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## Volatile Flavor Components of Leek

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The flavor complex from steam-distilled leek (*Allium porrum* L.) was studied by a combination of capillary gas chromatography and mass spectrometry. A total of 67 compounds were characterized, of which 57 have not been previously reported in leek. Odor properties were evaluated by running aromagrams on a thermal conductivity detector.

Much classical work has been done on aroma analysis since the advent of gas-liquid chromatography, especially in combination with mass spectrometry. Among vegetables, the *Allium* genus is one of the best investigated objects as to constitution, formation, and origin of volatile compounds.

The constitution of *Allium* species has been the subject of many publications. *Allium cepa* L. (onion) is undoubtedly the most important representative because of its very strong and pungent flavor. It has been studied intensively by Carson (1967), Bernhard (1968), Brodnitz et al. (1969, 1971), Boelens et al. (1971), and by Dembele and Dubois (1973). Other *Allium* species however, such as *A. chinense* G. Don (rakkyo), *A. sativum* L. (garlic), *A. schoenoprasum* L. (chive), *A. porrum* L. (leek), and *A. victorialis* L. (caucas), received little attention. A general and recent review of *Allium* constituents was published by Johnson et al. (1971).

The mechanism of flavor formation in *Allium* species has been investigated by Stoll and Seebeck (1948, 1949a,b, 1951), Schwimmer and Guadagni (1968), Schwimmer and Weston (1961), Calvallito and Bailey (1950), and some other workers.

This paper deals with the isolation, separation, and characterization of the major volatile constituents of leek oil obtained by steam distillation. The components were analyzed using gas-liquid chromatography and mass spectrometry. The structure of these components was identified by direct comparison of their mass spectra and retention times with those of reference products. Many of those products, although known to occur in other *Allium* species, were not reported earlier in leek.

### EXPERIMENTAL SECTION

**Sample Preparation.** About 30 kg of freshly harvested leek (Nov 1974) was chopped and placed in a 60-l. glass vessel of the pilot plant installation shown in Figure 1. Steam under atmospheric pressure was blown through the leek by means of a 6-kW steam generator. The volatile components were stripped and the vapor condensed and cooled, yielding a total distillate of about 25 l. in 8 h. This distillate was submitted to continuous ether extraction (Figure 2) during 24 h and the extract rectified over a column in order to remove the solvent. The yield was about 1.5 ml of a dark brown leek oil with a strong smell which was very similar to that of boiled leek soup.

**Gas Chromatography.** The components of the ethereal essence were analyzed on a Varian 2400 gas chromatograph, equipped with a flame ionization detector and a subambient temperature programmer. The subambient system was operated by connecting a liquid nitrogen Dewar

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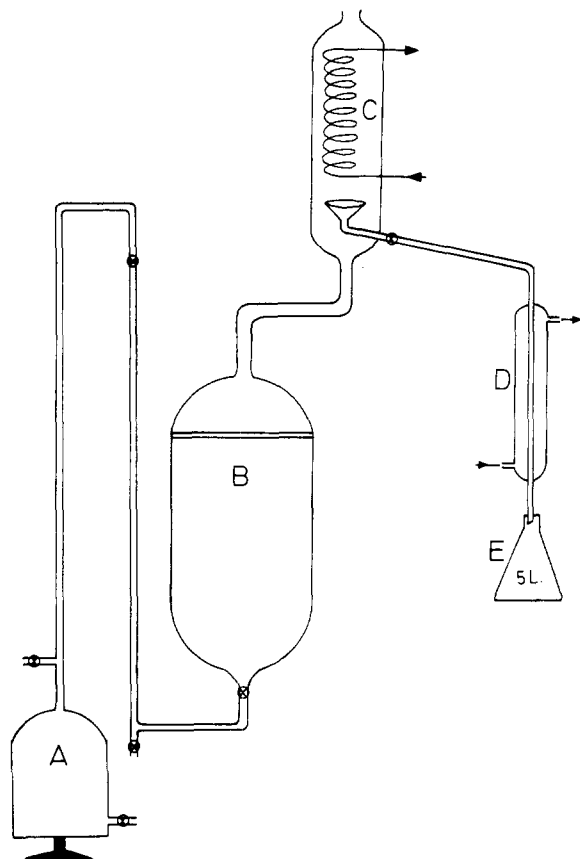


Figure 1. Steam distillation apparatus: (A) steam generator; (B) 60 l.; (C) condenser; (D) cooler; (E) recipient.

with its own pressure build-up (Cryoson), over a magnetic valve, to the GC oven. The valve was controlled by the linear temperature programmer.

