

THE NATURE OF THE FLAVORS OF FILBERT NUTS
(Corylus avellana)

by

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A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1955

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Date thesis is presented June 22, 1954

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ACKNOWLEDGMENTS

The author wishes to express his earnest gratitude to Dr. Oliver J. Worthington, Professor of Food Technology, for proposing the topic of this investigation and for his advice and direction in the course of the work as well as during the preparation of the manuscript.

Thanks are due Dr. H. D. Reese, Department of Chemistry, for determination of optical rotations, and Dr. E. C. Bubl, Agricultural Experiment Station, for chromatographic identification of sucrose.

Appreciation is represented to all the staff members and graduate students for their valuable participation in the sensory tests.

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CHAPTER I

INTRODUCTION

Flavor is probably the most important single factor that decides the palatability and, consequently, the consumer's acceptability of any food product. Jacobs (22, p.3) assigns the failure of the dehydration industry at the end of world wars I and II to consumer reluctance because of lack of palatability. Crocker (8, pp.32-35), Moncrieff (32, pp.1-20), and Kirchner (24, p.259) all acknowledge the relation between food flavors and food acceptability.

Methods of processing may be manipulated so as to bring forth the best flavor that can be obtained from any product. An example is the remarkably simple method developed by the Eastern Regional Research Laboratories for increasing the flavor strength of maple syrup as much as four fold, by boiling under reflux, after the importance of such treatment in flavor development was found out (49, pp.1-2).

Knowledge of ingredients to which the flavor is due may be used to great advantages in developing synthetic flavors. Such flavors are very important when economic factors forbid the use of natural flavors alone. A still greater importance of synthetic flavors would be their use in developing palatable synthetic foods from such sources as marine vegetation (31, pp.31-37). With the world's food output far below population needs, and the degree of population increase much greater than the rise in the rate of food production, the value of such synthetic foods cannot be overemphasized. The Japanese synthetic

rice (23, p.60) and the Swift and Company synthetic meat¹ are two examples of what may be achieved in this field.

Information on the sources and properties of specific flavors as well as off-flavors in food products may very well be the starting point of salvaging many foods that are now considered inedible because of the development of rancidity or other objectionable changes. Such information is also needed for developing entirely new foods such as the Quinoa which was discovered by the Food and Agriculture Organization of the United Nations (35, p.4).

In comparing the number of fruits and vegetables whose flavors have been studied with those whose flavoring components have not been studied, Kirchner (24, pp.259-296), in the most comprehensive review of fruit and vegetable flavors, stresses the limited information available in this field. The flavors of little more than a dozen fruits and vegetables have been investigated and in some cases the work is quite incomplete.

Although filberts do not represent one of Oregon's main crops, they have undergone quite an extensive investigation as to their ultimate analysis (10) and new uses (30, 37, 21, 44). Such investigations are quite rational when it is realized that Oregon produces nearly all of the United States' crop of filberts. The Oregon Filbert Commission (34) was organized in 1951 to provide for scientific research relating to the use of filberts, and to further the development of the domestic filbert industry.

¹ Schultz, Harold William. Private information to the author, 1954.

The distinctive, but little known flavor of filberts was thought of as one factor that may create public demand. This work was undertaken as an exploratory investigation of a completely unknown field to obtain as much information as possible and to point out the way for any further investigations. All filberts used were of the Barcelona variety.

CHAPTER II

REVIEW OF LITERATURE

Flavor is a composite sensation that involves taste, odor, and the common chemical sense. Moncrieff (32, pp.127-146) defines the common chemical sense as that sensation which is due to chemical irritation, such as the lachrymatory effect of ammonia, the sternutatory effect of diphenyl chloroarsine, as well as the pungency of hot or biting spices like pepper and the coolness of menthol. This sense is distinct from smell, taste, touch, and pain, and has a separate set of receptors. The receptors are the free nerve endings of spinal and cranial nerves, and are comparable in distinctiveness with heat, cold, or pain receptors, but are more localized.

It is generally agreed that there are four main tastes: sweet, sour, salt, and bitter. Tastes are quite important in all foods, and the ratio of sweet taste to sour taste, usually called sugar/acid ratio, is very important in the case of fruits.

Odor is the factor which has the greatest distinctiveness. Moncrieff (32, p.5) describes how grated turnips, grated apples, and grated onions all taste the same if the nose is held while they are eaten. Such a practice prevents the odor from reaching the odor-detection area which is located high in the nasal cavity (8, p.9).

The literature concerning the flavors of fruits, vegetables, and other food items is very meager. The excellent review of Kirchner (24, pp.259-296) discusses most of the work done until 1948 on the volatile flavors of apples, cherries, oranges, peaches,

pineapple, raspberries, strawberries, grapes, lemons, and bananas. He also discusses most of the work done on the essential oils and flavor components of carrots, celery, garlic, onion, *Allium scorodoprasum* L., parsley, parsnip, radish, watercress, garden cress, potatoes, cucumbers, bread, rye bread, mushrooms, maple syrup, molasses, and rather incidentally mustard oils. A great deal of work has been done on coffee, and Kirchner (24, pp.290-296) cites in his paper 19 references concerned with coffee flavor and off-flavor. The results obtained show the difficulties involved in flavor studies, and do not definitely establish the nature of the chemical components responsible for the flavor. The work on cocoa and tea resulted in the identification of different types of compounds, but those mainly or uniquely responsible for the flavor do not seem to be definitely identified.

Kirchner is of the opinion that deficiency of knowledge is mainly due to the very small quantities of flavoring material present, and in some cases to their unstable constitution, "Usually it is necessary to handle tons of raw material to obtain a mere hundred grams of the flavoring oil. Furthermore, when this oil is split into its numerous parts, the yields of some components may be only a fraction of a gram." Minute as they may be, these constituents inevitably provide their share to consummate the characteristic flavor of the product.

Kirchner and coworkers (25, pp.510-512) report on the volatile water-soluble constituents of grapefruit juice. They used 2760 gallons of freshly reamed Marsh seedless grapefruit juice, 2470 gallons

of freshly canned grapefruit juice, and 2470 gallons of stored canned juice. Acetaldehyde was identified in the fresh juice fraction as well as in the freshly canned juice and the stored canned juice. The amounts of acetaldehyde were 1.45, 0.33, and 0.6 p.p.m. respectively. Ethyl alcohol was identified in much greater amounts in all three fractions. The freshly canned juice had a small amount of volatile acids and a trace of furfural not present in the fresh juice. The stored juice had a considerable increase in the volatile acids, methanol and furfural. The amounts reported are 27.8, 23, and 8.2 p.p.m. respectively. Kirchner and Miller (26, pp.512-518) report on the volatile water-insoluble constituents of the same juices. They separated 21 compounds and three fractions of a complex nature. The amounts in which these compounds were present ranged from a trace to a maximum of 17.7 p.p.m. Both studies were concerned with the effect of canning and storage on those constituents.

Meat flavor has been studied by several workers and the information reported is very contradictory. Salomon (43, p.91) concluded that raw meat, in its fresh state, has no particular flavor. He assumed that the "roasted meat" taste is partially derived from the heated fat. Howe and Barbella (20, p.201) state that the responsible constituents of meat flavor appear to consist of a composite of salts, acids, and a group of products resulting from heating extractives, possibly disintegration products of proteins, and lipids. They claim the presence of inherent flavors in the fat of meat, that are characteristic of species, which become evident when the fat is heated. Crocker (9, pp.179-183) examined beef, lamb, pork and

chicken for the location and nature of their flavor. All the meats examined seemed to have a weak, fundamental flavor when raw, on which was superimposed flavors distinctive of the species, food, and environment of the animal. The flavors that developed on cooking likewise were similar for the various meats, again modified by the species, food, and environment of the animal, although even these characteristics tended to be lost with prolonged cooking. Crocker concluded that the flavor of raw meat resided in the juice, while most of the flavor created by heating came from action of heat on the solid protein. The differences seemed to be more in quantity than in quality. Bouthilet (3, pp.322-325) showed that chicken flavor could be steam-distilled from chicken broth. The flavor, when added to a broth of synthetic non-volatile materials, was indistinguishable from the flavor of the original natural chicken broth. The same author found later (4, pp.137-141 and 5, pp.201-204) by fractionation of the steam distillate that sulfur compounds are an integral part of the flavor, and concluded that the meaty flavor in chicken meat is due to a compound associated with the meat fibers rather than with the fat. In a study initiated at the Western Utilization Research Branch, Pippen and coworkers (41, pp.364-367) studied the physical localization of the flavor components of chicken by determining the relative contribution of poultry gross parts or fraction of the carcass to the flavor of the broth. Their results showed the fat to be of minor importance, though it contributes to the aroma of the broth. Meat was a better source of flavor than bones, skin, or a composite of all three parts. They found that the extraction of flavor precursors may

be readily accomplished from the cut-up raw meat by cold water.

