AN ABSTRACT OF THE THESIS OF

ROSS MARK SHELDON (Name) for the DOCTOR OF PHILOSOPHY (Degree)

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Title: FLAVOR CHEMISTRY OF ROASTED FILBERTS (CORYLUS AVELLANA)

Abstract approved: Dr. R. C. Lindsay

Dry-roasted filberts were subjected to qualitative and quantitative analyses in order to study the roasted filbert flavor. This was approached by (1) the characterization of the filbert lipid fraction and the assessment of its participation leading to the production of a roasted flavor; (2) qualitative and quantitative analyses of the filbert headspace volatiles; and (3) a qualitative analysis of the molecular distillate from oil samples obtained from roasted filberts by Soxhlet extraction.

The lipid fraction was shown to be primarily in the form of triglycerides, and oleic acid was observed to constitute a major portion of the triglyceride fatty acids. The development of measurable amounts of peroxidic compounds was not noted during the course of the roast.

The qualitative analysis 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. Experiments were conducted which demonstrate that ten of the twelve identified compounds are heat-induced. The amounts of these compounds were determined at selected times during the roasting period.

Thirty-eight compounds were positively identified and twelve compounds were tentatively identified from the roasted filbert. Those compounds positively identified include acetaldehyde, propanal, 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, hexanal, benzaldehyde, phenylacetaldehyde, acetic acid, hexanoic acid, methyl acetate, ethyl acetate, 2-pentyl furan, 2-furfural, acetyl-2-furan, 5-methylfurfural, furfuryl alcohol, 2, 5-dimethyl-4-hydroxy-3(2H)-furanone, 2-methyltetrahydrofuran-3-one, 2-methylpyrazine, 2-ethylpyrazine, 2, 5-dimethylpyrazine, 2, 3-dimethylpyrazine, 2-ethyl-5-methylpyrazine, 2-ethyl-3, 6-dimethylpyrazine, 2-ethyl-3, 5-dimethylpyrazine, acetone, diacetyl, dimethyl sulfide, γ-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, ethylmethylpyrazine, 2, 6- or 2, 5-diethyl-3-methylpyrazine, thiazole, N-furfurylpyrrole, N-methyl-2-pyrrole aldehyde,

3-pentene-2-one, methyl formate, allyl crotonoate and 1,2,4-trimethylbenzene.

The aldehydes, acids, furans and pyrazine derivatives were considered to be essential to the roasted flavor.

Flavor Chemistry of Roasted Filberts (*Corylus avellana*)

by

Ross Mark Sheldon

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Dean of Graduate School

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INTRODUCTION

The cultivation of filberts is very important to Oregon's agricultural economy. Oregon produces over ninety percent of the filberts grown in the United States. These nuts enter many avenues of today's food industry and they do so, largely in a roasted state. The roasted filbert has a very distinctive flavor which is considerably different from the flavor of the raw nut.

The development of heat-induced flavors in foods has always existed as an elusive problem for the flavor chemist. Studies concerned with the identification of flavor constituents and the characterization of their precursor systems have contributed greatly to an understanding of the basic mechanisms which are responsible for the formation of these flavors.

The development of flavors within roasted foods such as coffee and cocoa beans has been the subject of several recent investigations. With the enumeration of their flavor components, attention is quickly drawn to the qualitative similarity of each system. The identifications strongly implicate the reaction sequences of nonenzymatic browning, Strecker degradation and lipid autoxidation as being

essential for the development of a roasted flavor.

The purpose of this investigation was to study the flavor chemistry of the roasted filbert.

REVIEW OF LITERATURE

The Filbert

The filbert was introduced into Oregon in 1885 by Felix Gillette. Since that time, the filbert industry has grown and now holds a prominent position within Oregon's agricultural community. The Barcelona variety of Corylus avellana is the basis of Oregon's filbert industry. The development of this variety was achieved through the careful selection and hybridization of European stock. The Barcelona thrives on the cool, moist climate of the Pacific Northwest and the tree is characterized as being large, productive and bearing a quality nut.

Filbert Research

Past research on the filbert has been limited largely to two areas. One area of study has been concerned with those projects of commercial importance such as breeding and processing (13, 24, 53, 54, 73). The second area of research has emphasized studies on the filbert's composition. The following data evaluate the filbert's gross composition and compare the results with those obtained from the peanut (71).

	Percent by Weight	
	Filbert	Peanut
Protein	12.7	26.9
Carbohydrate	14.3	21.2
Fat	60.9	44.2
Crude Fiber	3.4	2.4
Ash	2.7	2.7
Calcium	0.287	0.071
Phosphorus	0.354	0.399

Characterization of the Lipid. Fifty to sixty percent of the filbert kernel is oil and the characterization of this oil has been the subject of several investigations (25, 40, 63, 71). Oxidative rancidity can be a critical problem within the filbert industry and therefore, this interest in the lipid content is most assuredly justified.

Attention has been drawn to the similarity which exists between the filbert and olive oils (40, 71). The data given below demonstrate this relationship:

	Percent Composition	
	Filbert (40)	Olive (15, p. 404)
Palmitic acid	5.0	13.5
Palmitoleic acid	0.1	1.5
Stearic acid	1.4	2.5
Oleic acid	77.0	73.0
Linoleic acid	16.0	8.5
Linolenic acid	0.3	Trace
Arachidic acid	0.1	
Eicosenoic acid	0.1	
C_{20} and higher (sat.)		0.5
C_{20} and higher (unsat.)		0.5

Wiegand (71) indicates that the level of free fatty acids is very low in the filbert, and therefore, the fatty acids must exist largely in the form of triglycerides. The presence of a phytosterol has also been observed (71). A report by Fang and Bullis (25) shows a divergence from the above data. Their results were obtained from Barcelona and Du Chilly varieties and indicate a 20.95 percent and 15.25 percent level for eicosenoic acid, respectively.

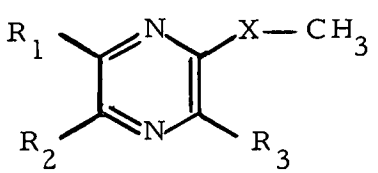
Filbert oil contains a high level of unsaturation and as a consequence, is susceptible to autoxidation. Research conducted by Cecil for the Oregon Agricultural Experiment Station (53) indicates, however, that the filbert kernel is relatively resistant to rancidity. Filberts stored at room temperature did not develop an off-flavor until after 7 to 9 months. Cecil also noted that samples stored at refrigeration temperatures (35°F and 2°F) remained indistinguishable from fresh filberts when observed during the ninth month of storage.

Amino Acid Composition. Fang and Butts (27) evaluated the amino acid content of two filbert 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 rats during a 28-day test. However, in 1920, Cajori (12) observed that satisfactory growth could be obtained with young rats using partly de-fatted, ground filberts as

a protein source. Prompted by these results, Fang, Bullis and Butts (26) measured the amino acid levels in oil-free filbert meal. They concluded that the amino acids showed an exceptional balance for a plant protein. In comparison to casein, the filbert protein was shown to be high in arginine and serine, but low in lysine, proline and tyrosine.

The Filbert: Flavor Applications

Filberts are generally consumed in a roasted form and are often incorporated into a variety of food products such as ice cream, cookies, assorted baked goods and confections. The development of a flavor concentrate or synthetic substitute would undoubtedly find wide commercial appeal. In a recent Japanese patent, E. T. Firmenich (29) indicated that nut-like flavors resembling cooked walnuts, peanuts or almonds could be obtained from compounds having the following general structure:



where X is sulfur or oxygen and the R groups consist of one methyl and two hydrogens. Firmenich (30) has continued their work in this area and now has a mixture available containing 2-methyl-3-methylmercaptopyrazine (70 percent) and 2-methyl-5-methylmercaptopyrazine

and 2-methyl-6-methylmercaptopyrazine. This mixture is reportedly able to impart a roasted filbert, peanut or almond flavor to foods.

Flavor Chemistry of Heated Foods

Although information pertaining to the roasted flavor of the filbert is not available outside of the patent literature, the development of heat-induced flavors has been the subject of numerous reports. The following discussion will briefly review the origin of heat-induced flavors and will present the results of several studies on individual food items. This discussion is based upon the premise that many similarities exist between foods and the manner in which they are processed. Therefore, an understanding of one system would undoubtedly be beneficial in anticipating possible results obtained during the course of this investigation.

A food flavor is the result of an interplay of many organic compounds. Jennings and Sevenants (41) broadly classified these components into two categories, namely, "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.

Role of Carbohydrates in the Formation of Heat-Induced Flavors

Carbohydrates serve as nonodorous precursors for a multitude of volatile flavor compounds. Caramelization and nonenzymatic browning constitute the major reaction sequences leading to the formation of these flavorful products. The distinguishing feature separating these pathways is the role of amino compounds in the case of nonenzymatic browning. Caramelization, on the other hand, defines those thermally induced reactions involving isolated carbohydrate reactants. The end result of each sequence is the production of some of the same compounds, however, the presence of the amino compounds allows for this production to occur at greatly reduced temperatures.

Caramelization. Caramelization is the gradual dehydration of sugars to form very active aldehydes (36). These newly formed aldehydes have several reactive options which include: cyclization, polymerization, assorted fission reactions and miscellaneous condensations. The end result of caramelization is a dark brown pigment, however, the careful control of this sequence produces the universally appreciated caramel flavor.

Several recent investigations (10, 42, 70) have studied the volatiles produced from several carbohydrate model systems. These experiments were conducted at temperatures ranging from 250° to

300°C and numerous reaction by-products were observed. Walter and Fagerson (70) observed at least 100 compounds arising from a thermally degraded sample of glucose at 250°C in a nitrogen atmosphere.

Nonenzymatic Browning. The Maillard reaction is the chemical description of the occurrence of nonenzymatic browning in foods. The reaction is endothermic and is initiated by the condensation of a reducing sugar and an amino compound to form an N-substituted glycosylamine. Hodge (35, 36) and Reynolds (56) have reviewed the existing information on the Maillard reaction. The flavors produced from the Maillard reaction in foods have been discussed by Hodge (36) at the 4th Symposium on Foods, Corvallis, Oregon. Figure 1 outlines important aspects of the Maillard reaction relative to the production of flavor compounds and formation of melanoidin pigments.

In a recent paper, Hodge (37) proposed three designations for the flavor compounds generated from the Maillard reaction. Structural relationships of the compounds from each class were noted and a correlation of structure to aroma was made. Table I briefly summarizes these observations.

