

taste thresholds (+)- and (-)-nootkatone and (+)- and (-)- α -vetivone have been tasted in a soft drink base by several experienced flavor chemists. (+)-Nootkatone was perceptible at a concentration of approximately 0.3 ppm and still had the flavor character of grapefruit. (-)-Nootkatone was perceptible at 40 ppm (much lower than the odor threshold value for aqueous solutions) and at that concentration tasted bitter and sour without any flavor impression. (+)- α -Vetivone was perceptible at 1.6 ppm and at that concentration is slightly reminiscent of grapefruit. It also has a strong woody flavor, not appreciated by flavor chemists. (-)- α -Vetivone, perceptible at approximately 8 ppm, is weaker than the (+)-form but has an even stronger woody note. The odor profiles are shown in Figure 5. Apparently the enantiomeric forms of the five sesquiterpenoid ketones do not only differ significantly in odor strength but in odor character as well. The largest differences are found again between (+)- and (-)-nootkatone.

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End of Part II on the Symposium on The Chemistry of Essential Oils and Related Products.

Volatile Components of Roasted Filberts

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Roasted filbert volatiles were isolated using the following techniques: steam distillation followed by solvent extraction; condensation of volatiles given off during steam distillation; and molecular distillation followed by fractionation using preparative gas chromatography. Extracts and fractions were analyzed by gc-ms using open tubular columns. 187 compounds are reported for the first time from

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roasted filbert volatiles including alkyl, alkenyl, oxygenated, and alicyclic pyrazines; pyrroles; pyridines; thiols, thiazoles, thiophenes, and sulfides; furans; phenols; acids; lactones; esters; terpenes; aromatic aldehydes, alkanals, 2-alkenals, and 2,4-alkadienals; aliphatic and olefinic alcohols and ketones; and aliphatic and aromatic hydrocarbons.

Filberts (*Corylus avellana*) are a thick-shelled, sweet-flavored tree nut which may be consumed raw or, preferably, roasted. Little has been published concerning the flavor components of roasted filberts, except for the work of Sheldon (1969), who identified 41 compounds in the volatiles of roasted filberts. The use of modern analytical techniques, particularly the coupled gas chromatograph-mass spectrometer (gc-ms), has revealed the complexity of such heat-processed foods as coffee (Friedel *et al.*, 1971), cocoa (van Praag *et al.*, 1968) and peanut (Walradt *et al.*, 1971). Our objective, in a more detailed investigation of the roasted filbert volatiles, was to provide a qualitative comparison with other roasted products. Our gc-ms identifications were greatly assisted by the recent availability of additional reference data, particularly for the nitrogen-containing compounds (Friedel *et al.*, 1971; Pittet *et al.*, 1971). This paper reports the com-

pounds which were obtained from roasted filberts by four different isolation techniques and identified by gc-ms.

EXPERIMENTAL

The methods of isolation used in our work were (A) headspace analysis, (B) collection of volatiles emitted during roasting, (C) steam distillation, and (D) molecular distillation.

Roasting conditions were identical for all methods. Oregon-grown filberts were roasted in a solid-shell roaster (Probat-Werke, Germany) to 200°C and held for 5 min or until a medium to dark brown color was obtained.

(A) The headspace analysis was of uncondensed volatiles emitted during an atmospheric pressure steam distillation. Roasted filberts (1 kg) were ground to a fine slurry in an industrial Waring blender with 2 l. of deionized water and steam distilled for 20 min. The bulk of the water vapor was condensed in a cold water condenser (15°C) and collected in a wet ice cooled receiver. The uncondensed volatiles were passed into a 4-in. \times 1/8-in. o.d. stainless steel tube packed with

*International Flavors & Fragrances, Union Beach, New Jersey 07735.