A thorough review of the literature since 1907 (1) revealed that nothing has been published on the nature of the flavors of edible nuts in general and filberts in particular. Griebel (16, pp.105-110) seems to have identified acetaldehyde in a large number of nuts and other materials. Due to the non-availability of the original reference it is not known whether filberts were included. The study seems to be concerned with intermediate metabolism of fruits, nuts, tubers, leaves, petals, and fungi, and not directly with flavor. Much work has been done on the flavor of bitter almonds which originates from the hydrolysis of the glycoside fraction of that nut to yield benzaldehyde.

Glycosides are widely distributed in nature but usually occur in small amounts. They are usually found in the fruit, bark or roots of plants, although they are frequently present in the leaves (15, p.713). The functions of glycosides in the plants are not definitely established, though a variety of functions has been suggested. According to McIlroy (29, p.9), glycosides may serve as sugar reserves, as waste products of plant metabolism, as a means of detoxication, to regulate osmosis, and to stabilize labile substances or regulate the supply of substances important in metabolism. Pigman (40, p.264) states that a great variety of naturally-occurring organic substances, such as natural coloring matters, aromatic flavoring principles, and drugs, are found in glycosidic combination.

The best known glycoside is probably amygdalin which is obtained from the kernels of the bitter almond, *Prunus amygdalus*, var. *amara*, in amounts ranging from 2.5 per cent to 3.5 per cent. It also occurs in

smaller amounts in the kernels of the peach, plum, apricot, and most fruits belonging to the Rosaceae. Benzaldehyde is the chief constituent of the essential oil of bitter almonds, prepared by distillation from the seed (50, p.483) after hydrolysis.

The commercial "Pure Almond Extract" is actually a solution of bitter almond oil, mainly benzaldehyde, in alcohol, according to the label. Other nut-flavors on the market are all synthetic, and are either formulated by trial and error methods, or the work involved in their discovery has never been published for special reasons.

The naturally-occurring glycosides are generally colorless, crystalline neutral compounds showing optical activity. With one or two rare exceptions (29, p.5), they have the β -configuration, and their enzymatic hydrolysis is achieved only by emulsin. They are all hydrolyzed by heating with dilute mineral acids to yield a sugar and an organic residue called the aglycone, which in some cases, is the principal characteristic flavor compound for their source materials.

On account of the very small amount of glycosides present in plant tissues and the fact that, as a rule, glycosides do not form characteristic insoluble derivatives which allow for their isolation and identification, it is difficult to discover new glycosides and still more difficult to determine their constitution (15, p.713).

A patent was issued to Stacom (47) in which is described the method of separating the fats and flavoring ingredients from the fibers, in fat-containing plant substances. The method comprises heating the substance to a temperature at which the fats become plastic

but not liquid and applying pressure of a predetermined degree to the heated material. It is claimed that this method is applicable to beans, seeds, and nuts, such as cocoabeans, peanuts, walnuts, almonds, filberts, cotton seeds, and such other fat-containing plant substances as fall within the general terminology of the terms. The method involves the use of a specially constructed press disclosed in another patent (46).

One of the major difficulties in flavor studies is the lack of a reliable method for the measurement of odor and the need for such a method is generally recognized (11, p.300). When the chemical entity of the compounds responsible for the aroma of a certain food product is known, those compounds may be chemically determined and a quantitative measure of the odor in the product may thus be obtained. The chemical estimation of aroma in butter and butter cultures by determination of acetylmethylcarbinol and diacetyl which compounds are known to impart butter aroma, is reported by Parker and Shadwick (36, pp.227-235). When the chemical composition of the flavor compounds is not known, as is the case with the absolute majority of food products, such quantitative determination introduces a very difficult problem.

Man has developed objective measures for most of his perceptions, like mass, color, sound, and texture, yet odor perception is still far from having a criterion. Many methods have been suggested for odor evaluation and estimation, but their use is generally limited to some restricted purposes.

Sensory methods depend on the use of trained judges to compare between odors and establish existing differences or preferences. These methods are usually subjective, but can be depended upon as an objective measure by the application of statistical methods.

Crocker (8, pp.12-14) describes the Crocker-Henderson system for measuring odor intensities. It is assumed in that system that the human nose is provided with four kinds of odor nerves, that every odorous substance stimulates all four kinds of these nerves simultaneously to an extent characteristic of that substance and of its concentration, and that the odor sensation chord thus created by the excitation of nerve endings is capable of originating a distinctive odor impression. According to this system an odor can be represented as a four-digit number: the first digit is the measure of fragrance, the second of acidity, the third of burntiness, and the fourth of caprylic character. Digits of 0 to 8 are assigned for each component in the odor in question, and this component is determined by comparison against the same component in the odors of the chemicals of a set of accepted standards. It is obvious that such a system requires a great degree of training and is dependent upon the acuity of the judges.

Moncrieff (32, pp.86-89) describes a number of methods by which the intensity of odors can be measured using certain devices. He especially describes Zwaardemaker's Olfactometer, the Fair and Wells Osmoscope, and different other methods. All these methods depend on human appraisal for the presence or absence of the odor under question. Such judgment is known to differ from person to person and to vary in

the same person according to many physical and psychological conditions. Such devices seem to have been used more for studying human olfaction than for measuring odors as such.

A new approach to flavor problems has been suggested by Cairncross and Sjöström (6, pp.303-311). The system involves a descriptive analysis of flavor which expresses in common language terms the characteristic notes of both aroma and flavor, their order of appearance and intensities, and the amplitudes of total aroma and flavor. The findings of the individual trained judges are later discussed in open panel, and a single composite decision is reached. This is the so-called "Flavor Profile" and may be easily represented by a diagram. To determine the effect of an experimental modification of a sample, it is only necessary to compare its composite profile with that of the original sample. It is apparent that this system, though it represents a promising approach to subjective analysis of the character of flavor with an attempt at quantification, yet its application will have to be of limited use until the descriptive terminology of flavor and aroma characteristics of the different materials are universally agreed upon.

The determination of odor intensity by chemical methods has been used by several workers. Such methods depend on the theory that to be odorous a substance must be oxidizable. Moncrieff (32, p.309) states that "No doubt there is a parallelism between odor, chemical reactivity and oxidizability." Lang and coworkers (27, pp.490-494) devised a method for determining the volatile constituents which may

be assumed to be responsible for the odors encountered in fish. The method is based on the fact that proteinaceous foodstuffs emit odorous substances as they undergo spoilage during deleterious handling and storage. Most types of volatile odorous organic compounds which conceivably might be formed during spoilage are oxidizable. A special apparatus was constructed by which a measured volume of purified air is aspirated through a suitably prepared sample of a material, then through an alkaline potassium permanganate solution, all solutions being at room temperature. The amount of reduction of this oxidizing reagent is used as the measure of the concentration of the volatile odoriferous substances. In preliminary studies, Farber (11, pp.300-304) applied this method to the determination of volatile reducing substances in a number of commodities associated with distinct osmotic stimulation. Coffee, bread, spices, food seasoning, fresh citrus peel, fresh fruits, dried fruits, flowers, and oils were all run and their corresponding volatile reducing substances determined. Farber and Cederquist (12, pp.478-480) represent data intended to point out that the determination of the volatile reducing substances content offers a useful tool in an approach to the establishment of a quality rating for packs of fish. Farber recognizes that this method permits only the measurement of total volatile reducing material present in a sample regardless of whether it is pleasing or otherwise. The size of the samples that may be used in Farber's apparatus ranges from 1 gram of the dry material either by itself or suspended in 10 ml of water for some products, to 5 ml of liquid for oils and

materials which can be pressed, to 10 grams for prunes and raisins. It is apparent that such small samples cannot be representative but of very small lots, and sampling of any medium sized lot, even for laboratory work, would have to be accomplished under very elaborate conditions. The apparatus itself is not compact and needs a train of five washing-bottles for air purification, in addition to the aeration flask, two reaction vessels, and an air measuring instrument. The aeration flask is a specially built piece which is very fragile and difficult to clean. Furthermore, introduction of air into samples creates the possibility of the oxidation of the volatile substances being measured. Those substances are assumed to be very reactive and easily oxidizable; an assumption which is actually the basis for the method itself.

