an average daily bread consumption in India of about 200 g, then at the 5% supplementation level with FPC this bread would give about 30 g of protein of high biological value. Consequently, not only is the quality improved but also the quantity of protein is increased.

In spite of the nutritional advantages that FPC has to offer, it should be stated that in regions where fish are abundant it would be more economical and practical for the people to consume the fish directly in the fresh or processed state. However, there are different marine species that cannot practically be used for direct human consumption. It is those species that man could utilize for the production of fish protein concentrate or fish meal. It would be illogical to convert most of the fish caught into some kind of fish protein concentrate if the same fish could be utilized in another less expensive and acceptable manner for direct human consumption, especially in regions where animal source proteins are needed most.

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Analysis of Leek Volatiles by Headspace Condensation

L. Schreyen,* P. Dirinck, F. Van Wassenhove, and N. Schamp

The flavor complex of freshly harvested leek (*Allium porrum* L.) was studied by a combination of capillary gas chromatography and mass spectrometry. Headspace condensation is used for isolation of the volatile flavor components. Possibilities and difficulties of the new isolation technique are examined. Odor properties are evaluated by running aromagrams on a thermal conductivity detector. The described method is very mild and produces a high quality flavor extract. This extract is compared with the essential oil obtained by steam distillation of leek.

The consumer's choice of fruits and vegetables is generally determined by appearance attributes such as color, shape, size, and defects. Those external features are no guarantee for a good internal sensorial quality such as flavor and consistency which, from the consumer's point of view, are even more important. For those reasons the establishment of methods to judge organoleptic qualities of fruits and vegetables on an objective base is up to date.

Such methods can lead to interesting applications such as flavor quality labeling of foods, selection of varieties by cultivators, and determination of the optimal harvesting time in order to obtain an optimum flavor quality. Since taste can be judged only on a subjective basis it is obvious that analysis of the volatile aroma determining components provides a means for objective flavor quality control. Complex mixtures of organic substances can now be analyzed by high-resolution gas chromatography. The gas–liquid chromatographic (GLC) pattern of aroma concentrates can be correlated with flavor quality. Therefore, it is necessary to determine contributory flavor components in a preliminary fundamental flavor analysis. The isolation of an aroma concentrate is at least as important as the analysis itself. In flavor quality control it can be important to use a simple and quick isolation method for flavors on small food quantities for economical reasons. Flavor quality of the obtained concentrate should be very high with minimum changes in composition and

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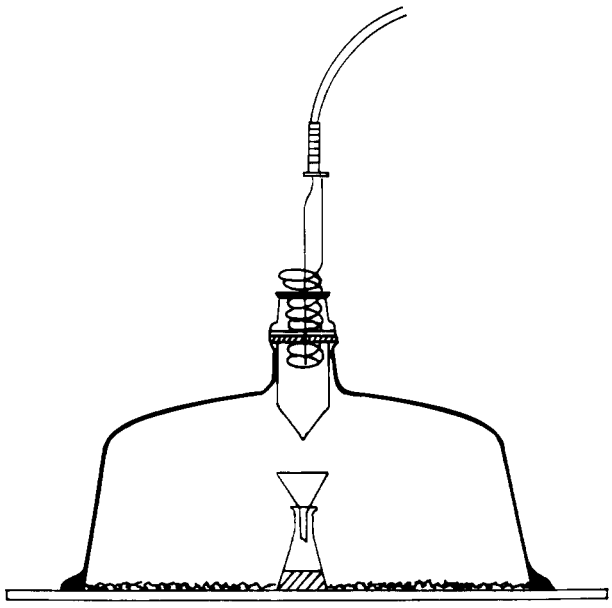

Figure 1. Apparatus used for headspace condensation of flavor compounds.

losses. This work deals with the description of such a simple isolation method which has been successfully applied in our laboratory to apples, leek, and tomatoes. The aroma concentrate of freshly chopped leek, obtained by headspace condensation, is analyzed and compared to that obtained by steam distillation. Identifications were carried out using capillary gas chromatography and mass spectrometry. Odor properties of the extract were evaluated by running aromagrams on a thermal conductivity detector.

