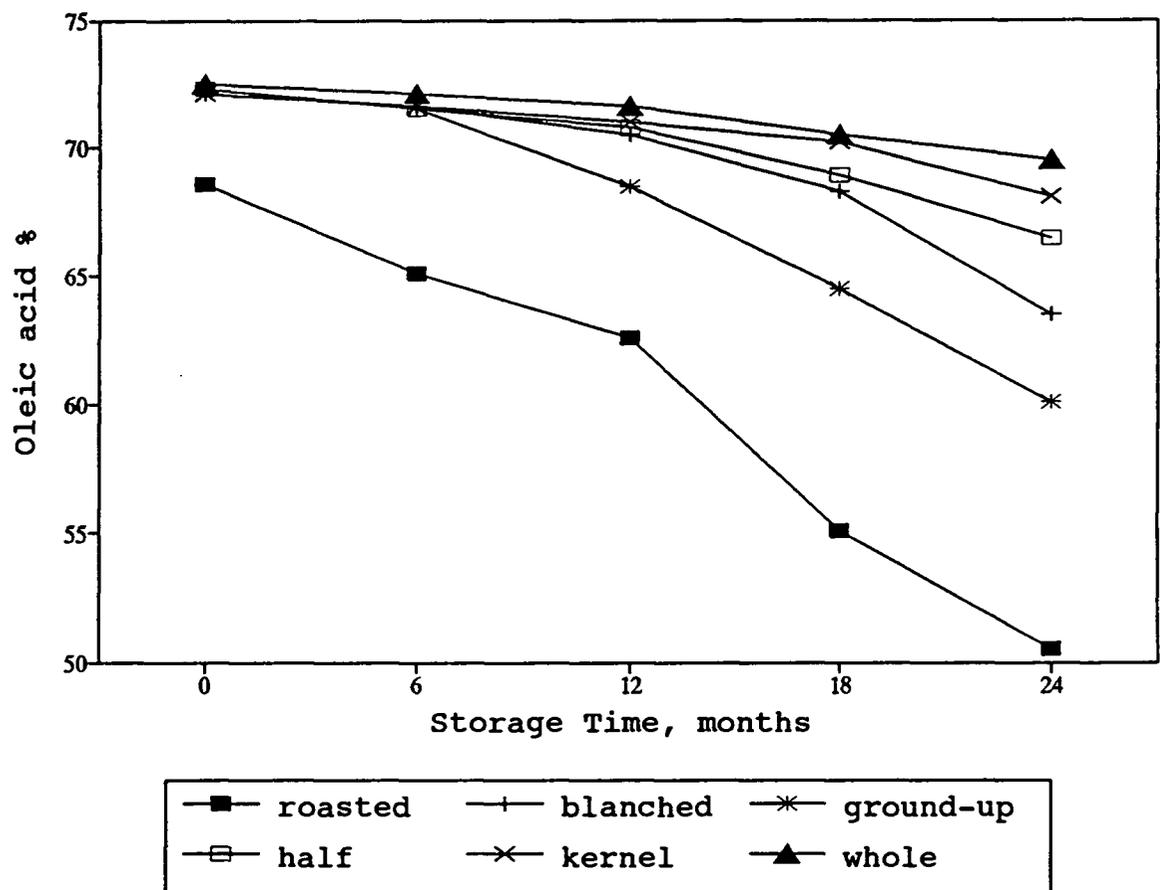


Fig. 6.32. Effect of storage duration on linoleic acid of treated hazelnuts, stored at 10°C. (Barcelona)

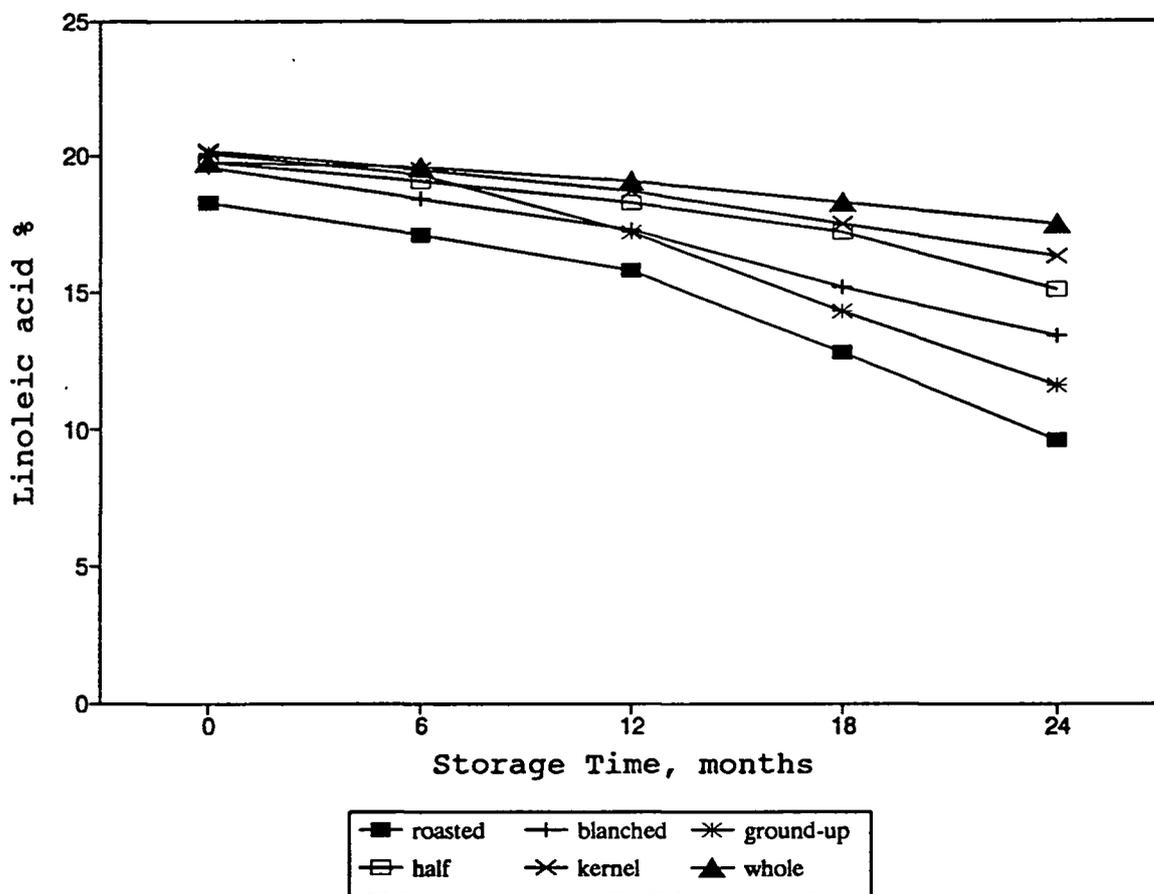


Fig. 6.33. Effect of different roasting temperatures on oleic acid of hazelnuts, stored at 0°C. (Barcelona)

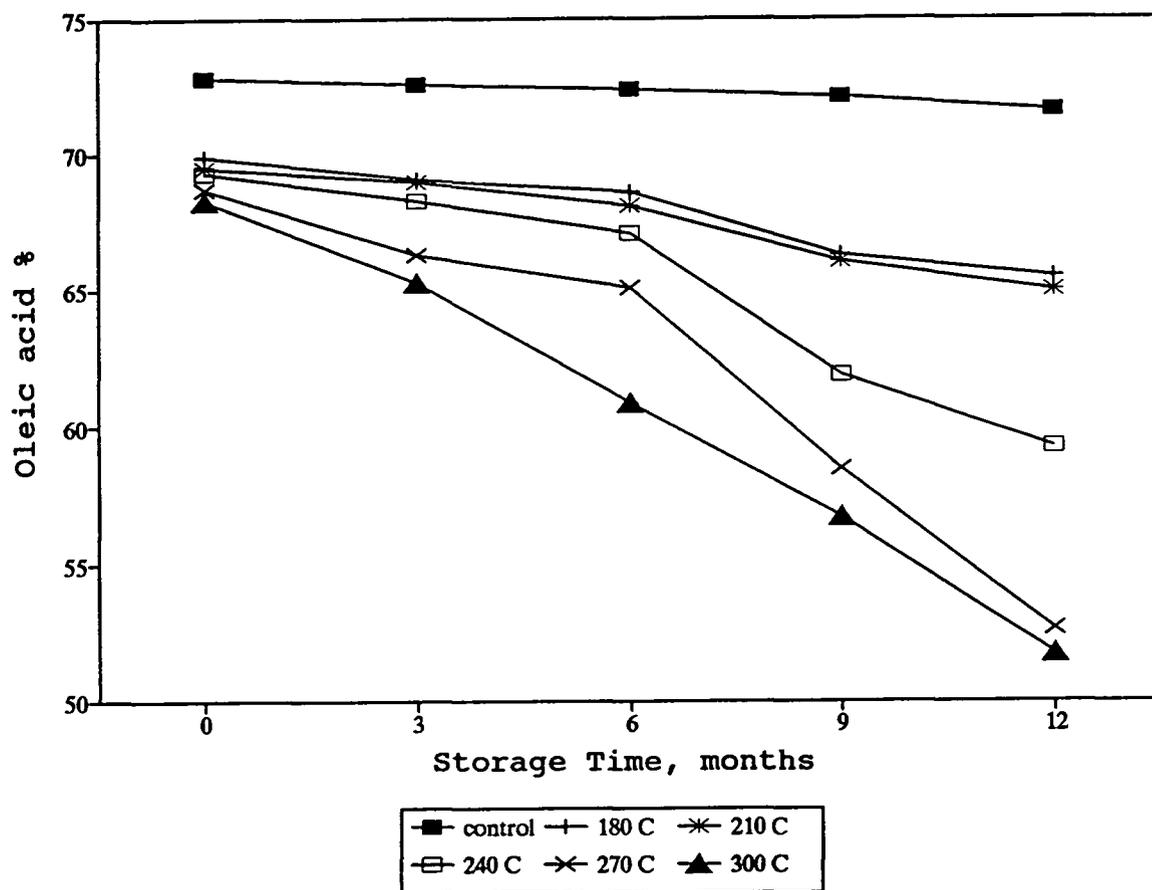


Fig. 6.34. Effect of different roasting temperatures on linoleic acid of hazelnuts, stored at 0°C. (Barcelona)

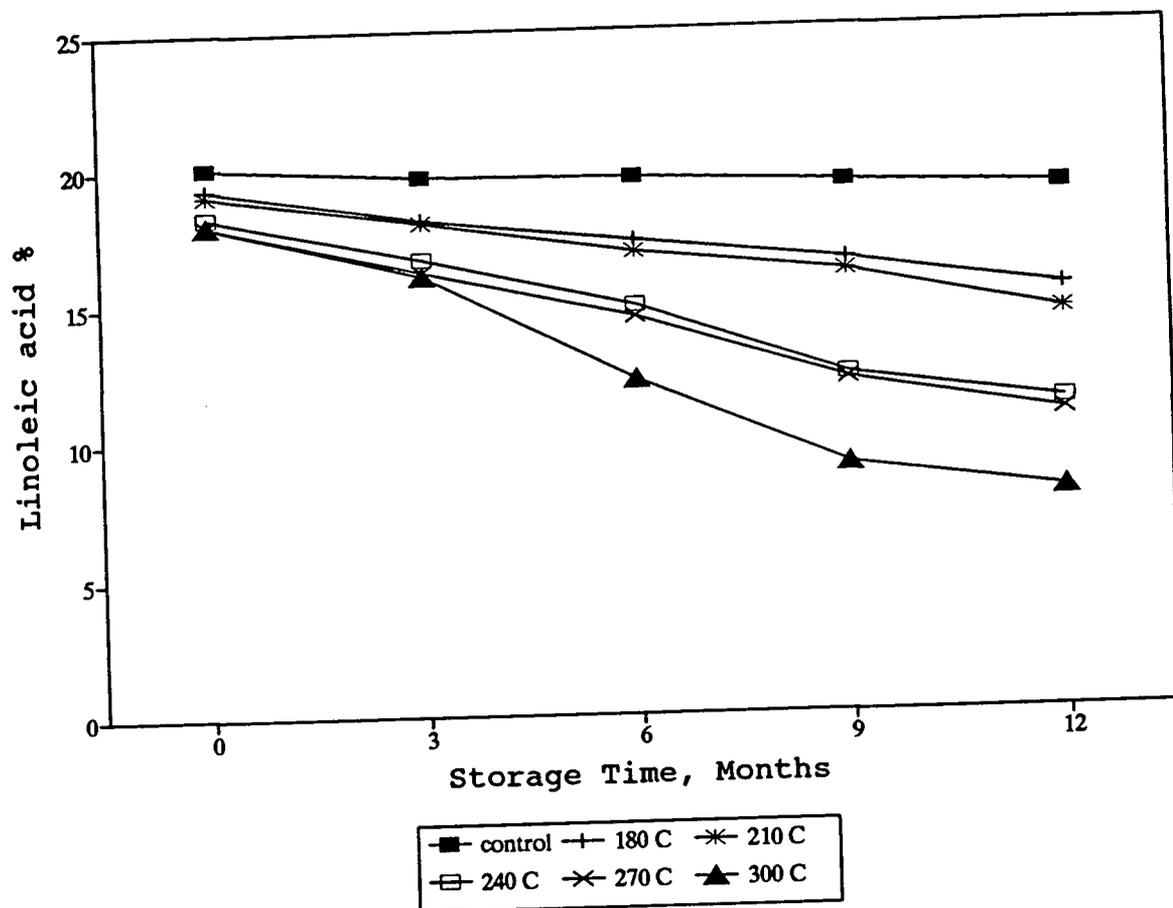


Fig. 6.35. The relationship between alpha-tocopherol and oleic acid.

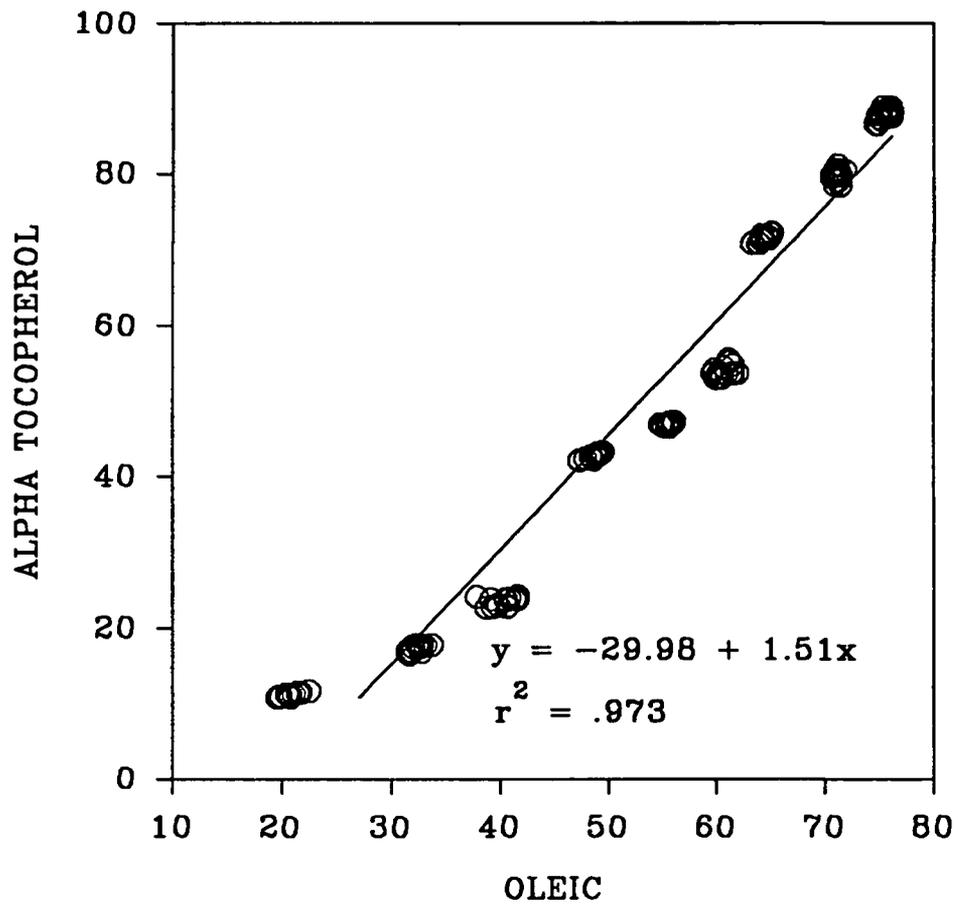


Fig. 6.36. The relationship between beta-tocopherol and linolenic acid.

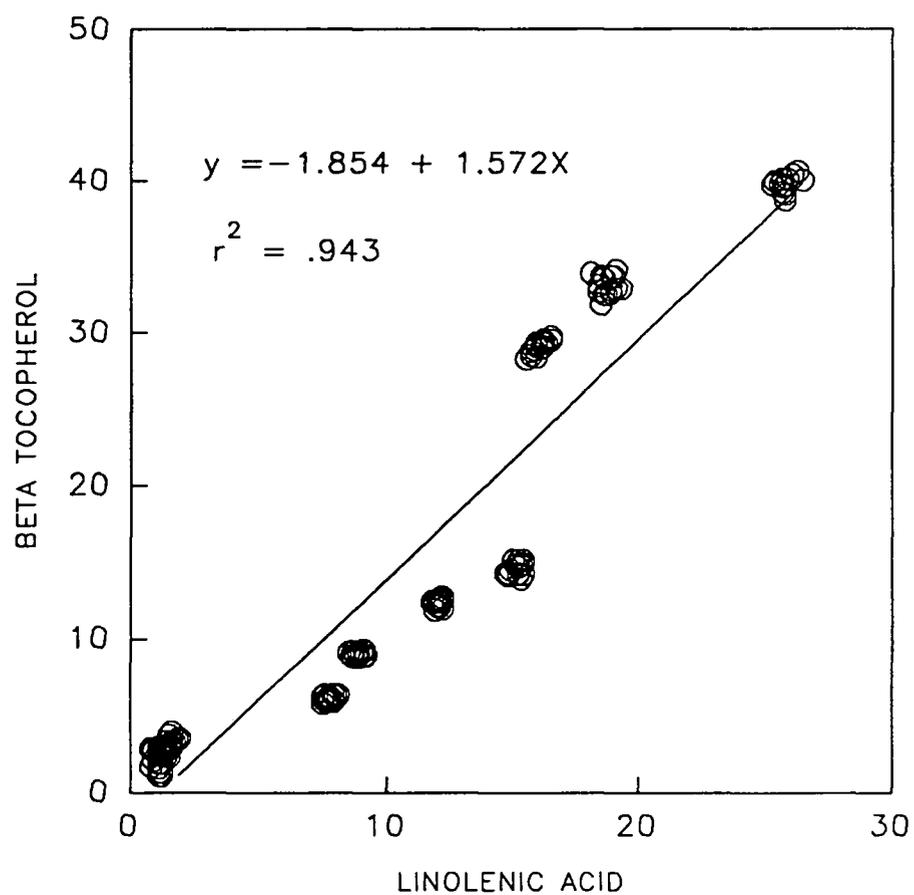
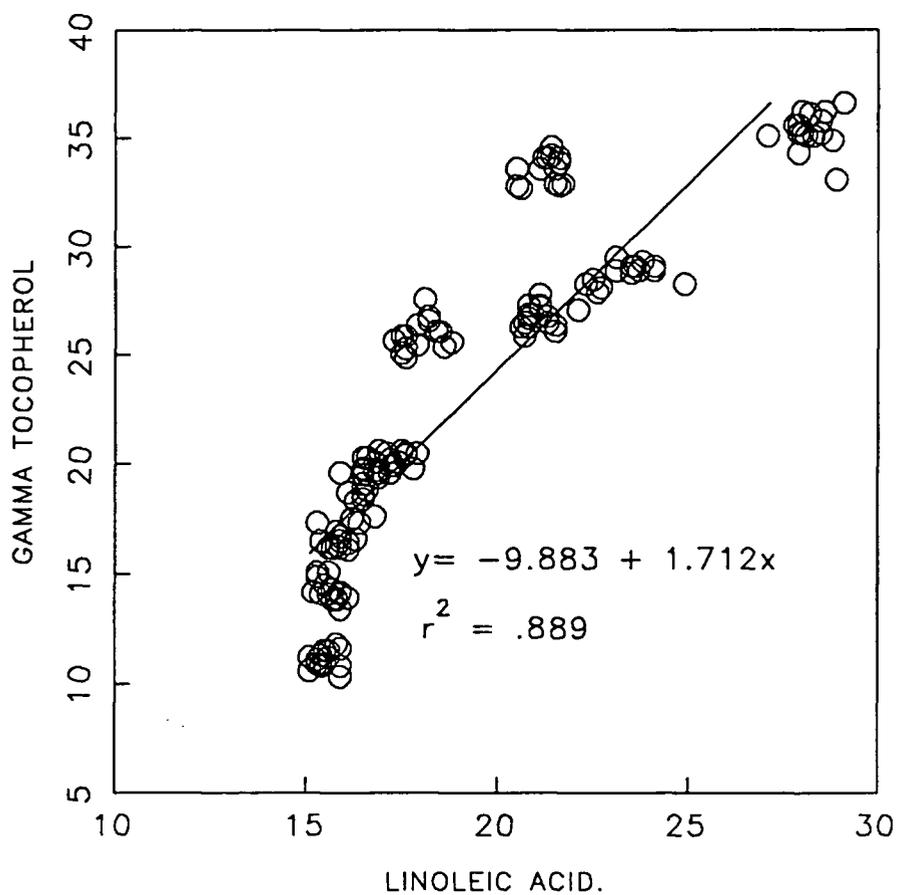


Fig. 6.37. The relationship between gamma-tocopherol and linoleic acid.



## Chapter 7. Conclusions

### Hazelnut Kernel White Mold

1. We have tentatively identified the hazelnut kernel white mold as Ramularia spp. While this identification has not rigorously applied Koch's postulates establishing pathogenicity, Ramularia was always present when mold was detected and was virtually ubiquitous in the interior of the shell of hazelnuts and occurs there from the very earliest stages of nut growth, and persists through harvest and storage. The fungus may gain entrance as early as flowering.

2. The year 1986 was a season of higher than normal rainfall, and kernel mold incidence was greater than (8.3%) in the dryer 1987 (2.6%), 1988 (1.8%) seasons.

3. "Barcelona" hazelnut variety is more susceptible to kernel mold than "Daviana" or "Ennis". Microclimate in the canopy and numbers of nuts per cluster had little, if any, effect on mold.

4. Storage temperatures near 0°C suppressed mold development, both incidence and severity compared to 10°C or 20°C.

### Hazelnut Developmental Biochemistry

1. A sigmoidal development pattern was observed in whole nut and kernels.

2. Moisture content decreased from 88% to 25% as oil synthesis proceeded from 3.5% to 61% at harvest.

3. Initially, as green tissue, linolenic acid was high, but steadily decreased to < 1% at harvest. Oleic acid rose to 70% and linoleic to 22% at harvest with triglycerides as the preponderant lipid class.