Friedman and Klaas (13, pp.47-61) used a very similar method for the determination of ethyl alcohol in blood, saliva, and urine. They separated the alcohol from other constituents by distillation after the addition of reagents which remove many of the commonly occurring volatile substances. These workers commend the high degree of reliability of the method as indicated by practically quantitative recovery of alcohol from pure solutions as well as when added to blood and urine. They obtained a consistent value for the normal alcohol content of blood, saliva, and urine. This method of separation of volatile components followed by determination of their oxidizability by an alkaline potassium permanganate solution was recently employed by the Western Regional Research Laboratory (17, pp.1169-1170) to obtain a measure of the volatile reducing components of different

fruits and fruit juices. A special vacuum distillation apparatus for the separation of volatile flavor compounds from fruit products was developed by which all the volatiles from fruit samples may be obtained without alteration due to heat damage such as occurs during steam distillation at atmospheric pressure. Representative data indicate that fairly reproducible results are given by that procedure. This method eliminates both the possibility of oxidizing the volatile components which may take place in aeration methods, and the danger of altering any heat sensitive compounds in atmospheric distillation methods.

CHAPTER III

PRELIMINARY ORGANOLEPTIC EXAMINATION OF FILBERT FLAVOR

1. Components of Filbert Flavor

The flavor of filberts, like all other flavors, comprises taste and odor. There are only three generally perceivable tastes in the filbert: sweetness, sourness, and bitterness. The sourness is barely detectable, and produces with the noticeable sweetness the recognizable taste of the peeled kernel. The bitterness seems to be provided by the pellicle, as the peeled nuts do not reveal a bitter taste, while saltiness is entirely indiscernible in the filbert. This is the over-all taste sensation procured from filberts masticated while the nasal cavities are closed. When the nasal cavities are open while eating the nut, an entirely different sensation manifests itself and makes the nut distinguishable. As a result of such observation with all persons available for this subjective sensory test, it was deduced that the odor of filberts constitutes the major fraction of flavor, and it may be decidedly concluded that the characteristic filbert flavor is principally due to the volatile components of the nut. The texture is identical with that realized from other common edible nuts and there is none of Moncrieff's common chemical sense (32, pp.127-146).

2. Effect of Removing the Pellicle on Organoleptic Evaluation of the Filbert

As removing the pellicle is thought of as a useful practice, and is being now studied in this department for commercial utilization, it

was decided to find out whether such treatment produces a difference in the flavor. An organoleptic, triangular test was run with one batch of nuts, part of which had been previously peeled. The nuts were ground in a peanut-butter mill (Bauer), then mixed evenly with a 1 per cent solution of Amaranth dye in distilled water in order to mask the difference in color between peeled and unpeeled nuts. This resulted in two similarly colored pastes that were undetectable from each other especially under the blue light of the testing booths. The judges were asked to point out the odd sample and to state their preference. Out of 45 judgments, 28 gave correct answers. This is significant at the 0.1 per cent level according to Roessler, Warren and Guymon (42, p.504), and it may be concluded that there is a flavor difference between peeled and unpeeled nuts. Of the 28 correct answers, 17 preferred the peeled nuts, 8 preferred the unpeeled, and 5 had no preference. According to Harrison and Elder (18, pp.434-438) this is not significant, and we can reach the conclusion that among the group of judges participating in this test there was no preference between peeled and unpeeled nuts. It may mean that some of the tasters preferred peeled nuts and others preferred unpeeled.

3. Volatile Reducing Substances from Different Species of Nuts

Filberts have been rated either as possessing a very strong flavor that is too potent for the people tasting them, or as having a very weak flavor. To find out how they compare with other common nuts, the odors of representative commercial samples of almonds, walnuts, pecans, and roasted peanuts have been quantitatively estimated by the method of

volatile reducing substances described in Chapter IV. The results obtained are compared with results obtained on typical filberts as shown in Table 1. No conclusive evidence is drawn from this comparison, as the volatile reducing substances estimated may completely differ as to reducing power from one kind of nuts to the other. However, if it is realized that those substances which volatilize under the same conditions of temperature and pressure probably possess the same or very similar composition, it may be safely assumed that the results obtained show filberts to possess an odor which is comparable in strength to odors of other common nuts. The filberts appear to have more volatile reducing substances, but one cannot vouch for the representativeness of the samples.

TABLE 1

VOLATILE REDUCING SUBSTANCES OF COMMERCIAL SAMPLES OF DIFFERENT SPECIES OF NUTS*

	Roasted Peeled Ground Filberts		Roasted Peeled Ground Peanuts		Raw, not peeled, ground							
	1	2	1	2	Filberts		Walnuts		Almonds		Pecans	
	1	2	1	2	1	2	1	2	1	2	1	2
a.	19.30	20.27	9.31	9.30	9.00	8.78	6.88	5.94	3.60	3.35	6.73	7.07
b.	19.67	20.12	8.96	9.12	9.00	8.33	6.36	5.71	3.22	2.98	5.90	6.76
c.	19.38	19.97	9.31	8.90	8.85	8.71	5.61	5.42	3.90	3.12	6.50	6.99
d.	19.45	20.12	9.20	9.11	8.95	8.61	6.28	5.69	3.57	3.15	6.37	6.94

* In microequivalents of reduction per gram

1 and 2 ——— Duplicate distillations

a., b., and c.— Triplicate titrations

d. ————— Column average

CHAPTER IV

EFFECT OF DIFFERENT COMMERCIAL PRACTICES ON THE ODOR INTENSITY
OF THE FILBERT NUT1. Method of Quantitative Estimation of Odor

The method used in this work is essentially the distillation of an accurately weighed sample of filberts with a known amount of distilled water, under a known and practically constant vacuum, at a low and quite a constant temperature, for a constant time. The distillate is collected volumetrically, and a 10 ml aliquot is oxidized by 5 ml of 0.1 N potassium permanganate solution in a 1 N sodium hydroxide solution. The oxidation is carried out in a 125 ml Erlenmeyer flask covered with a 100 ml beaker in a boiling water bath for 20 minutes. After cooling, the mixture is acidified with 5 ml of 6 N sulfuric acid, and 5 ml of a 20 per cent potassium iodide solution in 0.1 per cent sodium carbonate are added. The free iodine is titrated with 0.02 N sodium thiosulfate using a starch indicator. The difference between such a titration and a blank run on 10 ml of distilled water is multiplied by 20 to give the microequivalents of reduction per 10 ml of distillate. From this, the microequivalents of reduction per gram of filberts are calculated.

This method is based upon the assumption that volatile components responsible for the odor of filberts are reducing substances. It was originally used by Friedman and Klaas (13, pp.47-61) for the determination of ethyl alcohol in biological material, was used by Ueno (48, pp.611-617) to measure the aroma of tea, was adapted by

Lang and coworkers (26, pp.490-494) and by Farber (11, pp.300-304 and 12, pp.478-480) for chemical evaluation of odor intensity of fish and other products, and was recently used by Guadagni and Dimick (17, pp.1169-1170) for the estimation of volatile components in different fruits.

The apparatus used for the distillation is basically that described by Morrow and Sandstrom (33, p.71) for the preparation of amino acids. The condenser is modified by joining to it the bulb of a 200 ml round bottom flask as a receptacle for a constant volume of distillate. The guard flask is replaced by an ice-water trap which is connected to a vacuum gauge. This was considered satisfactory after a dry-ice trap before the vacuum pump did not contain any distillate. The aeration capillary is discarded to avoid any possibility of the oxidation of the volatile substances, and the temperature is recorded by a thermometer in the side arm of the Claisen distilling flask as well as a thermometer immersed in the distilling liquid. Distillation was possible under the prevailing conditions at a temperature average of 24° to 25°C, and a vacuum of 28.25" to 28.80" of mercury. The amount of distillate ranged from 183.5 ml to 200 ml, and the weight of the filberts used ranged from 50 gram to 51.20 gram samples. The time required to obtain the necessary amount of distillate was two hours. A blank distillation revealed that the rubber stoppers used in the apparatus do not incorporate any volatile reducing substances to the distillate. The apparatus is shown in Plate I, page 22.