Open tubular columns (600 ft, 0.03 in. i.d.) were prepared from widebore borosilicate glass tubings. The columns were drawn with a commercial glass drawing machine purchased from Hupe and Busch. Column coating was carried out according to the stationary method of Bouche and Verzele (1968) using silicone oil OV 1 at a concentration of 6 mg/ml of solvent. The solvent was dichloromethane. Special care was taken in order to avoid decomposition of products by means of contact with metal parts. Therefore, a 0.25 in. (0.02 in. i.d.) glass tubing was inserted in the injector block and drawn to a capillary end in the oven, in order to connect the column by means of P.T.F.E. shrink tubing. This shrink tubing was also used to connect 300-ft glass tubings in order to obtain a 600-ft column. Columns were conditioned by programming the temperature from 50 to 240°C at 1°C/min and leaving it overnight at 240°C. Operating conditions for GC are as follows: carrier gas nitrogen, 5 ml/min without make-up gas; hydrogen, 30 ml/min; air, 300 ml/min; injector and detector, 220°C; temperature programming, 0–230°C at 1°C/min.

Aromagrams were taken by analyzing the mixture with a microthermal conductivity detector under the following conditions: carrier gas hydrogen, 5 ml/min with make-up gas to 20 ml/min; injector, 220°C; detector, 240°C; isothermal, 15 min at ambient and later 1°C/min to 230°C; filament current, 225 mA.

**Gas Chromatography-Mass Spectrometry.** For GC-MS coupling a Varian 1200 gas chromatograph was modified and coupled to a MS 30 double beam mass spectrometer by means of a membrane separator sup-

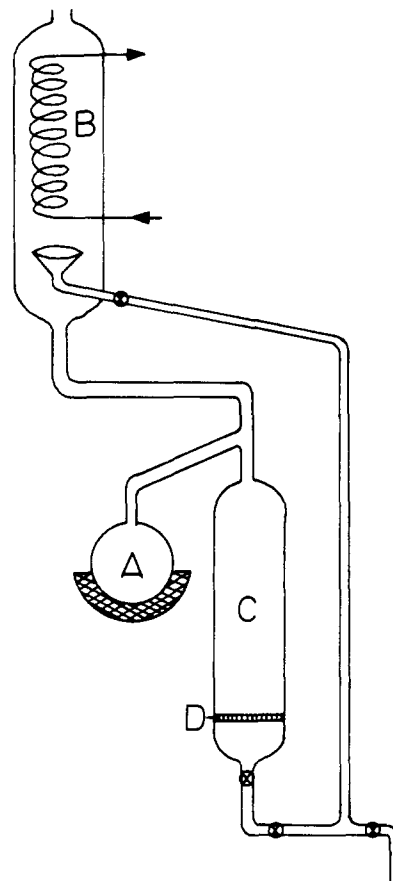


Figure 2. Continuous ether extractor: (A) ether recipient; (B) condenser; (C) extraction column; (D) sintered glass disk.

ported by A.E.I., Manchester. An effluent splitter was installed in order to send about 75% of the total gas flow to the separator and 25% to the F.I.D. When necessary, solvent peaks were eliminated by means of a solvent dump valve placed between the column exit and the separator. Makeup gas was added at the column exit in order to obtain an optimum gas flow through the separator ( $\pm 20$  ml/min). Operating conditions for GC-MS are: carrier gas helium, 6 ml/min, and make-up gas, to 20 ml; injector, 220°C; separator oven and interconnecting lines, 200°C; ion source pressure,  $10^{-5}$  mmHg; ion source, 200°C; trap current, 300  $\mu$ A; filament voltage, 70 V; scan speed, 3 sec/decade.