EXPERIMENTAL SECTION

Isolation Procedure. Isolation of the volatile components was performed by headspace condensation. For this purpose we used an apparatus (Figure 1) consisting of a hemispherical vessel cover with a diameter of 40 cm and a height of about 30 cm; this cover was part of the pilot plant installation used for steam distillation of leek. The cover was placed on a 1-cm thick glass plate and equipped with a cold finger, containing methanol, which was kept just above 0 °C with a cryostat in order to avoid freezing of the condensate. About 1 kg of freshly harvested and chopped leek was spread over the glass plate. At the center of the plate a small conical flask was placed (content 250 ml) into which any condensate from the cold finger was free to run. After 24 to a maximum 36 h of condensation, 250 ml of a dilute aqueous solution of volatiles was obtained. The temperature under the cover was kept at 30 °C in order to accelerate water evaporation.

Concentration. The isolation procedure yields a very dilute aqueous solution of organic components. Continuous extraction during 18 h with 50 ml of dichloromethane in a conventional liquid–liquid extractor is followed by fractional distillation in order to remove the solvent. At a volume of about 2 ml the extract is transferred to a second smaller distillation apparatus where the extract is further concentrated to 100 μl. This final concentrate is transferred with a syringe in a sealed reaction tube and stored at −20 °C.

An internal standard of 1 μl of dodecane can be added to the aqueous solution prior to extraction in order to follow the degree of solvent concentration. The addition of an internal standard permits us to run quantitative analyses whereby the degree of solvent concentration

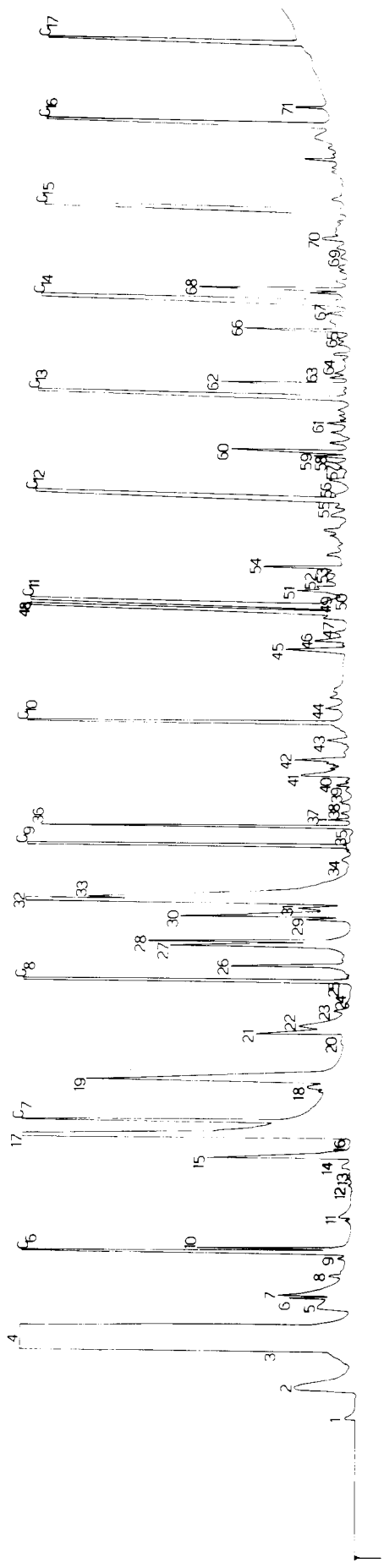

Figure 2. Gas chromatogram of leek volatiles isolated by headspace condensation. Peak numbers correspond to those of Table I. Normal alkanes are indicated on the chromatogram by their number of carbon atoms.