4.  $\alpha$ -tocopherol increased steadily over the season to about 350  $\mu\text{g/g}$  oil and this was in part due to progressive methylation of  $\beta$ -,  $\Gamma$ -, and  $\delta$ - tocopherols. There were only trace amounts of tocotrienols. Hazelnuts are a rich source of  $\alpha$ -tocopherol, highest of the nuts.

5. Oil content of hazelnut varieties ranged from a low of 58% in Hall's Giant to a high of 66% in Tombul.

#### Hazelnut compared to other nuts and oil seeds.

1. Seventeen varieties of hazelnuts were compared to 12 other types of nuts and 7 oil seeds for fatty acid composition, tocopherols and tocotrienols,  $\alpha$ -tocopherol equivalents, and total oil concentration.

2. Hazelnut oil composition was 70% oleic acid, 22% linoleic, 4% palmitic, 2% stearic, and less than 1% linolenic, palmitoleic, and arachidic.  $\alpha$ -tocopherol,  $\beta$ -tocopherol, and  $\Gamma$ -tocopherol were 366, 16, and 19  $\mu\text{g/g}$  oil respectively.

3. Hazelnut oil ranked second only to sunflower seed oil in  $\alpha$ -tocopherol equivalents, sunflower oil had 726  $\mu\text{g}$   $\alpha$ -toc equiv/g oil whereas hazelnuts had 369  $\mu\text{g/g}$  oil.

4. Recent implications of nut consumption and the prevention of coronary heart disease suggest that hazelnuts with their high  $\alpha$ -tocopherol and high mono-unsaturated,

linoleic acid oils would be highly desirable in the diet.

5. It appears that there are bio synthetic couplings of the type of vitamin E synthesized relative to fatty acid composition.

Storage studies and roasting effects on hazelnut quality.

1) Nut defects were mainly blanks (13.5%), kernel defects were, 2.7% underdeveloped, 4.5% shriveled, 0.1% black tip, 0.1% rotten, 0.1% worms, 0.1% split, 0.5% double, and 0.06% brown tip were found in "Barcelona." There were no significant differences found over three years.

2) Hazelnuts allowed to air dry at moderate temperatures (< 40°C) can be stored for long periods, up to 2 years, with less than 10% loss of  $\alpha$ -tocopherol, peroxide values less than 12 meq of O<sub>2</sub>/kg oil, and little change in fatty acid, and no rancidity. As the kernels lose their pellicle as are reduced to smaller pieces (halves, slices, chopped nuts), the oxidative rancidity processes are accelerated in storage.

3) Roasting at temperatures greater than 150°C had a dramatic effect on stimulating oxidation of the lipids as evidenced by greater losses of vitamin E, unsaturated fatty acids (linoleic > oleic), and increased peroxide values. Nuts roasted at 180°C for 25 minutes already had 23% less vitamin E prior to storage.

4) Low storage temperatures (0°C) were beneficial to reduce rancidity development.

5) Losses of tocopherols arise before peroxide values

begin to increase, but then peroxides increase more rapidly as tocopherols continue to decline. Peroxide values rise to a maximum, then decline as secondary rancidification breakdown products are formed and actual rancid flavors develop. Peroxide values are thus valuable as "early warnings" for incipient rancidity. Approximately: PV < 8 have no detectable rancid taste, very little oxidation, 10 < PV < 35 early oxidation but no or very little rancid flavor, PV > 50 oxidation is advanced, rancid flavors detectable, further oxidation leads to heavy rancid flavors, but PV values likely decrease after this as secondary products (shorter-chain aldehydes, acids, ketones, etc) develop, including malondialdehyde.

**Chapter 8. Bibliography**

- Adams, C.F. 1975. "Nutritive value of American foods" ARS, USDA. Agriculture handbook No. 456, Washington, DC.
- Adnan, M. 1980. Lipid properties and stability of partially defatted peanuts. Ph.D. thesis. Urbana, Illinois.
- Albers, N., G. Behm, D. Dressler, W. Klaus, K. Kuther, and H. Lindner. 1984. Vitamins in animal nutrition. Arbeitsgemeinschaft fur Wirkstoffe in der Tierernahrung eV (AWT), Bonn.
- Albert, D.S., Y.M. Peng, and T.E. Moon. 1978. Alpha-tocopherol pretreatment increases adriamycin bone toxicity. Biomedicine. 29:189-194.
- Al-Kishtaini, S.F. 1971. Methods of preparation and properties of water extracts of soybeans. PhD Thesis. Univ. of Illinois at Urban-Champaign.
- Andrikopoulos, N.K., M.N. Hassapidou, and A.G. Manoukos. 1989. The tocopherol content of Greek olive oils. J. Sci. Food Agric. 46: 503-509.
- Anon. 1916. Sources of supply of hazelnuts. Imperial Institute of Great Britian. 14:261-267.
- Anon. 1963. Filberts in Oregon. Oregon State University. Coop. Ext. Bull. 628.
- Anon. 1988. Hazelnut Hope. Sun-diamond Grower. Fall. pp.12-14.
- Anon. 1988a. The surgeon general's report on nutrition and health. Washington D.C.: U.S. government printing office. DDHS publication (PHS) 88-50,210,
- Anon. 1989a. Resolution No. 5. Nut grower society of Oregon, Washington, and British Columbia. pp.100.
- Anon. 1989b. Oregon hazelnut plantings register, healthy increase. Nut grower. July. pp.7.
- Anon. 1992. Vitamin E supplementation enhances immune response in the elderly. Nutrition Reviews. 50:85-87.
- A.O.A.C. 1975. Twelfth Edition. W. Horwitz, ed. Washington DC: Assc. Off. Anal. Chem.

- A.O.A.C. 1980. Official methods of analysis of the Association of Official Analytical Chemists. 13th edn. Washington, DC, USA.
- Appelquist, L.A. 1975. Biochemical and structural aspects of storage and membrane lipids in developing oil seeds, In: Recent Advances in the Chemistry and Biochemistry of Plant Lipids, Galliard, T. and E.I. Mercer, Eds., Academic Press, London. pp.247.
- Appelquist, L.A. 1986. Metabolism and control of lipid structure modification. Biochem. Cell Biol. 64:66-69.
- Assuncao, F.P., M.H.S. Bentes, and H. Serraya. 1984. A comparison of the stability of oils from brazil nut, Para rubber and passion fruit seeds. J. Amer. Oil Chem. Soc.. 61: 1031-1035.
- Ayres, J.L. 1977. Aflatoxin in pecans: Problems and solutions. J. Amer. Oil Chem. Soc. 54:229A-230A.
- Bahl, J., B. Francke, and R. Moneger. 1976. Lipid composition of envelopes, prolamellar bodies and other plastid membranes in etiolated, green and greening wheat leaves. Planta. 129: 193-201.
- Bailey, L.H. 1949. Manual of cultivated plants, Rev. Edition. Macmillan Co., New York.
- Ball, G.F.M. 1988. Applications of HPLC to the determination of fat-soluble vitamins in foods and animal feeds. (A review 1977-1987) J. Micronutr. Anal. 4:225-283.
- Barroso, M.A.T., F.M. Whiting, W.H. Brown, and J.W. Stull. 1973. Fatty acids of Brazilian cashew kernels. Hort Science. 8:99-101.
- Barthel, G., and W. Grosch. 1974. Peroxide value determination-comparison of some methods. J. Amer. Oil Chem. Soc. 51: 540-544.
- Bassil, N.V., W.M. Probesting, L.W. Moore, and D.A. Lightfoot. 1991. Propagation of hazelnut stem cuttings using agrobacterium. Hortscience. 26:1058-1060.
- Bauernfeind, J.C. 1977. The tocopherol content of food and influencing factors. Crit. Rev. Food Sci. and Nutr. March 337-338.
- Bauernfeind, J. C. 1986. Antioxidant function of L-Ascorbic acid in food technology. Vitamins, Nutrients and Therapeutic Agents. 27: 307-333.

- Behrens, W.A. and R. Madere. 1991. Tissue discrimination between dietary RRR- $\alpha$ - and all-rac- $\alpha$ -tocopherols in rats. *J. Vitam. Nutr. Res.* 61:454-459.
- Benson, M.W., R.H. Kurtzman Jr., W.U. Halbrook, and R.M. McCready. 1975. A research note: Aflatoxin production on some feeds and foods. *J. Food Sci.* 40:1085-1086.
- Berry, S.K. 1982. Fatty acid composition and cyclopropane fatty acid content of china-chestnuts (*Sterculia monosperma*, Venenat). *J. Amer. Oil Chem. Soc.* 59:57-58.
- Beuchat, L.R. 1975. Incidence of molds on pecan nuts at different points during harvesting. *Applied Microbiology.* 29: 852-854.
- Beuchat, L.R. 1978. Relationship of water activity to moisture content in tree nuts. *J. Food Sci.* 43:754-755.
- Beuchat, L.R., and R.E. Worthington. 1978. Technical note: Fatty acid composition of tree nut oils. *J. Food Tech.* 13: 355-358.
- Beuchat, L.R., and E.K. Heaton. 1980. Factors influencing fungal quality of pecans stored at refrigeration temperatures. *J. Food Sci.* 45: 251-253.
- Bieri, J.G. and R.P. Evarts. 1973. Tocopherols and fatty acids in American diet. The recommended allowance for vitamin E. *J. Am. Diet A.* 62: 147-152.
- Bieri, J.G., and R.P. Everts. 1975. Effect of dietary polyunsaturated fatty acids on tissue vitamin E status. *J. Nutr.* 108:392-398.
- Bieri, J.G., and P.M. Farrell. 1976. Vitamin E. *Vitamins Hormones.* 34:31-75.
- Billek, J.G. 1984. Lipid stability and deterioration. *J. Amer. Oil Chem. Soc.* 10:70-89.
- Birch, A.J. and W.F. Donovan. 1953. Studies in relation to biosynthesis. I. Some possible routes to derivatives of orcinol and phloroglucinol. *Aust. J. chem.* 6:360.
- Birch, A.J., R.A. Massey-Westropp, and C.J. Moyer. 1955. Studies in relation to biosynthesis. VII. 2-Hydroxy-6-methylbenzoic acid in *Penicillium griseofulvum* dierckx. *Aust. J. Chem.* 8:539.

- Blaser, P. and W.S. Lorenz. 1981. Aspergillus flavus kontamination von nussen, Mandeln und mais mit bekannten Aflatoxin-gehalten. *Lebensm. Wiss. U. Technol.* 14:252-259.
- Boone, P.D. 1924. Chemical constituents of pecan oil. *J. Ind. Eng. Chem.* 16:54-55.
- Booth, V.H. 1963. Alpha-Tocopherol, its Co-occurrence with chlorophyll in chloroplast. *Phytochemistry* 2: 421-429.
- Booth, V.H. 1964. The Alpha-Tocopherol content of forage crops. *J. Sci. Fd. Agric.* 15: 342-344.
- Bors, W. C., M. M. Erben-Russ, B. Kreileder, D. Tait And M. Saran. 1984. Oxygen radicals in chemistry and biology. Edited by W. Bors, M, Sarana and D. Tait-Walter de Gruyter, Berlin.
- Branch, W.D., T. Nakayama, and M. Chinnon. 1990. Fatty acid variation among U.S. runner type peanut cultivars. *J. Amer. Oil Chem. Soc.* 67:591-593.
- Branen, J.J. 1973. Synthesis of cationic surfactants with alkenyl group. *J. Amer. Oil Chem. Soc.* 50:59-63.
- Bright, S.E. 1983. Vitamin C and E (or fruit and vegetables) and the prevention of human cancer. In: *Nutritional factors in the induction and maintenance of malignancy.* Eds. Butterworth C.E. Jr., M.L. Huntchinson. New York, Academic press. pp.217-222.
- Brison, F.R. 1945. The storage of shelled pecans. *Tex. Agric. Ext. Stat. Bull.* 667: 1-3.
- Brooks, R.I. and A.S. Csallany. 1978. Effects of air, ozone, and nitrogen dioxide exposure on the oxidation of corn and soybean lipids. *J. Agric. Food Chem.* 26:1203-1209.
- Brown, C.M., E.J. Weber, and C.M. Wilson. 1970. Lipid and amino acid composition of developing oats. *Crop Science.* 10:488-491.
- Brown, F.J. 1952. The estimation of vitamin E. *J. Biochem.* 52: 523-526.
- Brown, F.J. 1953. The tocopherol content of farm feed-stuffs. *J. Sci. Food Agric.* 4: 161-165.
- Bucke, C. 1968. The distribution and stability of alpha-tocopherol in subcellular fractions of broad bean leaves. *Phytochemistry* 7: 693-700.

- Budowski, P., F.G. Menezenes, and F.G. Doller. 1950. Sesame oil, The stability of sesame oil. J. Amer. Oil Chem. Soc. 27:377-401.
- Budowski, P. 1964. Recent research on sesamin, sesamolin, and related compounds. J. Amer. Oil Chem. Soc. 41:260-265.
- Bukovits, G.J. and A. Lezerovich. 1987. Determination of individual tocopherols by derivative spectrophotometry. J. Amer. Oil Chem. Soc. 64:517-520.
- Ball, G.F.M. 1988. Applications of HPLC to the determination of fat-soluble vitamins in foods and animal feeds. Micronutrient. 4:255-283.
- Bunnell, R.H. 1971. Modern procedures for the analysis of tocopherols. Lipids. 6: 245-253.
- Burton, G.W., and K.U. Ingold. 1983. Autoxidation of biological molecules. 1. The antioxidant activity of vitamin E and related chain breaking phenolic antioxidants in vitro. J. Am. Chem. Soc. 103: 6472-6477.
- Burton, G.W., K.U. Ingold, D.O. Foster, S.C. Cheng, A. Webbs, L. Hughes, and E. Luszytk. 1988. Comparison of free alpha-tocopherol and alpha tocopherol acetate as sources of vitamin E in rats and humans. Lipids. 23: 834-840.
- Cajori, F.A. 1920. Some nutritive properties of nuts: Their proteins and content of water soluble vitamins. J. Biol. Chem. 43: 583-606.
- Cantoni, G.L. 1953. S-Adenoxylmethionine; A new intermediate formed enzymatically from L-methionine and adenosinetriphosphate. J. Biol. Chem. 204:403.
- Canvin, D.T. 1965. The effect of temperature on the oil content and fatty acid composition of the oil from several oil seed crops. Canadian J. Bot. 43:63-69.
- Carpenter, D.L., J. Lehmann, B.S. Mason and H.T. Slover. 1976. Lipid composition of select vegetable oils. J. Amer. Oil Chem. Soc.. 53: 714-716.
- Carpenter, J.R. and A.P. 1979. Determination of tocopherol in vegetable oil. J. Amer. Oil Chem. Soc. 56:361-363.
- Cecil, S.R. 1957. Progress report on various methods of storing filberts. Proc. Ore. Hort. Soc. 49: 156-158.

- Chan, H.W.S. 1987. Autoxidation of unsaturated lipids. Academic Press, London. pp.156.
- Chapman, D.J. and J. Barber. 1980. Influence of growth temperature on acyl lipids of leaves, In: Biogenesis and Function of Plant Lipids, Mazliak, P., P. Benveniste, C. Costes, and R. Douce, Eds., Elsevier, Amsterdam. pp.103.
- Chapman, R.A., and K. Mackey. 1949. The estimation of peroxides in fats and oils by the ferric thiocyanate method. J. Amer. Oil Chem. Soc. 26: 360-364.
- Cheel, E. and F.R. Morrison. 1935. The cultivation and exploitation of the Australian nut (Macadamia ternifolia). Technol. Museum, Sydney Australia, Bull. 20.
- Cheesbrough, T.M. 1989. Changes in the enzymes for fatty acid synthesis and desaturation during acclimation of developing soybean seeds to altered growth temperature. Plant Physiology. 90:760-764.
- Chen, L.H., G.A. Boissonneault, and H.P. Glauert. 1988. Vitamin C, vitamin E and cancer. Anticancer Res. 8:739-748.
- Chiba, T., K. Fujimoto, T. Kaneda, S. Kubota, and Y. Idegami. 1981. Radicals generated in autoxidised methyl linoleate by light irradiation. J. of Amer. Oil Chem. Soc. 58:587-590.
- Chimi, H.T., J. Cillard, P. Cillard, and M. Rahamni. 1991. Peroxyl and hydroxyl radical scavenging activity of some natural phenolic antioxidants. J. Amer. Oil Chem. Soc. 68:307-312.
- Chiou, R.Y.Y., Y.S. Chang, T.T. Tsai, and S. Ho. 1991. Variation of flavor related characteristics of peanuts during roasting as effected by initial moisture contents. J. Agric. Food Chem. 39:1155-1158.
- Chipault, J.R., G.R. Mizuno, J.M. Hawkins, and W.O. Lundberg. 1956. The antioxidant properties of spices in food. J. Food Sci. 10:209.
- Chow, C.K., and H.H. Draper. 1974. Oxidative stability and anti-oxidant activity of the tocopherol in corn and soybean oils. Int. J. Vit. Nutr. Res. 44: 369-371.
- Chow, C.K. 1985. Vitamin E in blood. Wld. Rev. Nutr. Diet. 45: 133-166.

- Christenson, C.M. 1957. Deterioration of stored grain by fungi. *Bot. Rev.* 23:108-134.
- Clegg, K.M. and A.D. Morton. 1968. The phenolic compounds of black currant juice and their protective effect on ascorbic acid. *J. Food Technol.* 3: 277-279.
- Cohen, L.A., M. Polansky, K. Furuya, M. Reddy, B. Berke, and J.H. Weisburger. 1984 Inhibition of chemically induced mammary carcinogenesis in rats by short-term exposure to butylated hydroxytoluene (BHT): Interrelationships among BHT concentration, carcinogen dose, and diet. *J. Nat. Cancer Inst.* 72:165.
- Combs, S.B. and G.F. Combs, Jr. 1985. Varietal difference in the vitamin E content of corn. *J. Agric. Food Chem.* 33: 815-817.
- Coppens, P. 1985. The antioxidant advantage. *Food.* 7:49.
- Cort, W.M. 1974. Antioxidant activity of tocopherol, ascorbyl palmitate and ascorbic acid and their mode of action. *J. Amer. Oil Chem. Soc.* 51: 321-325.
- Cort, W.M., W. Mergens, and A. Greene. 1978. Stability of alpha- and gamma- tocopherol: Fe<sup>+3</sup> and Cu<sup>+2</sup> interactions. *J. Fd. Sci.* 43:797-798.
- Cort, W.M., T.S. Vicente, E.H. Waysek, and B.D. Williams. 1983. Vitamin E content of feed stuffs determined by high performance liquid chromatographic florescence. *J. Agric. Food Chem.* 31:1330-1333.
- Crabtree, G.D., C.J. Weiser, S.D. Miles, J.L. Green, N.S. Mansour, A.R. Mosley, R.L. Stebbins, and B.C. Strik. 1987. 1988 profile of Oregon's high-value specialty crops. Oregon State University Extension Service.
- Crane, H.L. and M.B. Hardy. 1934. Interrelations between cultural treatment of pecan trees, the size and degree of filling of the nuts, and the composition of kernels. *J. Agric. Res.* 49:643-661.
- Crawford, D.L., R.O. Sinnhuber, and H. Aft. 1961. The effect of methylation upon the antioxidant and chelation capacity of quercetin and dihydroquercetin in a lard substrate. *J. Food Sci.* 26: 139-141.
- Crawford, M. A. 1987. The requirements of long chain n-6 and n-3 fatty acids for the brain. In Lands (1987), p 257-265.

- Cuculluy, A.F., L.S. Lee, R.Y. Mayne, and L.A. Goldblatt. 1966. Determination of aflatoxin in individual peanut section. *J. Amer. Oil Chem. Soc.* 43: 89-92.
- Curtis, P.E., E.R. Long, and R.H. Hageman. 1968. Developmental changes in oil and fatty acid content of maize strains varying in oil content. *Crop Science*. 8:689-693.
- Dacre, J.C. 1960. Metabolic pathways of the phenolic antioxidants. *J. New Zealand Inst. Chem.* 24:161.
- Dada, O.A., D.R. Threlfall, and G.R. Whistance. 1968. Biosynthesis of phytoquinones. Stereospecific biosynthesis of the polyprenyl side chains of terpenoid quinones and chromanols in maize shoots. *European J. Biochem.* 4:329.
- Dahmer, M., P. Fleming, G. Collings, and D. Hildebrand. 1989. A rapid screening method for the determination of the lipid composition of soybean seeds. *J. Amer. Oil Chem. Soc.* 66:543-548.
- Dale, L.K, E.G. Hill, and R.T. Holman. 1962. The thiobarbituric acid reaction and the autoxidation of polyunsaturated fatty acid methyl ester. *Arch. Biochem. Biophys.* 98:253.
- Davies, C.S., S.S. Nielson, and N.C. Nielson. 1987. Flavor improvement of soybean preparations by genetic removal of lipoxygenase 2. *J. Amer. Oil Chem. Soc.* 61:1428-1433.
- Davis, B.D. 1950. Aromatic biosynthesis. I. The role of shikimic acid. *Experientia* 6:141.
- De Leenheer, A.P., V.O. Bevere, A.A. Crayl, and A.E. Claeys. 1978. Determination of serum alpha-tocopherol (vitamin E) by high-performance liquid chromatography. *Clinic Chem.* 24: 585-590.
- De Luca, H. 1988a. Vitamin D metabolism. In Young and Shils (1988) *Fat-soluble vitamins assays in food analysis*. p. 313-341.
- De Luca, H. 1988b. The vitamin D story: A collaborative effort of basic science and clinical medicine. *FASEB J.*2: 224-226.
- De Lumen, B.O., and S. Fiad. 1982. Tocopherol of winged bean (*Psophocarpus tetragonalobus*) oil. *J. Agric. Food Chem.* 30:50-53.

- Desai, I.D. and L.J. Machlin. 1985. Vitamin E in methods of vitamin assay, 4th ed; Augustin, J., Klein, B.P., Becker, D., Venugopal, P.B., Eds. Wiley, New York. pp. 255-283.
- Dick-Buthnell, M.W. 1967. Column chromatography in the determination of tocopherol. J. Chromatog. 27: 96-101.
- Dilley, R.A., L.P. Kegel, and F.L. Carne. Biochemistry of Quinones . 1962. Plant Physiol. 37. suppl.11.
- Doehlert, D.C. and R.J. Lambert. 1991. Metabolic characteristics associated with starch, protein, and oil deposition in developing maize kernels. Crop Sci. 31:151-157.
- Dubois, C.W. and D.K. Tressler. 1943. Seasonings; their effect on maintenance of quality in storage of frozen ground pork and beef. Proc. Inst. Food Tech. 202:191-193.
- Draper, H.H. 1970. The tocopherols. In: Fat-soluble Vitamins. ed. R.A. Morton. Pergamon Press, New York. pp.333-393.
- Duke, J.A. 1985. Medicinal plants (letter), Science 229: 1036.
- Duke, J.A. and A.A. Atchley. 1986. Handbook of proximate analysis tables of higher plants. CRC press, Inc. Boca Raton, Florida. p.389.
- Duke, J.A. 1989. Handbook of nuts. CRC press, Inc. Boca Raton, Florida. pp.7.
- Duve, K.J. and P.J. White. 1991. Extraction and identification of antioxidants in oats. J. Amer. Oil Chem. Soc. 68:365-370.
- Dyszal, S.M. and C.P. Bruce. 1990. Determination of the country of origin of pistachio nuts by DSC and HPLC. J. Amer. Oil Chem. Soc. 67:947-951.
- El-Behadli, A.H. 1975. Mold contamination and infection of prunes and their control Ph.D dissertation. University of California, Davis. pp.80.
- Emanuel, N.M. and Y.N. Lyaskouskaya. 1967. The inhibition of fat oxidation processes. Pergamon Press, N.Y. pp. 212-256.