**Mass Spectrometry.** Reference mass spectra were recorded on the same instrument. The pure products were introduced through an all glass heated inlet system (AGHIS). Operating conditions were as follows: filament voltage, 70 V; accelerating voltage, 4 kV; trap current, 300  $\mu$ A; ion source pressure,  $5 \times 10^{-7}$  mm; AGHIS and ion source temperature, 200°C; scan speed, 10 sec/decade.

**Reference Compounds.** Some of the reference compounds are commercially available from Fluka, Merck, Riedel-de Haen, Union Chimique Belge, Schuchardt, or Aldrich. The supplier for each compound is indicated in Table I. Many reference spectra were obtained by GC-MS analysis of a commercially available onion oil with known composition (Naarden International, 1974). The composition of this oil has been earlier described in this journal by Boelens et al. (1971).

## RESULTS AND DISCUSSION

As a result of the present investigation 67 components were identified in leek essential oil. Fifty-seven of them have not been reported earlier in leek. A typical gas

Table I. Identification of Volatile Components Found in Leek

Peak no.	Component	Supplier <sup>a</sup>	Ip <sup>b</sup>	Identification	Peak no.	Component	Supplier <sup>a</sup>	Ip <sup>b</sup>	Identification
1	Methanal <sup>c</sup>			MS <sup>d</sup>	42	2,6-Dimethylpyrazine		891	MS, T
2	Ethanal	M		MS, RT, A	43	Allyl methyl disulfide <sup>c</sup>		895	MS, RT
3	Methanethiol <sup>c</sup>	S, F		MS, RT, A	45	Methyl propyl disulfide <sup>c</sup>		914	MS, RT
4	Propanal <sup>c</sup>	U		MS, RT, A	46	Methyl propyl disulfide <sup>c</sup>		922	MS, RT
5	Ethanol	U, A		MS, RT, A	47	Benzaldehyde	A, U	932	MS, RT, A
6	Diethyl ether <sup>e</sup>	U		MS, RT, A	48	Dimethyl trisulfide		948	MS, RT
7	Dichloromethane <sup>e</sup>	U		MS, RT, A	52	2-Octanone		972	MS, RT
9	Allyl alcohol	A		MS, RT, A	53	2-Ethyl furyl ketone		983	MS, RT
10	<i>n</i> -Propanol	U, A		MS, RT, A	55	Benzyl alcohol	U	1013	MS, RT, A
11	2-Butanone <sup>f</sup>	U		MS, RT, A	56	2-Pyrrolcarboxaldehyde		1023	MS, T
12	1-Propanethiol <sup>c</sup>			MS, RT	60	<i>n</i> -Octanol	A	1060	MS, RT, A
13	Ethyl acetate	U	603	MS, RT, A	61	2-Nonanone		1073	MS, RT
14	2-Methylpropanol	A	627	MS, RT, A	64	Dipropyl disulfide <sup>c</sup>	F	1092	MS, RT, A
15	3-Methylbutanal	A	633	MS, RT, A	65	2-Phenylethanol	M	1096	MS, RT, A
16	2-Methylbutanal		643	MS, RT	66	1,2-Dimethoxybenzene	R	1114	MS, RT, A
17	<i>n</i> -Butanol	U	664	MS, RT, A	67	Methyl propyl trisulfide		1132	MS, RT
18	<i>n</i> -Pentanal	A	675	MS, RT, A	69	<i>n</i> -Nonanol		1160	MS, RT
19	Allyl methyl sulfide		678	MS, RT	71	2-Decanone		1174	MS, RT
20	2-Hydroxy-3-butanone <sup>f</sup>	A	689	MS, RT, A	72	2,5-Dihydro-3,4-dimethylthiophen-2-one		1193	MS, RT
21	Pyridine	A	719	MS, RT, A	73	Benzothiazole	A	1196	MS, RT, A
22	Dimethyl disulfide		723	MS, RT	78	Decomposed		1291	
23	3-Methylbutanol <sup>f</sup>		722	MS, RT	79	Propenyl propyl trisulfide (isomer)		1310	MS, RT
24	2-Methylpentanal		740	MS, RT	80	Propenyl propyl trisulfide (isomer)		1317	MS, RT
25	Methylthiophene (2 isomers)		753-755	MS, RT	81	2,3-Dihydro-2- <i>n</i> -hexyl-5-methylfuran-3-one		1413	MS, RT
26	<i>n</i> -Pentanol	U	762	MS, RT, A	82	2-Tridecanone		1477	MS, RT
28	<i>n</i> -Hexanal	A	779	MS, RT, A	83	2,3-Dihydro-2- <i>n</i> -octyl-5-methylfuran-3-one		1619	MS, T
29	Methylpyrazine		798	MS, T	84	2-Pentadecanone		1681	MS, RT
30	2-Furaldehyde	F, A	804	MS, RT, A	85	Diphenylacetylene		>1700	MS, T
31	2-Methylpent-2-enal		811	MS, RT					
32	2-Methylpentanol	F	827	MS, RT, A					
33	<i>trans</i> -Hex-3-en-1-ol		843	MS, RT					
34	2-Furyl alcohol	F	846	MS, RT, A					
35	Dimethylthiophene (isomer)		855	MS, RT					
36	Allyl propyl sulfide		858	MS, RT					
37	<i>n</i> -Hexanol	U	859	MS, RT, A					
38	Dimethylthiophene (isomer)		861	MS, RT					
39	2-Heptanone		871	MS, RT					
40	<i>n</i> -Heptanal	A	881	MS, RT, A					
41	3,4-Dimethylthiophene		887	MS, RT					