Table I. Compounds Identified from Roasted Filbert Volatiles

Pyrazines	First reported	Isolate	Retention index		Ms data
			CBW	SF-96	
Pyrazine	X	B, D	5.77	3.75	80-53-26-52
Methylpyrazine		B, C, D	6.41 ¹	4.38	94-67-39-40-53
Ethylpyrazine		A, B, C, D	7.06 ¹	5.21 ¹	107-108-80-53-52-39
Isopropylpyrazine	X	D	7.34 ¹		107-122-94-27-52
Propylpyrazine	X	D	7.75 ¹	6.19	94-107-122-39
2,5-Dimethylpyrazine		A, B, C, D	6.86 ¹	5.17 ¹	108-42-39-40-81-28
2,6-Dimethylpyrazine	X	A, B, C, D	6.98 ¹		108-42-40-39-38-67
2,3-Dimethylpyrazine		B, C, D	7.10 ¹	5.26	67-108-80-42-40-26
2-Ethyl-6-methylpyrazine	X	B, C, D	7.53 ¹	6.06	121-122-39-94-56-40
2-Ethyl-5-methylpyrazine		C, D	7.57 ¹	6.07	121-122-39-56-94
2-Ethyl-3-methylpyrazine	X	B	7.67 ¹	6.17	121-122-67-94-39
2,6-Diethylpyrazine	X	D	8.14 ¹		135-136-39-108-53
2,5-Diethylpyrazine	X	D	8.18 ¹	6.93	136-121-135-39-27
2,3-Diethylpyrazine	X	D	8.24 ¹	6.88	136-121-27-135-39
2-Methyl-5-pentylpyrazine	X	D	10.46 ¹		108-121-39-109-135-164
Trimethylpyrazine	X	B, C, D	7.68 ¹	6.07	42-122-39-81
2-Ethyl-3,6-dimethylpyrazine		C, D	8.10 ¹	6.83	135-136-42-56-39-108
2-Ethyl-3,5-dimethylpyrazine		C, D	8.27 ¹		136-135-39-108-53-56
2,3-Diethyl-5-methylpyrazine	X	C	8.65		150-149-135-56-39
2,5-Diethyl-3-methylpyrazine	X	D	8.70		149-150-39-135
2,6-Diethyl-3-methylpyrazine		C	8.87	7.64	149-150-39-122-53-135
Dimethyl isobutylpyrazine	X	D	8.83		122-42-133-149-164
Triethylpyrazine	X	D	9.06		164-149-163-39-56-136
Tetramethylpyrazine	X	D	8.46 ¹	6.91	54-136-42-27-39-53
Diethyldimethylpyrazine	X	D	9.10		149-164-163
Vinylpyrazine	X	D	8.08 ¹		106-52-79-53-71
2-Methyl-6-vinylpyrazine	X	C, D	8.58 ¹		120-52-39-54-94-51
2-Methyl-5-vinylpyrazine	X	C, D	8.63 ¹		120-52-54-39-93-79
Acetylpyrazine	X	D	9.92 ¹	6.31	43-122-80-79-52-53
2-Methyl-5-acetylpyrazine	X	D	10.43 ¹		136-94-39
Ethylacetylpyrazine	X	D	10.90		150-107-108
6,7-Dihydro-5H-cyclopentapyrazine	X	D	10.25 ¹		120-119-39-41-66-65
2-Methyl-6,7-dihydro-5H-cyclopentapyrazine	X	D	10.73 ¹		134-133-39-66-40-107
5-Methyl-6,7-dihydro-5H-cyclopentapyrazine	X	D	9.93 ¹		119-134-133-39-52-78
2-Ethyl-6,7-dihydro-5H-cyclopentapyrazine	X	D	11.42 ¹		147-148-39-120-65-66
2,5-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine	X	D	10.26 ¹		133-148-39-147
3,5-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine	X	D	10.39 ¹		133-148-39-147
2,3-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine	X	D	11.54 ¹		148-43-147-66-107
Quinoxaline	X	D	12.7 ¹		130-76-103-50-75-51
5,6,7,8-Tetrahydroquinoxaline	X	D	11.14 ¹		134-133-52-39-106-41
2-Methyl-5,6,7,8-tetrahydroquinoxaline	X	D	11.30 ¹		148-147-52-39-120-79-133
(2'-Furyl)pyrazine	X	D	13.7 ¹		146-93-63-64-38

Table I. (Continued)