The recent identifications of alkyl-substituted pyrazines in food systems has created considerable interest (7, 22, 34, 47, 48, 57). Dawes and Edwards (20) and Newell, Mason and Matlock (52) have suggested that the pyrazines are formed from Maillard reaction

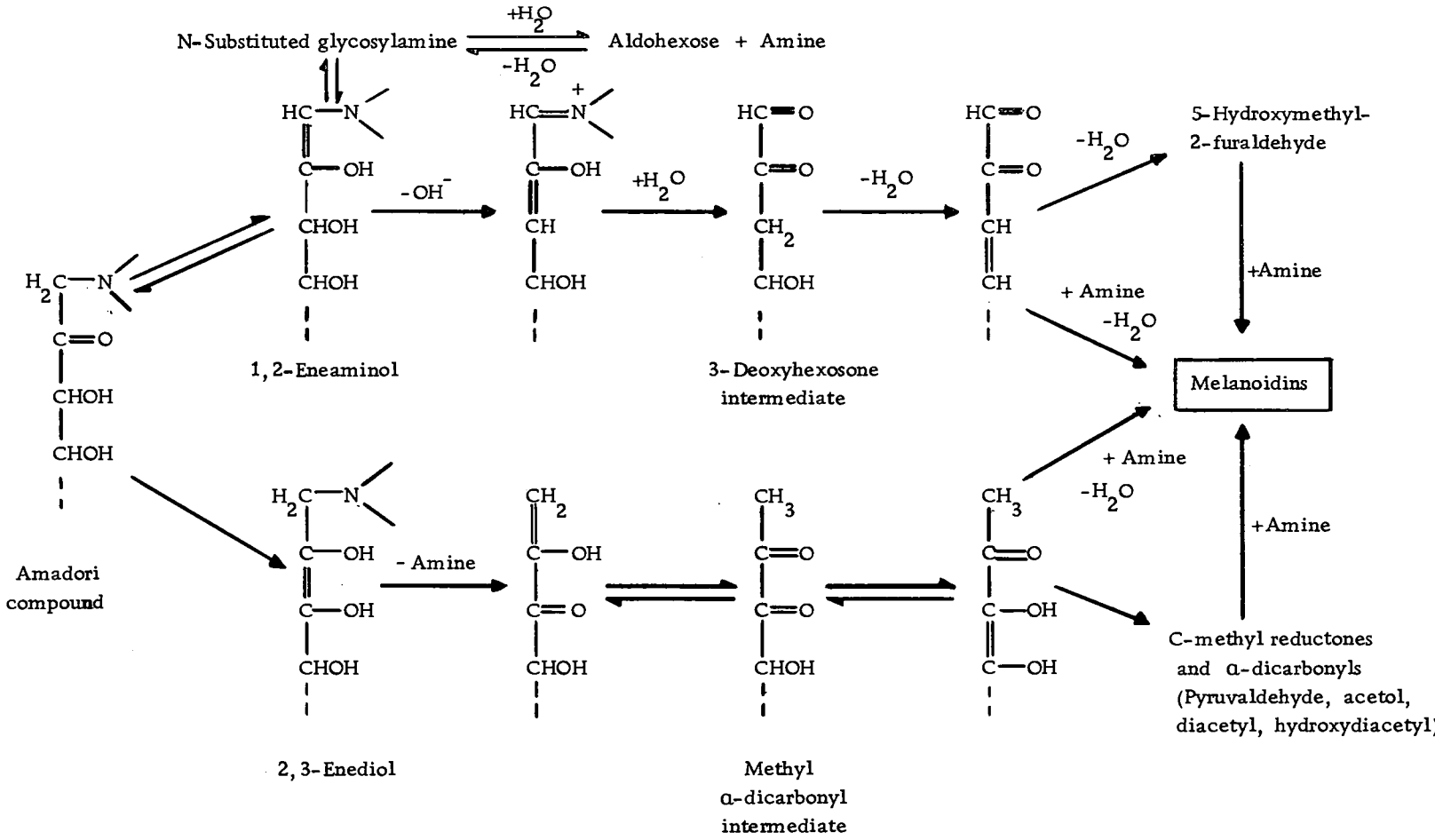
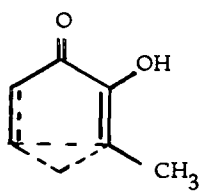
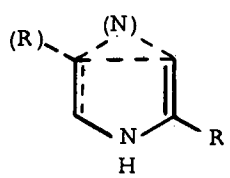


Figure 1. Two pathways of the Maillard reaction leading to the formation of flavor compounds and melanoidins (37).

Table 1. Correlation of flavor with structural characteristics (37).

Flavor Designation	Structural Characteristics	Classes of Compounds
1. Caramel	Non-nitrogenous, cyclic and planar containing a carbonyl, enolic hydroxyl and C-alkyl groups. 	Cyclopentenolones, Cyclohexenolones, Furenolones, Pyrones
2. Nutty, popcorny or bread-like	Nitrogenous heterocyclics with secondary or tertiary amino groups and with C-alkyl or C-acyl substituents. 	Pyrazines, Pyrroles, Pyrrolines, Δ^2-Piperidienes
3. Burnt, variable (aldehydic or ketonic)	Acyclic aldehydes, α,β-unsaturated aldehydes and α-dicarbonyl compounds	2-Pyrrole aldehydes, Strecker aldehydes, C_3-C_6 Methyl ketones, 2-Furaldehydes Pyruvaldehydes

intermediates. Koehler et al. (43) conducted experiments with labeled reactants and demonstrated that the sugars were the principle source of carbon while the amino acid provided only the nitrogen moiety for the pyrazine molecule. Evidence was also presented which indicates that the structure of the amino acid exerts an effect upon the quantitative distribution of the pyrazines formed. In a study of cocoa bean aroma (55), 11 alkyl-substituted pyrazines were identified. In an extended study designed to establish the mechanism responsible for the formation of the substituted pyrazines, several neutral amino acids were reacted with D-fructose and a similar distribution of pyrazines was obtained from each system. The same pyrazines could also be obtained using fructose or glucose and ammonia. These data suggest that the structure of the amino acid does not influence the course of the reaction and that ammonia appears to be an intermediate for this reaction. These reports appear to offer conflicting points of view however, it is probable that two reaction mechanisms are involved. The distinguishing feature is perhaps the water content. The system of van Praag, Stein and Tibbetts (55) employed an aqueous reflux whereas Koehler, Mason and Newell's (43) system contained only limited amounts of water.

Amino Acids, Peptides and Protein Degradation

Robertson and Merritt (58) conducted studies on the thermal

degradation of amino acids, peptides and protein substances. The samples were pyrolyzed at 1200°C for 10 to 30 seconds and the reaction by-products analyzed by gas liquid chromatography (GLC) and mass spectrometry. Numerous volatile compounds were produced and the complexity of the pyrolyzate was variable. Tyrosine, for example, yielded 98 percent toluene while the pyrolysis of cystine and insulin produced 12 and 20 major components, respectively. The relationship of these experiments to the production of flavors in foods must remain speculative until such experiments consider those conditions encountered during food processing.

Strecker Degradation. The reaction of α-amino acids with compounds containing -C:O-C:O- or -C:O(CH:CH)$_n$-C:O- groupings is termed Strecker degradation. Carbonyl containing reactants are readily formed during the Maillard reaction (see Figure 1). The end result of this reaction is the formation of an aldehyde containing one less carbon atom than the parent α-amino acid.

The Strecker reaction is extremely important to the flavor chemist. The aldehydes formed as a result of this thermally induced reaction can contribute significantly to the food's flavor. The commercial use of this reaction is the subject of several patents. One patent was granted to Kremers (44) who produced an imitation maple flavoring by heating α-aminobutyric acid and sugar.

Lipid Oxidation

Aliphatic carbonyl compounds, specifically alkanals, alk-2-enals, alk-2,4-dienals, α-dicarbonyls and β-dicarbonyls, are present in foods and constitute an important source of flavor. Members of each carbonyl class may be formed as a result of lipid oxidation (14, 21, 46). Lipid oxidation has traditionally been thought to include only those reactions of lipids containing sites of unsaturation. In a review, Frankel (31) discussed the mechanism by which this reaction proceeds and indicated that energy is required in order to initiate the oxidative process. Brodnitz, Nawar and Fagerson (8, 9) have recently completed a study in which they demonstrated that saturated lipid systems, heated to about 150°C, are also capable of undergoing oxidation. In the light of these observations, both saturated and unsaturated lipids must be considered as potential sources of flavor in thermally processed, lipid-containing foods.

Selected Studies on the Flavor Chemistry of Roasted Natural Products

Flavor investigations of roasted peanuts, pecans, coffee, chocolate and cocoa will be briefly discussed relative to the source and origin of their flavors.

Roasted Peanuts. Pyrazine derivatives have been cited as being significant to the development of a typical roasted peanut flavor.

Working with the flavor components isolated from roasted Spanish peanuts, Mason, Johnson and Hamming (48) identified five pyrazines and a pyrrole. Those compounds identified include methylpyrazine, 2,5-dimethylpyrazine, 2-methyl-5-ethylpyrazine, trimethylpyrazine, dimethylethylpyrazine and N-methylpyrrole. N-Methylpyrrole was not considered as an important component of the roasted aroma. The formation of the pyrazine components has already been discussed and shown to be a result of sugar-amino acid interactions.

Several important monocarbonyls were also identified in the volatile fraction from roasted peanuts (49). Some of the major components which were identified include acetaldehyde, 2-methylpropanal, 2-methyl and 3-methylbutanal, phenylacetaldehyde and benzaldehyde. The first five compounds are probably Strecker degradation aldehydes arising from alanine, valine, isoleucine, leucine and phenylalanine, respectively. These carbonyls were considered to be important to the development of a roasted peanut aroma.

Roasted Pecans. The volatiles from roasted pecans were recently the subject of a study conducted by Rudolph, Mason and Odell (61). The authors identified acetaldehyde, methyl disulfide and methanol from unroasted samples. Nine alkyl-substituted pyrazines were tentatively identified by mass spectrometry and were considered to be responsible for the aroma of roasted pecans. The pyrazines

were formed during the roasting process.