<sup>a</sup> Supplier: F = Fluka, M = Merck, U = Union Chimique Belge; A = Aldrich; R = Riedel-de Haen; S = Schuchardt. <sup>b</sup> Retention index on OV 1 between C<sub>6</sub> and C<sub>17</sub>, with linear temperature programming (Rasquinho, 1965). <sup>c</sup> Previously identified by other workers. <sup>d</sup> MS, mass spectrometry; RT, retention index; A, comparison with authentic compound. <sup>e</sup> Solvent peaks. <sup>f</sup> The steam distillation was carried out twice. This component was only present in one steam distillate.

chromatogram of steam-distilled leek oil, analyzed on OV 1, is shown in Figure 3. The volatile constituents were identified by comparing their mass spectra and retention times with those of reference materials. The compounds identified are presented in Table I and their peak numbers correspond to the numbers in Figure 3.

A weak lachrymatory factor is present in leek. It is noticed a few minutes after the leek tissue has been cut, and proved by the presence of *n*-propanal (peak 4) and 2-methylpent-2-enal (peak 31), two decomposition products from thiopropanal sulfoxide, the latter which is now proven to be the lachrymatory substance in *Alliaceae* (Brodnitz and Pascale, 1971).

Sulfur-containing components are the main flavoring constituents of leek essential oil, because of the high concentration in which they occur and their very low threshold values. Mainly saturated and unsaturated mono-, di-, and trisulfides are found in the analysis mixture besides some thiophene derivatives and thiols.

Typical for steam-distillation procedures are the presence of alkanals and furan derivatives which are formed by Maillard reactions between amino acids and reducing sugars. A lot of *n*-alkanals occur in the mixture besides the peaks 30 and 34 which are present in large concentration.

No explanation is found for the presence of the furan-3-one derivatives, peaks 81 and 83, in such large concentrations. Their formation is not clear. They could be formed via the respective C<sub>11</sub>- and C<sub>13</sub>-hydroxy ketones as is suggested by Boelens et al. (1971). Probably furan-3-ones can also be formed as an effect of heating upon sugars since Tonsbeek et al. (1968) isolated 4-hydroxy-5-methyl-2,3-dihydrofuran-3-one and its 2-methyl derivative from heated beef extract. The former product was due to reaction of ribose 5-phosphate and taurin or pyrrolidone carboxylic acid.