Pyrroles	First reported	Isolate	Retention index		Ms data
			CBW	SF-96	
2- <i>n</i> -Pentylpyrrole	X	D	12.4		80-137-53 [*]
2-Isobutylpyrrole	X	D	10.44		80-123-53-81 [*]
1-Methylpyrrole	X	A	5.09	3.41	81-80-39-53-66 [*]
1-Acetylpyrrole	X	D	9.03 ¹		67-109-39-43-41-40 [*]
2-Acetylpyrrole		B, C, D	13.7 ¹		94-109-66-39-43 [*]
2-Propionylpyrrole	X	D	13.7 ¹		94-123-39-66-37 [*]
1-Methylpyrrole-2-carboxaldehyde		D	9.86 ¹		109-108-80-78-53-39 [*]
5-Methylpyrrole-2-carboxaldehyde	X	B, D	14.4 ¹		109-108-80-53-29 [*]
Pyrrole-2-carboxaldehyde		B, C, D	13.5 ¹		95-94-39-66 [*]
1-Furfurylpyrrole		A, D	11.89 ¹	7.93 ¹	81-147-53-27-39-51 [*]
1-Methyl-2-pyrrolidinone	X	D		7.25	44-99-42-98-27-71-70-56 [*]
Indole	X	D	17.6 ¹		117-90-89-63-39-118-116 [*]
Pyridines					
2- <i>n</i> -Pentylpyridine	X	D	9.38 ¹		93-106-120-27-149 [*]
2-Acetylpyridine	X	D	9.73 ¹		79-78-121-43-51-52 [*]
3-Acetylpyridine	X	D	12.00		78-106-51-121-43-50 [*]
Methyl nicotinate	X	D	11.44 ¹	7.62	106-78-137-51-50-29 [*]
Sulfur compounds					
Methanethiol	X	A, D	0.38 ¹		47-48-45-15-44 [*]
Methyl disulfide		A, B, D	4.47 ¹	3.30 ¹	94-79-45-46-47-61 [*]
Ethyl disulfide	X	C	6.05 ¹	5.30	29-27-122-66-94-45 [*]
Methyl trisulfide	X	A, C	7.74 ¹	5.90	126-45-79-47-64-46 [*]
3-Methylthiopropionaldehyde	X	D	8.14 ¹	5.13	48-47-27-104-45 [*]
Dihydro-1 <i>H</i> -thiophen-3-one	X	D	9.29 ¹		46-102-45-27-26-60 [*]
Thiophene-2-carboxyaldehyde	X	B, C, D	10.59 ¹		111-112-39-29-45-83 [*]
4-Methyl-5-vinylthiazole	X	D	8.94		125-97-45-58-39-98 [*]
Benzothiazole	X	B, C	13.0 ¹		135-108-69-63-45-82 [*]
3,5-Dimethyl-1,2,4-trithiolan	X	A	9.50 ¹		152-45-59-92-88-64 [*]
Dimethyltrithiolan (isomer)	X	A			
Furans					
Furan	X	A	0.82 ¹		39-68-67 [*]
2-Methylfuran	X	A, B	1.87 ¹		53-39-82-81 [*]
2-Ethylfuran	X	A, B	3.00	3.06	81-39-96-41 [*]
2-Butylfuran	X	B	5.00 ¹		81-82-124-54 [*]
2-Pentylfuran		A, B, C, D	5.93 ¹	5.98 ¹	81-82-138-53 [*]
Phenylfuran	X	D	11.83		144-115-143 [*]
2-Hexylfuran	X	A, D	7.00		81-82-152 [*]
2-Heptylfuran	X	A, D	8.00		81-82-166 [*]
2-Octylfuran	X	D	9.00 ¹		81-82-180 [*]
Dimethylfuran	X	A	2.63		53-96-95-81 [*]
Dimethylfuran	X	A			96-95-43-81 [*]
2-Vinylfuran	X	A			94-65-66-39 [*]
2-Furfural		A, B, C, D	8.24 ¹	4.62 ¹	39-96-95-66 [*]

Table I. (Continued)