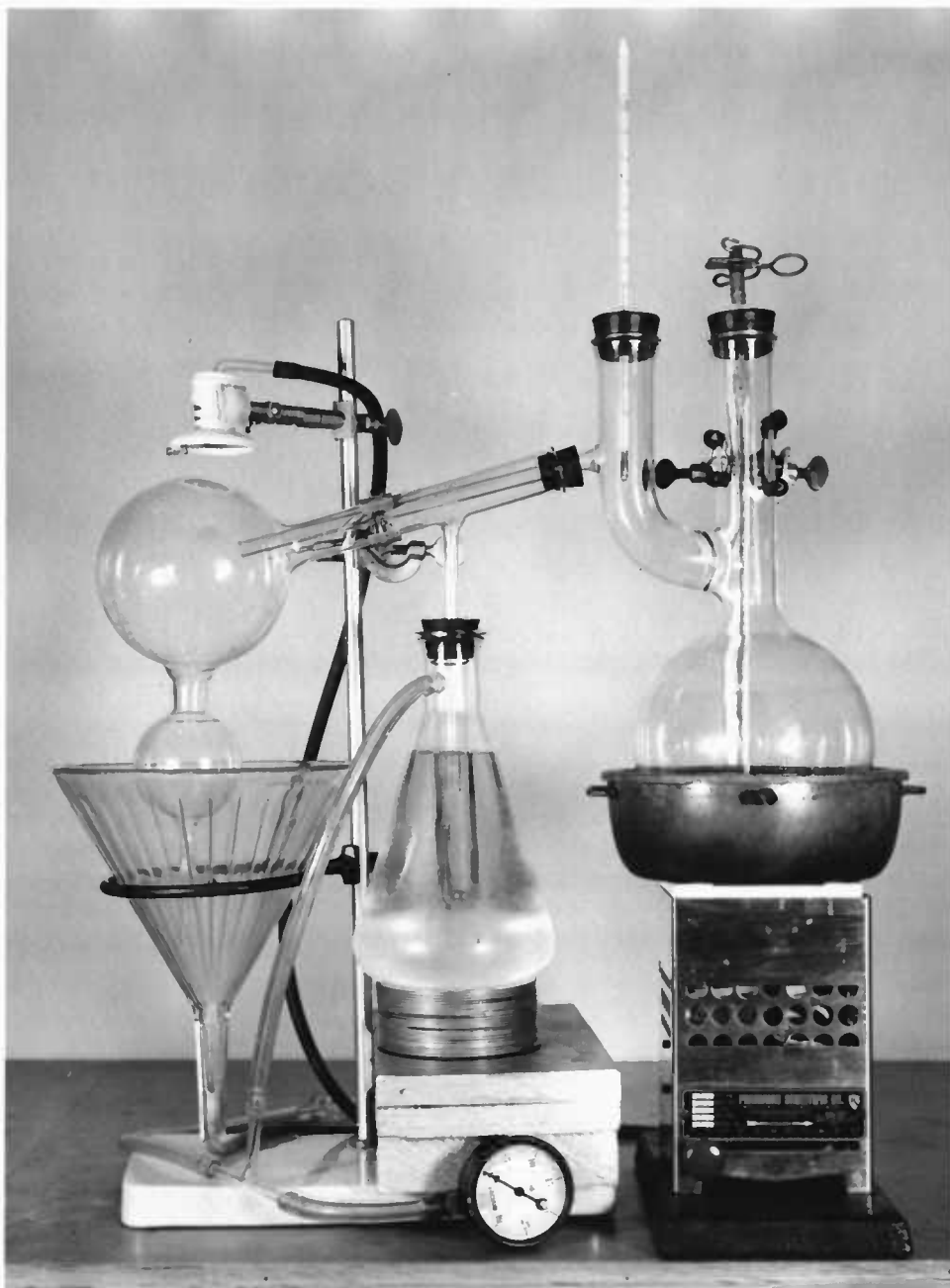


Plate I

2. Experimental Design and Results

To study the effect of peeling, grinding, roasting as well as enzyme action on the amount of volatiles of filberts, 18 different determinations were carried out on nine portions of a single batch of filberts receiving the following treatments:

1. Unpeeled, raw, and whole filberts.
2. Peeled, raw, and whole filberts.
3. Unpeeled, roasted, and whole filberts.
4. Peeled, roasted, and whole filberts.
5. Unpeeled, raw, and ground filberts.
6. Peeled, raw, and ground filberts.
7. Peeled, roasted, and ground filberts.
8. Peeled, raw, and ground filberts; incubated at 37°C for 10 minutes.
9. Peeled, raw, and ground filberts; enzyme inactivated.

Peeling includes an alkali dip, an acid dip, washing with water and drying.

Roasting was done in a baking oven at 350°F for 15 to 20 minutes.

Grinding was carried out, in a peanut-butter mill (Bauer), separately for each determination.

Incubation was tried to simulate conditions in the mouth while masticating the nuts.

Enzyme inactivation was undertaken after grinding by boiling 250 ml of distilled water and putting the nuts into them for 3 minutes; then cooling before distilling. The catalase and peroxidase inactivation tests were used to determine the suitability of this treatment

for inactivating the enzymes present in filberts.

All samples were mixed with 250 ml of distilled water before distillation, and three determinations of microequivalents of reduction were run on every distillate. Two lots of every treatment were used, and the results obtained are shown in Table 2.

Analysis of variance results, Table 3, show very plainly that the different treatments have an effect on the amount of volatiles distilled from the filberts as determined by the method used. The F value for preparation lots (duplicate runs) is not significant at the 5 per cent level, which is an indication of the accuracy of the method.

By pooling the means of the two lots of every treatment, finding the treatment mean, and applying the method of the least significant difference, the various treated filberts can be ranked according to the magnitude of the amount of volatiles as shown in Table 4.

TABLE 2

EFFECT OF DIFFERENT TREATMENTS ON VOLATILE REDUCING SUBSTANCES OF FILBERTS*

														Peeled raw ground incubated 37 C-10m.		Peeled raw ground enzyme inac.		
Unpeeled raw whole		Peeled raw whole		Unpeeled roasted whole		Peeled roasted whole		Unpeeled raw ground		Peeled raw ground		Peeled roasted ground						
1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	
a.	4.54	4.91	3.77	3.57	5.11	5.95	7.43	8.41	9.00	8.78	9.10	8.65	19.30	20.27	9.54	9.99	4.10	4.86
b.	4.69	3.63	3.30	3.64	5.70	6.33	7.86	7.75	9.00	8.33	8.34	9.02	19.67	20.12	9.91	9.99	4.25	4.42
c.	4.39	4.38	3.93	3.50	5.47	6.70	8.24	8.12	8.85	8.71	10.23	9.63	19.38	19.97	9.54	9.40	5.22	4.93
d.	4.54	4.31	3.67	3.57	5.43	6.32	7.84	8.09	8.95	8.61	9.22	9.10	19.45	20.12	9.96	9.79	4.52	4.73

* ————— In microequivalents of reduction per gram

1 and 2 ————— Duplicate distillations

a., b., and c.— Triplicate titrations

d. ————— Column average

TABLE 3
ANALYSIS OF VARIANCE

Variation Due to:	Sum of Squares	Degrees of Freedom	Mean Square	F	Remarks
Treatment	1147.5326	8	143.4416	796.81	Significant***
Prep. Lot	0.3112	1	0.3112	1.73	Not-significant
Error	7.9289	44	0.1802		
Total	1155.7727	53			

*** Significant at 0.001

3. Effect of Removal of Pellicle

Results of 6a and 7 in Table 4 seem to indicate that the pellicle may be contributing to the volatiles of the nut, though results of 3 and 3a indicate that the pellicle does not contribute to those volatiles. It is very possible that the peeling process affects the loss of some volatiles. Such loss is apparently very insignificant when compared to the total volatiles of the raw nut which become more pronounced upon grinding. Peeling also seems to insulate the nut somewhat, against roasting, as shown by treatments 4 and 5.

4. Effect of Grinding

Grinding increases the amount of volatiles in the raw as well as in the roasted nut. Comparing 1 and 4 for the roasted nuts, and 3 and 7 as well as 3a and 6a in Table 4 for the raw nuts indicate such a conclusion.

TABLE 4
TREATMENT RANK ACCORDING TO LSD
(LSD = 0.49 at the 5% level)

Treatment rank	Microequivalents of reduction per gram
1. Peeled, roasted, and ground	19.84
2. Peeled, raw, and ground (Incubated)	9.88
3. Peeled, raw, and ground 3a. Unpeeled, raw, and ground	9.16 8.78
4. Peeled, roasted, and whole	7.97
5. Unpeeled, roasted, and whole	5.88
6. Peeled, raw, and ground (Enzyme Inactivated)	4.63
6a. Unpeeled, raw, and whole	4.43
7. Peeled, raw, and whole	3.62

5. Effect of Roasting

Roasting also increases the volatiles of the nut. Results of 1 and 3, 4 and 7, and 5 and 6a in Table 4 show the effect of roasting to be significant.

6. Effect of Enzymes

Incubation at 37°C for 10 minutes seems to increase the amount of volatiles as shown by the increase in 2 over 3, Table 4, though the nuts were not moistened, as takes place during mastication, which does not give optimum conditions for enzymatic activity. Enzyme inactivation seems to prevent the development of volatiles as shown by comparing 3 and 6. The possibility of volatilizing some of the reducing substances while inactivating the enzyme was then thought of as a factor that may interfere. To eliminate such a possibility, the inactivation was carried out in the distillation flask with all openings closed, and the flask was immediately connected to the rest of the apparatus after cooling. The results obtained are shown in Table 5, and indicate the effect of enzyme inactivation in preventing the development of volatiles. The means show about the same increase of volatile reducing substances of the enzyme-active filberts over enzyme-inactivated filberts as that shown by the corresponding nuts in Table 4. However, both the former means are higher, showing that these nuts have more aroma than those analyzed in Table 4.