Alkanals and alcohols are difficult to recognize by mass spectrometry because most of them show no molecular ion

Table II. Mass Spectral Data of Constituents of Leek Oil

Allyl methyl sulfide	41 (100), 88 (91), 73 (62), 39 (52), 43 (48), 45 (42), 56 (38), 47 (21)
Dimethyl disulfide	94 (100), 79 (48), 45 (41), 46 (25), 47 (16), 61 (13), 48 (9), 64 (8), 96 (8)
2-Methylpentanal	43 (100), 58 (84), 41 (30), 29 (26), 27 (24), 71 (12), 100 (3)
<i>n</i> -Hexanal	43 (100), 44 (84), 41 (58), 56 (56), 45 (50), 72 (40), 57 (32), 55 (22), 100 (16), 82 (6)
Methylpyrazine	94 (100), 67 (50), 39 (21), 40 (20), 53 (20), 95 (6), 52 (6), 79 (5)
2-Furaldehyde	96 (100), 95 (89), 39 (75), 29 (23), 38 (17), 94 (15), 67 (11)
2-Methylpent-2-enal	41 (100), 98 (53), 39 (45), 69 (38), 27 (29), 55 (26), 43 (19), 29 (19), 83 (14)
2-Furyl alcohol	98 (100), 97 (54), 41 (57), 81 (50), 39 (50), 53 (39), 42 (31), 69 (24), 70 (22)
<i>n</i> -Heptanal	70 (100), 44 (97), 43 (91), 42 (89), 55 (71), 41 (63), 57 (61), 81 (31), 86 (20), 96 (9)
3,4-Dimethylthiophene	111 (100), 112 (76), 39 (63), 45 (26), 77 (15), 97 (5)
2,6-Dimethylpyrazine	108 (100), 42 (65), 40 (38), 39 (31), 109 (8), 81 (6), 67 (6)
Methyl propyl disulfide	80 (100), 122 (75), 43 (70), 41 (64), 45 (30), 47 (16), 39 (16), 64 (13)
Dimethyl trisulfide	126 (100), 45 (58), 79 (57), 47 (49), 46 (24), 64 (21), 48 (19), 111 (16), 94 (16), 128 (13), 61 (13)
2-Ethyl furyl ketone	95 (100), 124 (28), 39 (21), 27 (15), 41 (14), 29 (14)
Pyrrolecarboxaldehyde	95 (100), 94 (66), 66 (49), 39 (46), 29 (46), 41 (40), 43 (38), 45 (26)
Dipropyl disulfide	43 (100), 150 (29), 41 (24), 108 (19), 66 (8), 39 (7), 74 (5), 47 (5), 45 (5)
2-Phenylethanol	91 (100), 92 (57), 122 (23), 65 (12), 39 (8), 51 (6), 78 (4), 77 (4)
1,2-Dimethoxybenzene	138 (100), 123 (99), 95 (37), 77 (32), 41 (20), 65 (18), 52 (17), 51 (13)
Methyl propyl trisulfide	43 (100), 154 (96), 47 (70), 112 (63), 41 (60), 45 (44), 64 (38), 79 (30)
2,5-Dihydro-3,4-dimethylthiophen-2-one	128 (100), 85 (56), 67 (52), 39 (50), 41 (46), 55 (36), 81 (33), 45 (31), 99 (27), 73 (23), 59 (19), 83 (14), 100 (13)
Benzothiazole	135 (100), 108 (32), 69 (15), 45 (12), 82 (7), 63 (6)
Propenyl propyl trisulfide	41 (100), 74 (91), 180 (58), 45 (56), 106 (42), 115 (33), 116 (30), 83 (30), 39 (28), 47 (12), 182 (8)
2,3-Dihydro-2- <i>n</i> -hexyl-5-methylfuran-3-one	98 (100), 111 (53), 41 (23), 43 (18), 68 (13), 39 (13), 55 (12), 182 (7), 99 (7), 85 (6), 112 (4)
2,3-Dihydro-5-methyl-2- <i>n</i> -octylfuran-3-one	98 (100), 111 (56), 41 (19), 43 (14), 68 (11), 39 (10), 55 (8), 99 (6), 85 (5), 112 (4), 210 (3)
Diphenylacetylene	178 (100), 76 (21), 176 (20), 179 (17), 152 (15), 89 (15), 88 (13)

(see also mass spectral data). Alcohols, however, show tailing peaks in the chromatogram on the apolar phase OV 1 as is clearly illustrated by the peaks 5, 14, and 17.