Coffee. Numerous reports have considered many aspects of this very complex and elusive flavor (7, 32, 33, 34, 66, 67). Recently, Stoffelsma et al. (66) indicated that at least 318 volatile components have been shown to be present in coffee. Reviewing the list of identified components, attention is immediately drawn to the importance of the Maillard reaction, protein degradation and lipid oxidation leading to the development of the roasted coffee flavor.

Chocolate and Cocoa. Fermentative and heat curing processes are necessary for the development of the characteristic flavor in cocoa beans. Rohan (59, 60) established that phenolic and non-enzymatic browning reactants such as reducing sugars, amino acids and flavonoids, were released during the fermentation. He continued his study and showed that these compounds are the primary precursors of the chocolate aroma. Recently, two studies have been reported (31, 55) enumerating the many volatile compounds which have been isolated from cocoa bean flavor extracts. van Praag, Stein and Tibbetts (55) implicated several compounds which were thought to be essential to the cocoa aroma: acetaldehyde, isobutyraldehyde, isovaleraldehyde, benzaldehyde, phenylacetaldehyde, 5-methyl-2-phenyl-2-hexenal, 2-furfural, methyl disulfide, 11 alkyl-substituted pyrazines, acetic acid and isopentyl acetate.

The Study of a Flavor

The four examples presented in this review adequately demonstrate the complex nature of a flavor. A food consists of an assortment of macromolecules which, when exposed to a source of energy, can erupt into numerous reactions leading to the formation of many flavorful compounds. An understanding of flavor development is therefore synonomous with an understanding of the thermally induced interactions involving the food's macromolecular constituents, carbohydrates, proteins and lipids.

EXPERIMENTAL

Samples

Barcelona 30/40 filbert kernels (Corylus avellana) were used during the course of this investigation. The dried filbert kernels were obtained from the Norpac Growers, Inc. of Newberg, Oregon.

Sample Storage

The filbert kernels were received in bulk and immediately prepared for long term storage. Approximately 1800 gm quantities of the nut kernels were placed in No. 10 cans coated with a "C" enamel, evacuated, flushed with nitrogen and hermetically sealed. The sealed cans were stored at -10°C and held at this temperature until such time as they were needed for analysis. These precautions were considered necessary in order to prevent both chemical and enzymatic deterioration.

Sample Preparation

Prior to each analysis, a representative sample of nuts was evaluated organoleptically by a small laboratory panel in order to determine the quality of the nuts to be analyzed. Only filberts without noticeable flavor defects were used during the course of this investigation.

Roasted filbert samples were required throughout this study. The nuts were dry roasted in a gas oven at 177°C. A 17.5 minute roasting period produced a desirable roasted flavor.

Lipid Analysis

A study of the filbert's lipid composition was considered to be an important aspect of this investigation. The importance of this analysis was based upon the following consideration, namely, the potential of the lipid material to undergo autoxidation during roasting and serve as a source of flavor. To investigate this possibility, the lipid fraction was characterized and experiments were conducted in order to observe changes in the oil occurring as a result of roasting.

Extractable Lipids

Twenty-five to thirty gm quantities of coarsely ground, raw filberts[1] were extracted with 250 ml portions of purified hexane[2] for 48 hours in a Soxhlet apparatus having a 300 ml capacity. The

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[1] The filbert samples were obtained in a dried form and possessed a moisture content of 4.47 percent as determined using standard vacuum oven procedures.

[2] High purity grade hexane was treated for the removal of carbonyl compounds according to the method of Hornstein and Crowe (38). The hexane was then redistilled and used as indicated.

hexane extracts were dried over excess sodium sulfate, filtered and the solvent removed under vacuum. The quantity of the extracted lipid was recorded and the percent lipid determined.

Samples of the extracted lipid were analyzed by thin layer chromatography (TLC). A 20 x 20 cm plate, coated with a 0.25 mm layer of Silica Gel G, was used for the analysis. The plate was developed using a solvent system of hexane/ethyl ether/acetic acid, 80:20:1, v/v. After thorough drying, the plate was sprayed with a 50 percent sulfuric acid solution saturated with potassium dichromate, placed in an 110°C oven and heated until the spots charred. The separated lipid classes were identified by a comparison of the R_f values obtained from known laboratory standards.

Fatty Acid Composition

GLC was used to determine the identity and relative quantity of each fatty acid present in the extracted filbert oil. The samples were prepared using a boron trifluoride methylation procedure (28) and the fatty acids analyzed as their methyl esters. The reaction mixture[3] was heated for 30 minutes at 100°C in a sealed tube. After the heat treatment, the reaction mixture was extracted with 7 ml quantities of distilled water saturated with sodium sulfate and ethyl

[3]Reaction mixture: 1 ml 10 percent boron trifluroride in methanol, 1 ml benzene, 2 ml anhydrous methanol and 3 to 5 drops of oil.

ether. The ether layer was removed and washed with 7 ml of distilled water. The ether layer was again removed, dried over excess sodium sulfate, filtered and the solvent removed under vacuum. The isolated methyl esters were then analyzed by GLC.

The GLC identifications were made using relative retention times. The operating conditions were:

Column	15 percent Diethylene Glycol Succinate (DEGS), 0.05 percent Igepal CO-880 on 100-120 mesh AW-DMCS Chromosorb G, 10' x 1/8" OD stainless steel.
Instrument	F & M Model 810 Gas Chromatograph equipped with a hydrogen flame detector.
Column Temperature	200°C
Injection Block Temperature	250°C
Detector Temperature	250°C
Carrier Gas	Nitrogen
Flow Rate	20 ml/min

The peak area of each methyl ester was measured using a planimeter. Correction factors, correcting for the flame detector's non-linear response, were established by using a commercially

available, weighed standard mixture of selected compounds.[4] The corrected peak areas were recorded and the percent composition determined.

Peroxide Determination

The formation of peroxidic compounds in lipid systems is a widely accepted indicator of lipid autoxidation. The modified iodometric method for the semimicro determination of lipid peroxides of Dahle and Holman (19) was used during the course of this investigation. This measurement was considered necessary in order to provide a monitor of both the effect of the roasting process and sample handling on the filbert oil. The method has several advantages over conventional procedures. These advantages include the use of a single phase system, the elimination of iodine oxidation by air and the immediate titration of iodine.

Analysis of Headspace Volatiles

The headspace flavor volatiles from filbert oil samples were analyzed using GLC and mass spectrometry. The analysis was made by employing the gas entrainment, on-column trapping technique developed by Morgan and Day (51) and incorporating the

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[4] Applied Science Laboratories, Inc., State College Pennsylvania. Mixture H-104; Lot No. 568-18.

modification described by Bills (4). A diagram of the headspace assembly is shown in Figure 2.

This study was divided into two parts. The first segment was designed to establish the identity of the volatile components present in the headspace of the roasted filbert oil and the second, to note the effect of roasting upon the composition of the entrapped headspace components.

Gas-Liquid Chromatographic and Mass Spectrometric Analysis

The mass spectral analysis was conducted using an Atlas CH-4 Mass Spectrometer in tandem with an F & M Model 810 Gas Chromatograph. The entrapped volatile components were separated by GLC prior to their entry into the dual ion source of the mass spectrometer. The mass spectrometer was equipped with an EC-1 intake valve which was adjusted to permit approximately ten percent of the GLC column effluent to enter the ionization chamber. The remaining effluent was vented into the air through a heated tube. The operating conditions were:

GLC Conditions

Sample — Pressed filbert oil[5] from nut samples

[5] Pressed oil was obtained by pressing coarsely ground filberts at 8000 psi using a Carver Laboratory Press.

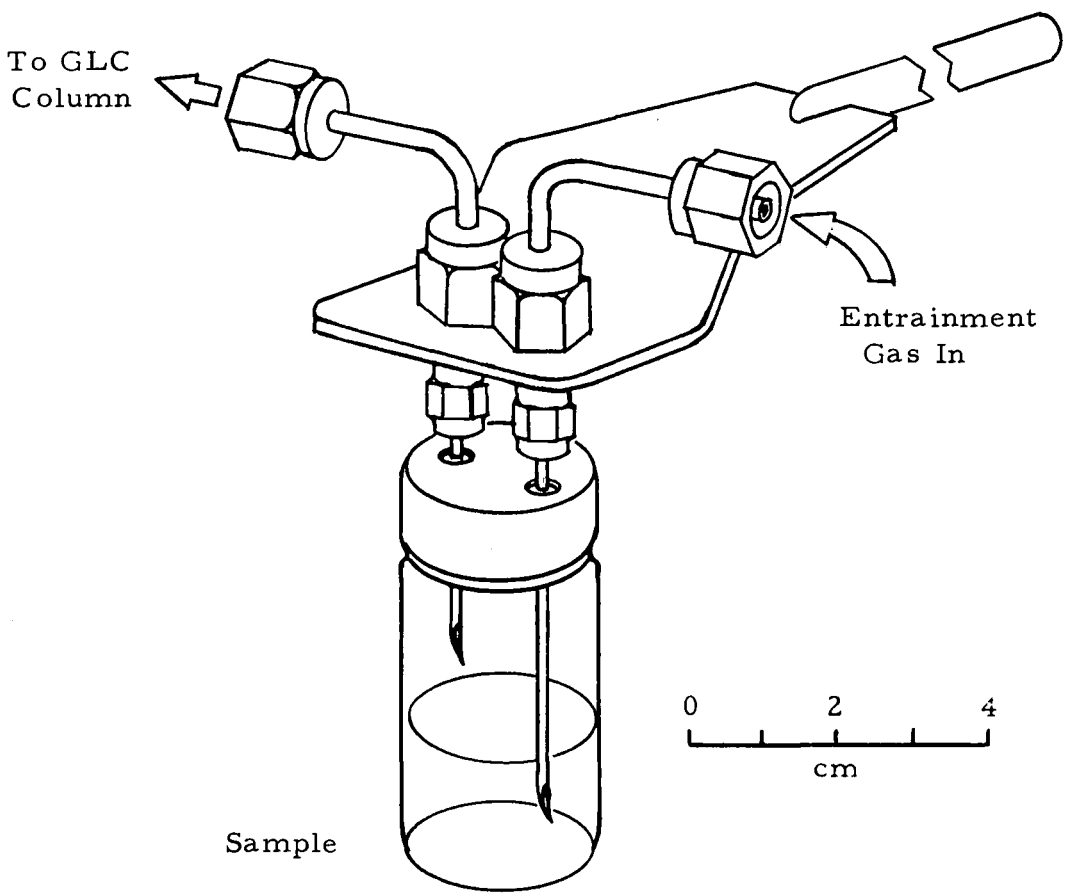


Figure 2. Headspace entrainment assembly used for the analysis of volatile constituents.

	roasted for 20 minutes, 10 ml.
Column	20 percent 1,2,3-tris(2-cyanoethoxy)-propane (TRIS) on 60-80 mesh Celite 545, 12' x 1/8" OD stainless steel.
Column Temperature	50°C
Carrier Gas	Helium
Flow Rate	20 ml/min
Water Bath Temperature	50-52°C
Purge Time	30 minutes
Pressure for Helium Purge	20 psig
	MS Conditions
Scan Speed	m/e 24 to 250 in 2.3 seconds
Filaments	Top Source - 20 eV, 48 uA
	Bottom Source - 70 eV, 30 uA
Pressure	1×10^{-6} mm Hg
Multiplier Voltage	1.60 KV
Source Temperature	250°C
EC -1 Valve Temperature	132°C

This instrument had two ion sources. The 20 eV source was used as a chromatographic readout and the 70 eV source provided the fragmentation patterns. An oscilloscope furnished a continuous monitor of the column effluent. The mass spectra were recorded using a Honeywell Visicorder Model 1508.