Furans	First reported	Isolate	Retention index		Ms data
			CBW	SF-96	
5-Methylfurfural		A, B, C, D	9.36 ¹	5.81 ¹	110-109-53-27-51*
2-Methyltetrahydrofuran-3-one		B, C	6.30 ¹		43-72-100-29-45-27*
2-Acetylfuran		B, C, D	8.70 ¹	5.29 ¹	95-110-39-43-96*
5-Methyl-2-acetylfuran	X	D	9.76 ¹		109-124-53-43-39-51-81*
Furfural acetate	X	B, D	8.97 ¹		81-43-98-52-53-140*
Methyl furoate	X	B, D	9.38 ¹	5.90	53-126-27-109-81-51*
Furfuryl alcohol		A, B, C, D	10.17 ¹	5.33 ¹	39-98-41-29-81-53*
Aldehydes					
Acetaldehyde		B, C, D	0.44 ¹	0.61	29-44-15-43-14-26*
Pentanal	X	A, B, C, D	3.26 ¹	2.86 ¹	44-29-58-41-57...86*
Hexanal		A, B, C, D	4.49 ¹	4.00 ¹	44-43-56-41-57...100*
Heptanal		A, B, C, D	5.55 ¹	5.01 ¹	44-43-70-41-55...114*
Octanal		A, B, D	6.58 ¹	6.03	44-41-57-56-84...128*
Nonanal	X	A, B, C, D	7.64 ¹	7.06	57-41-43-56-44...142*
Decanal	X	A, D	8.70 ¹	8.11	57-41-43-55-70...156*
Isobutyraldehyde		A, C, D	0.94 ¹	1.28 ¹	43-41-72-27-29*
Isovaleraldehyde		A, C, D	2.50 ¹	2.37	44-41-43-29-58...86*
2-Methylbutanal		A, D	2.43 ¹	2.47	57-29-41-58...86*
2-Methyl-2-butenal	X	D	4.61 ¹		55-29-84-27-39*
2-Heptenal	X	A, B, D	6.94 ¹	5.57	41-83-55-57-56...112*
2-Octenal	X	B, D	8.00 ¹	6.60	41-29-27-55-39...126*
2-Nonenal	X	A, D	9.10	7.65	41-29-43-27-55-37...140*
2-Decenal	X	A, D	10.07 ¹	8.73	41-43-27-55...154*
2-Undecenal	X	A		9.75 ¹	41-55-43-29-70...168*
Benzaldehyde		A, B, C, D	8.97 ¹	5.79	106-77-105-51-50*
Phenylacetaldehyde		A, B, C, D	10.14 ¹	6.59 ¹	91-120-92-65-39*
<i>p</i> -Tolualdehyde	X	C	10.24 ¹		119-91-120-39-65-63*
2,4-Nonadienal	X	D	10.66 ¹	8.24	81-41-27-49-67-138*
2,4-Decadienal (two isomers)	X	A, D			81-27-41-29-39-67-152*
<i>trans</i> -2, <i>trans</i> -4-Decadienal	X	A, B, C, D	11.69 ¹		81-27-41-29-39-67-152*
2-Phenyl-2-butenal	X	C, D	12.8 ¹		117-146-115-91-116*
4-Methyl-2-phenyl-2-pentenal	X	D			174-103-91-29-27-131*
5-Methyl-2-phenyl-2-hexenal	X	C	14.2 ¹	11.02	117-115-103...188*
Phenols					
Phenol	X	D	13.4 ¹		94-66-39*
2-Ethylphenol	X	B	14.0 ¹		107-122-77-39*
<i>m</i> -Cresol	X	B	14.0 ¹		107-108-77-79*
<i>p</i> -Cresol	X	B	14.1 ¹		107-108-79-77*
<i>o</i> -Methoxyphenol	X	D	12.2 ¹		109-124-81-53*
Ketones					
Acetone		A, D	1.00 ¹	0.97	43-58-27-26-42-29*
2-Butanone	X	A, C	2.21 ¹	1.74	43-29-27-72-42-57*
2-Pentanone	X	A	3.27		43-27-29-57-86-41*

Table I. (Continued)