TABLE 5
EFFECT OF ENZYME INACTIVATION ON THE VOLATILE REDUCING
SUBSTANCES OF GROUND FILBERTS*

	Raw, peeled, ground		Raw, peeled, ground Enzyme inactivated	
	1	2	1	2
a.	10.88	10.40	6.55	5.94
b.	11.25	11.90	6.92	5.42
c.	10.88	11.76	6.92	6.08
d.	11.00	11.35	6.76	5.81

* ----- In microequivalents of reduction per gram
 1 and 2 ----- Duplicate distillations
 a., b., and c.- Triplicate titrations
 d. ----- Column average

CHAPTER V

ISOLATION OF THE FLAVOR-CONTAINING FRACTION

Most of the flavor work described in the literature depends upon isolation of the flavor components by methods of distillation. These methods require handling of great amounts of raw material as well as the use of special equipment in order to obtain the flavor matter in manageable quantities (24, p.288). Furthermore, distillation introduces the possibility of changing the nature of the flavor components when steam or heat is utilized. This is undoubtedly the reason for always using different assumptions that may impair the issue of such work. The assumptions that if an alcohol and acid had been identified in a distillate that perhaps the ester was originally present, and if an aldehyde was identified, perhaps the original contained the corresponding alcohol, seem to be quite common (14, p.2).

The application of steam or heat to the distillation of filberts at atmospheric pressure effects an obvious change in the distilled flavor. Steam distillation of ground filberts that have been mixed with water and steeped for 3 hours results in a distillate which possesses an earthy-nutty odor that is not typical of filberts. The distillate has a pH of around 5.80 and upon acidification to pH 1.70 with hydrochloric acid no detectable change in odor takes place. Addition of sodium hydroxide to raise the pH to 12.00 results in a slight change in the odor as a faint ammonia-like smell seems to develop. Water-distillation under a reduced pressure results in distillates which parallel the filbert flavor to a greater extent. Preliminary

examination of all distillates, however, revealed the necessity of having the conventional large amounts of distillates for which the required equipment was not available.

The method of isolating different chemical fractions of the filbert and finding out the source of the flavor was thus decided upon as the most feasible procedure.

1. Lipid Extraction and Examination

Although the methods used for the isolation of the fat components of the filbert are the usual methods for oil extraction or expression, the term "lipid" seems to apply itself better to this fraction. Wittcoff (51, p.219) states that most of the phosphatides are carried along with the oil when the latter is removed from seeds either by solvent extraction or by mechanical means. The sludge which Wittcoff (51, p.219) describes as composed largely of phosphorus-containing lipides has been often noticed during the examination of filbert oil that was allowed to stand for some time.

A. Expressing the Lipid by Mechanical Means. The filberts were ground and subjected to a pressure of 2500 pounds per square inch for 30 minutes in a hydraulic press. The resulting oil was considered as a representative sample of the lipid fraction in the nut.

B. Solvent Extraction of the Lipid. The method used for solvent extraction of the lipid is essentially that of the Association of Official Agricultural Chemists (2, p.425). The only

differences were the extension of the extraction time in the Soxhlet to 24 hours instead of 16 hours as prescribed, as well as exclusion of drying the nuts as no quantitative estimation of the fat seemed necessary. In the course of the study some samples were ground and mixed with boiling 95 per cent ethanol for 3 minutes, the ethanol removed by suction-filtration, the nuts dried under vacuum and extracted according to the procedure mentioned. This treatment was used because of the known dissociating influence of alcohol on the phosphatides (51, p.156). The solvents used were ether (2, p.425), chloroform, and petroleum ether. Removal of the solvent from the lipid fraction was either accomplished by vacuum distillation or, in the case of ether, by evaporation at room temperature under the hood.

C. Results. Though it is not claimed that a quantitative isolation of the lipid fraction of the filbert nut has been accomplished, it is very safe to assume that the fraction obtained represents the lipids of filberts. This fraction does not possess any flavor that may contribute to the typical filbert flavor.

2. Globulin Extraction and Examination

According to Fang (10, p.12), the filbert nut contains about 20 per cent protein. Two methods of extraction were used for the isolation and examination of filbert globulins.

A. Extraction with a 10 per cent Sodium Chloride Solution.

The nuts were ground in a peanut-butter mill, and the oil extracted

with ether in a Soxhlet apparatus. The meal was dried at room temperature and 100 grams of the resulting powder mixed with 250 ml of a 10 per cent solution of sodium chloride and allowed to stand, with occasional mixing, at room temperature for 12 hours. The mixture was centrifuged at 2000 RPM for 15 minutes, and the residue discarded. The supernatant liquid was placed in cellophane bags and dialyzed against running water until free from chloride ions. The precipitate (globulins) was removed by centrifugation at 2000 RPM for 30 minutes, washed with methanol and ether, and allowed to dry at room temperature. The supernatant liquid (albumins) was preserved for examination.

B. Extraction with a 5 per cent Sodium Chloride Solution. The nuts were ground in a peanut-butter mill, and the oil extracted with ether. The meal was dried at room temperature and 100 grams of the resulting powder mixed with 150 ml of a 5 per cent solution of sodium chloride and stirred continuously for 3 hours with an electric stirrer. The procedure then continued as in the previous method. This method is essentially the one used by Shah and Worthington (44) for the preparation of extracts for testing the proteolytic activity of filbert nuts (37), and was used to eliminate the possibility of flavor deterioration due to the prolonged extraction used in the first method.

C. Results. The globulins prepared by either method were examined organoleptically for any similarity to filbert flavor and the results were definitely negative. Examination of the supernatant

liquid resulting after the dialysis revealed that filbert albumins (15, p.347), if present, are also not involved in its flavor.

3. Carbohydrate Extraction and Examination

Several methods were used to extract the carbohydrate fraction from filberts. The extraction was usually carried out on ground, and ether-defatted nuts, though ground, and non-defatted nuts were also used.

After trying several procedures for the extraction of sugars (2, p.425) and carbohydrates (33, pp.182-185) with different concentrations of ethanol ranging from 50 per cent to 95 per cent, it was established that the flavor constituents of the filbert are extracted with ethanol at a concentration of 95 per cent. Ethanol at a concentration of 80 per cent extracts very little of the flavor constituents of the filbert. Extraction in a Soxhlet apparatus was found to give better results than boiling with alcohol on a water bath, while extraction with 95 per cent ethanol at room temperature did not extract the flavor constituents. A procedure was then developed for the most adequate extraction of the flavor components of the nut.

4. Procedure for Extracting the Flavor Components of Filberts

1. The nuts are preferably peeled to eliminate the incorporation of any bitter principles or coloring matters from the pellicle, then ground in the peanut-butter mill (Bauer) to a fine paste.

2. The ground nuts are then immersed in boiling 95 per cent ethanol for 3 to 5 minutes to inactivate the enzymes and dissociate

the phospholipids. The alcohol is removed by suction-filtration on a Buchner funnel, and the nuts freed from as much alcohol as possible by drying under the hood. Boiling ethanol does not seem to extract any of the flavor constituents of the nut in this short time.

3. Ethylether-extraction of the nuts is then carried out in a large Soxhlet apparatus for 24 hours. The fat is extracted to avoid the subsequent separation of part of it with the ethanol, as well as to change the ground nuts to a fine powder that can be thoroughly extracted with alcohol. The ether is removed by suction-filtration, and the nuts dried under the hood to a fine powder.

4. The powdered nuts are then mixed with 2 per cent of their weight of precipitated calcium carbonate to neutralize any naturally-occurring plant acids, and extracted with 95 per cent ethanol for 12 hours in a large Soxhlet apparatus.

5. The alcohol extract is concentrated under reduced pressure to approximately 1/10 of its original volume.

6. The concentrated alcohol extract is left standing until crystallization of a sugar (identified as sucrose, Chapter VI) is complete and the clear extract decanted.