- Emmerie, A. and C. Engel. 1938. Colorimetric determination of dl- $\alpha$ -tocopherol. II. Absorption experiments. *Nature*. 142:873.
- Emken, E.A. 1980. Nutritive value of soybean oil. Ch. 20. In "Handbook of soy oil processing and utilization". D.R. Erickson, E.H. Pryde, O.L. Brekke, T.L. Mounts, and R.A. Falb (Ed.), P. 439. Am. Soybean Association and J. Amer. Oil Chem. Soc. St. Louis, Mo.
- Erdei, L., C.E.E. Stuiver, and P.J.C. Kuiper. 1980. The effect of salinity on lipid composition and on activity of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  stimulated ATPase in salt-sensitive and salt-tolerant Plantago species. *Physiol. Plant Pathol.* 49:315.
- Erridge, I., W. Reeve, and R. Fritz. 1989. A look at the tree nut market. Nut growers society of Oreg., Wash., and Brit. Col. 74th Annual meeting. 69-84.
- Escher, F.E., P.E. Koehler, and J.C. Ayres. 1973. Effect of roasting on aflatoxin content of artificially contaminated pecans. *J. Food Science*. 38:1127-1129.
- Escher, F.E., P.E. Koehler, and J.C. Ayres. 1974. A study on aflatoxin and mold contaminations in improved variety pecans. *J. Food Sci.* 39: 1127-1129.
- Eustace, H.J. 1989. There is only one way. Nut grower society of Oreg., Wash., and Brit. Col. 74th Annual meeting. 113- 120.
- Evans, H.M. and K.S. Bishop. 1922. On the existence of a hitherto unrecognized dietary factor essential for reproduction. *Science* 56:650.
- Evans, H.M., O.H. Emerson, and G.A. Emerson. 1936. The isolation from wheat-germ oil of an alcohol,  $\alpha$ -tocopherol, having the properties of vitamin E. *J. Biol. Chem.* 113:319.
- Fang, S.C. and J.S. Butts. 1949. Investigation of Barcelona and Duchilly filbert nuts I. Chemical study of Barcelona and Duchilly filbert nuts and oils. *J. Amer. Oil Chem. Soc.* 26:512-515.
- Fang, S.C. and J.S. Butts. 1950. Investigation of Barcelona and Duchilly filbert nuts II. Isolation, nutritional evaluation, and amino acid distribution of filbert globulins. *J. Nutrition* 40:329-333.

- Fang, S.C., D.E. Bullis, and J.S. Butts. 1953. Investigation of Barcelona and Duchilly filbert nuts III. Amino acid and B-vitamin contents of oil-free nut meals. Food Research. 18:555-559.
- FAO. 1972. Food composition table for use in East Asia. Food and Agric. Organ. of United Nations, Rome.
- Farmer, F.H., G.R. Bloomfield, A. Sundralingam, and D.A. Sutton. 1942. The course and mediums of autoxidation reaction in olefinic and polyolefinic substances, including rubber. Trans. Faraday Soc. 38: 348.
- Fedeli, E. 1977. Lipids of olives. Prog. Chem. Fats Other Lipids. 15:57-74.
- Feilding, J.L. and A. Goldsworthy. 1980. Tocopherol levels and aging in wheat grains. J. Food Sci. 46:453-456.
- Fernandez-Martinez, J. 1974. Variability in the fatty acids composition of the seed oil of Helianthus spp. MS thesis. University of California.
- Ferrando, R., G. Morice, and C. Furlon. 1971. Polyunsaturated fatty acid and vitamin E. Clin. Rec. Med. Vet. 147:955.
- Finch, A.H. and C.W. Van Horn. 1936. The physiology and control of pecan nut falling and maturity. Arizona Agric. Exp. Stat. Tech. Bull. 62.
- Finlayson, S.A. and D.T. Dennis. 1980. NAD<sup>+</sup>-specific glycerol 3-phosphate dehydrogenase from developing castor bean endosperm. Arch. Biochem. Biophys. 199:179.
- Finley, J.W. and P. Given. 1986. Technological necessity of antioxidants in the food industry. Food Chem. Toxic. 24:999-1002.
- Fleischman, A.I., A. Florin, J. Fitzgerald, A.B. Caldwell, and G. Eastwood. 1963. Tocopherols and fatty acids in American diets. J. Amer. Diet. Assoc. 42:394.
- Folch, J., M. Lees, and G.H. Sloane-Stanley. 1957. A simple method for the isolation and purification of total lipids from animal tissues. J. Biol. Chem. 226: 497-509.
- Forbes, W.R. Jr., S.D. Senter, B.G. Lyon, and H.P. Dupey. 1980. Correlation of objective and subjective measurements of pecan kernel quality. 45: 1378-1379.

- Forbes, W.R. Jr., S.D. Senter, and R.L. Wilson. 1983. Cultivar, processing, and storage effects on pecan kernel color. *J. Food Sci.* 48: 1646-1649.
- Fore, S.P., N.J. Morris, C.H. Mack, A.F. Freeman, and W.G. Bickford. 1953. Factors affecting the stability of crude oils of 16 varieties of peanuts. *J. Amer. Oil Chem. Soc.* 30: 298-301.
- Forss, D.A. 1972. Lipid oxidation. In: *Progress in the chemistry of fats and other lipids*, Vol. 3. (Holman, R.T., Ed. Pergamon Press, Oxford. p. 207.
- Fourie, P. C. and D. S. Basson. 1989. Change in the tocopherol content of almond, pecan and macadamia kernels during storage. *J. Am. Chem. Soc.* 66: 1113-1114.
- Frankel, E.N., C.D. Evans, and J.C. Cowan. 1957. Determination of tocopherol in oxidized fats. *J. Amer. Oil Chem. Soc.* 34: 544-546.
- Frankel, E.N., C.D. Evans, and P.M. Cooney. 1959. Tocopherol oxidation in natural fats. *J. Agric. Food Chem.* 7: 438-441.
- Frankel, E.N. 1980. Lipid oxidation Prog. *Lipid Research.* 19:1-22.
- Frankel, E.N. 1982. Volatile lipid oxidation products. *Prog. Lipid Res.* 22:1-33.
- Frankel, E.N. 1984. Lipid oxidation: Mechanisms products, and biological significance. *J. Amer. Oil Chem. Soc.* 61:1908-1917.
- Frankel, E.N. 1985. Chemistry of free radical and singlet oxidation of lipids. *Prog. Lipid Res.* 23:197-221.
- Franzen, J., J. Bausch, D. Glatzle, and E. Wagner. 1991. Distribution of vitamin E in spruce seedling and mature tree organs, and with the genus. *Phytochemistry.* 30:147-151.
- Franzen, J. and M.M. Haab. 1991. Vitamin E content during development of some seedlings. *Phytochemistry.* 30:2911-2913.
- Fraser, G.E., Sabate, J., Beeson, W.L., and Strahan, T.M. 1992. A possible protective effect of nut consumption on risk of coronary heart disease. *Arch. Intern. Med.* 152:1416-1424.

- Frazer, A.C., and J.G. Lines. 1967. Studies on changes in flour tocopherol following ageing and treatment of the flour with chlorine dioxide. *J. Sci. Food Agric.* 18: 203-207.
- Fukuba, H. and T. Murota. 1985. Determination of tocopherols in foodstuffs, especially nuts and spices, by HPLC. *J. Micronutr. Anal.* 1:93-105.
- Fukuda, Y. and M. Namiki. 1988. Recent studies on sesame seed and oil. *Nippon Shokutin Kogyo Gakkaishi.* 35:552-555.
- Fukuzawa, K. A. Tokumura, S. Ouchi, and H. Tsukatani. 1982. Antioxidant activities of tocopherols on Fe<sup>+2</sup>-ascorbate-induced lipid peroxidation in lecithin liposomes. *Lipids* 17:511-513.
- Fukuzawa, K., Y. Kurotori, A. Tokumura, and G. Tsukatani. Vitamin E deficiency increases the synthesis of platelet-activating factor (PAF) in rat polymorphonuclear leukocytes. *Lipids* 24:236-239.
- Fuller, B., W.W. Spooncer, A.D. King, J. Schade Jr., and B. Mackey. 1977. Survey of aflatoxins in California tree nuts. *J. Amer. Oil Chem. Soc.* 54: 231-234.
- Garces, R., C. Sarmiento, and M. Mancha. 1992. Temperature regulation of oleate desaturase in sunflower (Helianthus annuus L.) seeds. *Planta.* 11:461-465.
- Garcia-Olmedo and M.A. Marcos-Garcia. 1971. Contribucion al Estudio de los Aceites de Frutos Secos Espanoles. Composicion Acidica. *Anal. Bromatol.* 23:253-258.
- Gardner, H.W. 1968. Preparation isolation of monogalactosyl and digalactosyl diglycerides by thin-layer chromatography. *Lipids* 9:139-141.
- Garrone, W., M. Antonucci, U. Bona, and S. Clement. 1988. Determination of hazelnut content by means of their protein fraction in chocolate bars, chocolates, and milk containing spreads. *Lebensm. Wiss. U. Technol.* 2:76-82.
- Gaydou, E.M., Y. Lozano, and J. Ratovohery. 1987. Triglyceride and fatty acid compositions in the mesocarp of Persea americana during fruity development. *Phytochemistry.* 26:1595-1597.
- Ghaly, T.F. and J. W. Sutherland. 1984. Heat damage to grain and seeds. *J. Agri. Engr. Res.* 30:337-345.

- Glover, J. 1965. In: Biochemistry of quinones, Ed. R.A. Morton. Academic Press inc. London. pp.207.
- Glover, J. 1970. Biosynthesis of the fat-soluble vitamins. In: Fat-soluble vitamins. Ed. R.A. Morton. pp199-209.
- Gould, M.N., J.D. Haag, W.S. Kennan, M.A. Tanner, and C.E. Elson. 1991. A comparison of tocopherol and tocotrienol for the chemoprevention of chemically induced rat mammary tumors. Am. J. Clin. Nutr. 53:10,685-10,705.
- Gray, J.I. 1978. Measurement of lipid oxidation. J. Amer. Oil Chem. Soc.. 55: 539-543.
- Gregory, D. 1984. Antioxidants. The radical answer. Food. 6:18.
- Green, J. 1958. The distribution of tocopherol during the life cycle of some plants. J. Sci. Food Agric. 9: 801-812.
- Greve, L.C. and J.M. Labavitch. 1985. Development of rancidity in walnuts. Walnut Res Reports. UC Davis. pp.235-243.
- Greve, L.C., R. Darnell, and J.M. Labavitch. 1986. Development of rancidity in walnuts. Walnut Res. Reports, UC Davis. pp.102-106.
- Greve, L.C., G. McGranahan, J. Hasey, R. Snyder, K. Kelly, D. Goldhamer, and J.M. Labavitch. 1992. Variation in polyunsaturated fatty acids composition of Persian walnut. J. Amer. Soc. Hort. Sci. 117(3):518-522.
- Griewahn, J., and B.F. Daubert. 1948. Delta-tocopherol as an antioxidant in lard. J. Amer. Oil Chem. Soc. 25: 26-30.
- Groeschke, F. 1887. Die Hazelnues, Ihre Arten und Ihre Kulture. 1099, Berlin, Germany.
- Gunstone, F.D. 1984. Reaction of oxygen and unsaturated fatty acids. J. Amer. Oil Chem. Soc. 61:441-447.
- Gunstone, F.D. and F.A. Norris. 1983. Lipids in Foods. Oxford: Pergamon Press.
- Gurr, M.I. 1980. The biosynthesis of triacylglycerols, In: The Biochemistry of Plants, Vol. 4, Stumpf, P.K. and E.E. Conn, Eds., Academic Press, New York. pp.205.
- Gutfinger, T. and A. Letan. 1975. Tocopherols in several vegetable oils. Ri. Ital. Sostanze Gras. 52:191.

- Guzman, G.J., and P.A. Murphy. 1986. Tocopherol of soybean seeds and soybean curd (tofu). *J. Agric. Food Chem.* 34: 791-795.
- Hadansson, B., M. Jagerstad, and R. Oste. 1987. Determination of vitamin E in wheat products by HPLC. *J. Micronutr. Anal.* 3:301-318.
- Haigh, R. 1986. Safety and necessity of antioxidants. EEC approach. *Food Chem. Tox.* 24: 1031-1033.
- Hakansson, B., M. Jagerstad, and R. Oste. 1987. Determination vitamin E in Wheat products by HPLC. *J. Micronutr. Anal.* 3: 301-318.
- Hammond, E.G. and W.R. Fehr. 1984. Improving the fatty acid composition of soybean oil. *J. Amer. Oil Chem. Soc.* 61:1713-1716.
- Han, T.J. and J. Liston. 1987. Lipid fractionation and phospholipid hydrolysis in fish muscle microsomes and frozen fish. *J. Food Sci.* 52:294-296.
- Hansberry, R., L. Holden, R. Malone, and W. Wilson. 1988. Oregon industry view of European operations. Nut growers society of Oreg, Wash, and Brit. Col. 49-57.
- Hara, S. and Y. Totani. 1968. A highly sensitive method for the micro-determination of lipid hydroperoxides by potentiometry. *J. Amer. Oil Chem. Soc.* 65:1948-1950.
- Harris, P.L. and N.D. Embrae. 1963. Quantitative consideration of the effect of polyunsaturated fatty acid content of the diet upon the requirements of vitamin E. *Am. J. Clin. Nutr.* 13:385.
- Harris R.V., A.T. James, and P. Harris. 1967. Effect of temperature on fatty acid synthesis in sunflower seeds. *Biochem. Chloroplasts Proc.* 2:241-253.
- Hartung, M.E. and W.B. Storey. 1939. The development of the fruit of Macadamia ternifolia. *J. Agr. Res.* 59:397-406.
- Harwood, J.L. 1980. Fatty acid synthesis. In: Biogenesis and function of plant lipids. Ed. P. Mazliak, P. Benveniste, C. Costes, R. Douce. Elsevier, Amsterdam. pp.143-152.
- Harwood, J.L. and P.K. Stumpf. 1971. Control of fatty acid synthesis in germinating seeds. *Arch. Biochem. Biophys.* 142:281.

- Harwood, J.L. 1983. Adaptive changes in the lipids of higher plant membranes. *Biochem. Soc. Trans.* 11:343-346.
- Harwood, J.L. 1984. Effects of the environment on the acyl lipids of algae and higher plants, In: *Structure, Function, and Metabolism of Plant Lipids*, Siegenthaler, P.A. and W. Eichenberger, Eds., Elsevier, Amsterdam. pp.543.
- Harwood, J.L. 1987. Medium and long chain fatty acid synthesis, in *The Metabolism, Structure and Function of Plant Lipids*, Stumpf, P.K., J.B. Mudd, and W.D. Nes. Eds., Plenum Press, New York. pp.465.
- Harwood, K.P. and H.J. Teede. 1988. Fatty acid metabolism. *Ann. Rev. Plant Physiol.* 39:101-103.
- Hatam, L.G. and H.J. Kayden. 1979. A high performance liquid chromatographic method for the determination of tocopherol in plasma and cellular elements of the blood. *J. Lipid Res.* 20:639-645.
- Hathway, D.E. 1967. Metabolic fate in animals of hindered phenolic antioxidants in relation to their safety evaluation and antioxidant function. *Advan. Food Res.* 15:1.
- Heath, R. L. 1984. Air pollutant effects on biochemicals derived from metabolism: Organic, fatty and amino acids, in *Gaseous Air Pollutants and plant metabolism*, Koziol, M. J. and Whatley, F. R. Ed., Butterworths, London, P:275-284.
- Heaton, E.K. and J.G. Woodroof. 1970. Humidity and weight loss in cold stored pecan. *ASHRAEJ.* 12:49-51.
- Heaton, E.K., R.E. Worthington, and A.L. Shewfelt. 1975. Pecan nut quality effect of time of harvest on composition, sensory and quality characteristics. *J. Food Sci.* 40:1260-1263.
- Heaton, E.K., A.L. Shewfelt, A.E. Badenhop, and L.R. Beuchat. 1977. Pecan: Handling storage, processing and utilization, Univ. Georgia. Athens, Georgia, USA. *Agric. Res. Bull.* 197:pp. 77.
- Heaton, E.K., and L.R. Beuchat. 1980. Quality characteristics of high-moisture pecans stored at refrigeration temperature. *J. Food Sci.* 45: 255-261.

- Heinman, W. 1980. Fats and associated substances (lipids). In: Fundamentals of Food Chem. USA: Ellis Horwood. pp.109-114.
- Hellyer, A., H.E. Bambridge, and A.R. Slabas. 1986. Plant acetyl-CoA carboxylase. Biochem. Soc. Trans. 14:565.
- Herrmann, K. 1976. Flavonols and flavones in food plants: A review J. Food Technol. 11: 433-435.
- Hills, G.L. and C.C. Thiel. 1946. The ferric thiocyanate method of estimating peroxide in the fat of butter, milk and dried milk. J. Dairy Res. 14: 340-344.
- Hirose, M., M. Shibata, A. Hagiwara, K. Imaida, and N. Ito. 1981. Chronic toxicity of butylated hydroxytoluene in wistar rats. Food Cosmet. Toxicol. 19:147.
- Hitchcock, C. and B.W. Nichols. 1971. Plant Lipid Biochemistry, Academic Press, London.
- Hjarde, W., E. Leerbeck, and T. Leth. 1973. The chemistry of vitamin E including its chemical determination. Acta Agri. Scand. Suppl. 19: 87-92.
- Horwitt, M.K. 1961. Vitamin E in human nutrition. Bordens Rev. of Nutr. Res. Handl. 22:1-5.
- Hove, E.L., and P.L. Harris. 1951. Note on linoleic acid. Tocopherol relationship in fat and oil. J. Amer. Oil Chem. Soc. 38:405-407.
- Howes, F.N. 1948. Nuts, their production and everyday uses. 1-264. Faber and Faber, London.
- Hudson, B.J.F. and S.E.O. Mahgoub. 1980. Naturally occurring antioxidants in leaf lipids. J. Sci. Food Agric. 31:646.
- Hudson, B.J.F. and S.E.O. Mahgoub. 1981. Synergism between phospholipids and naturally occurring antioxidants in leaf lipids. J. Sci. Food Agric. 32:208.
- Hudson, B.J.F. and J.I. Lewis. 1983. Polyhydroxy flavonoid antioxidants for edible oils. Structural criteria for activity. Food Chem. 10: 47-50.
- Husain, S.R., J. Cillard, and P. Cillard. 1987. Hydroxy radical scavenging activity of flavonoids. Phyto-Chemistry. 26:2489.

- Ikeda, N., and K. Fukuzumi. 1977. Quantitative analysis of tocopherol in autoxidized methyl linoleate. *J. Japan Oil Chem. Soc.* 26: 343-346. In: *Food Sci. Tech. Abstr.* (1978). 10: 2A133.
- Imaida, K., S. Fukushima, T. Shivai, M. Ohtani, K. Nakanishi, and N. Ito. 1983. Promoting activities of butylated hydroxyanisole and butylated hydroxytoluene on 2-stages urinary bladder carcinogenesis and inhibition of Y-glutamyl transpeptidase-Positive foci development in the liver of rats. *Carcinogenesis.* 4:895.
- IUPAC-IUB. 1973. Commission on biochemical nomenclature (CBN) nomenclature of tocopherols and related compounds. *Eur. J. Biochem.* 46:217-219.
- Jan, M., D.I. Langerak, T.G. Wolters, J. Farkas, H.J.V.D. Kamp, and B.G. Muuse. 1988. The effect of packaging and storage conditions of the keeping quality of walnuts treated with disinfestation doses of gamma rays. *Acta Alimentaria.* 17:13-31.
- Janiszowska, W. and G. Korczak. 1980. Observation on the biosynthesis of phytoterpenoid Quinone and chromanol nuclei. *Phytochemistry.* 19:139-1392.
- Janiszowska, W. 1987. Intracellular localization of tocopherol and biosynthesis in Calendula officinalis. *Phytochemistry.* 26: 1403-1407.
- Jennings, W.G. and M.R. Sevenants. 1969. Volatile esters of Bartlett pears. *J. Food Sci.* 29:158-163.
- Johnson, F.C. 1971. A critical review of the safety of phenolic antioxidants in food. *CRC. Crit. Rev. Food Tech.* Oct: 267.
- Johnson, F.C. and J.A. Pye. 1979. The antioxidant vitamins. Critical reviews in food science and nutrition. 11:217-309.
- Jones, W.W. 1937. The physiology of oil production in the macadamia. *Proc. Amer. Soc. Hort. Sci.* 35:239-245.
- Jones, W.W. 1939. A study of developmental changes in composition of the macadamia. *Plant Physiol.* 14:755-768.
- Jones, W.W. 1943. The process of oil formation and accumulation in the macadamia. *Plant Physiol.* 18:1-6.

- Jung, M.Y. and D.B. Min. 1990. Effect of  $\alpha$ -,  $\Gamma$ -,  $\delta$ -tocopherol on oxidative stability of soybean oil. *J. Food Sci.* 55:1464-1464.
- Kadman, A. and E. Slor. 1983. "Yonik" macadamia. *Hort. Sci.* 17:991.
- Kanner, J., I. Shegalovich, S. Harel, and B. Hazan. 1988. Muscle lipid peroxidation dependent on oxygen and free metal ions. *J. Agric. Food Chem.* 36:409-412.
- Karahadian, C. and R.C. Lindsay. 1989. Action of tocopherol type compounds in directing reactions forming flavor compounds in auto-oxidizing fish oils. *J. Amer. Oil Chem. Soc.* 66:1302-1308.
- Kashani, G.G.. 1982. The effect of roasting and of gamma irradiation on various chemical constituents of six varieties of Iranian pistachio nuts. PhD thesis. University of London.
- Kashani, G.G. and L.R.G. Valaden. 1983. Effect of salting and roasting on the lipids of Iranian pistachio kernels. *J. Food Technol.* 18: 461-467.
- Kashani, G.G. and L.R.G. Valaden. 1984. Effect of gamma irradiation on the lipids, carbohydrates, and proteins of Iranian pistachio kernel. *J. Food Tech.* 19:631-638.
- Kawashima, K., H. Itoh, and I. Chibata. 1977. Antioxidant activity of browning products prepared from low molecular carbonyl compounds and amino acids. *J. Agric. Food Chem.* 25:202.
- Kay, S.J. 1979. Pecan kernel color changes during maturation harvest, storage, and distribution. *The pecan quarterly.* 13:4-6.
- Kim, M.A., T. Matoba, and K. Hasegawa. 1988. Thermal oxidation stability of interesterified oils under continuous heating conditions. *Agric. Biol. Chem.* 52:1239-1244.
- King. A. D. Jr., W.U. Halbrook, G. Fuller, and L.C. Whitehand. 1983. Almond nutmeat moisture and water activity and its influence on fungi, flora, and seed composition. *J. Food Science.* 48:615-617.