Quantification of Headspace Volatiles

The headspace flavor volatiles were analyzed using the aforementioned entrainment technique. Filbert samples, approximately 150 gm quantities, were roasted for 0, 5, 10, 15, 17.5, 20 and 25 minute time periods. Pressed oil samples were obtained from each lot. The prepared samples contained 9 ml of the pressed oil and a 1 ml aliquot of a butanone internal standard solution. Screw-capped vials were used during the analysis. The internal standard solution consisted of 10 ppm of butanone in a stream-stripped corn oil[6] medium. Authentic compound controls were prepared in the same manner except that specified dilutions of the authentic compounds in the stream-stripped corn oil were used in place of the pressed filbert oil sample. The conditions for the analysis were:

Column	20 percent 1,2,3-tris(2-cyanoethoxy)-propane (TRIS) on 60-80 mesh Celite 545, 12' x 1/8" OD stainless steel.
Instrument	Aerograph Model 1200 equipped with a hydrogen flame detector.

[6] Mazola - Pure Corn Oil; Best Foods Division, Corn Products Company, Englewood Cliffs, New Jersey. Two gallons of corn oil were stream-stripped for five hours at 1 mm Hg. The oil temperature was 90-95°C and 1 liter of glass distilled water was used. The finished oil was free of volatiles as determined by GLC headspace analysis.

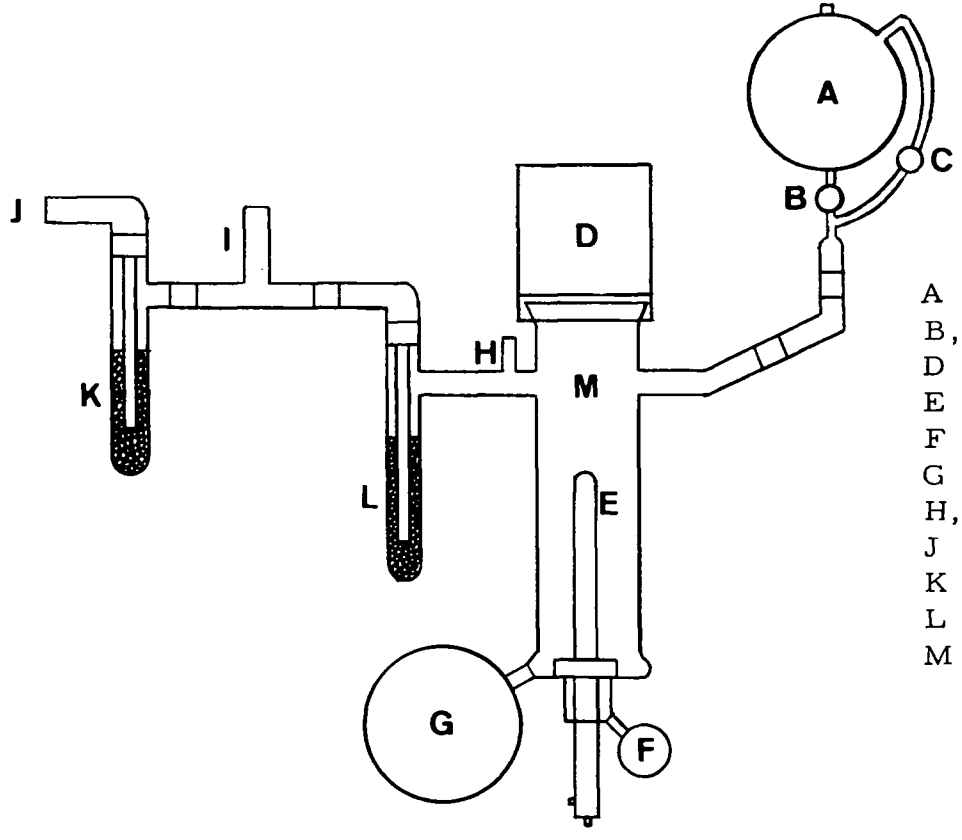
Column Temperature	50°C
Detector Temperature	240°C
Carrier Gas	Nitrogen
Flow Rate	20 ml/min
Water Bath Temperature	50-52°C
Purge Time	Ten minutes
Pressure for Nitrogen Purge	20 psig

Recovery and Evaluation of Flavor Volatiles

Samples of roasted filbert oil were subjected to a molecular distillation and the distillates analyzed using GLC, mass spectrometry and TLC. A similar procedure was employed by Libbey, Bills and Day (45) in a study of Cheddar cheese volatiles.

Distillation Apparatus

Approximately 900 ml quantities of Soxhlet extracted filbert oil were distilled using a Rota-Film Molecular Still, Model 30-2, a product of the Arthur F. Smith Company of Rochester, New York. Figure 3 is a diagram of the distillation apparatus. The overall dimensions of the apparatus were approximately three feet in length and three feet in height. Prior to the distillation, the sample was degassed in order to achieve the desired operating pressure. The degassing was accomplished by opening stopcock C and evacuating



A - Feed Flask
B, C - Stopcocks
D - Wiper Blade Motor
E - Cold Finger Cooled by Tap Water
F - Cold Finger Trap
G - Residue Container
H, I - Vacuum Gauge Monitoring Sites
J - Vacuum Pump Line
K - Liquid Nitrogen Safety Trap
L - Liquid Nitrogen Trap
M - Distillation Chamber

Figure 3. Diagram of molecular distillation apparatus.

until the appropriate operating pressure was obtained. During the course of the distillation, the pressure was maintained between 0.6×10^{-3} to 3.0×10^{-3} mm Hg and was monitored electronically at positions H and I, according to the diagram.

The system was designed to allow for a continuous distillation of the oil sample. Fresh sample was introduced through stopcock B and flowed at a rate of approximately 2 ml/min into the distillation chamber, M. As the oil flowed down the chamber's wall, wiper blades immediately spread the oil into a thin film covering the entire circumference of the wall. The wiper blade assembly was driven by a motor designated as D on the diagram. The oil eventually drained to the bottom of the distillation chamber and was retained in the residue container (G). The wall of the distillation chamber was maintained at a temperature of $45^{\circ}C$.

As the oil flowed through the distillation chamber, the volatile components were vaporized and condensed at one of two sites depending upon the compound's volatility. The compounds which were readily vaporized, were swept from the distillation chamber and condensed in the liquid nitrogen cooled trap designated as L. Less volatile components condensed on the cold finger, E.

After the distillation, both the liquid nitrogen trap, L, and the cold finger, E, were separately washed with purified ethyl ether[7].

[7]Reagent grade ethyl ether was treated to remove peroxides

Ethyl ether was choosen because of its low boiling point and relative inertness.

Concentration of Flavor Compounds

The ether extract which was obtained from trap L was subjected to a fractional distillation in order to remove the excess ethyl ether and thereby concentrate the extracted compounds. The distillation employed a 1 x 60 cm fractionation column packed with glass helices, and the rate of distillation was electronically controlled at a reflux ration of 1:3. The distillation was continued until the residue reached a volume of approximately 40 ml. The residue reached a volume of approximately 40 ml. The residue was then transferred and stored in a 50 ml Bantamware pear-shaped flask. Portions of the residue were subsequently transferred to a 2 ml chromatographic storage tube (Kontes K-42256) and allowed to evaporate at room temperature under a slow stream of nitrogen. As the evaporation progressed, the residue was repeatedly recharged from the 50 ml reservoir. By this procedure, the original 40 ml volume was concentrated to 0.05 ml thereby rendering the sample suitable for GLC and mass spectral analyses.

The cold finger ether extract was analyzed by TLC. The

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according to the method of Valseth (69). Following the peroxide treatment, the ether was slowly glass distilled.

solvent was removed under vacuum and the sample analyzed using the previously described procedure.

Gas-Liquid Chromatographic and Mass Spectrometric Analysis of Flavor Concentrate

GLC and mass spectrometry were used to analyze the roasted filbert flavor concentrate. The mass spectral analysis was conducted in a manner similar to that described. The GLC parameters were modified in order to achieve the desired chromatographic separation and were:

Column	15 percent DEGS, 0.05 percent Igepal CO-880 on 100-120 mesh AW-DMCS Chromosorb G, 10' x 1/8" OD stainless steel.
Temperature Program	55°C for 16 minutes, 2°/min, 200°C
Injection Block Temperature	200°C
Detector Temperature	220°C
Carrier Gas	Helium
Flow Rate	25 ml/min

GLC retention time data were obtained from authentic standard compounds. An Aerograph Model 204 Gas Chromatograph was used for this analysis and the conditions employed were identical to those used with the mass spectrometer except that nitrogen was chosen as

the carrier gas. The gas chromatograph was equipped with an effluent splitter which permitted the simultaneous evaluation of the component's aroma as retention time and mass spectral data were obtained. Component identifications were made by evaluating the accumulated retention time and mass spectral data.