However, the 2-methyl ketones are very easily recognized by their base peak *m/e* 58 and characteristic spectral pattern.

As another result of heating, the formation of large amounts of 3,4-dimethylthiophene, in addition to two other positional isomers has to be mentioned. These products can be formed by heating alkenyl disulfides with a loss of hydrogen sulfide as is unambiguously proven by Boelens

Table III. Odor Description of Figure 4

1. Rotten	M <sup>a</sup>	52. Pungent	M
2. Rotten	S	53. Sweet	M
3. Aldehyde	M	54. Fresh	W
4. Diethyl ether	M	55. Onion	W
5. Brussels sprouts	S	56. <i>Allium sativum</i>	M
6. Onion	M	57. Violet	W
7. Alcoholic	W	58. Cabbage blossom	S
8. Buttery	M	59. Burnt potatoes	S
9. Fresh cut leek	S	60. <i>Allium sativum</i>	M
10. Pleasant	M	61. Burnt potatoes	S
11. Buttery	M	62. Fruity	S
12. Musty	M	63. Aromatic	M
13. Aldehyde	W	64. Moldy	VS
14. Unpleasant	S	65. Peas	S
15. <i>Allium sativum</i>	W	66. Rubbery	S
16. Rotten	VS	67. Pleasant	M
17. Pyridine	M	68. Leek	S
18. Alcoholic	W	69. Unpleasant	M
19. Aromatic	W	70. Leek, sweet	S
20. <i>Allium sativum</i>	W	71. Aromatic	S
21. Buttery	W	72. Leek, pungent	S
22. Burnt rubber	S	73. Green carrots	M
23. Fruity	M	74. Musty	S
24. <i>Allium sativum</i>	W	75. Moth balls	M
25. Gaseous	W	76. Moldy	S
26. Nutty	W	77. Unpleasant	M
27. Aromatic	S	78. Onion, irritating	M
28. Pleasant, aldehyde	S	79. Onion	S
29. Burnt	M	80. Tomatoes	W
30. Rotten	W	81. Rubbery	M
31. <i>Allium sativum</i>	S	82. Onion, irritating	S
32. Flowers	M	83. Onion	M
33. Green, pleasant	S	84. Caramel, hay	S
34. Burnt potatoes	S	85. Menthol	S
35. Peas	M	86. Boiled leek	W
36. Sweet	W	87. Onion, irritating	S
37. Caramel	M	88. Carrots, pleasant	S
38. Burnt potatoes	VS	89. Musty	W
39. Musty, pungent	S	90. Rubbery	M
40. Burnt potatoes	VS	91. Leek, irritating	W
41. Leek	M	92. Pleasant, meaty	M
42. <i>Allium sativum</i>	M	93. Almonds	W
43. <i>Allium sativum</i> , fried	S	94. Steam distillate leek	M
44. Leek, irritating	VS	95. Pleasant	M
45. Onion	S	96. Green carrots	M
46. Onion, irritating	W	97. Steam distillate leek	S
47. Onion, irritating	S	98. Leek	W
48. Cabbage	S	99. Steam distillate leek	M
49. Leek, irritating	M	100. Meaty, pleasant	M
50. Spinach	S		
51. Sweet, alcoholic	M		

<sup>a</sup> Odor intensity: W = weak; M = medium; S = strong; V = very.

and Brandsma (1972). Peak 78 disappeared during GC-MS coupling and is also not found when taking the aromagram, indicating the fact that there is still some thermal decomposition during the analysis.