- King, A.D. Jr., and J.E. Schade. 1986. Influence of almond harvest, processing and storage on fungal population and flora. *J. Food Sci.* 51: 202-205.
- Kinsella, J. E. 1987. Effects of polyunsaturated fatty acids on factors related to cardiovascular disease. *Am. J. Cardiol.* 60: 23G.
- Kinsella, J. E. 1988. Food lipids and fatty acids: Importance in food quality, nutrition, and health. *Food Technol.* 11:124-230.
- Kiritsakis, A.K. and L.R. Dugan. 1984. Effect of selected storage conditions and packaging materials on olive oil quality. *J. Food Sci.* 54:251-253.
- Kiritsakis, A.K. and L.R. Dugan. 1985. Studies in photooxidation of olive oil. *J. Amer. Oil Chem. Soc.* 62:892-896.
- Kivimae, A., and C. Carpena. 1973. The level of vitamin E content in some conventional feeding stuffs and the effects of genetic variety harvesting, processing and storage. *Acta Agric. Scand. Suppl.* 19: 161-168.
- Klauri, H. 1971. The functional (technical) uses of vitamins. In: *The University of Nottingham Seminar on Vitamins.* ed. M. Stein. Churchill Livingstone, Edinburgh and London. pp.110-143.
- Knekt, P., A. Aromaa, J. Maatela, R Aaran, M. Hadama, and L. Tepp. 1991. Vitamin E and cancer prevention. *Am. J. Clin. Nutr.* 53:2835-2865.
- Komada, M., and I. Harada. 1969. A dimeric oxidation product of gamma-tocopherol in soybean oil. *J. Amer. Oil Chem. Soc.* 46: 18-21.
- Kroll, J., and M. Roloff. 1974. On the formation of peroxides, carbonyls and free fatty acids and on the degradation of DL- gamma-tocopherol during autoclaving and storage of fat in water emulsions. *Nahrungs,* 18: 451-455. In: *Food Sci. Tech. Abstr.* (1975) 7: 6N 246.
- Labavitch, J.M., C.M. Heintz, H.L. Rae, and A. Kader. 1982. Physiological and compositional changes associated with maturation in 'Kerman' pistachio nuts. *J. Amer. Soc. Hort. Sci.* 107:688-692.
- Labavitch, J.M., L.C. Greve, and A.A. Kader. 1984. Factors effecting rancidity of walnuts. *Walnut research reports.* pp.184-185.

- Labuza, T.P. 1971. Kinetics of lipid oxidation in foods. *Critical Rev. Food Technol.* October: 355-403.
- Ladiko, D. and V. Lougovois. 1990. Lipid oxidation in muscle foods. *Food Chem.* 35:295-314.
- Lagerstedt, H.B. and G.E. Hubert. 1975. A progress report on propagating filbert trees by means of budding and cutting. *Nut growers society of Oregon, Washington, and British Columbia.* pp.58-69.
- Lagerstedt, H.B. 1977. The occurrence of blanks in the filbert *Corylus avellana* and possible causes. *Botany.* 31:153-159.
- Lagerstedt, H.B. 1982. Three promising filbert propagation techniques. *Nut growers society of Oregon, Washington, and British Columbia.* pp.58-68.
- Lajara, J.R., U. Diaz, and R.A. Quidiello. 1990. Definite influence of location and climatic conditions on the fatty acid composition of sunflower oil. *J. Amer. Oil Chem. Soc.* 67:618-623.
- Lambertsen, G., H. Myklestad, and O.R. Brekkan. 1962. Tocopherol in nuts. *J. Sci. Food Agric.* 13: 617-620.
- Lauer, C. 1986. Hazelnuts in the candy industry. *Nut grower society of Oregon, Washington, and British Columbia.* pp.43-53.
- Law, B.A., C.M. Cousins, M.E. Sharpe, and F.L. Davies. 1979. In: Cold tolerant microbes in spoilage and the environment (Russell, A.D. and Fuller, K. Eds) *Society for Applied Bacteriology, Technical series No. 13, Academic press London, p.144.*
- Lea, C.H. 1952. Methods for determining peroxide in lipids. *J. Sci. Food Agric.* 3: 386-389.
- Lea, C.H., and R.J. Ward. 1959. Relative antioxidant activities of the seven tocopherols. *J. Sci. Food Agric.* 10: 537-540.
- Lea, C.H. 1960. On the antioxidant activities of the tocopherol. II. Influence of substrate, temperature and level of oxidation. *J. Sci. Food Agric.* 11: 212-215.
- Lea, C.H. 1962. Lipid oxidation. In: *Symposium on foods: Lipids and their oxidation.* H.W. Schultz, E.A. Day, and R.O. Sinnhaber, Eds. AVI publishing, Westport, Conn. Chap 1.

- Lee, C.Y., A.P. Pennesi, and M.H. Dickson. 1984. Characterization of the cauliflower peroxidase isoenzyme. *J. Food Chem.* 32:18.
- Lee, L.S., Cucullu, A.F. and L.A. Goldblat. 1968. Appearance and aflatoxin content of raw and dry roasted peanut kernels. *Food Tech.* 22:1131-1133.
- Lehmann, J., and H.T. Slover. 1976. Relative autoxidative and photolytic stabilities of tocols and tocotrienols. *Lipids* 11: 853.
- Leng, E.R. 1967. Changes in weight, germ ratio, and oil content during kernel development in high oil corn. *Crop Sci.* 7:333-334.
- Lercker and Pallotta. 1984. Cashew seed and oil composition. In: *Cashew research and development*. Ed. Bhaskara E.V. and Khan H.H. pp.184-195.
- Letan, A. 1966a. The relation of structure to antioxidant activity of quercetin and some of its derivatives. I. Primary activity. *J. Food Sci.* 31:359.
- Letan, A. 1966b. The relation of structure to antioxidant activity of quercetin and some of its derivatives. II. Secondary (metal complexing) activity. *J. Food Sci.* 31:518-519.
- Leverington, R.E. 1963. Evaluation of methods of roasting macadamia nut. *J. Agric. Sci.* 19:131-132.
- Lillard, H.S., R.T. Hanlin, and D.A. Lillard. 1970. Aflatoxigenic isolate of Aspergillus flavus from pecan. *Appl. Microbiol.* 19:128-131.
- Linghart, H. and C.E. Erikson. 1983. Characterization of antioxidative maillard reaction products from histidine and glucose. *ACS sym. ser.* 215:335.
- Linschneer, W. G., and A. J. Vergroesen. 1988. Lipid digestion and metabolism. Fat soluble vitamins. In: *Young and Shils (1988)*, Ed. G.F.M. Ball p.72.
- Lips, H.J. 1957. Stability of d-alpha-tocopherol alone in solvents and in methyl esters of fatty acids. *J. Amer. Oil Chem. Soc.* 34:513-516.
- Lozano, Y.F., J.V. Ratovohery, and E.M. Gaydou. 1991. Compositional changes in triglycerides of avocado mesocarps associated with fruit development. *Lebensm. Wiss. U. Technol.* 24:46-52.

- Luan, N.T., J. Pokorny, J. Couper, and S. Pokorny. 1977. Fractionation of the oxidation products of alpha-tocopherol and their condensation products with L-lysine by combined thin layer and gel chromatography. *J. Chromatog.* 130: 378-380.
- Lubin, B.V., L.J. Machlin. eds. 1982. *Vitamin E*. Ann. N.Y. Acad. Sci. 393.
- Lynen, F. 1961. How to estimate quality changes in frozen food. *Fed. Proc.* 20:941.
- Maeura, Y., J.H. Weisburger, and G. Williams. 1984. Dose-dependent reduction of N-2-fluorenylacetylamide - induced liver cancer and enhancement of bladder cancer in rats by butylated hydroxytoluene. *Cancer Res.* 44:1604-1606.
- Maia, G.A., W.H. Brown, F.M. Whiting, and J.W. Stull. 1975. Cashew fatty acids. *Hortscience.* 10:233-234.
- Marero, L.M., S. Homma, K. Aida, and M. Fujimaki. 1986. Changes in the tocopherol and unsaturated fatty acid constituents of spices after pasteurization with super heated steam. *J. Nutr. Sci. Vitaminol.* 32: 131-136.
- Marshall, P.S., S.R. Morris, and D.R. Threlfall. 1985. Biosynthesis of tocopherol: A re-examination of the biosynthesis and metabolism of 2-methyl-6-phytyl-1, 4 benzoquinol. *Phytochemistry.* 24:1705-1711.
- Martin, D. 1988. Filberts reach the breakfast table. *Nut growers society of Oregon, Washington, and British Columbia.* pp.28.
- McCarthy, M.A. and F.I. Meredith. 1988. Nutrient data on Chestnuts consumed in the United States. *Econ. Bot.* 42:29-36.
- McDonald, R.E. and H.O. Hultin. 1987. Some characteristics of the enzyme lipid peroxidation system in the microsomal fraction of flounder skeletal muscle. *J. Food Sci.* 52:15-21.
- McKeon, T.M. and P.K. Stumpf. 1982. Purification and characterization of the stearyl-ACP desaturase and acyl-ACP thioesterase from maturing seeds of safflower. *J. Biol. Chem.* 257:12141.
- McLaughlin, P.J. and J.L. Weihrauch. 1979. *Vitamin E contents of foods.* *J. Am Diet. Assoc.* 75: 647-781.

- McLeanahan, F.M. 1959. The development of fat in the black walnut. *J. Amer. Oil Chem. Soc.* 31:1093-1098.
- Mead, J.F. 1972. Dietary polyunsaturated fatty acids as potential toxic factors. *Chemtech.* 2:70-71.
- Mead, J. F., R. Alfin-Slater, D. Howton, and R. Popjack. 1986. "Lipids: Chemistry, Biochemistry and Nutrition." Plenum Press, New York.
- Mehlenbacher, S.A. 1988. The Oregon hazelnut breeding program. *Nut growers society of Oregon, Washington, and British Columbia.* pp.75-76.
- Mehlenbacher, S.A. and A.N. Miller. 1988. Pollenizer management in a hazelnut orchard. *Nut growers society of Oregon, Washington, and British Columbia.* pp.67-82.
- Mehlenbacher, S.A. and D.C. Smith. 1988. Heritability of ease of hazelnut pellicle removal. *HortScience.* 23:1053-1054.
- Mehlenbacher, S.A. 1989. Hazelnut. *U. sun-diamond grower.* Fall: 28-33.
- Mehlenbacher, S.A. 1991. Genetic resources of temperate fruit and nut crops (hazelnuts) 290. *Acta Hort.* Ch.17 pp.809-810.
- Mehlenbacher, S.A., M.M. Thompson, and H.R. Cameron. 1991. Occurrence and inheritance of resistance to Eastern filbert blight in 'Gasaway' hazelnut. *HortScience.* 26:410-411.
- Mehlenbacher, S.A., A.N. Miller, M.M. Thompson, H.B. Lagerstedt, and D.C. Smith. 1991. 'Willamette' hazelnut. *HortScience.* 26:1341-1342.
- Mehlenbacher, S.A. and M.M. Thompson. 1991. Inheritance of a chlorophyll deficiency in hazelnut. *HortScience.* 26:1414-1416.
- Mehlenbacher, S.A. and D.C. Smith. 1992. Effect of spacing and sucker removal on precocity of hazelnut seedling. *J. Amer. Soc. Hort. Sci.* 117:523-526.
- Mehran, M. and M. Filsoof. 1974. Characteristics of Iranian almond nuts and oils. *J. Amer. Oil Chem. Soc.* 51:433-434.

- Meissonnier, E. 1983. The supply of vitamins to dairy cattle. F. Hoffmann-La Roche and Co. Ltd, Basle, Switzerland.
- Metcalf, L.D. and A.A. Schmitz. 1961. The rapid preparation of fatty acid esters for gas chromatography. *Anal. Chem.* 33:363-364.
- Miller, A. 1991. Pollenizer selection and spacing. Nut grower society of Oregon, Washington, and British Columbia. pp.74-79.
- Min, D., and T. Smouse. 1988. "Lipids and Food Flavors." *J. Amer. Oil Chem. soc.* 57: 342-342.
- Miruish, S.S. 1986. Effect of vitamins C and E on N-nitroso compound formation, carcinogenesis, and cancer. *Cancer.* 58:1842-1850.
- Mitsumoto, M.C., R.G. Faustman, R.N. Cassen, and K.K. Scheller. 1991. Vitamin E and C improve pigment and lipid stability in ground beef. *J. Food Sci.* 56:194-197.
- Min, D.B. and J. Wen. 1983. Qualitative and quantitative effects of antioxidant on the flavor stability of oil. *J. Food Sci.* 48:1172.
- Mohan, S.R. and R.G.O. Kekwick. 1980. Acetyl-CoA carboxylase from avocado plastids and spinach chloroplasts. *Biochem. J.* 187:667.
- Moore, T., I.M. Sharman and R.J. Ward. 1957. The destruction of vit. E in flour by chlorine dioxide. *J. Sci. Food Agric.* 8:97-101.
- Morino, K. N. Matsukura, T. Kawachi, S. Ohgaki, and I. Hirono. 1982. Carcinogenicity test of quercetin and rutin in golden hamsters by oral administration. *Carcinogenesis.* 3:93.
- Morton, I.D. 1977. In: Physical, chemical and biological changes in food caused by thermal processing (Hyem, T. and Kvale, O. Eds) Applied Science Publications, London.
- Munshi, S.K., P.S. Sukhija, and I.S. Bhatia. 1983. Lipid biosynthesis in developing kernels of almond, Prunus amygdalus. *Phytochemistry.* 22: 79-83.

- Munshi, S.K. and P.S. Sukhija. 1984. Compositional and biosynthesis of lipids in the developing kernels of almonds (Prunus amygdalus). J. Sci. Food Agric. 35:689-697.
- Murphy, D.J. and P.K. Stumpf. 1981. The origin of chloroplastic acetyl-CoA. Arch. Biochem. Biophys. 212:730.
- Nagao, M., N. Morita, T. Yahagi, M. Shimizu, M. Kuroyanagi, M. Fukuaka, K. Yoshihira, S. Natori, T. Fujino, and T. Sugimura. 1981. Mutagenicities of 61 flavonoids and 11 related compounds. Environ. Mutag. 3:401.
- Namiki, M., A. Shigeta, and T. Hayashi. 1982. Antioxidant effect of the reaction mixture of dehydroascorbic acid with tryptophan. Agric. Biol. Chem. 46:1199.
- Namiki, M. and T. Kobayashi. 1989. goma no kagaku (science of sesame) Asakura Shoten, Tokyo.
- Namiki, M. 1990. Antioxidants/antimutagens in food. Critical Review Food Sci. Nutr. 29:273-300.
- NAS-NRC. 1974. Recommended dietary allowances, 8th ed., National Academy of Sciences, National Research Council, Washington, D.C.
- NAS-NRC. 1980. Recommended Dietary Allowances, 9th ed; National Academy of Sciences, National Research Council, Washington DC.
- NAS-NRC. 1982. "Diet Nutrition and cancer" Natl. Acad. of Science, Natl. Res. Council. National Academy Press, Washington, D.C.
- NAS-NRC. 1988. "Designing Foods: Animal product Portions in the Market Place". Board on Agriculture, National Academy Press, Washington, D.C.
- NAS-NRC. 1989. Recommended dietary allowances. 10th ed. National Academy of Sciences, National Research Council, Washington DC.
- Nassar, A.R., B.S. El-Tahawi, and A.S. El-Deen. 1977. Chromatographic identification of oil and amino acid constituents in kernels of some almond varieties. J. Amer. Oil Chem. Soc. 54:553-556.
- Newton, R.P., and J.F. Pennock. 1971. The intracellular distribution of tocopherol in plants. Phytochemistry. 10: 2323-2328.

- Nilsson, J.L.G., G.D. Daves, Jr., and K. Folders. 1968. New tocopherol dimers. *Acta Chem. Scand.* 22:200-206.
- Nishibori, S. and K. Namiki. 1988. Antioxidative substances in the green fractions of lipids of aonori. *Nippon kaseigaku kaishi.* 39:1137-1175.
- Nishina, A., K. Kubota, H. Kameoka, and T. Osawa. 1991. Antioxidizing component, Musizin, in *Rumex Japonicus* Houtt. *J. Amer. Oil Chem. Soc.* 68:735-739.
- Notermans, S., J. Dufrenne, and P.S. Soentoro. 1988. Detection of molds in nuts and spices: The mold colony count versus the enzyme linked immunosorbent assay (ELISA). *J. Food Sci.* 53:1831-1834.
- Ohlrogge, J.B. 1987. Biochemistry of plant acyl carrier proteins, In: *The Biochemistry of Plants, Vol 9*, Stumpf, P.K. and E.E.Conn. Academic Press, New York. pp.137.
- Okuda, T., Y. Kimura, T. Yoshida, and S. Arichi. 1983. Studies on the activities of tannins and related compounds from medicinal plants and drug. I. Inhibitory effect on lipid peroxidation in mitochondria and microsomes of liver. *Chem. Pharm. Bull.* 31:1625-1632.
- Olcott, H.S. 1938. A weighing method for measuring the induction period of marine and other oils. *Nutr.* 15:221.
- Omaye, S.T. 1984. Safety of megavitamin therapy. In: *Nutritional and Toxicological Aspects of Food Safety.* ed. M Friedman. Plenum Press, New York. pp.169-203.
- Ong, D. E. 1985. Vitamin A-binding proteins. *Nutr. Rev.* 43: 231-234.
- Osawa, T. and M. Namiki. 1981. A novel type of antioxidant isolated from leaf wax of *Eucalyptus* leaves. *Agric. Biol. Chem.* 45:735.
- Osawa, T. and M. Namiki. 1985. Natural antioxidants isolated from *Eucalyptus* leaf waxes. *J. Agric. Food Chem.* 33:777.
- Ohata, H., S. Aibara, H. Yamashita, F. Seklyama, and Y. Morita. 1990. Post-harvest drying of fresh rice grain and its effects on deterioration of lipids during storage. *Agri. Biol. Chem.* 54:1157-1164.

- Pamukou, A.M., S. Yalciner, J.F. Hatcher, and G.T. Bryan. 1980. Quercetin, a rat intestinal and bladder carcinogen present in bracken. *Cancer Res.* 40:3468.
- Papadopoulous, G. and D. Boskou. 1991. Antioxidant effect of natural phenols on olive oil. *J. Amer. Oil Chem. Soc.* 68:669-671.
- Pappenheimer, A.M. and M. Goettsch. Measurement of vitamin E by polography. 1931. *J. Exp. Med.* 53:11.
- Paquette, G., D.B. Kupranycz, and F.R. Van de Voort. 1985. The mechanisms of lipid autoxidation II. Non volatile secondary oxidation products. *Canadian Institute Food Sci. Technol. J.* 18:197-206.
- Parkhurst, R.M., W.A. Skinner, and P.A. Sturm. 1968. The effect of various concentrations of tocopherol and tocopherol mixture on the oxidative stability of sample of lard. *J. Amer. Oil Chem. Soc.* 45: 641-643.
- Parrish, D.B. 1980. Determination of vitamin E in food, a review. *Crit. Review Food Science Nutrition.* 13:161-185.
- Parson, W.W. and H. Rudney. 1964. Fat soluble vitamin. *Proc. Nat. Acad. Sci. Washington.* 51:444.
- Payne, J.A., R.A. Jaynes, and S.J. Kays. 1983. Chinese chestnuts production in the United States: practice, problems, and possible solutions. *Econ. Bot.* 37(2):187-200.
- Pearce, R.S. and I.M.A. Samual. 1980. Change in fatty acid content of polar lipids during aging of seeds of peanut. *J. Exp. Bot.* 31:1283-1290.
- Peker, K. 1962a. Human health and the filbert, a medical history. *Peanut J. and Nut World.* 41(5): 30-31, 38-40, (6) 38-39.
- Peker, K. 1962b. Human health and the filbert, a medical history. *Nut Grower Society of Oreg., Wash., and Brit. Col.* 27.
- Percheron, E. and J. Loliger. 1990. Influence of drying technology on precooked cereal autoxidation. *Lebensm. Wiss. U. Tech.* 4:400-403.
- Pennock, J.F., F.W. Flemming and J.D. Kerr. 1964. A reassessment of tocopherol chemistry. *Bioch. Biophys. Res. Comm.* 17: 542-546.

- Peraino, C. R.J.M. Fry, E. Staffeldt, and J.P. Christopher. 1977. Enhancing effects of phenobarbitone and butylated hydroxytoluene on 2-acetylaminofluorene induced hepatic tumorigenesis in the rat. *Food Cosmet. Toxicol.* 15:93.
- Pham, Thi, A.T., C. Flood, and J.V. da Silva. 1982. Effects of water stress on lipid and fatty acid composition of cotton leaves, In: *Biochemistry and Metabolism of Plant Lipids*, Wintermans, J.F.G.M. and P.J.C. Kuiper, Eds., Elsevier, Amsterdam. pp.451.
- Phillips, D.J., M. Uota, D. Monticelli, and C. Curtis. 1976. Colonization of almond by Aspergillus flavus. *J. Amer. Soc. Hort Sci.* 101:19-23.
- Pilrenen, V., P. Varo, E.L. Syvaaja, K. Salminen, and P. Koivistoinen. 1984. High-performance liquid chromatographic determination of tocopherol and tocotrienols and its application to diets and plasma of Finnish men I: Analytical method, *International J. Vit. Nutr. Res.* 53: 35-40.
- Piironen, V., P. Varo, E.L. Syvaaja, K. Salmien, and P. Koivistoinen. 1983. High-performance liquid chromatographic determination of tocopherols and tocotrienols and its application to diets and plasma of Finnish men. *Internal J. Vit. Nutr. Res.* 53: 35-40.
- Piironen, V., Eeva-Liisa Syvaaja, K. Salminen, and P. Koivistoinen. 1985. Tocopherol and Tocotrienols in Finnish foods: meat and meat products. *J. Agric. Food Chem.* 33:1215-1218.
- Piironen, V., E.L. Syvaaja, P. Varo, K. Salminen, and P. Koivistoinen. 1986. Tocopherols and tocotrienols in Finnish foods: Vegetables, fruits, and berries. *J. Agric. Food Chem.* 34: 742-746.
- Podlaha, O., A. Eriksson, and B. Toregard. 1978. An investigation of the basic conditions for tocopherol determination in vegetable oils and fats by differential phase polarography. *J. Amer. Oil Chem. Soc.* 55:530.
- Pollard, M.R. and S.S. Singh. 1987. Fatty acid synthesis in developing oilseeds, In: *The Metabolism, Structure and Function of Plant Lipids*, Stumpf, P.K., J.B. Mudd, and W.D. Nes. Eds., Plenum Press, New York. pp.465.
- Pompella, A., E. Maellaro, A.F. Casini, M. Ferrali, and M. Comporti. 1987. Measurement of lipid peroxidation in vivo: A comparison of different procedures. *Lipids* 22:206-211.