Ketones	First reported	Isolate	Retention index		Ms data
			CBW	SF-96	
2-Hexanone	X	A	4.55 ¹	3.85 ¹	43-58-29-27-41... [*] 100
2-Heptanone	X	A, B, C, D	5.49 ¹	4.95	43-58-71-29... [*] 114
2-Octanone	X	A, B, C, D	6.55 ¹		43-58-71... [*] 128
2-Nonanone	X	A, B, C, D	7.60 ¹		43-58-71... [*] 142
2-Decanone	X	A, C	8.61 ¹	7.95 ¹	58-43-71-59-41-156 [*]
2-Undecanone	X	A	9.62		58-43-71... [*] 170
3-Methyl-2-pentanone	X	A, B, C, D	3.66 ¹		43-29-57-41-72... [*] 100
5-Methyl-2-hexanone	X	C	5.00 ¹		43-58-27-41-57-39... [*] 114
3-Penten-2-one		A, B, C, D	4.90 ¹	3.39	69-41-43-39-84-15 [*]
5-Methyl-3-hexen-2-one	X	D	6.06 ¹	5.04	43-41-97-69-112-39-53 [*]
2-Hepten-4-one	X	D	6.42 ¹		69-41-39-97-84... [*] 112
3-Hepten-2-one	X	D	6.68 ¹	5.50	55-97-43-112-41 [*]
3-Octen-2-one	X	D	7.72 ¹		55-43-111-41-97-39-126 [*]
3-Hexanone	X	A		3.80	43-57-29-27-71-41-100 [*]
2,3-Butanedione		A, B, C, D	3.17 ¹	1.69	43-86-42-44 [*]
2,3-Pentanedione	X	A, B, C, D	4.13 ¹	2.84	43-29-57-27-100 [*]
2,5-Hexanedione	X	B	8.70 ¹		43-99-27-71-57-114 [*]
6-Methyl-3,5-heptadien-2-one	X	D	9.61 ¹		109-81-43-124-39-41 [*]
<i>p</i> -Mentha-6,8-dien-2-one	X	D	11.09 ¹		82-39-54-27-41... [*] 150
2-Cyclopentenone	X	B, D	7.30		39-82-27-54-53-26 [*]
2-Cyclohexenone	X	B	8.15		68-39-96-40-27-42 [*]
3-Methyl-2-cyclohexen-1-one	X	B, C, D	9.66 ¹		82-39-110-54-27-41-67 [*]
3,5,5-Trimethyl-2-cyclohexen-1-one	X	D	9.71		82-39-138-27-54 [*]
2-Hydroxy-3-methyl-2-cyclopentenone	X	D	11.77 ¹		112-55-41-27-69-39-43 [*]
Acetophenone	X	B, C, D	10.26 ¹	6.66	105-77-120-51 [*]
1-Phenyl-1-propanone	X	B	10.85		105-77-51... [*] 134
1-Phenyl-2-propanone	X	B	10.94		43-91-92-134-65-39 [*]
Alcohols					
Methyl alcohol		A	0.40 ¹		31-32-29-28-18 [*]
Ethyl alcohol		B, C	2.44 ¹		31-45-46-27-29-43 [*]
1-Propyl alcohol	X	B	3.71 ¹		31-27-29-59-42... [*] 60
1-Butyl alcohol	X	B, C	4.91 ¹		56-31-41-43-42... [*] 74
1-Pentyl alcohol	X	A, B, C, D	6.00 ¹	3.88 ¹	42-31-29-41-55... [*] 88
1-Hexyl alcohol	X	A, B, D	7.00 ¹	4.87 ¹	56-43-55-41-31... [*] 102
1-Heptyl alcohol	X	B, C, D	8.00 ¹	5.88	41-70-56-43-55-31-29... [*] 116
1-Octyl alcohol	X	C, D	9.04 ¹		41-56-43-55-29-31-130 [*]
2-Methyl-1-butyl alcohol	X	D	5.54 ¹	3.50	29-57-41-56-31... [*] 88
2-Propyl alcohol	X	A, B, C	2.30 ¹		45-43-27-29-41-59... [*] 60
2-Butyl alcohol	X	B	3.55 ¹	1.83	45-27-29-31-43-59... [*] 74
2-Pentyl alcohol	X	B, C, D	4.61 ¹	3.06	45-43-55-27-29-44... [*] 88
2-Heptyl alcohol	X	D	6.66 ¹		45-43-55-27-29-41... [*] 116
2-Methyl-1-propyl alcohol	X	B	4.36 ¹		43-41-42-31-33... [*] 74
3-Methyl-1-butyl alcohol	X	B, C, D	5.55 ¹	3.48	31-41-55-57-70-56... [*] 88