Infrared Spectroscopy

One major component within the flavor concentrate was isolated and subjected to an infrared analysis. The acquisition of this data was considered necessary in order to provide additional structural information for identification. The compound was trapped from the effluent splitter on the Aerograph Model 204 Gas Chromatograph into a 1/6 inch by 12 inch glass capillary tube. The isolated compound was subsequently washed from the tube and the solution collected in a 0.05 mm KBr micro cavity cell. Both spectro grade carbon tetrachloride and carbon disulfide were used. A Beckman Model IR5 spectrophotometer,[1] equipped with a 5 x KBr lens type beam condensor, was employed for the infrared study.

RESULTS AND DISCUSSION

Lipid Characterization

Thermally induced autoxidation reactions of lipid materials were thought to be a potential source of flavor for the roasted filbert. Experiments were conducted in order to test this hypothesis.

Extractable Lipid

Ground filberts were subjected to a Soxhlet extraction with hexane, and the lipid content was determined to be 58.6 percent of the filbert kernel. Portions of the extracted lipid were analyzed by TLC and the results of this analysis are shown in Table 2. The data indicate the presence of two lipid classes. On the basis of their R_f values, spots #1 and #2 have been characterized as triglyceride and phytosteroid compounds, respectively. These results are consistent with earlier literature (71). The triglyceride fraction constituted approximately 90 percent of the total lipid.

Table 2. Thin layer chromatographic results from unroasted filbert lipid samples.

Sample	R_f Value
Filbert Oil	
Spot #1 (ca 90%)	0.484
Spot #2	0.134
Tristearin	0.478
Triolein	0.465
Linolenic Acid	0.242
Lecithin	0.000
Cholesterol	0.146
Cholesterol Palmitate	0.930

Fatty Acid Composition

The fatty acids were analyzed as their methyl esters. Ester identifications were made using gas chromatography and were based on the coincidence of relative retention times of authentic compounds with those of the unknowns. The retention time data is presented in Table 3 and has been recorded relative to the retention time of methyl octadecanoate (18: 0) which was assigned a value of 1.000.

Despite the presence of 18 fatty acids, the composition of the oil is relatively simple since many of the fatty acids are present in only trace amounts. The fatty acid methyl esters were quantitated and the percent composition determined. Methyl esters present in trace

Table 3. Gas chromatographic identification of filbert fatty acids analyzed as their methyl esters.

Compound	Symbol	t_R/t_R 18:0	
		Filbert Oil	Authentics
Methyl Decanoate	10:0	0.137	0.141*
Methyl Undecanoate	11:0	0.174	0.180*
Methyl Dodecanoate	12:0	0.250	0.233*
Methyl Tetradecanoate	14:0	0.379	0.371*
Unknown No. 1		0.388	
Methyl 9-Tetradecenoate	14:1	0.428	0.421*
Methyl Pentadecanoate	15:0	0.473	0.477*
Methyl Hexadecanoate	16:0	0.596	0.588
Methyl 9-Hexadecenoate	16:1	0.701	0.701
Methyl Heptadecanoate	17:0	0.759	0.770*
Unknown No. 2		0.886	
Methyl Octadecanoate	18:0	1.000	1.000
Methyl 9-Octadecenoate	18:1	1.187	1.191
Methyl 9,12-Octadecadienoate	18:2	1.415	1.420
Methyl Eicosanoate	20:0	1.588	1.592
Methyl 9,12,15-Octadecatrienoate	18:3	1.806	1.818
Methyl Eicosenoate	20:1	2.105	2.111*
Methyl Docosanoate	22:0	2.586	2.591

*Determined by log plot technique for homologous compounds under isothermal conditions.

amounts (< 0.1 percent) were not considered for this determination. The data are presented in Table 4 and are compared to the results obtained by Jart (40) in 1963.

Table 4. Quantitative evaluation of filbert fatty acids.

Fatty Acid	Percent Composition	
	Present Investigation	Jart, 1963 (40)
16:0	7.3	5.0
16:1	0.3	0.1
Unknown No. 2	0.1	
18:0	2.0	1.4
18:1	67.3	77.0
18:2	22.4	16.0
18:3	0.4	0.3
20:0	0.1	0.1
20:1	0.1	0.1

Lipid Autoxidation

The level of peroxides was measured iodometrically during all phases of the experiment which utilized lipid materials. These measurements normally reflect the oxidative activity within the lipid fraction and serve as a monitor of lipid autoxidation resulting from roasting and/or sample handling. The method of Dahle and Holman (19) was used and at no time were peroxides detected. These results suggest that the filbert's lipid fraction does not constitute an important

source of flavor for the roasted nut.

Withycombe (72) has demonstrated the potential of methyl oleate (18:1) to autoxidize at 150°C for time periods ranging from ten to 30 minutes. The filbert's lipid material did not show this tendency during the roasting process. The lipid's apparent stability might be explained by the presence of natural antioxidants, such as tocopherols.

Analysis of Roasted Filbert Volatile Constituents

The volatile components of the roasted filbert were analyzed in order to satisfy two objectives. This first objective of this particular study was to establish the identity of the volatile components present in the headspace of roasted filbert oil and the second, to observe the effect of roasting upon the composition of the entrained volatile components.

Gas-Liquid Chromatographic and Mass Spectrometric Analysis

Pressed filbert oil was obtained from filbert nuts roasted for 20 minutes. GLC and mass spectrometry were used to analyze the headspace volatiles from the oil sample. The compounds were identified by comparing their mass spectra with tabulated standard spectra of authentic compounds. GLC relative retention time data were obtained and used to compliment the mass spectral identifications.

Figure 4 is a chromatogram obtained from the headspace of the roasted filbert oil chromatographed isothermally at 55°C on a TRIS column. The component identifications are listed in Table 5. The retention data are recorded relative to the retention time of 2-methylpropanal which was assigned a value of 1.000.

Quantitative Study

The effect of roasting upon the composition of the filbert headspace volatiles was quantitatively determined. The quantitative measurements were made from standard curves obtained by plotting peak height versus concentration. Methanol and acetone (Peak no. 8) were not resolved by GLC. This peak was quantified as acetone. 2-Methylbutanal and 3-methylbutanal were also not completely resolved and produced an asymmetric peak. The quantitative measurements for these compounds were obtained by plotting the peak area of 3-methylbutanal standards versus concentration. Typical standard curves are shown in Figure 5 and the results of this analysis are presented in Table 6.

Significance of the Qualitative and Quantitative Results

The results presented in Table 6 indicate that the roasting process is responsible for the creation and/or increase in the concentration of ten of the 12 headspace components. Only benzene and ethanol

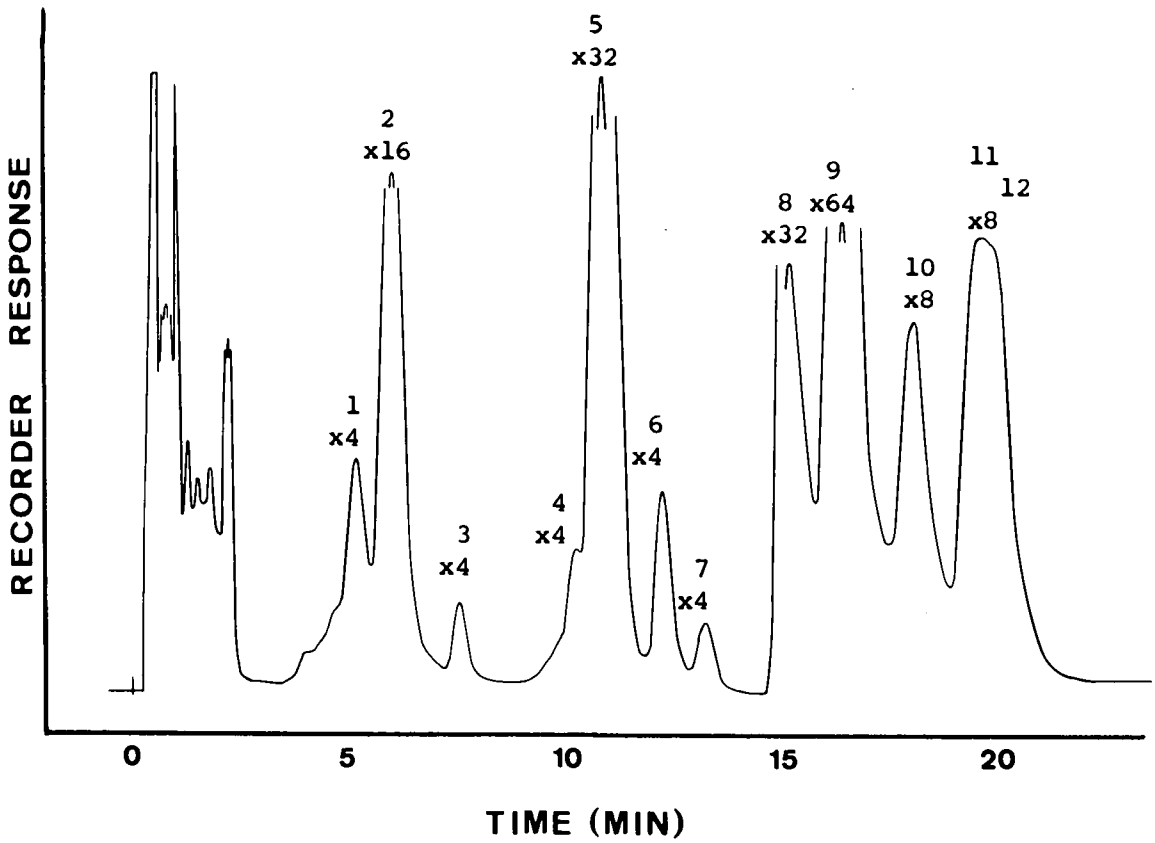

Figure 4. Analysis of the headspace volatiles of the oil obtained from filbert nuts roasted for 20 minutes using a TRIS column.

Table 5. Component identifications of roasted filbert oil headspace volatiles: gas chromatogram is shown in Figure 4.