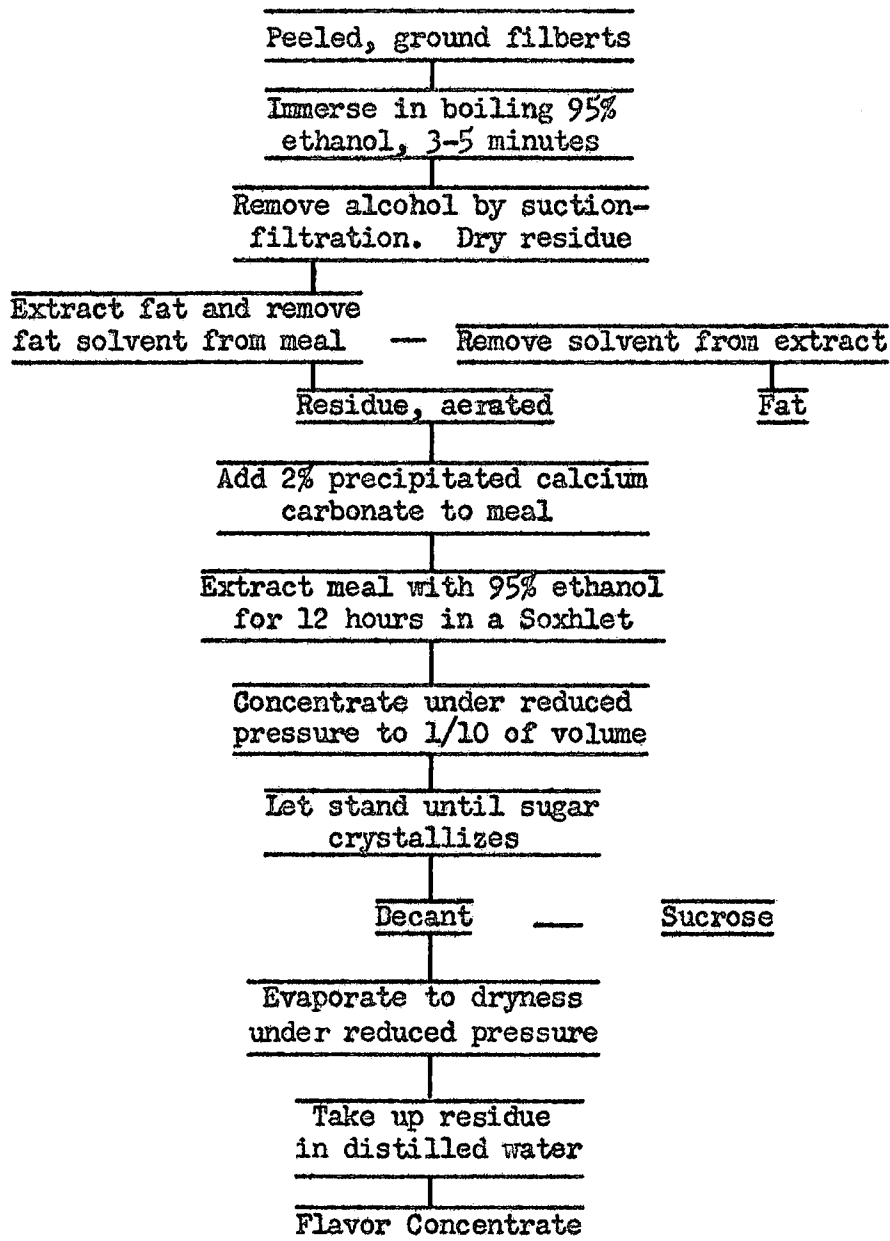
7. The flavor-containing fraction is then obtained by evaporation of this clear alcohol extract to dryness under reduced pressure, and taking up the residue in distilled water. This is called the flavor concentrate.

This procedure is shown schematically in Figure I, page 36.

FIGURE I

SCHEMATIC DIAGRAM OF PROCEDURE FOR EXTRACTING THE FLAVOR

COMPONENTS OF FILBERTS



5. Reconstitution of Ground Natural Filberts from Extracted Filbert-meal plus Flavor Concentrate

To find out whether the flavor-concentrate contains all components of aroma in the nut, the extract was added back to the ether-defatted and alcohol-extracted nuts. It was impossible to incorporate the extract to the nuts because of their non-wettability, and addition of oil was necessary before any incorporation of the extract was possible. Enough filbert oil was added to make the final concentration of the oil in the reconstituted nuts of natural magnitude, approximately 60 per cent (10, p.12). Comparison of the reconstituted nuts with raw, ground filberts revealed a very close similarity between the flavor of the two in character and in intensity though an obvious difference in texture was apparent. To eliminate the effect of texture on the evaluation of the flavor, equal samples of ether-defatted, alcohol-extracted nuts were each mixed with enough filbert oil to make the final concentration of the oil in the reconstituted nuts of natural magnitude. To one sample was then added 0.5 ml of the flavor-concentrate, which was approximately the correct amount of flavor for that weight of reconstituted nuts, while to the other was added 0.5 ml of distilled water. Organoleptic evaluation of both samples showed the one with the added extract to possess a definite filbert flavor while the other was odorless and practically tasteless.

6. Evaluation of the Flavor Concentrate

One hundred grams of filberts were used to extract the flavor according to the standard procedure and the residue taken up in 25 ml

of distilled water. Exactly 2.5 ml of this flavor concentrate, which originated from 10 grams of nuts, were then put in a covered 50 ml beaker and the odor compared organoleptically with the odor of 10 grams of freshly ground filberts from the same lot in a similar beaker. The judges were asked to decide whether the odors from the two beakers were the same, and to compare their strength. The 10 judges participating in this test agreed unanimously that the two odors were the same and that the odor of the extract was stronger than the odor from the 10 grams of fresh nuts.

CHAPTER VI

CHARACTERIZATION OF THE PRINCIPAL FLAVOR COMPOUNDS

In the succeeding discussion the following terms will be used as designated below:

"Flavor Extract": meaning the alcohol-extract of the ether-defatted nuts after concentrating.

"Flavor Concentrate": meaning the aqueous suspension of the residue left after concentrating the alcohol-extract, removal of the crystallized sugar, and evaporation to dryness.

1. Preliminary Examination

The flavor concentrate as prepared by the method outlined in Chapter V, is quite acidic in nature and possesses a pH of about 4.00. This pH is obtained whether precipitated calcium carbonate is mixed with the nuts to neutralize the naturally occurring plant acids before the alcohol extraction or not. It is very possible that calcium carbonate does not exhibit any effect due to the dry state the nuts are in when extracted, as well as the insolubility in alcohol.

Addition of dilute hydrochloric acid, dilute sulfuric acid, or dilute nitric acid to the flavor concentrate results in the separation of a flocculent precipitate. On filtration, the precipitate was found to possess a nutty odor, while the filtrate possesses an "ethereal," ester-like, fruity aroma. Neither the precipitate, nor the filtrate can be said to represent the filbert odor, though the two of them together do exhibit the typical odor of the nut.

Addition of a 5 per cent solution of sodium hydroxide to the flavor concentrate results in the development of a fruity odor. When heated to boiling and cooled, the fruity odor disappears, and the color darkens. Subsequent acidification with dilute hydrochloric acid results in a nutty odor manifesting itself.

The action of certain classification reagents on portions of the flavor concentrate was then determined and the results are shown in Table 6. All tests were run according to Shriner and Fuson (45).

2. Characterization of the Aroma Compounds

A. The Nutty Odor. As results of preliminary tests revealed that the main acidic fraction of the flavor concentrate is probably phenolic, a large portion of the concentrate was acidified with 5 per cent hydrochloric acid until precipitation took place and the precipitate was separated by filtration. The precipitate is insoluble in water, and was washed on the filter paper until the washings were neutral to litmus. It exhibits a nutty flavor on tasting and possesses a nutty odor. It is a waxy substance that splutters upon heating, and melts readily to a brownish liquid which has an odor similar to roasted filberts.

Application of the Schotten-Baumann reaction for alcohols, phenols, and amines (45, p.88) to the flavor concentrate results in the precipitation of a greyish jelly-like substance which gives the ferric hydroxamate test for esters (7, p.121). It was thus concluded that the main acidic fraction of the flavor extract is definitely phenolic in nature, and is responsible for the nutty part of the

filbert flavor.

TABLE 6
THE ACTION OF CERTAIN CLASSIFICATION REAGENTS ON THE
FLAVOR CONCENTRATE

Reagent	Result	Conclusion
1. Bromine water	Decolorization, and precipitation on excess. White, yellowish precipitate	Unsaturated compounds
2. Potassium permanganate solution	Decolorization	Unsaturated compounds
3. Ferric chloride solution	Greenish coloration	Phenols
4. Gelatine solution, 5%	No precipitation	Tannins not present
5. Benzoyl chloride	Precipitate in 10 minutes	Phenols, alcohols, or amines

B. The Ethereal Odor. The filtrate resulting from the separation of the acidic fraction of the flavor concentrate, by precipitation with dilute hydrochloric acid, was subjected to certain classification tests and the results are recorded in Table 7.