- Pratt, D.F. 1980. Natural antioxidants of soybeans and other oil seeds, In: Antioxidants in Food and Biological Systems. Simic, M.G. and Karel M. Ed. Plenum press, New York.
- Preston, C.M. and B.,G. Sayer. 1992. What's in a nutshell: An investigation of structure by carbon-13 cross-polarization magic-angle spinning nuclear magnetic resonance. J. Agr. Food Chem. 40:206-210.
- Privett, O.S., K.A. Dougherty, W.L. Erdahyl, and A. Stolyhwo. 1973. Studies on the lipid composition of developing soybeans. J. Amer. Oil Chem. Soc. 50:516-520.
- Pryor, W.A., J.P. Stanley, and E. Blair. 1976. Autoxidation of polyunsaturated fatty acids. 2. A suggested mechanism for the formation of TBA-reactive materials from prostaglandin-like endoperoxids. Lipids. 11:370.
- Pryor, W.A. 1991. The antioxidant nutrients and disease prevention. What do we know and what do we need to find out? Am. J. Clin. Nutr. 53:3915-3935.
- Purcell, S.L., D.J. Phillips, and B.E. Mackey. 1980. Distribution of Aspergillus flavus and other fungi in several almond growing areas of California. Phytopathology. 70:926-929.
- Ramanujan, R.A., and Anantakrishnan. 1958. Stability of tocopherol in fats during storage and eating. Indian J. Dairy Sci. 11: 179-181.
- Ramaratham, N., T. Osawa, M. Namiki, and S. Kawakishi. 1988. Chemical studies on novel rice hull autoxidants, I. Isolation fractionation, and partial characterization. J. Agr. Food Chem. 36:732-736.
- Ramaratham, N., T. Osawa, M. Namiki, and S. Kawakishi. 1989. Chemical studies on novel rice hull autoxidants, II. Identification of isovitexin, a C-glycosyl flavonoid. J. Agr. Food Chem. 37:316-320.
- Rammell, C.G. and J.J.L. Hoogenboom. 1985. Separation of tocols by HPLC on an amino-cyano polar phase column. J. Liquid Chromat. 8:707-717.
- Rao, M.K.G., and K.T. Achaya. 1967. Role of tocopherol as an antioxidant in safflower oil. Fette, Seifen, Anstrich mittel. 67: 711. In: Biol. Abstr. (1968) 49: 44310.

- Rawls, H.R., and P.J. Van Santen. 1970. A possible role for singlet oxygen in the initiation of fatty acid autoxidation. *J. Amer. Oil Chem. Soc.* 47: 121.
- Raymond, W.D. 1966. Mycotoxin problems in the United Kingdom and the tropics. *Food Technol.* 20:904-910.
- Rehder, A. 1956. Manual of cultivated trees and shrubs hardy in North America, 2nd edition. MacMillan Co. New York.
- Rehwoldt, R. 1986. Tracking the use of antioxidants through industry surveys. *Food Chem. Toxic.* 24: 1039-1041.
- Reid, J.T. and E.K. Heaton. 1977. The effect of mechanical harvesting and cleaning operation of shell-breaking and nutmeat quality of pecan. *Trans. Amer. Cos. Agric. Eng.* 20: 623-626.
- Rennie, B.D. and J.W. Tanner. 1989. Fatty acid composition of oil from soybeans grown at extreme temperatures. *J. Amer. Oil Chem. Soc.* 66:1622-1624.
- Rhee, C.O. and Z.U. Kim. 1982. Analysis of the lipid components in chestnut (Castanea crenata). Part 1. Composition of lipid fraction of inner and outer part of chestnut. *J. Korean Agric. Chem. Soc.* 25(4):239-247.
- Richardson, D.G. 1988. Hazel nut quality. Nut growers society of Oreg., Wash., and Brit. Col. 83-86.
- Rockland, L.B., D.M. Swarthout, and R.A. Johnson. 1961. Studies on English walnuts. Juglans regia III. *Food Technol.* 15:112-116.
- Robak, J. and R.J. Gryglewski. 1988. Flavonoids are scavengers of super oxide anion. *Biochem. Pharmacol.* 37:837.
- Robertson, J.A., G.W. Chapman, and R.L. Wilson. 1978. Relation of days after flowering to chemical composition and physiological maturity of sunflower seed. *J. Amer. Oil Chem. Soc.* 55:266-269.
- Robertson, J.A., R.G. Roberts, and G.W. Chapman Jr. 1985. Changes in oil type sunflower seed stored at 20 C at three moisture levels. *J. Amer. Oil Chem. Soc.* 62: 1335-1339.
- Rosengarten, F.Jr. 1984 The book of edible nuts. Walker and Company, New York. pp.384.

- Rosenthal, I., U. Merin, D. Basker, and A. Kadman. 1984. A study of macadamia nuts of the "Yonik" variety. *J. Food Qual.* 7:67-73.
- Rosenthal, I., U. Merin, and A. Kadman. 1989. Comparison of some properties of macadamia nuts of the "Yonik" and "Beaumont" cultivars. *Lbensm. Wiss. U. Technol.* 19:35-55.
- Rossell, J.B. 1983. Measurement of rancidity. In: *Rancidity in Foods.* J.C. Allen Ed. pp 21-29.
- Rubel, A., R.W. Rinne, and D.T. Canvin. 1972. Protein, oil, and fatty acid developing soybean seeds. *Crop Sci.* 12:739-741.
- Rudney, H. and W.W. Parson. 1963. The conversion of p-hydroxybenzaldehyde to the benzoquinone ring of ubiquinone in Rhodospirillum rubrum. *J. Biol. Chem.* 238:137.
- Rudolph, C.J. 1971. Factors responsible for flavor and off-flavor development in pecans. Ph-D thesis, Oklahoma State Univ. p.233.
- Russell-Eygitt, P.W. and L.D. Ward. 1953. The chemical estimation of vitamin E activity in cereal products. *J. Sci. Food Agric.* 4: 569-572.
- Saleeb, W.F., D.M. Yermanos, C.K. Huszar, W.B. Storey, and C.K. Labanauskas. 1973. The oil and protein in nuts of Macadamia tetraphylla L. Johnson, Macadamia integrifolia Maiden and Betcher, and their F<sub>1</sub> hybrid. *J. Amer. Soc. Hort. Sci.* 98:453-456.
- Samant, S.K. and D.V. Rege. 1988. Carbohydrate composition of cashew nut and choral. *Lebensm. Wiss. U. Technol.* 22:164-168.
- Sanchis, V., S. Sala, A. Palomes, P. Santamarina, and P.A. Burdaspal. 1986. Occurrence of aflatoxin and aflatoxigenic molds in foods and feed in Spain. *J. Food Prot.* 49:445-447.
- Saura-Calixto, F., J. Canellas, and A. Garcia-Raso. 1985. Characteristics and fatty acid composition of almond tegument oil. Comparison with almond kernel oil. *Fette, Seifen, Anstrichm.* 87: 4-6.
- Schade, J.E., K. McGreevey, A.D. King, B. Mackey, and G. Fuller. 1975. Incidence of aflatoxin in California almond. *Appl. Microbiol.* 29:48-51.

- Schade, J.E. and A.D. King Jr. 1984. Fluorescence and aflatoxin content of individual almond kernels naturally contaminated with aflatoxin. *J. Food Sci.* 49: 493-497.
- Scharch, K.M. 1980. Free radical initiation in proteins and amino acids by ionizing and ultra-violet radiations and lipid oxidation. Part III: Free radical transfer from oxidizing lipid. *Critical Reviews in food science and nutrition.* 13:189-245.
- Schnass, I.S. and H. Pabst. 1988. Influence of vitamin E on physical performance. *Int. J. Vit. Nutr. Res.* 58:49-54.
- Scott, M.L. 1978. Vitamin E In: *The fat-soluble vitamins.* ed. H.F. De Luca. Plenum, New York, New York. pp.133-210.
- Senter, S.D., and R.J. Horvat. 1976. Lipids of pecan nut meats. *J. Food Sci.* 41: 1201-1203.
- Senter, S.D. and R.J. Horvat. 1979. Lipid constituents of black walnut kernels. *J. Food Sci.* 44:266-268.
- Senter, S.D., R.J. Horvat, and W.R. Forbus. 1982. GLC-MS analysis of fatty acids from five black walnut cultivars. *J. Food Sci.* 47:1753-1755.
- Senter, S.D., W.R. Forbus Jr., S.O. Nelson, R.L. Wilson Jr., and R.J. Horvat. 1984. Effect of dielectric and steam heating treatments on the storage stability of pecan kernels. *J. Food Sci.* 49:893-895.
- Senter, S.D., R.J. Horvat, and W.R. Forbus. 1985. Comparative GLC-MS analysis of phenolic acids of selected tree nuts. *J. Food Sci.* 48:798-800.
- Serr, E.F. 1964. The nut crops of Turkey. *Proc. Nut Grow. Soc. Ore, Wash, and Brit. Col.* 50, 11-20.
- Sharma, K.D. 1977. Biochemical changes in stored oil seeds. *Indian J. Agric. Res.* 11:137-141.
- Sheldon, R.M., R.L. Lindsey, and L.M. Libbey. 1972. Identification of volatile compounds in roasted filberts. *J. Food Sci.* 37:313-316.
- Shen, C.S.J. and A.J. Sheppard. 1980. A rapid high-performance liquid chromatographic method of separation tocopherols. *J. Micronutrient Anal.* 2:43-53.

- Shewry, R.R. and A.K. Stobart. 1973. Acyllipid metabolism in germinating hazelseeds (Corylus avellana L.). J. Exper. Bot. 24:1106-1116.
- Shewry, R.R., N.J. Pinfield, and A.K. Stoelbart. 1973. Phospholipid and the phospholipid fatty acids of germination hazelseeds. J. Exper. Bot. 24:1100-1105.
- Shewry, R.R. and A.K. Stobart. 1974. Effect of Gibberellic acid on sterol production in Corylus avellana seed. Phytochemistry. 13:347-355.
- Shewry, R.R., N.J. Pinfield, and A.K. Stobart. 1974. Effect of gibberellic acid on mevalonate activation in germinating Corylus avellana seeds. Phytochemistry. 13:341-346.
- Shokriaii, E.H. 1977. Chemical composition of the pistachio nuts of Kerman, Iran. J. Food Sci. 43: 244-246.
- Shuhart, E.V. 1927. Morphology and anatomy of the fruit of pecan. Bot. Gaz. 93:1-20.
- Singer, S. J., and G. L. Nicholosl. 1972. The fluid mosaic of the structure of cell membranes. Science 175: 720-731.
- Singleton, J.A. and H.E. Pattee. 1987. Characterization of peanut oil triacylglycerols by HPLC, GLC, and EIMS. J. Amer. Oil Chem. Soc. 64:534-538.
- Sinnhuber, R.O. and T.C. Yu. 1958. 2-Thiobarbituric acid method for the measurement of rancidity in fishery products. 2. The quantitative determination of malonaldehyde. Food Tech. 12:9.
- Sinnhuber, R.O. and T.C. Yu. 1977. 2-Thiobarbituric acid reaction an objective measure of the oxidative deterioraton occurring in fats and oils. J. Japan Oil Chem. Soc. 26:259.
- Slaga, T.J. and W.M. Bracken. 1977. The effect of antioxidants on skin tumor initiation and aryl hydrocarbon hydroxylase. Cancer Res. 37:1631.
- Slate, G.L. 1930. Filberts. N.Y. State Agric. Exp. Stn. Bull. (Geneva)558.
- Slover, H.T. 1971. Tocopherols in foods and fats. Lipid. 26:291-295.

- Smith, J.R. 1977. Tree crops: A permanent agriculture. Deven-Adair Co., Old Greenwich, Conn. p.408.
- Soler, L., J. Canellas, and F. Saura-Calixto. 1988. Oil content and fatty acid composition of developing almond seeds. J. Agric. Food Chem. 36: 695-697.
- Soll, J. and G. Schultz. 1980. 2-methyl 6-phytylquinol and 2,3-dimethyl 5-phytylquinol as precursors of tocopherol synthesis in spinach chloroplast. Phytochemistry. 19:215-299.
- Sonntage, N.O.V. 1979. Reactions in the fatty acid chain. Ch. 2 in "Bailey's Industrial Oil and Fat Products," D. Swern (Ed.), P. 135.
- Speek, J.J., J. Schriguer, and W.H.P. Schreurs. 1985. Vitamin E composition of some seed oils as determined by high-performance liquid chromatography with fluorometric detection. J. Food Sci. 50:121-124.
- Sporn, M. B., A. Roberts, and D. Goodman. 1984. The Retinoids, Vols. 1 and 11. Academic Press, New York.
- Srinivasan, R.R., H.T. Shigeura, M. Sprecher, B.D. Sprinson, and D.B. Davis. 1956. The conversion of various carbohydrates to 5-dehydroshikimic acid by bacterial extracts. J. Biol. Chem. 223:477.
- Srinivasan, R.R. and B.D. Sprinson. 1959. The conversion of phosphoenolpyruvic acid and D-erythrose 4-phosphate to 5-dehydroquinic acid. J. Biol. Chem. 234:716.
- Stebbins, R.L. and J. Kent. 1982. The influence of various treatments and timings on rootings of suckers of Barcelona hazelnuts in sawdust. Nut growers society of Oregon, Washington, and British Columbia. pp.69-73.
- Stebbins, R.L. 1984. What's known about brownstain. Nut growers society of Oregon, Washington, and British Columbia. pp.101-108.
- Stone, J., L. Young, T. Larson, D. Pierce, and D. Anderson. 1988. The Eastern filbert blight panel. Nut growers society of Oregon, Washington, and British Columbia. pp.33-48.
- Stowe, H.D. 1963. Separation of beta and gamma-tocopherol. Arch. Biochem. Biophys. Acta. 103: 42-46.

- Stuiver, C.E.E., L.J. de Kok, A.E. Hendriks, and P.J.C. Kuiper. 1982. The effect of salinity on phospholipid content and composition of two Plantago species, differing in salt tolerance, In: Biochemistry and Metabolism of Plant Lipids, Wintermans, J.F.G.M. and P.J.C. Kuiper, Eds., Elsevier, Amsterdam. pp.455.
- Stumbs, J. 1987. Hazelnut market heats up. Sun-diamond Grower. Spring, 44-47.
- Stumpf, P.K. 1981. Plants, fatty acids, compartments. Trends Biochem. Sci. 8:173.
- Sturm, P.A., R.M. Parkhurst, and W.A. Skinner. 1966. Quantitative determination of individual tocopherol by thin layer chromatographic separation and spectrophotometry. Anal. Chem. 38: 1245-1248.
- Stymne, S. and A.K. Stobart. 1987. Triacylglycerol biosynthesis, In: The Biochemistry of Plants, Vol 9, Stumpf, P.K. and E.E. Conn, Academic Press, New York. pp.175.
- Su, J.D., T. Osawa, M. Namiki. 1986. Screening for antioxidative activity of crude drugs. Agric. Biol. Chem. 50:199-203.
- Su, J.D., T. Osawa, S. Kawakishi, and M. Namiki. 1988. Tannin antioxidants from Osbeckia Chinensis. Phytochemistry. 27:1315-1319.
- Suarna, C. and P.T. Southwell-Keely. 1988. New oxidation product of 2,2,5,7,8-pentamethyl-6-chromanol. Lipids 23:1129-1131.
- Suarna, C. and P.T. Southwell-Keely. 1991. Antioxidant activity of oxidation products of  $\alpha$ -tocopherol and of its model compound 2,2,5,7,8-penta methyl-6-chromanol. Lipids 26:187-190.
- Syvaoja, E.L., V. Piironen, P. Varo, P. Koivistoinen, and K. Salminen. 1986. Tocopherols and tocotrienols in Finnish foods: oils and fats. J. Amer. Oil Chem. Soc. 63:328-329.
- Takahama, U. 1985. Inhibition of lipoxygenase dependent lipid peroxidation by quercetin. Mechanism of antioxidative function. Phytochemistry. 24: 1443-1445.

- Tan, M.H., M.A. Dickinson, J.J. Albers, R.J. Havel, M.C. Cheung, and J. Vigne. 1980. The effect of a high cholesterol and saturated fat diet on serum high-density lipoprotein cholesterol apoprotein A-1, and apoprotein E levels in normolipidemic humans. *Am J. Clin. Nutr.* 33:2559-2565.
- Tan, B. 1989. Palm carotenoids, tocopherols, and tocotrienols. *J. Amer. Oil Chem. Soc.* 66:770-776.
- Tangney, C.C., J.A. Driskell, and H.M. McNair. 1979. Separation of vitamin E isomers by high-performance liquid chromatography. *J. Chromatography.* 172: 513-515.
- Tappel, A.L., F.W. Knapp, and K. Urs. 1957. Oxidative fat rancidity in food products. II. Walnuts and other nut meats. *Food Res.* 22: 287-289.
- Tappel, A.L. 1962. Vitamin E as the biological lipid antioxidant. *Vitamin Horm.* 20:493-496.
- Tappel, A.L. 1980. The role of free radical reaction in biological systems. In: *Free radicals in biology.* Vol. IV. edited by W.A. Pryor. New York: academic press. pp.1-24.
- Tashiro, T., Y. Fukuda, T. Owasa, and N. Namiki. 1990. Oil and minor components of sesame strains. *J. Amer. Oil Chem. Soc.* 67:508-511.
- Taylor, P. and P. Barnes. 1981. Analysis for vitamin E in edible oil by high performance liquid chromatography. *Chemistry and Physics of Lipid.* 20: 951-956.
- Tevini, M. 1977. Light, function, and lipids during plastid development, In: *Lipids and Lipid Polymers in Higher Plants,* Tevini, M. and H.K. Lichtenthaler, Eds., Springer-Verlag, Berlin. pp.121.
- Theimer, R., G. Wanner, and R. Eggersmann. 1986. Cellular compartmentation for seed oil storage. *J. Amer. Oil Chem. Soc.* 63:59-63.
- Terao, J. and S. Matsushita. 1977. Products formed by photosensitized oxidation of unsaturated fatty acid esters. *J. Amer. Oil Chem. Soc.* 54:293-238.
- Thompson, J.N. and G. Hatina. 1979. Determination of tocopherol and tocotrienols in foods and tissues by high performance liquid chromatography. *J. Liq. Chromatography.* 2: 327-344.

- Thompson, J.N. 1982. Determination of vitamin E and K in food and tissue using high performance liquid chromatography. In: Trace Analysis. Vol. II, Lawrence, J.F. (Ed), Academic Press, New York, pp. 1-67.
- Thompson, G.A. 1986. Metabolism and control of lipid structure modification. *Biochem. Cell Biol.* 64:66-69.
- Thompson, M.M. 1967. Role of pollination in nut development. *Proc. Nut Growers Soc. of Oregon and Washington.* 53:31-36.
- Thompson, M.M. and D.G. Richardson. 1978. Is there an effect of pollenizers on filbert kernel quality? Nut growers society of Oregon, Washington, and British Columbia. pp.52-58.
- Thompson, M.M. 1979a. Growth and development of the pistillate flower and nut in Barcelona filberts. *J. Amer. Soc. Hort. Sci.* 104:427-432.
- Thompson, M.M. 1979b. Genetics of incompatibility in Corylus avellana L. *Theor. Appl. Genetics.* 54:113-116.
- Thompson, M.M. 1979c. Incompatibility of alleles in Corylus avellana L. *Theor. Appl. Genetics.* 55:29-33.
- Thompson, M.M. 1982. Breeding for filbert varieties suitable for shelling. Nut growers society of Oregon, Washington, and British Columbia. pp.35-42.
- Thor, C.J.B. and C.L. Smith. 1935. A physiological study of seasonal changes in the composition of the pecan during fruit development. *J. Agr. Res.* 50:99-121.
- Threlfall, D.R., W.T. Griffith, and T.W. Goodwin. 1967. Observation on the biosynthesis of phytosterpenoid quinone and chromanol nuclei. *Biochem. J.* 103:831.
- Tkhagushev, N.A., V.V. Grinenko, and Y.A. Merzhanian. 1971. *Izvestiy Vysshikh Uchebnykh Zavedenii. Pishchevaya Tekhnologiya.* 2: 39-42.
- Toda, S., T. Miyase, H. Arichi, H. Tamizawa, and Y. Takino. 1985. Natural antioxidants. II. Antioxidative compounds isolated from seeds of Plantago asiatica. *Linne. Chem. Pharm. Bull.* 33:1725-1728.
- Truswell, A.S. 1985. ABC of nutrition. Vitamins 2. *Brit. Med. J.* 291:1103-1106.

- Tsuchia, T. 1970. Phenolic substance from rice bran and rice germ oil. Japanese patent. 70:744-745.
- Tsuchia, T. 1982. Rice bran oil antioxidant for food. Japanese patent. 82:248-251.
- USDA. 1977. USDA: U.S. fats and oils statistics, 1961-1976. (Statistical bull no. 574) USDA, Washington, DC.
- USDA. 1984. Composition of foods: nut and seed products; raw, processed, prepared. USDA Agric. Handbook. 8-1.
- Van Nickerk, P.J. 1973. The direct determination of free tocopherols in plant oils by liquid-solid chromatography. Anal. Biochem. 52: 533-536.
- Vereshchagin, A.G. 1991. Comparative kinetic analysis of oil accumulation in maturing seeds. Plant Physiol. Biochem. 29:385-393.
- Volp, J. J., and P. R. Vagelos. 1976. Mechanisms and regulation of biosynthesis of saturated fatty acids. Physiol. Rev. 56: 339-417.
- Walker, K.A. and J.L. Harwood. 1985. Localisation of chloroplastic fatty acid synthesis de novo in the stroma. Biochem. J. 226:551.
- Wallerstein, I.S., U. Merin, and I. Rosenthal. 1989. Comparison of kernels of three Virginia-type peanut cultivars. Lebensm. Wiss. U. Technol. 22:179-181.
- Wanner, G., H. Formanek, and R.R. Theimer. 1981. The ontogeny of lipid bodies in plant cells. Planta. 151:109.
- Warner, K., E.N. Frankel, and T.L. Mount. 1988. Flavor evaluation of crude oil to predict the quality of soybean oil. J. Amer. Oil Chem. Soc. 65:386-391.
- Wehner, F.C. and C.J. Rabic. 1970. The micro-organisms in nuts and dried fruits. Phytophylactica. 2:165-168.
- Weisburger, J.H. 1991. Nutritional approach to cancer prevention with emphasis on vitamins, antioxidants, and carotenoids. Am. J. Clin. Nutr. 53:2265-2375.
- Weiser, H. and M. Vecchi. 1982. Stereoisomers of  $\alpha$ -tocopherol acetate. Biopotences of all eight stereoisomers, individually or in mixture, as determined by rat respiration-gestation test. Int. J. Vit. Nutr. Res. 52:351-370.