Peak No.	Compound	t_R/t_R 2-Methylpropanal		Mass Spectral Ident.	MS Ref.	Aroma
		Roasted Filbert Oil	Authentics			
1	Dimethyl sulfide	0.481	0.476	Positive	17	+
2	Acetaldehyde	0.558	0.562	Positive	17	+
3	Methyl formate	0.697	0.672			
4	Propanal	0.939	0.937	Positive	17	
5	2-Methylpropanal	1.000	1.000	Positive	17	+
6	Methyl acetate	1.129	1.136	Positive	17	
7	_____	1.216				
8	Methanol	1.369	1.350	Positive	17	
	Acetone		1.391	Positive	17	
9	Benzene	1.497	1.495	Positive	17	
10	Ethanol	1.665	1.659	Tentative	17	
11	2-Methylbutanal	1.803	1.779	Positive	17	+
12	3-Methylbutanal	1.832	1.811	Positive	17	+

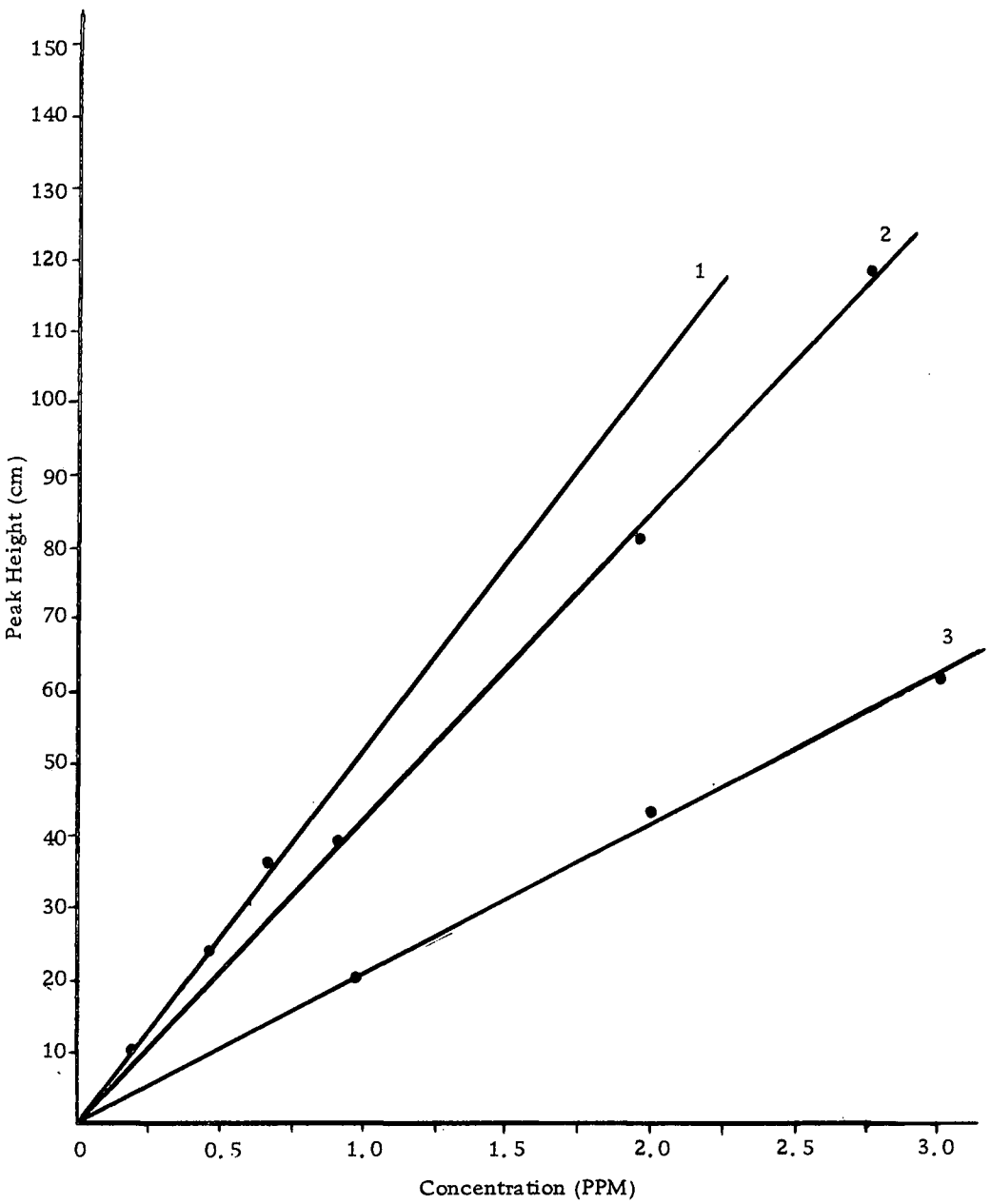

Figure 5. Peak heights obtained from various concentrations of known compounds. (1) Dimethyl sulfide; (2) Propanal; (3) Methyl acetate.

Table 6. Quantitative results of the headspace analysis taken with filbert oil from nuts which were roasted for different time periods.

Compound	Roasting Time (min)						
	0	5	10	15	17.5	20	25
Dimethyl sulfide[a]			0.04	0.11	0.33	0.66	0.43
Acetaldehyde[a]	0.06	0.11	0.22	0.81	5.01	10.65	8.76
Methyl formate[a]					0.02	0.19	0.70
Propanal[a]				0.05	0.14	0.48	0.81
2-Methylpropanal[a]	11.72	9.47	15.21	11.78	23.01	79.56	45.44
Methyl acetate[a]				0.15	0.33	1.28	2.85
Acetone & Methanol[a]	0.10	0.13	0.19	1.80	5.36	12.60	13.51
Benzene[a]	27.19	29.26	36.20	28.88	39.71	27.56	15.04
Ethanol[a]	2.60	2.29	2.89	2.44	1.98	2.68	1.49
2-Methyl- & 3-Methylbutanal[a]			0.42	0.78	4.95	13.05	15.75
Flavor Evaluation	Typical raw filbert nut	Raw taste present with no indication of a roasted flavor	Slight roasted flavor but raw taste predominates	Roasted flavor established with slight raw taste	Good roasted flavor	Nuts are thoroughly roasted and in some cases - over-done	Quite over-done - flavor is bitter, nuts are dry

[a]Concentrations expressed in p. p. m.

were observed to remain at relatively constant concentrations throughout the duration of the heat treatment. Their presence in natural products has been the subject of several documented studies. Benzene has been shown to arise as a result of ethylene metabolism in plant systems (39). Ethanol has frequently been identified in the flavor extracts of a variety of natural products (1, 62).

A striking feature of the results obtained during this study is the presence of acetaldehyde, 2-methylpropanal, 2-methylbutanal and 3-methylbutanal. The Strecker degradation is a probable source of these aldehydes. The amino acid precursors for these compounds are alanine, valine, isoleucine and leucine, respectively. The flavor thresholds for these compounds have been determined in water and the results indicate that they can be detected at less than 1 p.p.m. (64).

Dimethyl sulfide was also shown to be a heat-induced component of the roasted filbert and was observed to be present at very significant concentrations. The flavor threshold for this compound is several parts per billion and, as a consequence, trace quantities cause it to be an important flavor compound for many food systems. Bills and Keenan (5) traced the development of dimethyl sulfide in canned corn and established that the thermal degradation of an S-methylmethionine sulfonium salt was responsible for its formation.

The methyl formate, methyl acetate, propanal and

acetone-methanol peaks were observed to increase during the roasting process. The formation of the two esters is thought to occur as a result of a mass action, acid catalyzed esterification reaction. The production of propanal can be attributed to two reaction pathways. Hodge (36) has indicated that propanal is a common end-product of nonenzymatic browning while Day (21) indicates that propanal can also arise from lipid autoxidation. Finally, one is only able to postulate which component or what percentage of each component is responsible for the increase of the acetone-methanol peak. Rudolph, Mason and Odell (61) identified methanol in unroasted pecans, and acetone is a known end-product of nonenzymatic browning (36).

Dimethyl sulfide, acetaldehyde, 2-methylpropanal, 2-methylbutanal and 3-methylbutanal contribute significantly to the roasted filbert flavor and aroma.

Identification of Flavor Compounds Isolated from the Roasted Filbert

GLC and mass spectrometry were used to analyze the flavor concentrate obtained from the roasted filbert. The distillation procedure was not quantitative and therefore, only qualitative significance can be placed upon these results. The flavor components were positively identified by comparing their mass spectra with known fragmentation patterns. The coincidence of GLC relative retention

times of authentic compounds with those of the unknowns provided information which was useful in confirming the mass spectral interpretations.

Figure 6 is a chromatogram obtained from a temperature programmed GLC analysis on a 15 percent DEGS, 0.05 percent Igepal CO-880 column for the roasted filbert flavor concentrate. The retention time data were recorded relative to the retention time of 2-furfural which was assigned a value of 1.000. Marion et al. (47) present data which were also obtained from a temperature programmed GLC analysis using a DEGS column. These data provided elution orders for some commercially unavailable compounds of interest to this study. The identification of the peaks shown in Figure 6 is given in Table 7. Table 8 summarizes the constituents identified from the roasted filbert.

In several cases, chromatographic resolution was not achieved. The identification of these mixtures was, nevertheless, possible when definitive mass spectral fragmentation patterns could be obtained. Aroma perception of these mixtures played a significant role during this investigation.