Table I. (Continued)

Alcohols	First reported	Isolate	Retention index		Ms data
			CBW	SF-96	
1-Octen-3-ol	X	D	8.00		57-43-41-72-55-27-128*
Benzyl alcohol	X	B, D	12.2 ¹		79-108-107-77-51-91*
Phenethyl alcohol	X	D	12.6 ¹		91-92-122-65-39-41-51*
Lactones					
γ -Butyrolactone		B, D	10.00 ¹		42-86-41-56*
γ -Valerolactone	X	B, D	9.85 ¹	3.41	56-85-41...100*
γ -Hexalactone	X	B, C, D	10.78 ¹		85-29-27-56-41...114*
γ -Heptalactone	X	B, D	11.65 ¹		85-29-27-56-41...128*
γ -Octalactone	X	B, C	12.9 ¹		85-29-27-41-56...142*
γ -Nonalactone	X	B, D	14.0 ¹		85-29-27-41-42...156*
δ -Valerolactone	X	D			42-41-56-27...100*
δ -Octalactone	X	D			99-42-27-71-55...142*
γ -Crotonolactone	X	D			55-27-84-53-26*
Terpenes					
α -Pinene	X	D	4.00 ¹		93-92-91-77-41...136*
β -Pinene	X	D	4.93 ¹		93-41-69-39-27...136*
Sabinene	X	D	5.00 ¹		93-77-41-91-79...136*
Myrcene	X	D	5.32 ¹		41-93-69-81...136*
β -Phellandrene	X	D	6.02 ¹		93-136-94-77-91*
α -Terpinene	X	A, D	6.23 ¹		93-136-91-77-43-121*
<i>p</i> -Cymene	X	A, D	6.48 ¹		119-134-91-39-41-77*
4-Terpineol	X	C	9.68 ¹		71-43-111-93-154*
Limonene	X	A, D	6.79 ¹		68-67-93-94-78-121...136*
Esters					
Ethyl formate	X	A, C	1.00 ¹	1.00 ¹	31-28-29-47-45-74*
Ethyl acetate		B, C, D	2.00 ¹	2.00	43-29-45-61-88*
Butyl acetate	X	C, D	4.34 ¹		43-56-87-41-116*
2-Methylbutyl 2-methylbutyrate	X	D	6.61 ¹		70-57-85-43-41-29...172*
Ethyl heptanoate	X	A, D	7.00 ¹	7.00 ¹	88-43-27-41-60-113-158*
Ethyl decanoate	X	D	10.00 ¹		88-27-41-101-45...200*
Methyl undecanoate	X	D	11.63		74-87-43-41...200*
Benzyl acetate	X	D	10.92 ¹		108-91-43-90-79...150*
Dimethyl succinate	X	D	9.46 ¹		115-55-59-114-29...146*
1-Hydroxy-2-propanone acetate	X	B, D	8.22 ¹		43-86-73-116*
Acids					
Acetic acid		B			43-45-60-15-42*
Valeric acid	X	D			60-73-41-45...102*
Aromatic hydrocarbons					
Benzene		A, D	2.92 ¹	2.52 ¹	78-51-52-49-39-77*
Toluene		A, C, D	4.14 ¹	3.75 ¹	91-92-65*
<i>p</i> -Xylene		A, B, C, D	5.10 ¹	4.84	91-106-105*
<i>m</i> -Xylene		C	5.17 ¹		91-106-105*
<i>o</i> -Xylene	X	C, D	5.61 ¹		91-106-105*

Table I. (Continued)