- Wellburn, A.R. 1969. The stereochemistry of hydrogen transfer during the reduction of G20 isoprenoid in higher plants. *Phytochemistry*. 7:1523-1528.
- Wellburn, A.R. 1970. Studies on the biosynthesis of the tocopherols in higher plants. *Phytochemistry*. 9:743-748.
- Whistance, G.R., D.R. Threlfall, and T.W. Goodwin. 1967. Observation on the biosynthesis of phytoterpenoid Quinone and chromanol nuclei. *Biochem. J.* 105:145-153.
- Whistance, G.R. and D.R. Threlfall. 1967. Biosynthesis of phytoquinones: An outline of the biosynthetic sequences involved in terpenoid quinone and chromanol formation by higher plants. *Biochem. Biophys. Res. Commun.* 28:295-302.
- Whistance, G.R. and D.R. Threlfall. 1968. Biosynthesis of phytoquinones: utilization of homogentisic acid by maize shoots for the biosynthesis of plastoquinone. *Biochem. J.* 109:482-483.
- Whitehouse, W.E., E.J. Koch, L.E. Jones, J.C. Long, and C.L. Stone. 1964. Influence of pollen from diverse pistachio species on development of pistachio nuts. *J. Amer. Soc. Hort. Sci.* 84:224-229.
- Whittle, K.J. and J.F. Pennock. 1967. The examination of tocopherols by two-dimensional thin-layer chromatography and subsequent colorimetric determination. *Analyst*. 92: 423-428.
- Wiegand, E.H. 1943. The future of the filbert. *Food Manufacture*. 18:409-412.
- Widdowson, E. M. 1987. Atwater: A personal tribute from the U.K. *Amer. J. Clin. Nutr.* 45: 898-992.
- Williamson, P.M. 1991. The hazelnut industry, measuring its growth. *Nut growers society of Oregon, Washington, and British Columbia.* pp.34-40.
- Wintermans, J.F.G.M. and P.J.C. Kuiper., Eds. 1982. *Biochemistry and Metabolism of Plant Lipids*, Elsevier, Amsterdam.
- Witting, L.A. 1975. Vitamin E as a food additive. *J. Amer. Oil Chem. Soc.* 52:64-67.

- Wong, M.L., R.E. Timms, and E.M. Gosh. 1988. Colorimetric determination of total tocopherols in palm oil, Olein and Stearin. J. Amer. Oil Chem. Soc.. 65: 258-261.
- Woodroof, J.C. and N.C. Woodroof. 1927. The development of the pecan nut from flower to maturity. J. Agr. Res. 34:1049-1063.
- Woodroof, J.C. 1967. Filberts. In: Treenuts; Production, Processing, Products. Vol. 1. Westport, Conn. Avi. pp 277-312.
- Yamaoka, M., H.J. Maria, K. Kamiyama. 1991. Antioxidative activities of tocotrienols on phospholipid liposomes. J. Amer. Oil Chem. Soc. 68:114-118.
- Yoshida, H., M. Tatsumi, and G. Kajimoto. 1991. Relationship between oxidative stability of vitamin E and production of fatty acids in oil during microwave heating. J. Amer. Oil Chem. Soc. 68:566-570.
- Yuki, E. and Y. Ishikawa. 1976. Tocopherol contents of nine vegetable frying oils, and their changes under simulated deep fat frying condition. J. Amer. Oil Chem. Soc. 53:673-678.
- Zielinski, Q.B. 1959. The search for new varieties of filberts for Oregon. Nut Grow. Soc. Ore, Wash, and Brit. Col. 45, 2-4.

## **APPENDICES**

Table A.1. Percentage of mold on hazelnuts from tree and ground for 1986, 1987, and 1988.\* 368

Year	Variety	Position	% Mold*
1986	Barcelona	Tree	9.4 a
		R-Tree	9.3 a
		Ground	6.7 d
		R-Ground	7.7 c
	Ennis	Tree	7.7 c
		R-Tree	7.9 c
		Ground	6.9 d
		R-Ground	7.3 c d
	Daviana	Tree	7.7 c
		R-Tree	8.6 b
		Ground	5.8 e
		R-Ground	6.6 d
1987	Barcelona	Tree	3.8 f
		R-Tree	3.3 f
		Ground	3.2 f g
		R-Ground	2.9 g
	Ennis	Tree	2.0 h
		R-Tree	2.2 h
		Ground	1.7 h
		R-Ground	1.7 h
	Daviana	Tree	2.9 f g
		R-Tree	3.2 f g
		Ground	2.1 g h
		R-Ground	2.3 g h
1988	Barcelona	Tree	2.0 h
		R-Tree	2.2 h
		Ground	1.2 i
		R-Ground	1.7 h i
	Ennis	Tree	1.4 i
		R-Tree	1.5 i
		Ground	1.5 i
		R-Ground	1.8 h i
	Daviana	Tree	1.8 h i
		R-Tree	2.0 h
		Ground	1.8 h i
		R-Ground	2.0 h i

\*Each tree and R-tree equal 120 replicates, 36,000 nuts. Each ground and R-ground equal 72 replicates, 18,000 nuts. Four different farms. Means followed by the same letter are not significantly different,  $p=0.05$ .

Table A.2. Change in hazelnut kernel moisture (%) content for different storage times, (months) 1986.\*

Variety	0	6	12	18	24	30	36
Tombul	5.7	5.1	5.6	5.3	5.3	5.3	5.2
OSU 43-58 Willamette	5.4	5.3	5.1	5.1	5.1	5.1	5.0
Casina	5.8	5.3	5.2	5.2	5.1	5.1	5.1
Tombul Ghiaghli	5.3	5.5	5.2	5.2	5.2	5.1	5.1
Imperial	5.9	5.2	5.5	5.3	5.2	5.2	5.1
Mortarella	5.1	5.1	5.1	5.2	5.1	5.0	5.0
Tonda Romana	5.3	5.3	5.1	5.2	5.1	5.0	5.0
Negret	5.1	5.7	5.2	5.2	5.1	5.1	5.1
Tonda di Giffoni	5.3	5.4	5.2	5.1	5.1	5.0	4.9
Daviana	5.6	4.9	4.3	4.3	4.3	4.3	4.3
Hall's Giant	6.5	6.6	6.1	6.0	5.7	5.7	5.6
TGDL	5.7	5.4	5.3	5.3	5.2	5.2	5.1
OSU 49-73	5.3	5.0	5.1	5.1	5.1	5.0	5.0
Montebello	5.4	5.1	4.9	4.9	4.9	4.9	5.0
Butler	5.8	4.6	4.3	4.3	4.3	4.3	4.3
Barcelona	5.3	5.1	4.8	4.8	4.8	4.7	4.7
Ennis	5.1	4.8	4.3	4.3	4.2	4.2	4.2

\*Each value represents the mean of 3 replicates.

Table A.3.

Change in hazelnut kernel moisture (%) content for different storage times, (months) 1987.\*

370

Variety	0	6	12	18	24
Tombul	5.5	5.2	5.1	5.1	5.0
OSU 43-58 Willamette	5.2	5.6	5.1	5.1	5.0
Casina	5.8	5.5	5.1	5.0	5.0
Tombul Ghiaghli	5.6	5.3	5.2	5.1	5.0
Imperial	5.3	5.4	5.4	5.1	5.0
Mortarella	5.2	5.2	5.2	5.1	5.0
Montebello	5.2	5.2	5.2	5.1	5.0
Negret	5.8	5.3	5.2	5.2	5.1
TGDL	6.0	5.6	5.2	5.1	5.1
Hall's Giant	5.9	5.1	5.1	5.2	4.9
Tonda di Giffoni	5.5	5.6	5.5	5.3	5.0
Tonda Romana	5.5	5.2	5.1	5.0	5.1
Daviana	6.3	5.3	5.1	5.1	5.0
Barcelona	6.1	5.5	5.6	5.4	5.0
Butler	6.0	5.6	5.5	5.4	5.1
Ennis	5.5	5.5	5.2	5.1	5.1
OSU 49-73	5.3	5.0	5.1	5.0	5.0

Each value represents a mean of 3 replicates.

Table A.4. Change in hazelnut kernel moisture 371  
 (%) content for different storage  
 times, (months) 1988.\*

Variety	0	6	12
Casina	6.1	5.8	5.3
OSU 43-58 Willamette	5.5	5.4	5.3
Tombul	5.6	5.5	5.1
Imperial	5.8	5.8	5.2
Mortarella	6.1	5.6	5.5
Tombul Ghiaghli	5.4	5.2	5.0
Hall's Giant	5.1	5.1	4.9
Negret	5.5	5.1	5.1
Tonda di Giffoni	5.8	5.3	5.3
TGDL	5.8	5.4	5.4
Tonda Romana	5.6	5.2	5.5
Montebello	5.2	5.1	5.1
OSU 49-73	5.8	5.4	5.1
Daviana	5.9	5.9	5.5
Butler	5.9	5.8	5.4
Barcelona	5.5	5.2	5.1
Ennis	5.7	5.5	5.0

Each value represents the mean of 3 replicates.

Table A.5.

Oil content (%) of hazelnut varieties during different storage times, (months) 1986.

372

Variety	0	6	12	18	24	30	36
Tombul	65.7	65.8	65.2	65.4	65.4	65.8	65.9
OSU 43-58 Willamette	63.4	62.6	63.9	64.1	64.2	64.2	64.3
Casina	65.3	64.9	65.3	65.4	64.6	65.5	65.5
Tombul Ghiaghli	65.4	65.6	65.8	65.7	65.4	65.7	65.2
Imperial	61.8	61.7	61.8	61.7	62.1	62.2	62.1
Mortarella	63.4	63.2	63.7	63.7	63.1	63.9	63.0
Tonda Romana	62.9	63.1	62.9	62.9	63.3	63.1	63.0
Negret	64.9	64.8	64.9	65.1	65.5	65.3	65.6
Tonda di Giffoni	62.9	62.9	62.5	62.0	62.1	62.2	62.5
Daviana	60.4	61.7	61.5	61.6	61.9	62.6	62.7
Hall's Giant	57.9	58.7	56.7	57.3	57.9	58.1	58.1
TGDL	62.3	62.3	62.3	62.4	62.9	61.8	62.1
OSU 49-73	62.9	62.7	62.8	63.0	63.4	63.5	63.5
Montebello	61.3	61.5	62.0	62.4	62.4	61.1	61.2
Butler	61.4	62.7	63.1	63.1	63.2	63.2	63.2
Barcelona	62.8	62.9	63.2	63.3	63.7	63.7	63.7
Ennis	61.4	61.3	62.8	62.9	63.1	63.2	63.3

Each value represents the mean of 3 replicates.

Table A.6.

Oil content (%) of hazelnut varieties during different storage times, (months) 1987.\*

373

Variety	0	6	12	18	24
Tombul	64.1	63.9	64.5	64.5	64.1
OSU 43-58 Willamette	63.5	61.9	62.3	62.5	63.2
Casina	64.0	63.9	64.3	63.8	64.3
Tombul Ghiaghli	64.3	64.3	65.1	64.9	65.3
Imperial	60.7	60.9	60.8	60.4	60.3
Mortarella	62.2	63.9	63.6	63.2	63.4
Montebello	62.5	62.6	62.6	62.9	63.1
Negret	65.1	65.1	65.1	65.3	65.1
TGDL	64.6	64.1	64.5	64.6	64.6
Hall's Giant	56.8	56.4	57.1	56.7	56.6
Tonda di Giffoni	62.9	62.9	62.9	62.7	62.8
Tonda Romana	64.5	65.3	65.8	65.2	64.9
Daviana	60.0	60.9	60.9	60.8	60.5
Barcelona	60.5	61.7	61.2	60.5	60.5
Butler	60.8	60.9	61.9	61.6	61.2
Ennis	60.2	60.1	60.3	60.8	60.6
OSU 49-73	63.5	62.8	62.7	62.2	62.6

Each value represents a mean of 3 replicates.

Table A.7. Oil content (%) of hazelnut varieties during different storage times, (months) 1988.\*

Variety	0	6	12
Casina	64.5	64.9	64.8
OSU 43-58 Willamette	63.4	62.9	63.8
Tombul	64.5	65.3	65.8
Imperial	63.3	63.3	63.3
Mortarella	62.1	62.3	62.3
Tombul Ghiaghli	64.6	64.1	64.8
Hall's Giant	56.4	56.6	57.3
Negret	63.6	63.4	63.6
Tonda di Giffoni	63.5	63.4	63.1
TGDL	64.8	63.1	64.2
Tonda Romana	63.4	63.1	63.4
Montebello	60.5	60.5	60.7
OSU 49-73	62.1	62.2	62.5
Daviana	61.6	60.4	60.8
Butler	61.9	61.7	62.7
Barcelona	62.0	61.2	61.2
Ennis	59.2	59.4	60.4

Each value represents the mean of 3 replicates.

Table A.8.

Change in  $\beta$ -tocopherol concentration for different storage times, (months) 1986. Tocopherols are expressed as  $\mu\text{g/g}$  oil. 375

Variety	0	6	12	18	24	30	36
Tombul	36	35	32	26	19	13	11
OSU 43-58 Willamette	32	31	28	25	20	17	14
Casina	19	19	16	13	11	10	9
Tombul Ghiaghli	30	29	15	10	8	8	8
Imperial	14	13	12	11	10	9	9
Mortarella	12	13	12	11	11	10	8
Tonda Romana	12	12	11	10	9	8	8
Negret	14	13	11	10	9	8	6
Tonda di Giffoni	10	9	7	6	6	5	5
Daviana	15	15	14	11	10	10	9
Hall's Giant	13	12	11	9	7	6	5
TGDL	13	13	9	8	7	7	5
OSU 49-73	14	14	12	9	7	6	6
Montebello	16	15	12	11	10	8	7
Butler	15	14	14	13	11	10	9
Barcelona	10	10	9	8	7	6	6
Ennis	8	8	8	7	7	5	5

Each value represents the mean of 3 replicates.

Table A.9.

Change in  $\beta$ -tocopherol concentration for different storage times, (months) 1987.\* Tocopherol is expressed as  $\mu\text{g/g}$  oil.

376

Variety	0	6	12	18	24
Tombul	19	18	15	12	10
OSU 43-58 Willamette	11	10	9	6	6
Casina	15	14	13	11	10
Tombul Ghiaghli	17	17	15	14	12
Imperial	12	12	10	11	10
Mortarella	13	13	8	7	7
Montebello	8	8	6	6	5
Negret	12	12	10	10	8
TGDL	8	8	7	7	7
Hall's Giant	10	10	8	7	5
Tonda di Giffoni	7	7	6	6	4
Tonda Romana	9	9	7	7	6
Daviana	11	11	9	8	8
Barcelona	11	10	9	9	8
Butler	12	11	10	9	7
Ennis	11	11	10	9	8
OSU 49-73	7	7	7	7	5

Each value represents a mean of 3 replicates.

Table A.10.

Change in  $\beta$ -tocopherol concentration for different storage times, (months) 1988.\*  
Tocopherol is expressed as  $\mu\text{g/g}$  oil.

377

Variety	0	6	12
Casina	17	17	15
OSU 43-58 Willamette	20	20	15
Tombul	9	8	7
Imperial	13	13	11
Mortarella	10	9	9
Tombul Ghiaghli	11	9	9
Hall's Giant	14	13	13
Negret	16	16	15
Tonda di Giffoni	11	9	9
TGDL	13	12	11
Tonda Romana	13	12	10
Montebello	17	14	11
OSU 49-73	16	15	14
Daviana	10	9	9
Butler	13	13	13
Barcelona	10	10	9
Ennis	14	12	11

Each value represents a mean of 3 replicates.

Table A.11.

Change in  $\Gamma$ -tocopherol concentration for different storage times, (months) 1986. Tocopherols are expressed as  $\mu\text{g/g}$  oil.

378

Variety	0	6	12	18	24	30	36
Tombul	42	41	36	29	24	18	18
OSU 43-58 Willamette	42	41	33	23	22	20	19
Casina	39	38	35	34	29	21	18
Tombul Ghiaghli	29	29	17	11	10	8	6
Imperial	17	16	16	14	12	11	11
Mortarella	19	16	15	12	12	8	7
Tonda Romana	16	15	14	13	12	12	11
Negret	14	14	12	9	7	7	5
Tonda di Giffoni	12	11	10	8	6	5	3
Daviana	20	19	17	10	9	9	8
Hall's Giant	14	13	11	7	6	6	4
TGDL	18	18	12	11	10	9	6
OSU 49-73	11	11	11	7	7	7	6
Montebello	14	14	11	9	8	5	5
Butler	11	11	10	10	7	7	6
Barcelona	11	10	10	11	10	8	6
Ennis	9	9	8	8	8	5	5

Each value represents the mean of 3 replicates.

Table A.12.

Change in  $\Gamma$ -tocopherol concentration for different storage times, (months) 1987.\* Tocopherol is expressed as  $\mu\text{g/g}$  oil.

379

Variety	0	6	12	18	24
Tombul	65	61	59	49	36
OSU 43-58 Willamette	38	35	33	25	20
Casina	39	38	37	33	28
Tombul Ghiaghli	27	25	20	18	13
Imperial	17	16	16	14	10
Mortarella	17	17	17	13	9
Montebello	10	9	8	6	4
Negret	11	10	9	7	5
TGDL	25	24	23	20	15
Hall's Giant	6	5	5	5	4
Tonda di Giffoni	8	8	7	7	4
Tonda Romana	13	13	9	9	6
Daviana	16	15	14	10	9
Barcelona	9	9	9	8	7
Butler	10	10	9	8	7
Ennis	14	13	13	8	8
OSU 49-73	9	9	8	8	8

Each value represents a mean of 3 replicates.

Table A.13.

Change in  $\Gamma$ -tocopherol concentration for different storage times, (months) 1988.\* Tocopherol is expressed as  $\mu\text{g/g}$  oil.

380

Variety	0	6	12
Casina	41	40	34
OSU 43-58 Willamette	51	50	46
Tombul	59	53	44
Imperial	20	12	11
Mortarella	13	11	11
Tombul Ghiaghli	15	14	13
Hall's Giant	17	12	11
Negret	14	14	13
Tonda di Giffoni	12	11	11
TGDL	18	16	15
Tonda Romana	16	16	15
Montebello	11	10	10
OSU 49-73	13	12	11
Daviana	11	10	8
Butler	13	13	11
Barcelona	11	10	9
Ennis	14	13	12

Each value represents a mean of 3 replicates.

Fig. A.1. Mean percent of kernel mold for three hazelnut varieties, over three years. (Barcelona, Ennis, and Daviana)

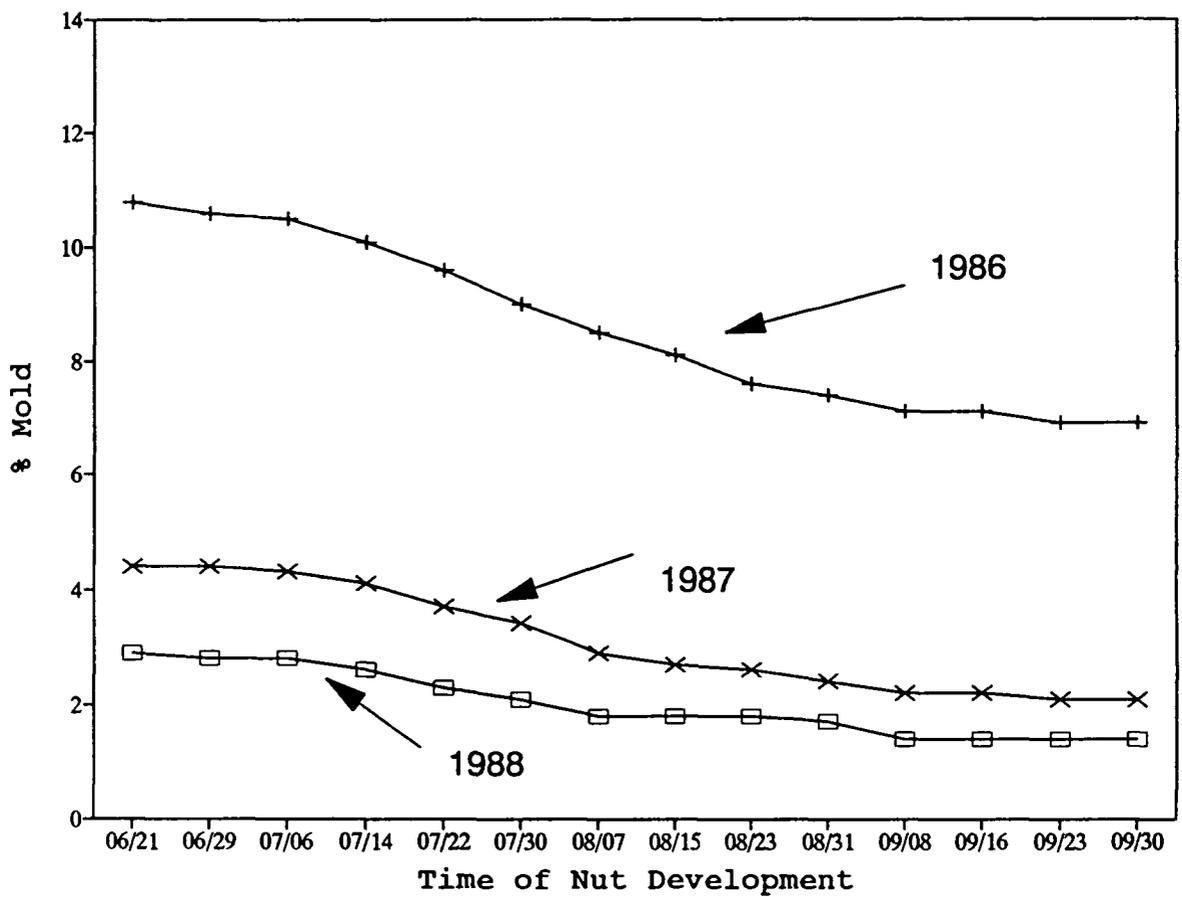


Fig. A.2. Growth of the kernel of seven hazelnut varieties, 1987 and 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