Mass spectral data of the identified components are summarized in Table II. The peaks are given with their intensities (in parentheses) relative to that of the base peak (100%).

Four aromagrams were taken by sniffing the eluting products from the column at the collector exit of a microthermal conductivity cell. Three trained persons were involved in running the aromagrams. The mean results of these analyses are illustrated in Figure 4 and Table III where an odor description is given for each peak together with its odor strength. The numbers of Table III correspond to the peak numbers of Figure 4.

The aromagram indicates 11 leek-like odors in addition to a lot of onion odors. Sometimes it is very difficult to distinguish both. Components which are believed to contribute to the specific leek flavor are propanethiol, allyl

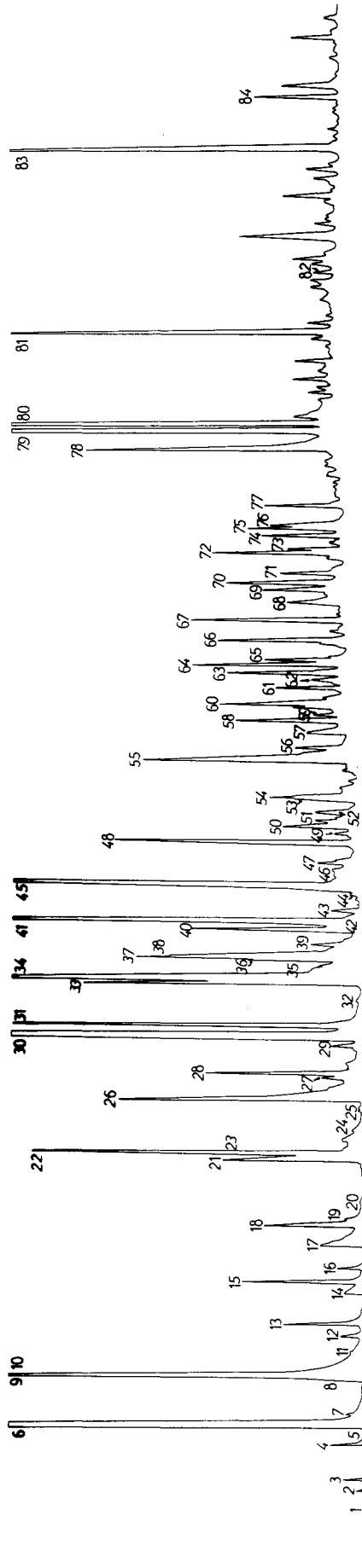


Figure 3. Gas chromatogram of steam-distilled leek oil (for identification see Table I): OV 1 coated Gelay column, temperature programmed from 0 to 230°C at 1°C/min.