As a result of these classification tests it was decided that the ethereal odor associated with the filbert flavor is due to an ester

TABLE 7

THE ACTION OF CERTAIN CLASSIFICATION REAGENTS ON THE NON-ACIDIC
FRACTION OF THE FLAVOR CONCENTRATE

Test	Result	Conclusion
1. Potassium perman- ganate	Very slight decolo- rization	Indefinite
2. Bromine water	Negative	No unsaturation
3. Ceric nitrate	No reaction	No alcoholic hydroxyl group
4. Ferric chloride	No coloration	No indication of phenols
5. Benzoyl chloride	No reaction	No alcohols, phenols, or amines
6. Benedict's reagent (On neutralized solution)	Negative	No active aldehyde group
7. Fehling's solution (On neutralized solution)	Negative	No active aldehyde group
8. Sodium bisulfite	No immediate reac- tion, turbidity overnight	Probable ketone
9. 2,4, Dinitrophenyl- hydrazine	No immediate reac- tion, turbidity in 20 minutes, slight precipitate overnight	Probable ketone
10. Ferric hydroxamate	Positive	Esters present

fraction and probably a ketone fraction. Those fractions could not be separated by steam distillation under either atmospheric conditions or reduced pressure. Steam distillation under reduced pressure was carried out in a special apparatus, Plate II, page 44, where steam distillation is possible at 25° to 30°C. This apparatus has been used by the Western Regional Research Laboratory for separation of volatile components of fruit flavors (17, p.1169). It is very possible that the failure to detect those two fractions in the distillate was due to very low concentrations.

3. Taste Compounds

A. The Sweet Taste. The crystals which separate from the alcohol extract of filberts on concentration were separated and recrystallized from 95 per cent ethanol. They are odorless, colorless, and possess a definite sweet taste. The following tests were run and the results obtained are discussed:

a. Solubility. The crystals are very soluble in water and very slightly soluble in 95 per cent ethanol.

b. Melting Point. The melting range of the crystals was between 170° to 180°C with browning and decomposition. The melting point is determined according to Shriner and Fuson (45, p.19). Sucrose is reported to have a melting range of 170° to 186°C with decomposition (28, p.625).

c. Optical Rotation. The specific rotation of a 9.4 per cent solution of the crystals in distilled water was found to be +67.4°, as

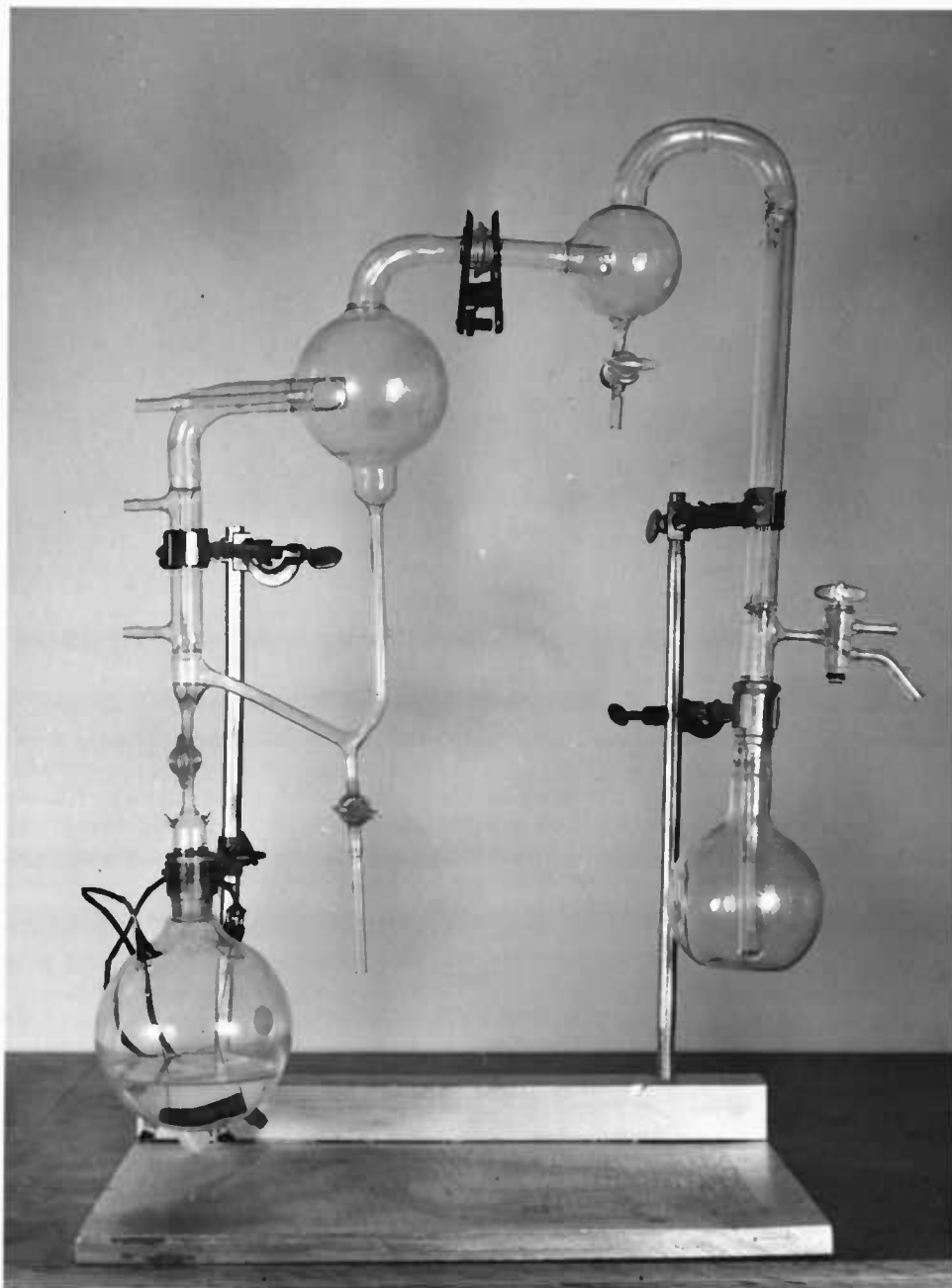


Plate II

compared to a specific rotation of $+66.5^{\circ}$ for sucrose (33, p.174).

d. Reducing Power. The crystals' solution did not exhibit any reducing power towards Fehling's (45, p.98) or Benedict's (45, p.90) solutions, which is true of sucrose.

e. Hydrolysis. Hydrolysis with a 5 per cent hydrochloric acid solution is very easily accomplished, while emulsin does not affect hydrolysis after 18 hours incubation at 36°C . The tests for reducing power of the hydrolyzate were used as an indication of the hydrolysis. This applies to sucrose.

f. Fermentation. Commercial baker's yeast effects fermentation of solutions of the unknown crystals very readily as run according to the method of Morrow and Sandstrom (33, p.155).

g. Seliwanoff's Resorcinol Test. An intense red color develops in about 2 minutes indicating a ketose sugar (33, p.154) when this test is run on a solution of the original crystals as well as the hydrolyzed product.

h. Osazone Formation. Using the phenylhydrazine reagent, as described by Morrow and Sandstrom (33, p.161), on the original crystals no precipitate separated until after heating for about 30 minutes. The appearance of the osazone crystals under the microscope is identical with glucosazone crystals prepared from pure glucose.

i. Chromatographic Identification. The unknown compound was found to have an R_f value of 0.14 as compared to an R_f value of 0.13 for pure sucrose. Both values were determined according to the method of Partridge (38, pp.238-248) for chromatographic identification of sugars.

It was thus definitely concluded that the unknown crystals are the disaccharide sucrose.

B. The Bitter Taste. The flavor concentrate possesses a definite bitter taste which was thought to be associated with the glycoside in the nut. Addition of ether to the alcohol extract, after crystallization of the sucrose, results in the precipitation of a whitish, gummy precipitate which turns to a brown mass upon exposure to air. Washing with ether, drying, and dissolving in distilled water, results in a bitter solution which is neutral to litmus.

Classification tests on this solution fail to detect alcohols, aldehydes, or phenols, but it gives a precipitate with the 2,4, dinitrophenylhydrazine reagent in about 6 hours, and develops appreciable turbidity with the sodium bisulfite reagent in 5 hours. This may indicate the presence of ketones. Equal volumes of this solution were subjected to acid hydrolysis, alkali hydrolysis, and enzyme (emulsin) hydrolysis.