Study of a Major Heat-Induced Component

A major heat-induced component (Peak no. 34, Figure 6) was observed during the GLC analysis of the roasted filbert flavor

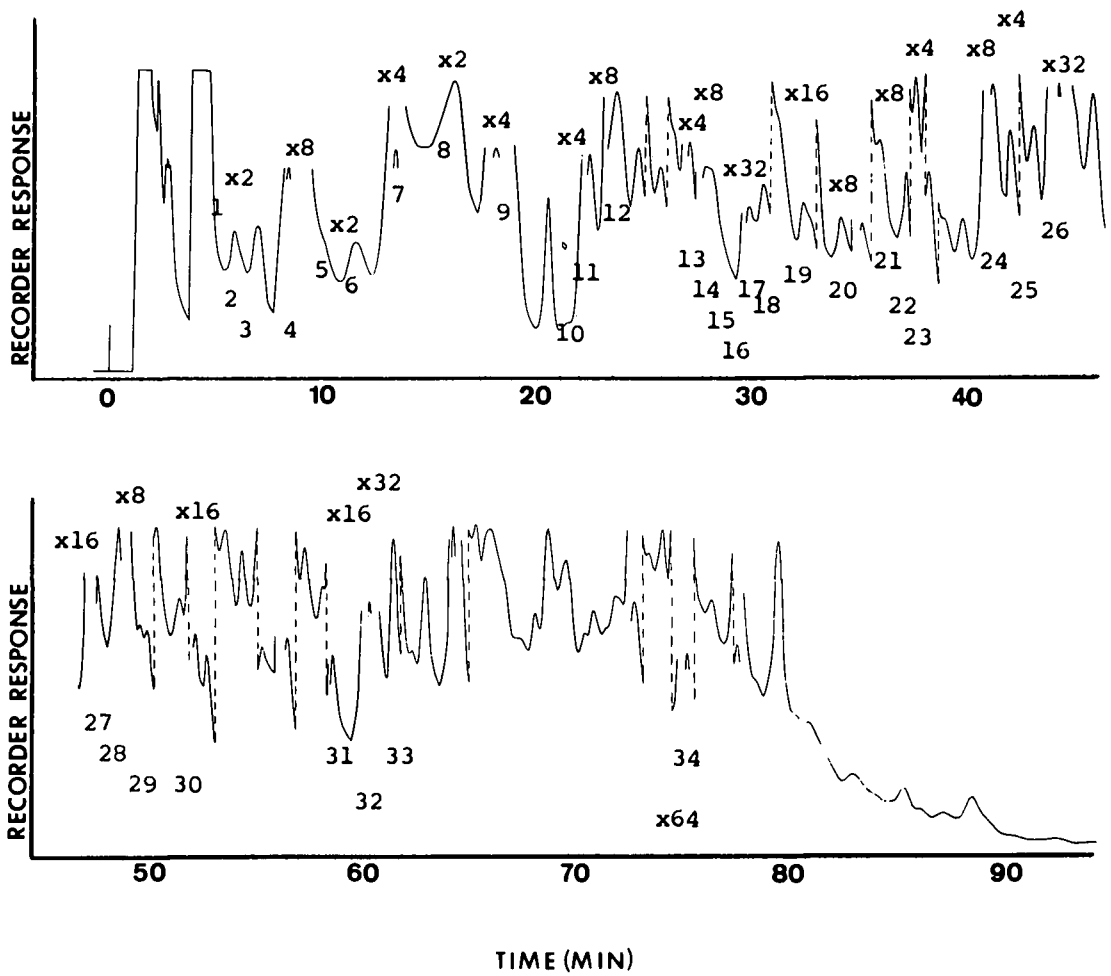

Figure 6. Gas chromatogram of the roasted filbert flavor concentrate using a DEGS column.

Table 7. Gas chromatographic and mass spectral identifications of roasted filbert components; gas chromatogram is shown in Figure 6. (The initial peaks are due to those compounds previously identified from the headspace studies and to residual solvent.)

Peak No.	Compound	$^tR/^tR$ 2-Furfural		Mass Spectral Ident.	MS Ref.	Aroma
		Roasted Filbert	Authentics			
1	Ethyl acetate	0.110	0.113	Positive	17	
2	Toluene	0.161	0.174	Positive	17	
	Diacetyl		0.178	Positive	17	+
3	n-Decane	0.189	0.208	Positive	17	
4	Hexanal	0.229	0.264	Positive	17	+
5	Xylene (m or p)	0.273	(m) 0.288	Positive	17	
			(p) 0.298			
6	Unknown	0.317				
7	Mixture - 3-Pentene-2-one	0.366	0.384	Tentative	17	
8	Heptanal	0.444	0.452	Tentative	17	
	2-Pentyl furan		0.516	Positive	6	
9	1,2,4-Trimethylbenzene	0.499	0.586	Tentative	17	
10	Thiazole	0.595	0.589			+
11	Octanal	0.623	0.649			+
12	Allyl crotonoate	0.659		Tentative	17	
	2-Methylpyrazine		0.658	Positive	7	
	2-Methyltetrahydrofuran-3-one		(47)	Positive	67	
13	2-Ethylpyrazine	0.754	(47)	Positive	7	
14	2,5-Dimethylpyrazine	0.775	0.767	Positive	7	+
15	Acetic Acid	0.780	0.791	Positive	17	+
16	2,3-Dimethylpyrazine	0.791	0.801	Positive	7	
17	2-Ethyl-5-methylpyrazine	0.832	0.841	Positive	7	+
18	2-Ethyl-3,6-dimethylpyrazine	0.850	0.917	Positive	7	+
19	Ethylmethylpyrazine	0.902		Tentative	7	
20	2-Ethyl-3,5-dimethylpyrazine	0.950	0.948	Positive	7	
21	2-Furfural	1.000	1.000	Positive	17	+
	2,6- or 2,5-diethyl-3-methylpyrazine			Tentative	7	
22	Acetyl-2-furan	1.037	1.016	Positive	17	
23	Benzaldehyde	1.048	1.058	Positive	17	+
24	5-Methylfurfural	1.147	1.163	Positive	17	
25	N-Methyl-2-pyrrole aldehyde	1.201	1.218	Tentative	67	
26	Phenylacetaldehyde	1.234	1.241	Positive	17	+
	Furfuryl alcohol		1.241	Positive	17	+
27	γ-Butyrolactone	1.321	1.337	Positive	18	
28	Hexanoic acid	1.348	1.341	Positive	17	+
29	N-Furfurylpyrrole	1.385	1.444	Tentative	67	
30	Butylated hydroxytoluene	1.447	1.456	Positive	17	
31	Acetyl-2-pyrrole	1.627	1.632	Positive	11	
32	Pyrrole-2-carboxaldehyde	1.673	1.700	Positive	11	
33	3-Hydroxy-2-methyl-4-pyrone	1.704	1.707	Positive	67	
	2,5-Dimethyl-4-hydroxy-3 (2H)-furanone		1.707	Positive	65	+
34	Heat-induced Unknown	2.086				

Table 8. Summary of compounds identified in the roasted filbert flavor concentrate.[a]

Acids	
Acetic acid	+
Hexanoic acid	+
Alcohols	
Ethanol	±
Methanol	+
Aldehydes	
Acetaldehyde	+
Propanal	+
2-Methylpropanal	+
2-Methylbutanal	+
3-Methylbutanal	+
Hexanal	+
Heptanal	±
Octanal	±
Benzaldehyde	+
Phenylacetaldehyde	+
Esters	
Methyl formate	±
Methyl acetate	+
Ethyl acetate	+
Allyl crotonoate	±
Furans	
2-Pentyl furan	+
2-Furfural	+
Acetyl-2-furan	+
5-Methylfurfural	+
Furfuryl alcohol	+
2, 5-Dimethyl-4-hydroxy-3 (2H)-furanone	+
2-Methyltetrahydrofuran-3-one	+
Hydrocarbons	
Benzene	+
Toluene	+
Xylene (m or p)	+
1, 2, 4-Trimethylbenzene	±
n-Decane	+
Pyrazines	
2-Methylpyrazine	+
2-Ethylpyrazine	+
2, 5-Dimethylpyrazine	+
2, 3-Dimethylpyrazine	+
2-Ethyl-5-methylpyrazine	+
2-Ethyl-3, 6-dimethylpyrazine	+
Ethylmethylpyrazine	±
2-Ethyl-3, 5-dimethylpyrazine	+
2, 6- or 2, 5-Diethyl-3-methyl-pyrazine	±
Miscellaneous Compounds	
Dimethyl sulfide	+
Thiazole	±
Acetone	+
Diacetyl	+
3-Pentene-2-one	±
3-Hydroxy-2-methyl-4-pyrone	+
γ-Butryolactone	+
2-Pyrrole aldehyde	+
N-Furfurylpyrrole	±
N-Methyl-2-pyrrole aldehyde	±
Acetyl-2-pyrrole	+

[a] (+) denotes those compounds which have been positively identified while (±) indicates tentative identifications.

concentrate. This component was present in sufficiently high concentration to warrant a study leading to its characterization. The compound was repeatedly trapped from the GLC column effluent and approximately 100μg were obtained for mass spectral and infrared (IR) analyses.

The mass spectral fragmentation pattern is shown in Table 9. The compound also possessed two meta-stable fragments at m/e 45.6 and 71.3. The data presented by Beynon, Saunders and Williams (2) for meta-stable transistions interpret their presence as being indicative of two, one step fragmentations, namely,

$$\text{m/e } 121 \xrightarrow{71.3^*} \text{m/e } 93 \xrightarrow{45.6^*} \text{m/e } 65$$

Table 9. Mass spectrum of Peak no. 34, Figure 6. Base Peak: m/e 93. Parent Peak: m/e 121.

m/e	Relative Intensity
27	16
38	25
39	19
64	13
65	38
66	13
93	100
121	56

Mass spectrometry was used to establish an empirical formula for both the parent and base peaks (50, p. 25). The parent peak was

shown to be 121. This assignment was confirmed by noting an increase in the intensity of the m/e 121 peak and the observed absence of larger fragments during a low energy scan of the spectrum. Since the molecular weight is an odd number, the structure was presumed to contain an odd number of nitrogen atoms (50, p. 33). Scanning slowly through the parent and base peak regions and evaluating the (P) and the (P+1) peaks, empirical formulas of C_7H_7NO and C_6H_7N were obtained for m/e 121 and m/e 93, respectively (3). An interesting feature of this spectrum is the two successive losses of 28. The first loss is due to the elimination of CO.

The IR spectra of Peak no. 34 were obtained using carbon tetrachloride and carbon disulfide as solvents and are shown in Figure 7. A strong carbonyl band was observed at 1700 cm^{-1}. The IR spectra also show the presence of several other prominent bands, namely, 1378 cm^{-1}, a doublet at 1310 & 1304 cm^{-1} and 1065 cm^{-1}. An evaluation of the IR spectrum was made by considering the band assignments of Colthup, Daly and Wiberley (16). The following conclusions were made concerning the structural properties of the compound as shown in Table 10.