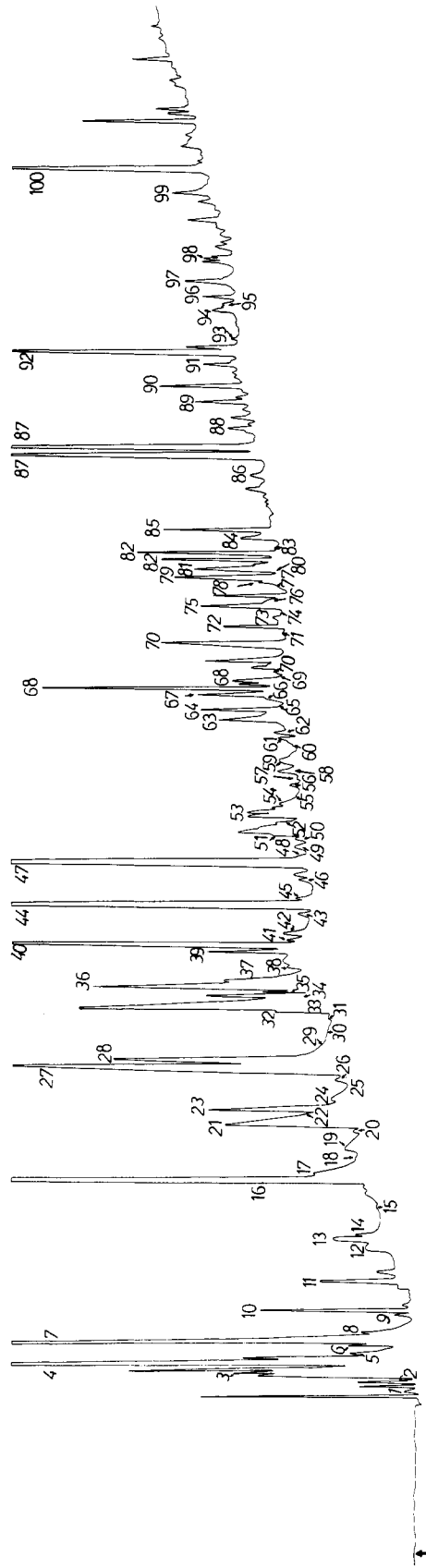


Figure 4. Aromagram of steam-distilled leek oil: OV 1 coated Gelay Column, 200 m.

methyl disulfide, methyl propyl disulfide, dipropyl disulfide, methyl propyl trisulfide, and some unidentified products.

From Ip 1500 it becomes difficult to distinguish odors at all, for a specific leeklike odor lasts around the collector exit.

#### ACKNOWLEDGMENT

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## Effects of Storage Temperature and Container Lining on Some Quality Attributes of Papaya Nectar

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Papaya nectar in plain tin- and enamel-lined cans was stored at 55, 75, and 100°F for 1 year. Samples were analyzed periodically to determine quality of the product. Corrosion of the tin lining was most rapid at 100°F; after 1 year, the tin content of the nectar was 400 ppm. Iron content increased more rapidly in enamel- than in tin-lined cans. Acid hydrolysis of sucrose was a first-order reaction. The samples stored at 100°F were dark and of poor flavor. Samples at 55°F were virtually unchanged after a year. Type of can lining was not as important as low temperature for quality retention in storage.

Papaya is marketed chiefly as fresh fruit, but interest in its processed products such as canned nectar has increased. The nectar is made from papaya puree, water, sugar, and citric acid. The stability of canned papaya nectar, as of any processed food product, is important to the producer. Storage temperature and type of can lining generally affect the stability of a product.

Enamel-lined cans have been recommended for papaya nectar because of the corrosiveness of papaya products on plain, tin-lined cans (Lloyd, 1972). A positive correlation between nitrate content and rate of detinning has been established (Farrow et al., 1970; Board, 1973). Extensive detinning can cause container failure and may affect product flavor. Tolerance of tin in high acid foods has not been established in the U.S., but limitations have been imposed on the amount of SnCl<sub>2</sub> that can be added to some canned vegetables. No toxic effects were shown from ingestion of fruit juices that contained 730 ppm of Sn (Benoy et al., 1971).

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The characteristic carotenoid color of products is often, but not always, retained better in tin- than in enamel-lined cans (Payumo et al., 1968; Lloyd, 1972). The rate of darkening of fruit products has been associated with hydrolysis of sucrose to reducing sugars (Stadtman, 1948; Hodge, 1953; Loeffler, 1941), which then enter the Maillard reaction or other reactions producing brown pigments. Inversion of sucrose in a fruit juice product can thus be viewed as a phenomenon associated with the early stages of quality deterioration.

We report herein our investigation of the effects of storage temperature and type of can lining on quality and composition of papaya nectar.

#### MATERIALS AND METHODS

Papaya nectar (13.4° Brix; pH 3.5) was prepared from papaya puree (25%), water, and sugar (10%). The puree had been prepared by the method of Brekke et al. (1972) and stored at 0°F for 1 year.

Half of the nectar (about 150 lb) was then canned in enamel-lined cans (G enamel; no side seam spray, 0.25 lb electrolytic inside, 1.00 lb electrolytic outside, MR 85 lb tin plate). The remaining 150 lb was canned in differential bright tin plate (1.00 lb inside and 0.5 lb outside). After vacuum sealing, the cans were spin-cooked in flowing steam for 3 min (Wang and Ross, 1965), then spin-cooled in water