Hydrolysis with either dilute hydrochloric or sulfuric acids for 6 hours and distilling, results in the production of an unidentified alcohol which possesses a pleasant fruity odor. The alcohol was detected by the development of a red coloration with the ceric nitrate reagent (45, p.96). The residue reduces Fehling's solution and when chromatogrammed with glucose, galactose, and fructose, according to the method of Partridge (39, p.57), only glucose was identified by an R_f value of 0.34 which was identical with the R_f value obtained with pure glucose.

Hydrolysis with 30 per cent sodium hydroxide for 6 hours and distilling does not give any results comparable to acid hydrolysis. The distillate possesses a foul caustic odor and does not react with classification reagents for alcohols, aldehydes, ketones, or phenols (45, pp.83-151).

Hydrolysis with emulsin after adjusting the pH of the extract to pH 6.15 with a phosphate buffer (15, p.85) and incubation at 36°C does not result in the development of alcohol within 72 hours. Due to the limited supply of emulsin, the results obtained cannot be considered conclusive.

Solutions of this bitter tasting fraction in distilled water exhibit a positive optical rotation.

CHAPTER VII

COMPARATIVE CHARACTER OF FLAVORS OF RAW AND ROASTED FILBERTS

During the course of this work, it was realized that roasting of filberts results in the development of a more pronounced aroma than that encountered in the raw nut. Roasting seems to have been associated with the development of flavor in the fats of certain meats (20, p.201), and seems to develop some browning reactions which are considered to produce desirable effects, as in bread crust, roasted cereals, soy beans, coffee, and nuts (19, p.1436). Sucrose is known to decompose on heating and produces caramel with its brown color and distinct odor. The possible effect of the contribution of fat, browning reactions, and caramelization of sucrose to the flavor of the roasted filbert was then thought of as a means of studying the factors which seemed to be involved in the flavor of the roasted nut.

1. The Fat

The fat fraction extracted from filberts according to the methods mentioned in Chapter V does not possess any filbert odor. Heating this fraction by several methods ranging from heating at 350°F for 15 to 20 minutes in a baking oven to heating on a Bunsen burner for one hour does not result in the development of any odor whatsoever. It can be very definitely concluded that the filbert fat is not responsible to any degree for the aroma of the roasted nuts.

It must be mentioned, however, that the fat extracted from roasted filberts possesses a definite "roasted-nut" odor. This can

only be explained by the solubility of the components responsible for the "roasted-nut" odor in the fat or the fat solvent and, consequently, their separation with the fat fraction. These components are easily steam-distilled from the fat.

2. The Browning Reactions

The filbert-meal remaining after ether-defatting and alcohol-extracting of the raw nut is a very fine, white powder that does not possess any odor. Subjecting this powder to the same heat treatment the nuts undergo during roasting does not result in any browning. Lengthening the time of roasting results in charring accompanied by a burnt odor. Such burnt odor is not encountered in the adequately roasted nuts.

The filbert-meal remaining after ether-defatting and alcohol-extracting of the roasted nut is a very fine powder which is light brown in color, and does not possess any odor.

Extracting the soluble protein according to the methods described in Chapter V from both raw and roasted nuts revealed the fact that the filbert protein is affected by roasting, and develops a definite light brown color. No distinct taste or odor could be detected, however, to differentiate between the protein prepared from roasted filberts and that prepared from the raw nut.

The Molisch test (33, p.110) revealed the presence of carbohydrate groups in both the protein prepared from raw nuts and that prepared from roasted nuts. However, when both proteins were dissolved in 5 per cent sodium chloride solution they did not exhibit

any reducing power toward Fehling's solution. These results suggest that the carbohydrate is combined to the protein and not present as a separate constituent.

3. Caramelization

Pure sucrose was used to prepare caramel, and caramel solutions in distilled water were prepared in different concentrations. Addition of those solutions to reconstituted-filberts prepared as described in Chapter V does not produce any similarity to the roasted aroma. This was taken as an indication that caramelization of sucrose does not play any part in the pronounced aroma developed by roasting. It is obvious that the roasting temperature does not heat the inside of the nut to the temperature where sucrose caramelizes. The roasting temperature does not exceed 176.6°C (350°F) and sucrose is known to require a temperature of 210°C (15, p.617) to bring about caramelization.

4. Comparison of the Phenolic Fraction in the Flavor Concentrates from Roasted and Raw Nuts

When it was realized that the fat, the sucrose, and typical protein/reducing sugar browning reactions do not seem to be principally involved in the enhanced aroma of the roasted nuts, a comparison between the phenolic fractions of the roasted and raw nuts seemed necessary, especially with the observation that heating the phenolic fraction from raw nuts results in the development of an aroma similar to that of roasted nuts.

The Schotten-Baumann reaction for alcohols, phenols, and amines (45, p.88) was then applied to 5 ml each of the flavor concentrate

from roasted and raw nuts. After the reaction took place, the mixtures were centrifuged. In the case of the raw flavor concentrate a homogenous, grey, jellylike precipitate settled at the bottom of the centrifuge tube. The roasted flavor concentrate produced two distinct layers of precipitate: a yellow, oily liquid and the grey, jellylike precipitate. The ferric hydroxamate test for esters (7, p.121) gave a definite wine red color with the three precipitates. It is very possible that roasting affects the phenolic constituents of raw filberts in such a way as to produce other phenolic substances. It must be mentioned here that while the flavor concentrate of raw nuts gives green coloration with the ferric chloride reagent, the concentrate from roasted nuts gives a brownish-green coloration. This may be an indication of the change that takes place in the phenolic substances.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

No work has ever been done before on the flavors of edible nuts. Information on food flavors in general is very meager, and the need for more studies in this field is quite obvious.

Preliminary organoleptic examination revealed that the characteristic filbert flavor is principally due to volatile components. The tastes perceivable from the nut are sweetness, sourness, and bitterness. The pellicle seems to contribute to the bitterness of the unpeeled nut. Although there is definitely a flavor difference between peeled and unpeeled nuts, no consumer preference could be established with the limited taste-panel available for this work.

A method is described by which the volatile reducing substances responsible for the filbert odor are distilled under regulated conditions, oxidized with an alkaline potassium permanganate solution, and a quantitative estimate of the filbert odor is thus obtained. The method gives reproducible results which agree with factual observations on filberts subjected to different commercial practices. Results obtained with this method show that removal of the pellicle does not affect the odor intensity of the ground, raw nuts, yet adds a little to the odor intensity of whole, raw nuts. The contribution of the pellicle to the odor of the nut seems to be so little that it becomes insignificant upon grinding, which was found to increase the odor intensity of the nut by about 150 per cent.

Roasting also increased the odor intensity of filberts by more than 115 per cent in the case of peeled nuts, but the increase did not exceed 33 per cent when the nuts were not peeled possibly due to the insulating effect of the pellicle.

Enzyme action was proven to be involved in the development of volatiles in the ground, raw nuts. Enzyme inactivation reduces the amount of volatiles by over 40 per cent, while incubation of the nuts results in a significant increase in the amount of volatiles.

Steam and water distillation of filberts under atmospheric conditions change the characteristic filbert odor somewhat as determined organoleptically. Water distillation under reduced pressure results in distillates which resemble the filbert odor to a great extent. However, the non-availability of large vacuum-distillation equipment made it impossible to obtain distillates in amount yielding manageable contents of flavor components. The investigation of the major constituents of the filbert nut was thus decided upon as the only feasible means for studying the flavor of the nut.

The filbert oil was found to be devoid of any filbert flavor. Heating the oil at elevated temperature does not result in the development of any flavor. The soluble proteins were also found to be not responsible for the filbert flavor.

The filbert flavor was found to be associated with the carbohydrate fraction of the nut as proven by the method of extraction, and a procedure was developed for the laboratory isolation of the flavor-containing fraction. Further investigations may yield a more

feasible method for commercial purposes. The method depends on grinding the filberts, subjecting them to boiling 95 per cent ethanol for a few minutes, extracting the fat with fat solvents, and extracting the meal with warm 95 per cent ethanol. Evaporation of the alcohol under reduced pressure results in a residue which when taken up in distilled water was found to possess all of the typical filbert odor according to organoleptic evaluation.

Two main odors seem to constitute the typical aroma of the nut. A nutty odor was found to be associated with unidentified phenolic substances, and a fruity odor which is associated with unidentified esters and ketones.

Sucrose was definitely identified in the filbert nut. It is the main compound responsible for the sweet taste.

A bitter tasting compound is also found in the flavor extract. There is evidence that this may be a glucoside, as acid hydrolysis results in the production of an unidentified alcohol and the monosaccharide glucose.

Roasting the nuts results in a change in the flavor of the nut as determined organoleptically. This change was found to be not resulting from the effect of the roasting temperature on the fat, the protein or the sucrose of the filberts. A change in the phenolic constituents associated with the nutty odor was found to take place.

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