Aromatic hydrocarbons	First reported	Isolate	Retention index		Ms data
			CBW	SF-96	
Propylbenzene	X	D	5.83 ¹		91-120-65 *
Styrene	X	A, D	6.32 ¹	4.49 ¹	104-103-78-51-77 *
1,2,4-Trimethylbenzene		A, D	6.61 ¹		105-120-119-39-27-77 *
Ethylbenzene	X	A, D	6.94 ¹	4.74	91-106-51-39 *
Butylbenzene	X	A			91-92-134-27 *
2,3-Dihydroindene	X	D			117-118-115-39-91-116 *
Indene	X	D	8.61 ¹		116-115-63-39-89 *
Naphthalene	X	C, D	11.15 ¹		128-127-64 *
1-Methylnaphthalene	X	A, D	12.6 ¹		142-141-115-143-139 *
2-Methylnaphthalene	X	A, D	12.1 ¹		142-141-115-143-139 *
Ethylnaphthalene	X	D			141-156-115-142 *
Biphenyl	X	C	13.5 ¹		154-153-152-76-155-51 *
Methylethylbenzene	X	D			105-120-39-91 *
Miscellaneous					
Hexane	X	A			43-42-41-27...86 *
Heptane	X	A, D		3.05	43-41-29-27...100 *
Octane	X	A			43-41-27-57...114 *
Nonane	X	D	2.44		43-57-41-29-27...128 *
Decane		D			43-57-41-29...142 *
Undecane	X	A			43-57-41-29-71...156 *
Dodecane	X	D			43-57-41-71...170 *
Tridecane	X	D			43-57-41-81...184 *
+ Chloroform	X	A	3.66 ¹		83-85-47-87-48-49...118 *
+ Dichlorobenzene (two isomers)	X	D			146-148-111-75 *
Benzonitrile	X	B	9.70		103-76-50-51-26 *
+ Ionol	X	C	12.6 ¹	11.29	205-57-220-41 *
+ Diethyl phthalate	X	D	16.8 ¹		149-177-29-150...222 *

X = not previously reported in roasted filberts. A = headspace analysis. B = condensate. C = steam distillate. D = molecular distillate. ¹ = retention index of unknown and known standard are in agreement. * = molecular weight of compound. + = probable solvent artifact.

Porapak Q (Schultz *et al.*, 1971) and held at room temperature. This process was facilitated by the application of slightly reduced pressure at the exit end of the Porapak trap. After collection, the Porapak trap was removed from the distillation apparatus and connected to a stainless steel 6-in. \times 0.03-in. i.d. U-tube held in liquid nitrogen. The Porapak trap was wrapped with heating tape and heated to 130°C while the volatile compounds were back-flushed with helium (10 ml/min) into the U-tube. With the carrier gas shut off, the U-tube was coupled between the injection port and a 500-ft \times 0.03-in. i.d. SF-96 open tubular column in the gc-ms system. The temperature program of 60–190°C @ 2°C per min was begun when the carrier gas flow was started after a 2-min equilibration period at 60°C.

The gc-ms system consisted of a Hewlett-Packard 5750 gas chromatograph coupled to a Hitachi RMU-6E mass spectrometer by means of a porous glass separator (Watson and Biemann, 1965). The effluent from the open tubular column was split, with 5 ml per min being directed through the sepa-

rator to the mass spectrometer and the remaining 5 ml per min to the flame ionization detector of the gas chromatograph.

(B) Five kilograms of filberts were roasted and the vapors emanating from the roaster were directed by means of a negative pressure gradient through a series of cold traps [cold water (15°C), ice water and 2-propanol-dry ice]. Upon completion of roasting, the traps were rinsed with 300 ml of distilled water. The aqueous solution obtained was subjected to two successive extractions with different solvents, a procedure found to be more efficient than the use of either solvent exclusively. The initial extraction was with 2 \times 250 ml of redistilled Ucon 11 (trichloromonofluoromethane, Union Carbide) followed by 2 \times 250 ml of diethyl ether (Matheson Coleman & Bell, ACS reagent grade). The two separate solvent extracts, after drying over sodium sulfate, were initially concentrated in a Kuderna-Danish concentrator (Kontes Glass Co., Vineland, N.J.) to about 5 ml and, finally, to about 1 ml using a stream of nitrogen. The extracts were then combined and analyzed by gc for the presence of sulfur-

and/or nitrogen-containing compounds. The instrument used was a Tracor MT 220 modified in our laboratory as follows. One side of the Tracor dual flame ionization detector was modified by the addition of a rubidium sulfate bead (Craven, 1970) for detection of nitrogen-containing compounds; the column effluent was split between the alkali flame and a Melpar flame photometric detector, which also incorporated a flame ionization output. Thus, with the addition of a third electrometer and appropriate recorders, simultaneous sulfur, nitrogen, and flame ionization detection signals could be monitored.