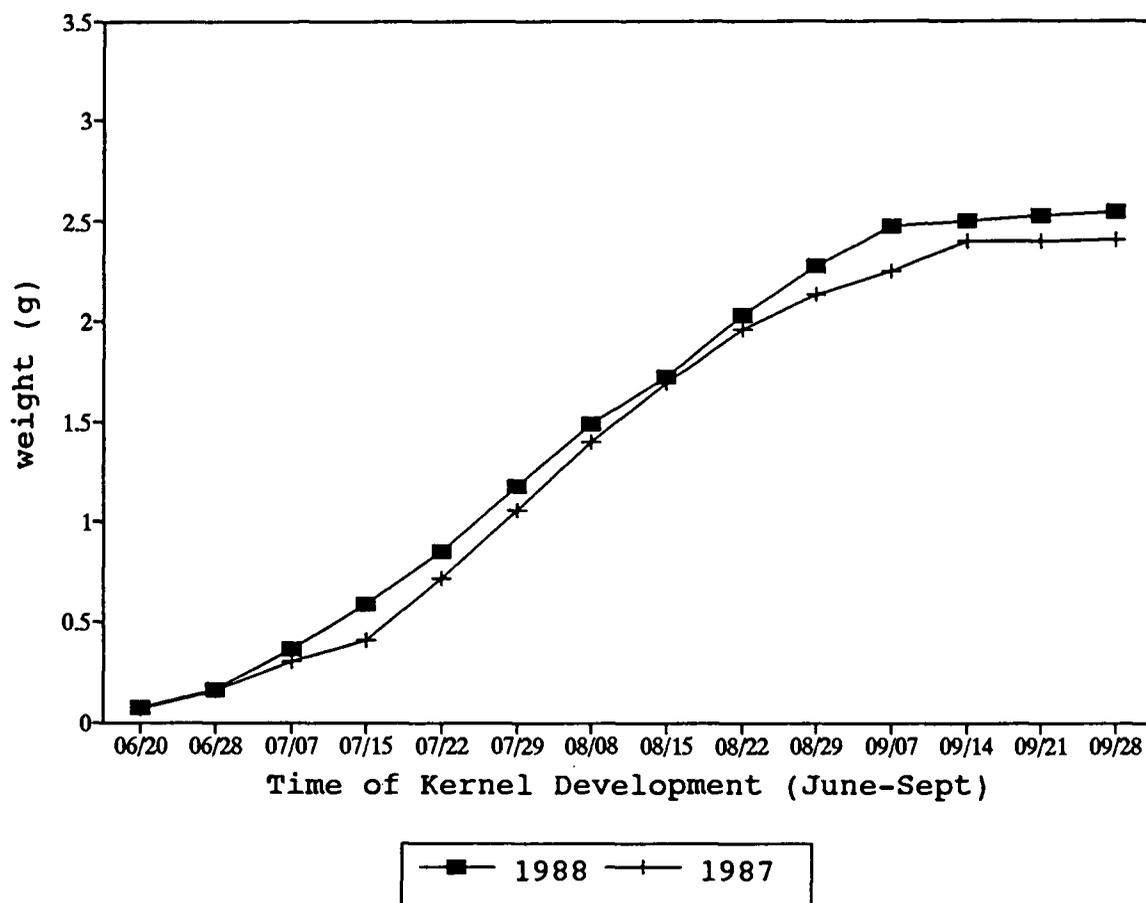


Fig. A.3. Oleic acid development in seven hazelnut varieties, 1987 and 1988. (Barcelona, Ennis, Daviana, Tonda Romana, Tonda Gentile delle Langhe, Tombul, and Tombul Ghiaghli)

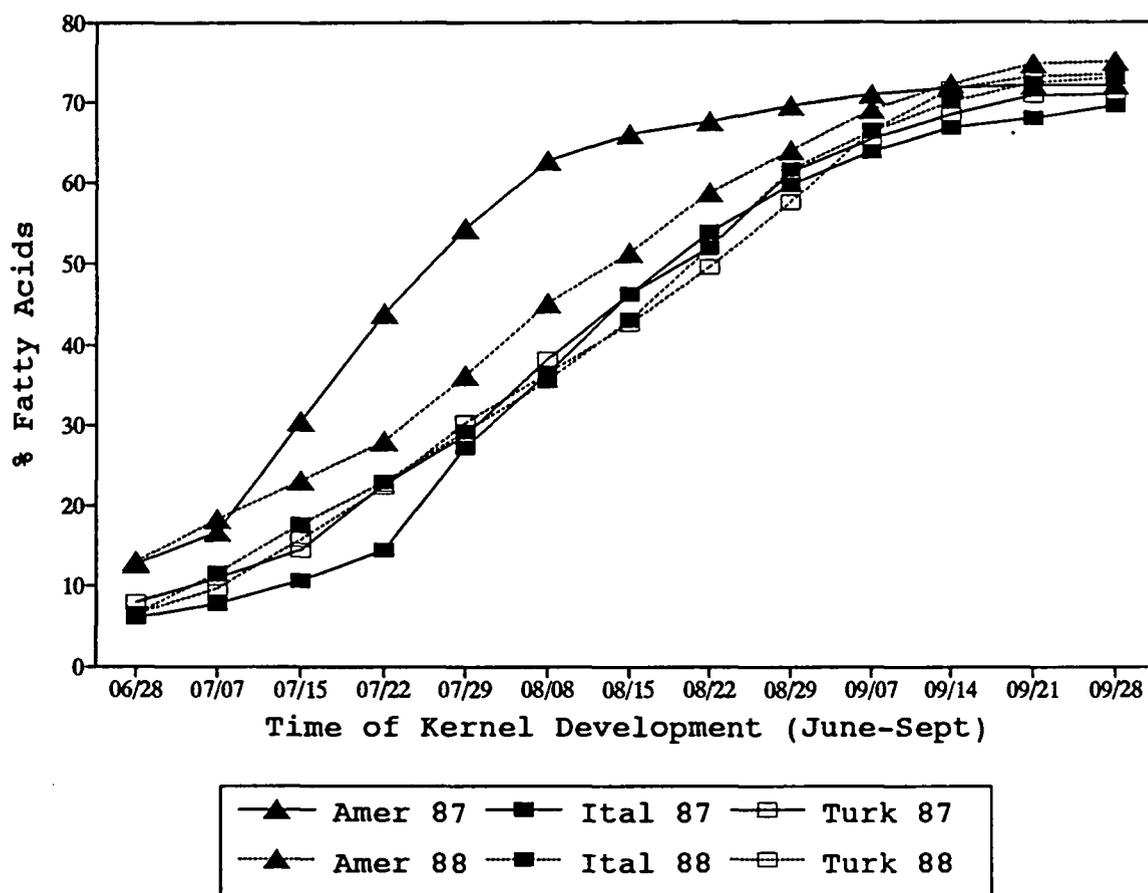


Fig. A.4. Standard curve of tocopherol by HPLC.

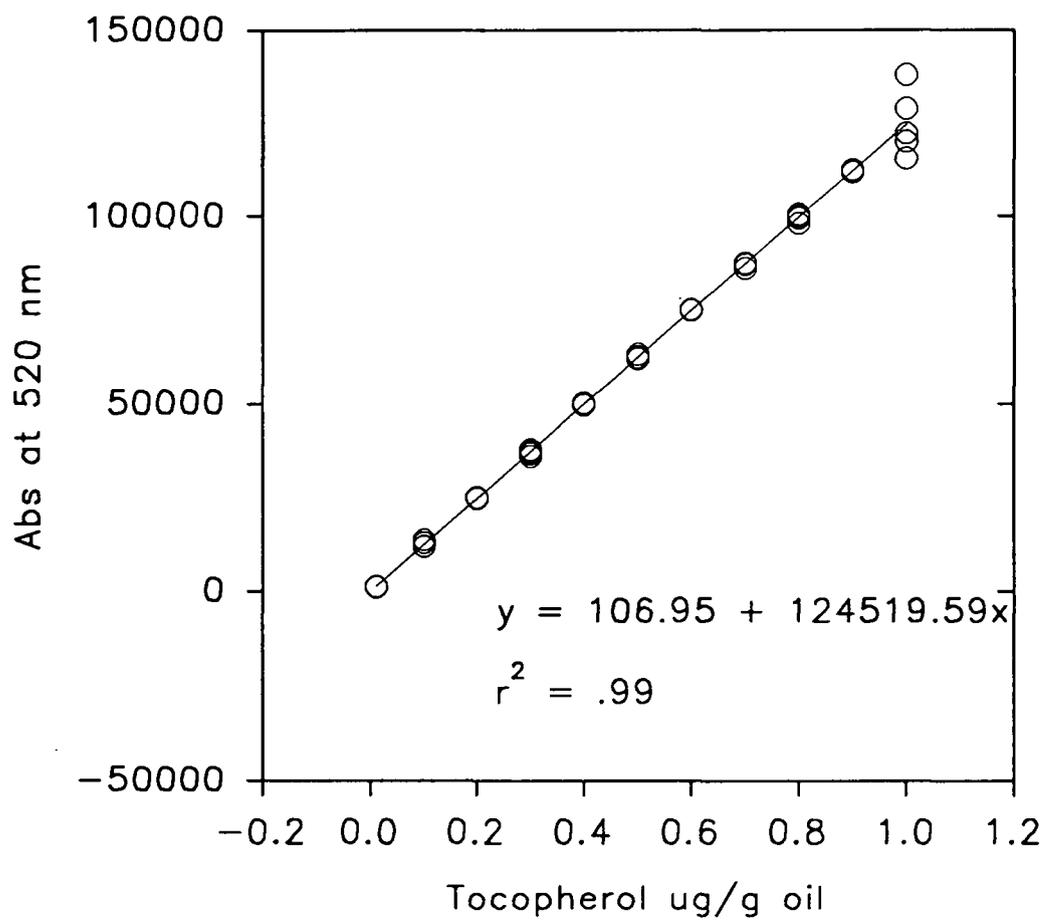


Fig. A.5. Temperatures of June, 1987.

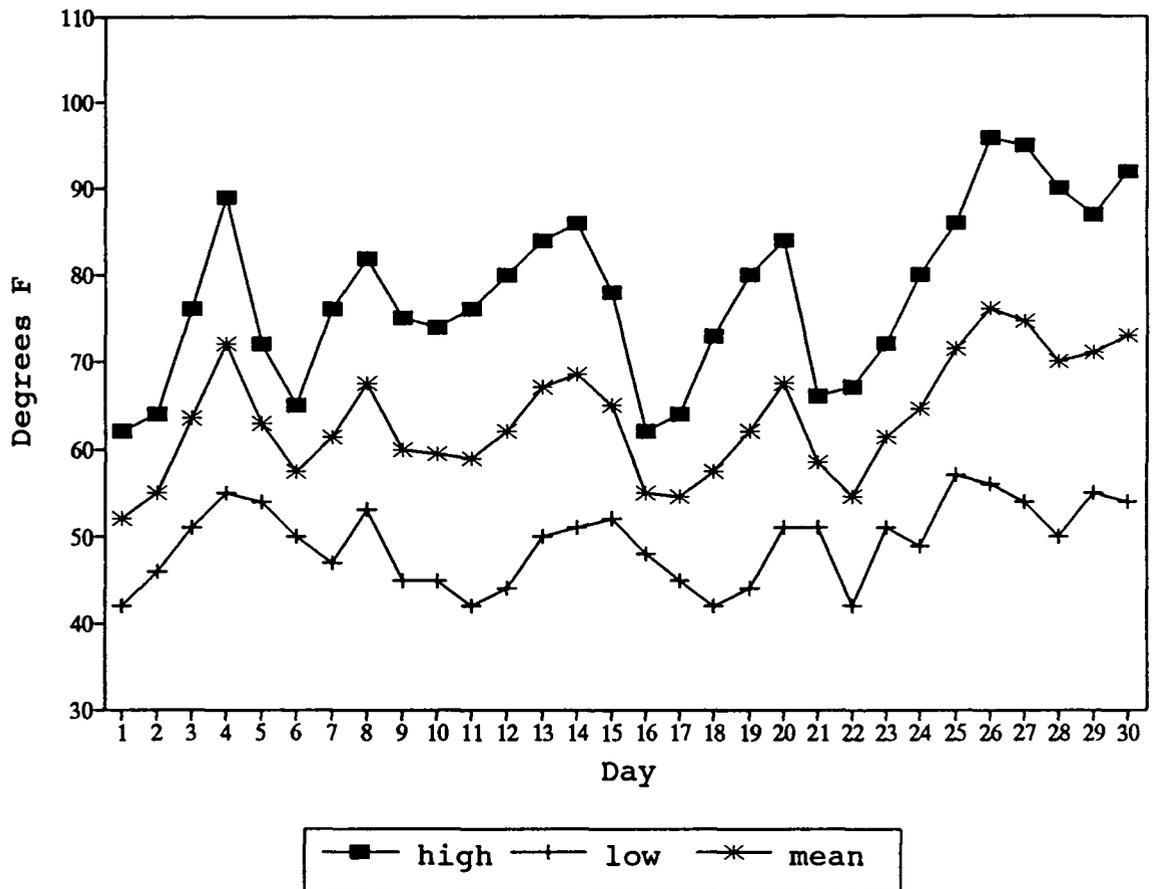


Fig. A.6. Temperatures of June, 1988.

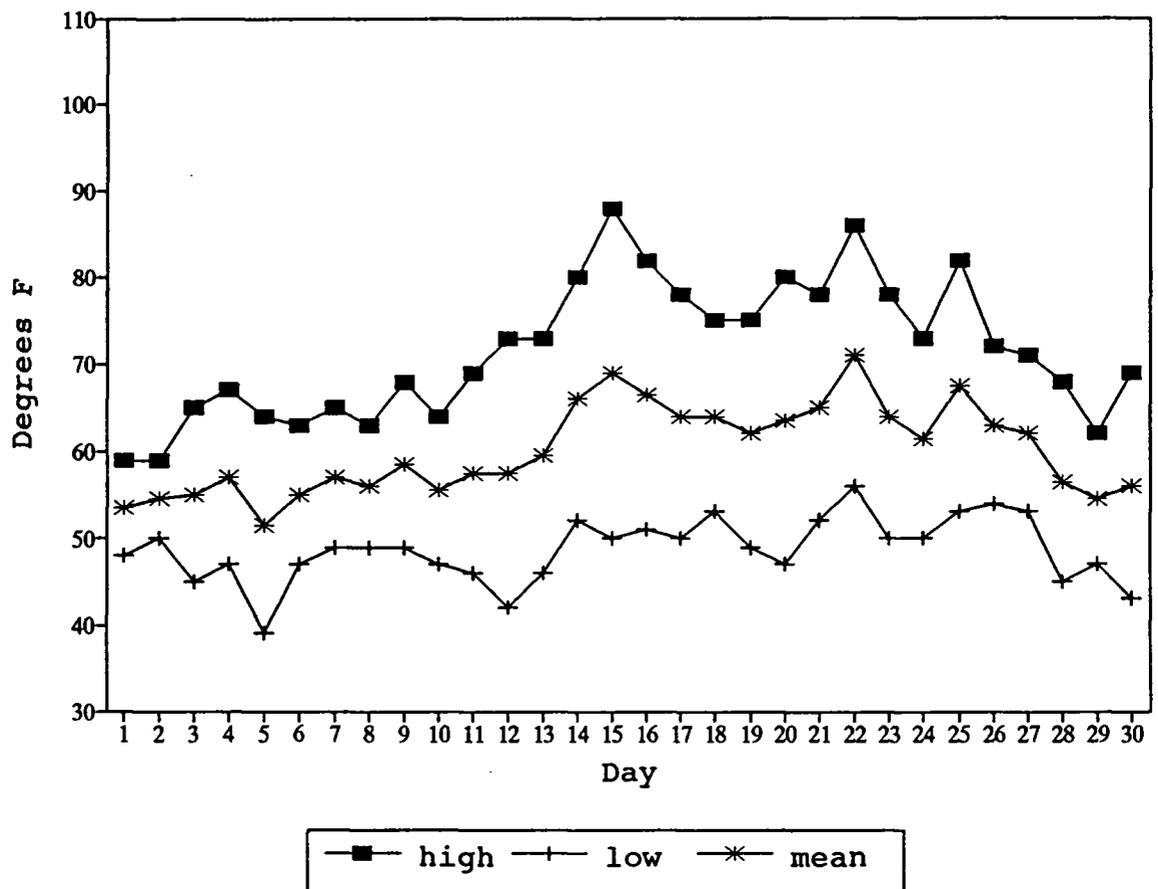


Fig. A.7. Temperatures of July, 1987.

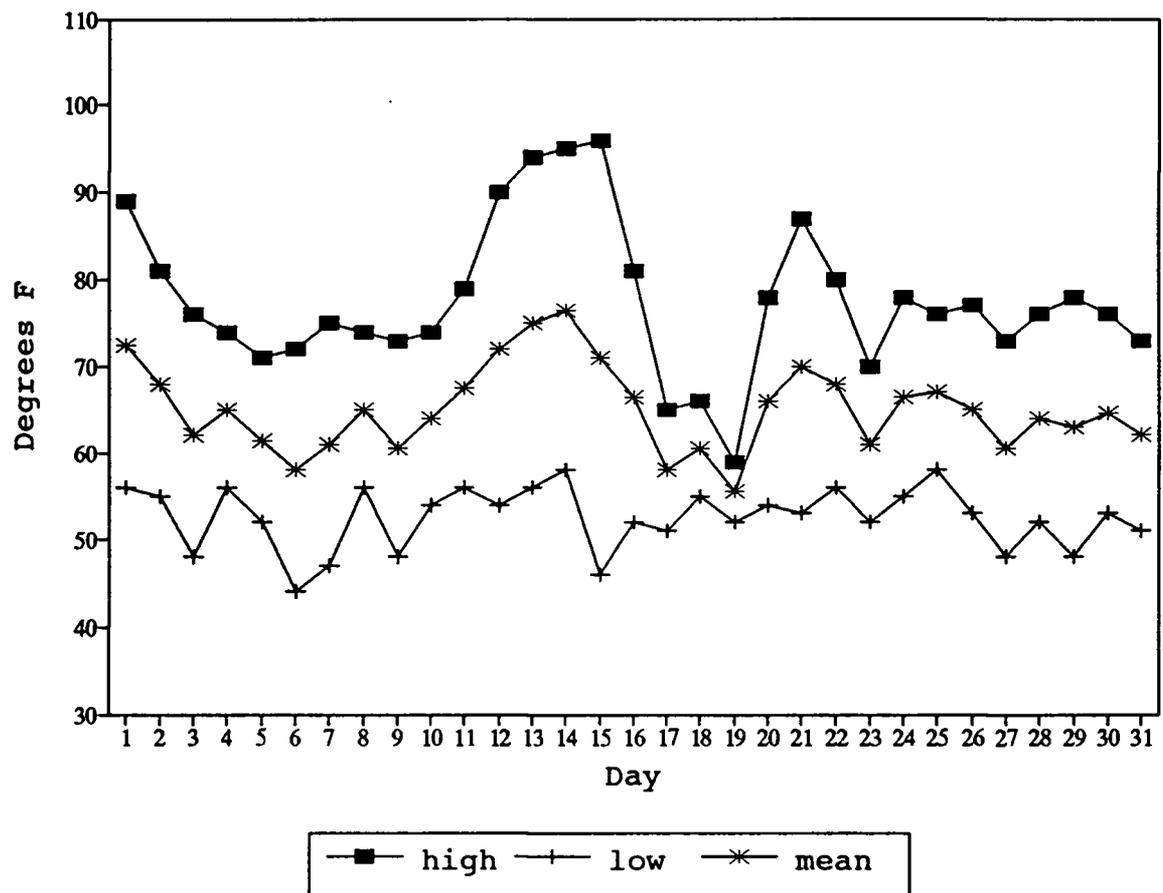


Fig. A.8. Temperatures of July, 1988.

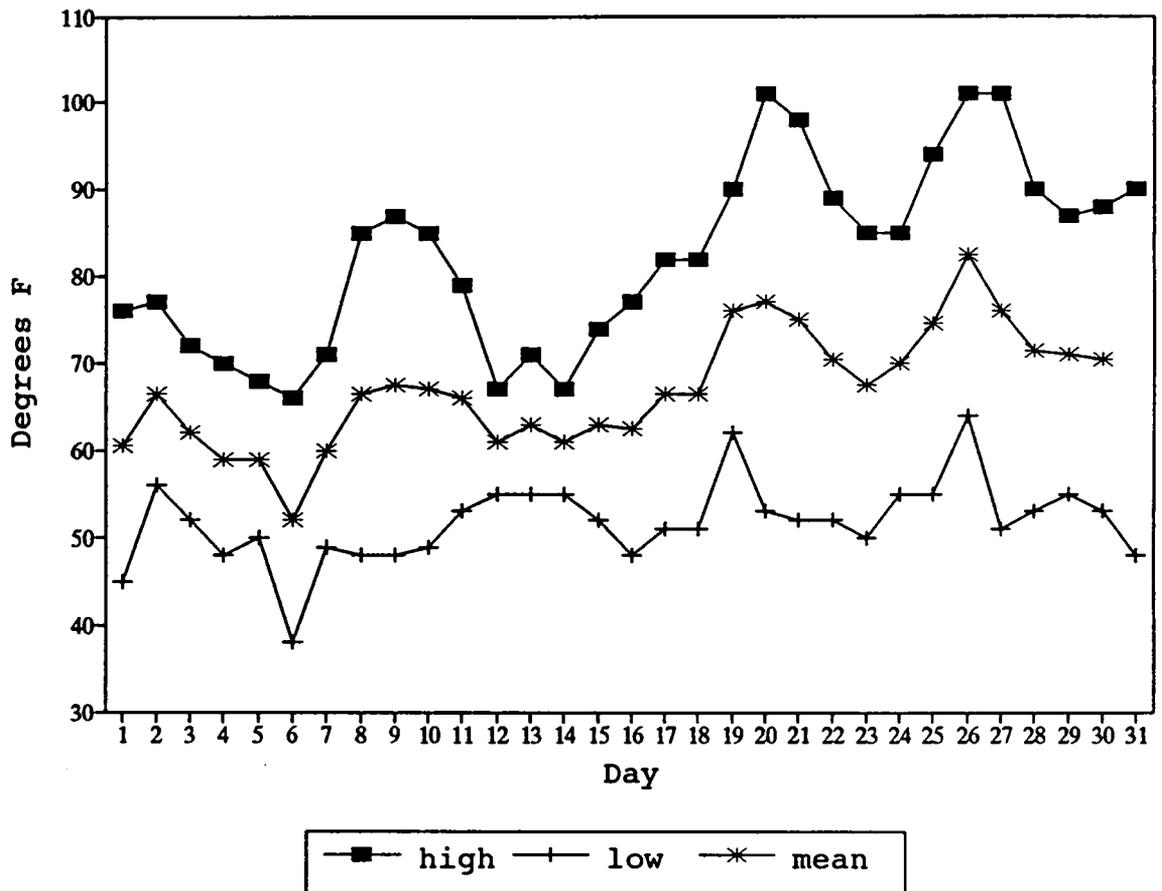


Fig. A.9. Temperatures of August, 1987.

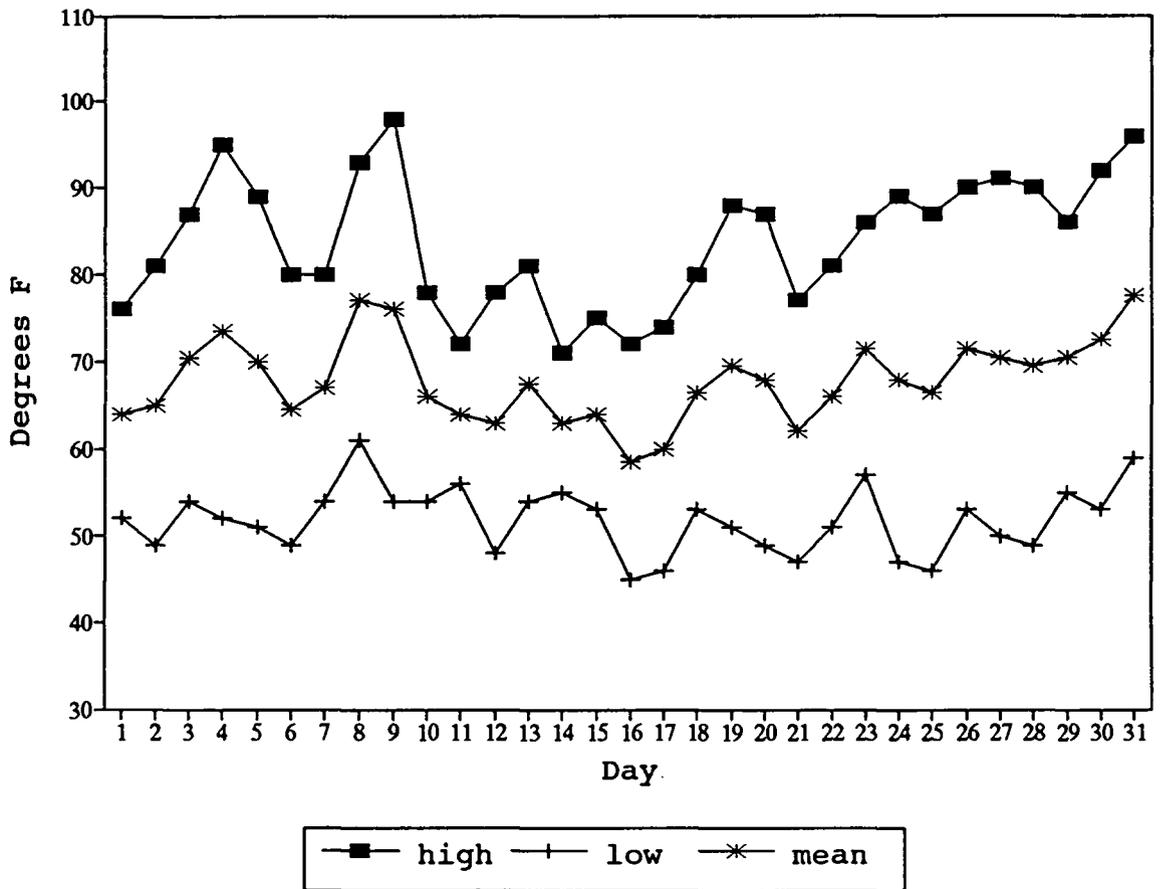


Fig. A.10. Temperatures of August, 1988.