These spectral data suggest that the compound is a carbon-nitrogen heterocycle containing a carbonyl moiety within the ring system. The possibility of a γ-lactam was considered, however, a satisfactory structure could not be postulated. Sufficient structural

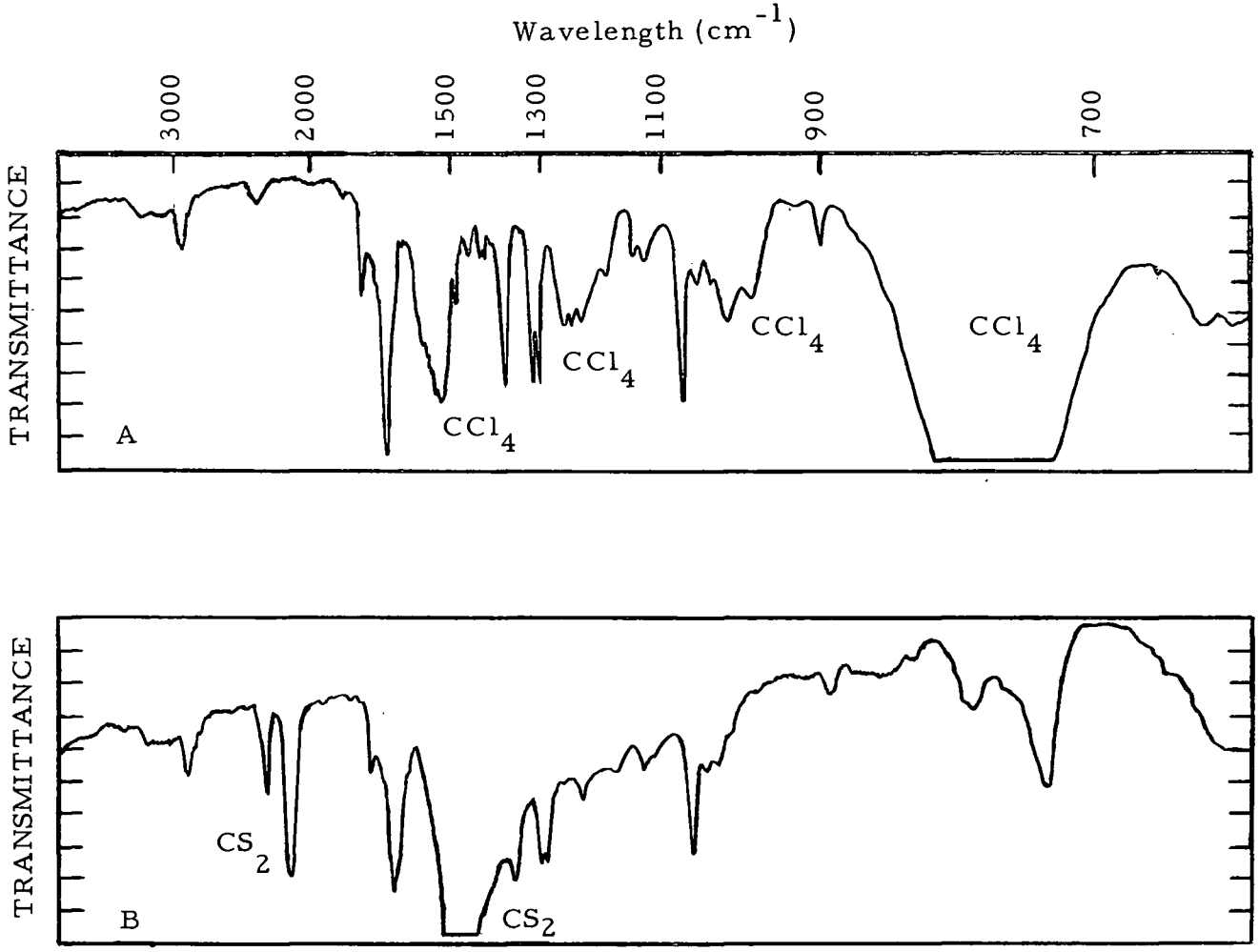

Figure 7. Infrared spectrum of Peak no. 34, Figure 6. A - Carbon tetrachloride; B - Carbon disulfide.

Table 10. Structural properties of Peak no. 34, Figure 6.

Structural Property	Evidence
Aliphatic CH's and no NH	CH absorption below 3000 cm^{-1}, absorption is absent for NH.
Ring structure is probable	Relatively stable parent ion; m/e 65 and m/e 39 are suggestive of cyclic compounds.
Type of carbonyl:	
carbonyl is in the ring	Only a loss of 28 was observed-m/e 121 to m/e 93.
carbonyl is probably not conjugated	A strong band at 1650 cm^{-1} is absent.
no indication of a CH_2-CO-CH_2 structure	The characteristic band at 1230-1100 cm^{-1}.
γ -lactam	Possibility--the carbonyl absorption of the unknown is in the correct position, 1700 cm^{-1}. C-N stretching vibrations for lactams appear in the region of 1350-1310 cm^{-1}. Absorption for the unknown was observed in this region.

data were not available to provide a complete identification of this compound.

Development of the Roasted Filbert Flavor

Throughout this investigation, considerable attention has been focused upon the involvement of major reaction sequences and their role in the development of flavor. Lipid autoxidation has already been discussed and concluded to be of minor importance for this particular flavor. The nonenzymatic browning and Strecker degradation pathways, however, are essential to the production of a roasted filbert flavor.

The aldehydes, acids, furans, pyrazines and several miscellaneous compounds listed in Table 8 were considered to be essential to the flavor of the roasted nut. Their origin will be discussed in the following sections.

Aldehydes

The origin of the volatile aldehydes such as acetaldehyde, propanal, 2-methylpropanal, 2-methylbutanal and 3-methylbutanal has been previously discussed and both nonenzymatic browning and the Strecker degradation reactions have been implicated as an important source of these compounds (36). These compounds contribute significantly to the roasted flavor. The branched chain C_4 and C_5

aldehydes possess "malty" flavor notes. Phenylacetaldehyde is another Strecker aldehyde and is a product of the oxidative degradation of phenylalanine. This compound possesses a floral characteristic which may contribute to the background of the flavor.

Hexanal was positively identified while tentative identifications were obtained for both heptanal and octanal. Fatty acid precursors are generally cited as being responsible for the presence of straight chain aldehydes.

Acids

Only two acids were identified in the flavor concentrate. Non-enzymatic browning is a documented source of acetic acid (36), however, the origin of hexanoic acid is not clear. The possibility could exist whereby hexanal is a participant in a redox reaction and is oxidized to the corresponding acid. Hexanoic acid, on the other hand, may be a by-product of the browning reaction.

Furans

Furans containing aldehyde, alcohol and ketone functional groups were identified from the flavor concentrate. These compounds are formed as a result of the thermal degradation of carbohydrate material within the nut and contribute roasted and caramel flavors (37). Furfural is an important representative of this group

and is formed largely from pentosan precursors (23, p. 289). Hodge (36) and Reynolds (56) have surveyed the literature on the Maillard reaction and have referred to the production of many substituted furans.

4-Hydroxy-2,5-dimethyl-3(2H)-furanone has been identified in pineapple (65) and in beef broth (68) flavor extracts. This compound was also observed during this study and possesses a very distinctive caramel flavor which is undoubtedly an important contributor to the roasted filbert flavor.

Pyrazines

Seven alkyl-substituted pyrazines were positively identified during the course of this investigation. Pyrazines are reportedly reaction by-products of sugar-amine systems (43, 55). These compounds have been found in many roasted systems and possess flavor properties which Hodge (37) describes as being nutty, popcorny and bread-like. Pyrazines have been implicated as being responsible for the roasted flavor of the pecan (61) and peanut (48).

Miscellaneous Compounds

Dimethyl sulfide, diacetyl, 3-hydroxy-2-methyl-4-pyrone (maltol) and γ-butyrolactone were considered to contribute significantly to the roasted flavor. The origin of dimethyl sulfide has already been discussed. Diacetyl and maltol are common by-products

of the Maillard reaction (36, p. 468, 469, respectively). The formation of diacetyl is thought to occur as a result of fission reaction involving the reductone structures shown in Figure 1. Diacetyl possesses important "buttery" and "heated" flavor notes. Maltol, on the other hand, possesses a caramel-like aroma and is assumed to arise from 4-O-substituted glucose derivatives such as maltose and lactose. γ-Butyrolactone is another important compound and imparts a very sweet aroma to the mixture. Lactones are generally considered to form as a result of dehydration reactions involving hydroxy acids.

Concluding Remarks

This discussion has considered the roasted filbert flavor with respect to those compounds which have been identified during the course of the study. No single component can be named which possesses a flavor resembling the roasted nut, and therefore, this flavor is an expression of a combination of compounds. In this regard, the pyrazine derivatives are probably responsible for much of the roasted character of the nut.

Aromas from the GLC column were perceived, however, which were suggestive of that of the unroasted nut. The most noticeable character-impact aroma was noted in the region of peaks 6 and 7 according to Figure 6. Attempts to yield identifications for this

region were not entirely successful. Peak no. 6 was present in very low concentrations and rendered attempts for spectral identifications impossible. Peak no. 7 was tentatively identified as 3-pentene-2-one. The mass spectrum for this peak, however, indicated a mixture and contained several fragments which could not be correlated. Odor evaluations of the authentic sample did not produce a distinctive filbert aroma. It is, nevertheless, conceivable that overlapping compounds are modifying the effect of the ene-one to give a filbert-like aroma.

SUMMARY AND CONCLUSIONS

The attention of this investigation was focused upon the roasted filbert flavor. The study was divided into three parts. These were: (1) the characterization of the lipid fraction and the assessment of its participation leading to the production of the roasted flavor; (2) qualitative and quantitative analyses of the headspace volatiles; and (3) a qualitative analysis of the vacuum distillate from roasted filbert oil samples obtained by Soxhlet extraction.

The lipid fraction was shown to be primarily in the form of triglycerides and oleic acid was observed to constitute a major portion of the triglyceride fatty acids. The development of measurable amounts of peroxidic compounds was not noted during the course of the roast.

The qualitative analysis of the headspace volatiles yielded ten positive identifications 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. Experiments were conducted which demonstrate that ten of the 12 identified compounds were heat-induced. The amounts of these compounds were determined at selected times during the roasting period.

The volatile compounds of the roasted nut were analyzed from

the Soxhlet extracted oil. The oil was subjected to a vacuum distillation and an ether extract prepared. The extract was concentrated and the flavor concentrate analyzed by GLC and mass spectrometry. Twenty-nine compounds were positively identified and ten compounds were tentatively identified from the flavor concentrate.

The following conclusions were reached from the findings of this investigation:

1. The qualitative analysis of the roasted filbert flavor components yielded 38 positive and 12 tentative identifications.
2. The roasted filbert flavor depends upon the interaction of a combination of compounds. The identified aldehydes, acids, furans and pyrazines were considered to be essential to the roasted filbert flavor.
3. Nonenzymatic browning and the Strecker degradation reaction sequences were considered to be the principle source of flavor constituents.
4. The lipid fraction did not appear to be an important precursor of flavor components.

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