After sulfur- and nitrogen-containing compounds were located, the gc-ms system was used to complete identifications. A 1000-ft \times 0.03-in. i.d. Carbowax 20M open tubular column was used with a temperature program of 70 to 190°C @ 1°C/min after a 30-min post-injection hold at 70°C.

(C) 1.5 kilograms of roasted filberts were ground to a fine slurry in an industrial Waring blender with 3 l. of deionized water and the resulting slurry was steam distilled at atmospheric pressure. The distillate (1 l.) was extracted with 4 \times 125 ml of redistilled Ucon 11 and then with 4 \times 125 ml of diethyl ether. The samples were concentrated and analyzed as described above.

(D) The fourth method of isolation, similar to that used by Sheldon (1969), was a molecular distillation of oil expressed from roasted filberts. The oil was obtained from 5 kg of roasted filberts using a Model C Carver Press with a cage assembly (F. S. Carver, Summit, N.J.). The oil was filtered through glass wool and centrifuged to obtain 1500 ml of a clear golden oil. The aroma of the oil was substantially reduced in four or five repeated passes through a falling film molecular still (Nester-Faust Corp., Newark, Del.) at a rate of 300 ml per day. Volatiles were collected in two liquid nitrogen cooled traps. The first pass was made at a pressure of 1 mm to degas the oil and removed most of the moisture, with the following passes made at 10^{-4} – 10^{-5} mm. The jacket temperature of the still was held at 60–65°C. The contents of the cold traps were extracted each day with 4 \times 50 ml of Ucon 11 and 4 \times 50 ml of diethyl ether. After extracting the trap contents, the solvent layer was concentrated in the Kuderna-Danish system and the solvent recovered for re-use the following day. In this manner the possibility of solvent impurities in the final total extract was minimized. The final accumulated and concentrated extract was subjected to preparative gc on a stainless steel 13-ft \times 1/8-in. column packed with 12% SF-96 + 0.6% Igepal CO-880 on 100–120 mesh Chromosorb W. Effluent fractions were collected in Dry Ice-cooled glass tubes. The contents of each trap were then further resolved in the gc-ms system using a 1000-ft \times 0.03-in. Carbowax 20M open tubular column with a program rate of 70–190°C @ 1°C/min.

IDENTIFICATION

Identification was accomplished by matching mass spectra and gas chromatographic retention indices, I_E values, relative to ethyl esters (van den Dool and Kratz, 1963) of the unknowns with those of known standards on Carbowax and/or SF-96 columns. Mass spectral interpretation was simplified

by knowing which compounds contained sulfur and/or nitrogen. As a result, there was greater confidence in the designation of such compounds as being "positively identified."

DISCUSSION AND RESULTS

The use of a cold-water condenser and an ice trap in conjunction with the Porapak trap during the headspace analysis enabled the collection of sufficient volatiles for good mass spectra without the interference of large amounts of water.

Suggested pathways for the formation of some of the identified components were discussed in a previous paper on roasted peanuts (Walradt *et al.*, 1971) and the synthesis and spectral properties of alicyclic pyrazines have been summarized (Pittet *et al.*, 1971) and will be submitted for publication.

Three compounds reported by Sheldon (1969) from packed column gc-ms work were not found in the present investigation. They were: 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone; 3-hydroxy-2-methyl-4-pyrone (maltol); and hexanoic acid. It has been our experience that these compounds and the higher carboxylic acids usually do not elute as discernible peaks from the 500-ft and 1000-ft open tubular columns within a reasonable time. Observations of this type should serve to remind the researcher that no single method of isolation or analysis can be expected to provide a complete picture of the components of a particular natural product.

Only those compounds considered to be positively identified are listed in Table I. The table is a composite of compounds from all four methods of isolation. Also given for each compound is its retention index on Carbowax 20M and SF-96 columns, when available, and the major mass spectral fragments listed in decreasing order of intensity.

SUMMARY

As a result of our work, 229 compounds have been identified and 187 are reported for the first time as roasted filbert constituents. As has been the case with other roasted products (peanut and coffee for example), many of the components identified were considered to contribute to the overall flavor but none was isolated which could be considered to have the typical roasted filbert character.

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