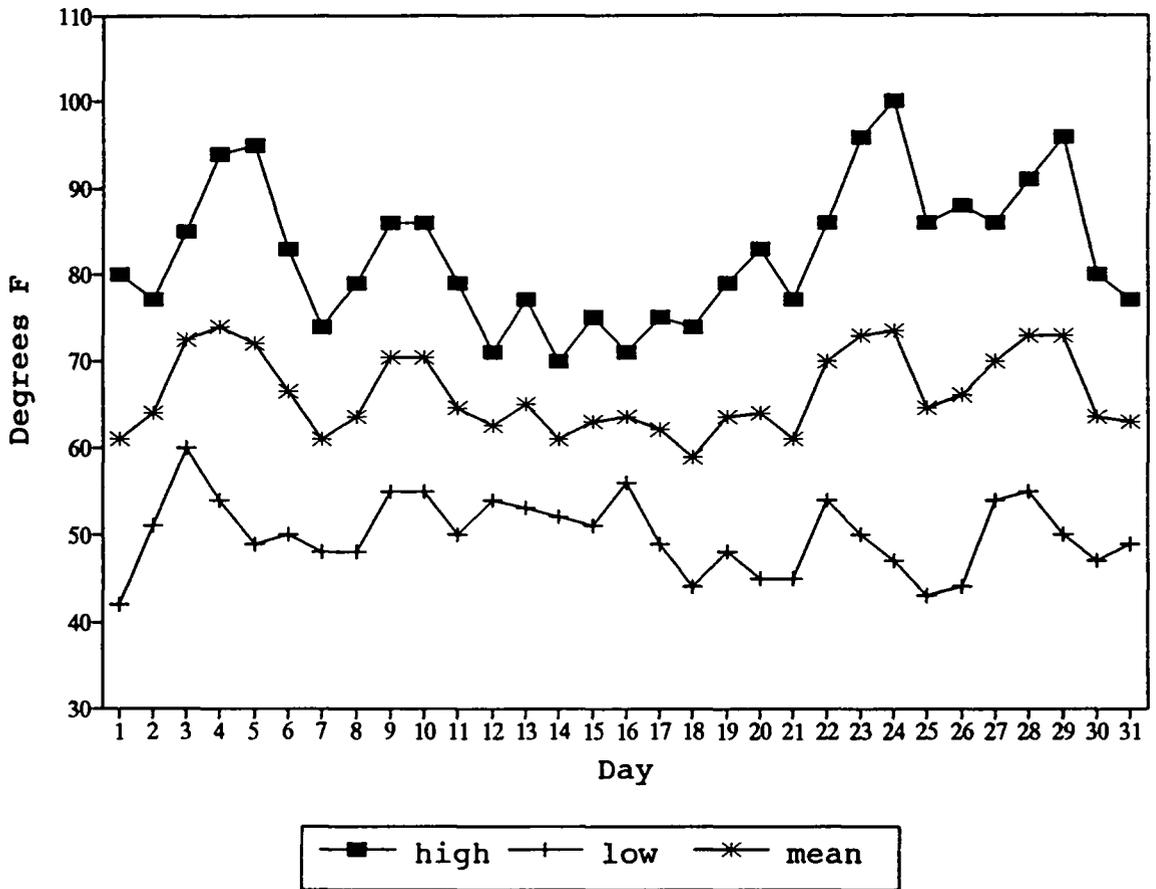


Fig. A.11. Temperatures of September, 1987.

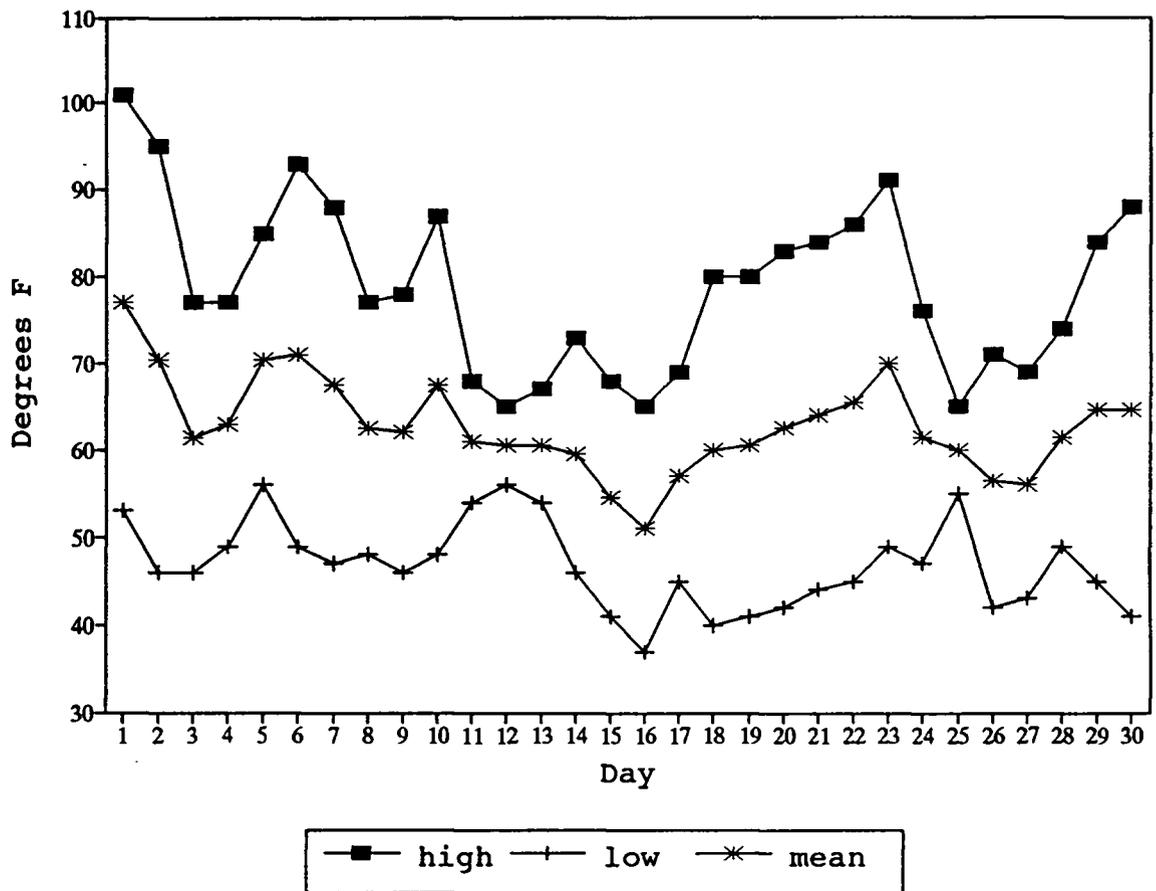


Fig. A.12. Temperatures of September, 1988.

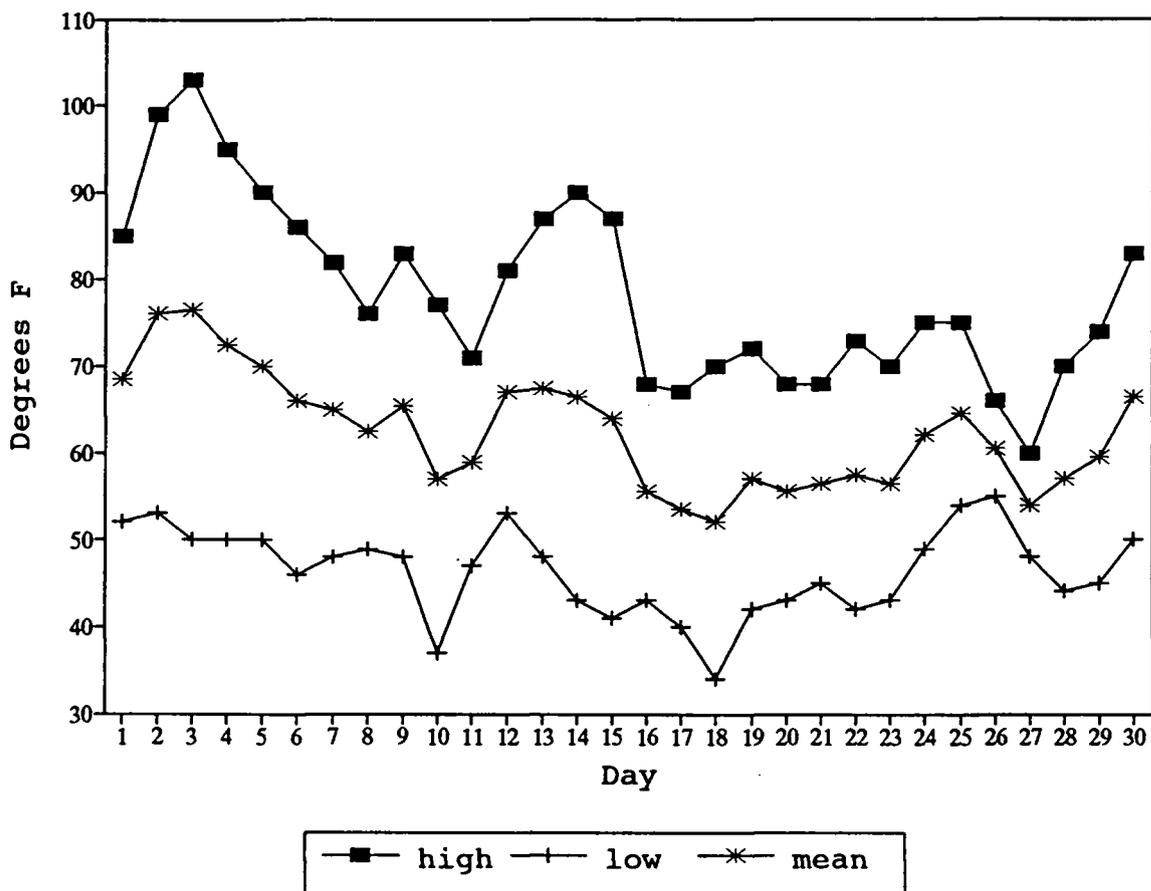


Fig. A.13. Standard curve for peroxide value.

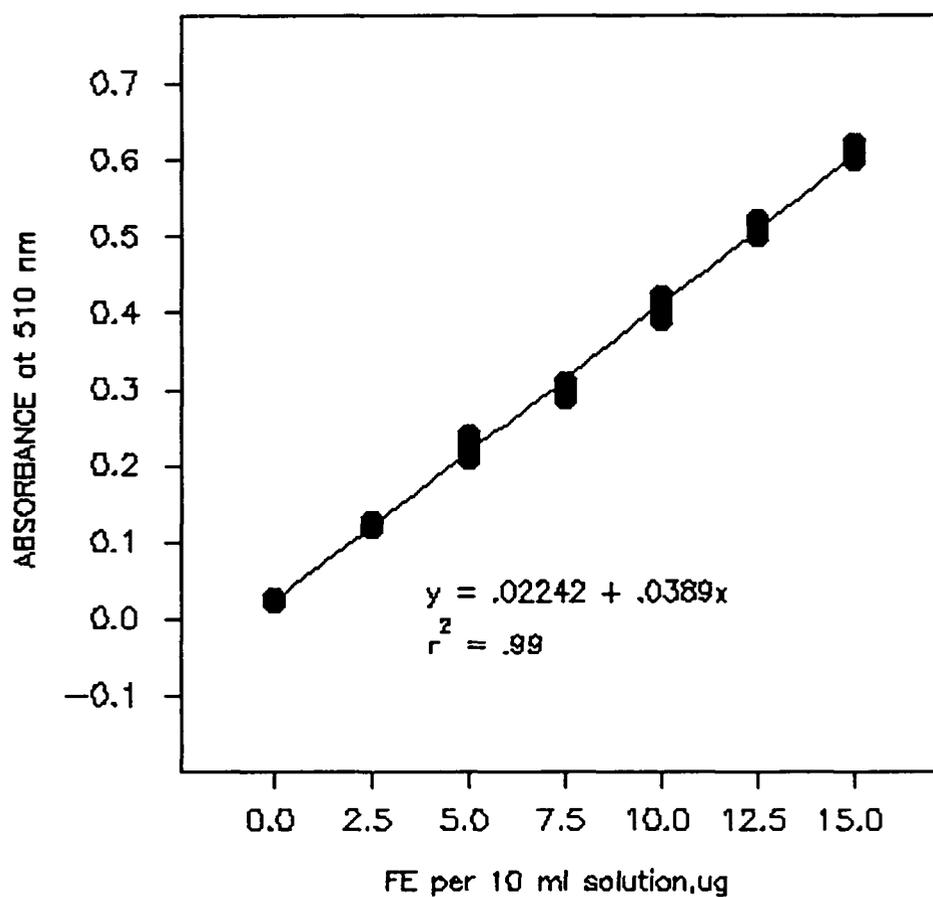


Fig. A.14. Tree nut per capita U.S. consumption (Anon, 1988).

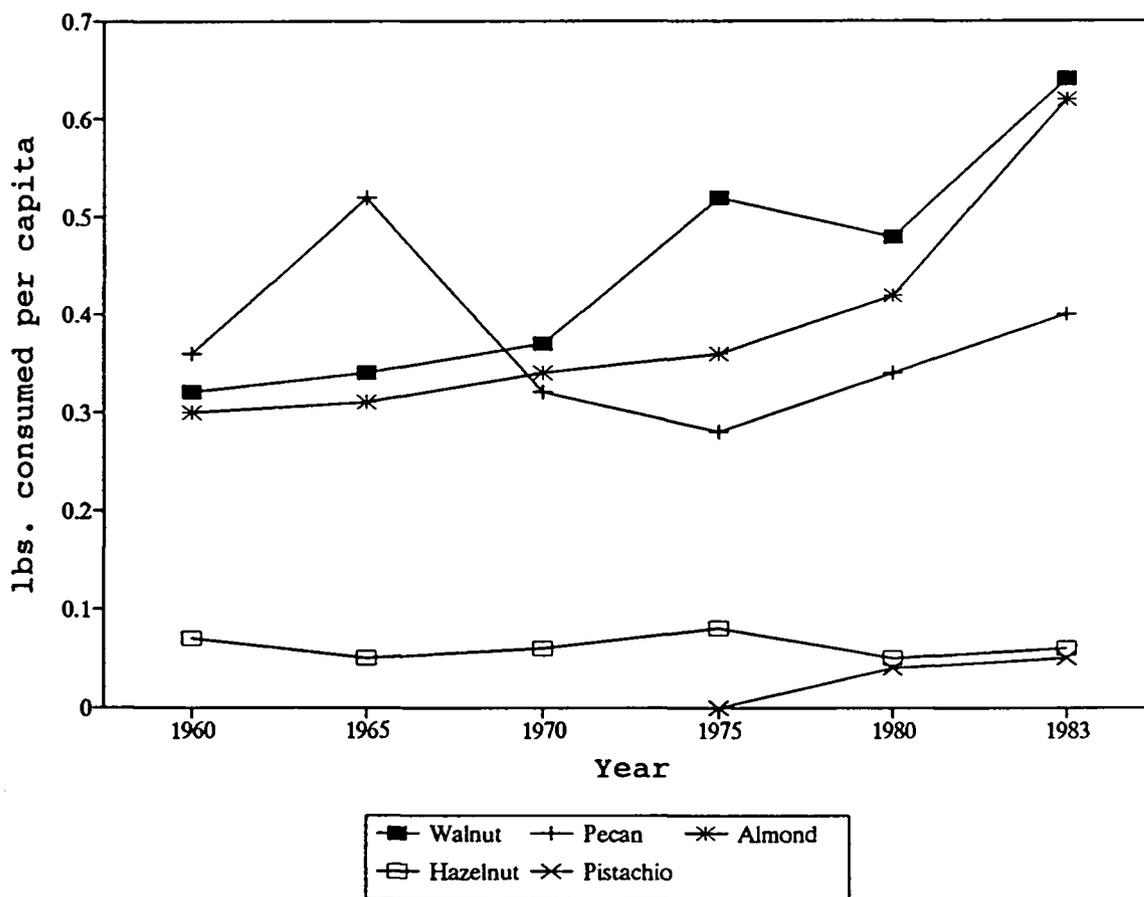


Fig. A.15. The relationship between alpha-tocopherol and oleic acid. (quadratic fit)

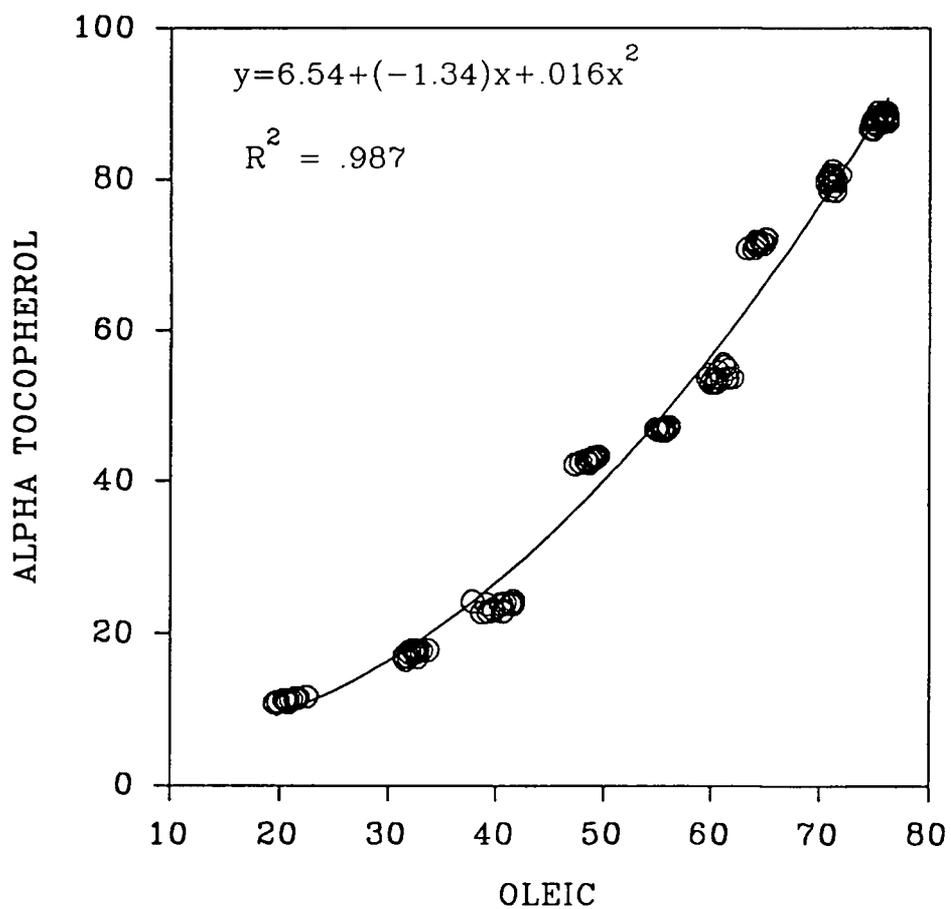


Fig. A.16. The relationship between gamma-tocopherol and linoleic acid. (quadratic fit)

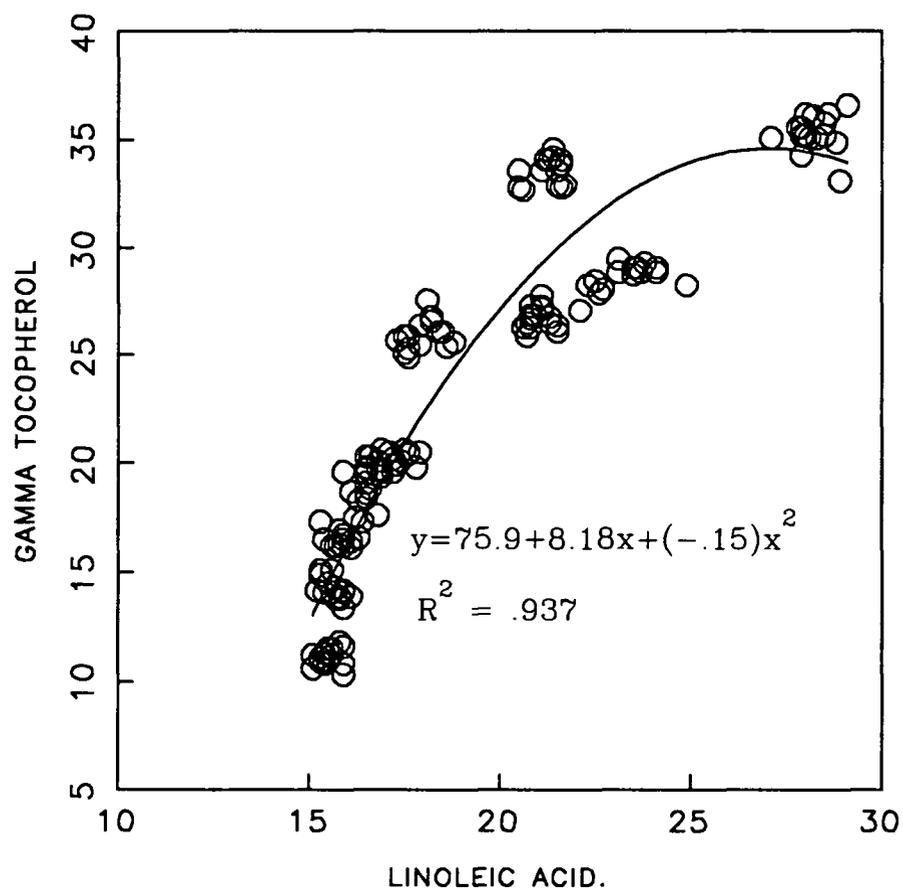


Fig. A.17. The relationship between beta-tocopherol and linolenic acid. (quadratic fit)