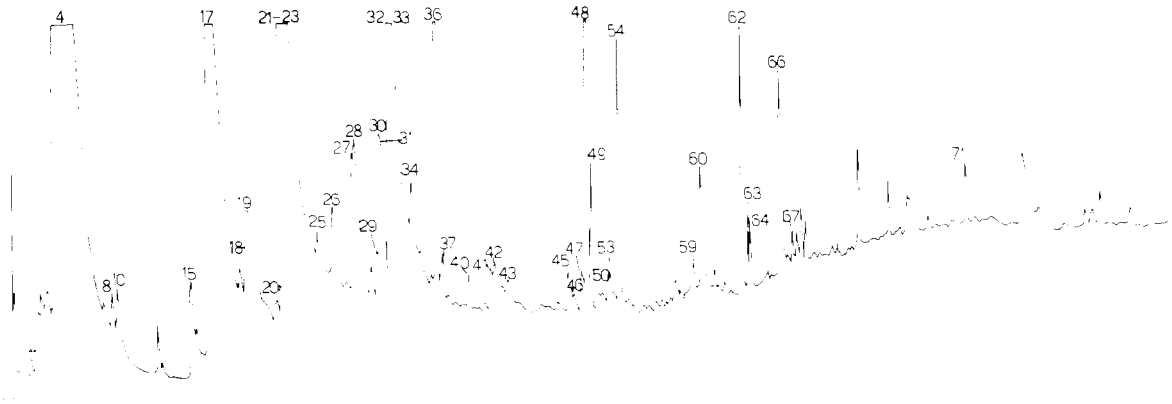

Figure 3. Aromagram of leek volatiles isolated by headspace condensation. Peak numbers correspond to Table I where odor descriptions are listed.

should be known in order to calculate aroma yields.

Gas Chromatography. The volatile components were analyzed on a Varian 2400 F.I.D. gas chromatograph equipped with a subambient temperature programmer. Open tubular glass columns of 600 ft length and 0.03 in. i.d. were used, statically coated with OV_1 as stationary phase (Bouche and Verzele, 1968). Operating conditions are as follows: carrier gas, nitrogen, 4 ml/min with make-up gas to 20 ml/min; hydrogen, 30 ml/min; air, 300 ml/min; injector and detector temperature, 220 °C; temperature programming from 0 to 230 °C at 1 °C per min.

Aromagrams were taken by running analyses with a microthermal conductivity detector (cell volume 140 μl; supplier Gow-Mac) under the following conditions: carrier gas, hydrogen, 5 ml/min with make-up gas to 20 ml/min; injector, 220 °C; detector, 240 °C; filament current, 225 mA; oven temperature isothermal for 15 min at ambient, followed by temperature programming to 230 °C at 1 °C per min.

GC–MS. A Varian 1200 gas chromatograph was modified and coupled to a MS 30 mass spectrometer (A.E.I., Manchester) by means of a membrane separator. An effluent splitter was installed in order to split 75% of the gas flow to the separator and the remainder to the F.I.D. Make-up gas was added at the column exit in order to obtain an optimum gas flow through the separator. Operating conditions for the GC–MS coupling are as follows: carrier gas, helium, at 5 ml/min and make-up gas to 30 ml/min; separator oven and interconnecting lines, 200 °C; ion source pressure, 10^{-5} mmHg; ion source temperature, 200 °C; filament voltage, 70 V; trap current, 300 μA; scan speed, 3 s per decade. Technical details which are not mentioned in this paper are the same as in a previous publication concerning leek in this journal (Schreyen et al., 1976).

RESULTS AND DISCUSSION

Leek oil, isolated by headspace condensation and continuous dichloromethane extraction, has been analyzed in order to identify aroma components of leek, as well as for evaluating this new isolation method. The volatile constituents were identified by comparing their mass spectra and retention times with those of reference spectra. Figure 2 shows us a typical gas chromatogram of the isolated leek oil. The components identified are listed in Table I and their peak numbers correspond to the numbers of Figure 2.

On comparison of Table I and the results obtained by steam distillation we notice that most of the sulfur-containing products, contributing to the leek aroma, are present in comparable concentrations, such as *n*-propanethiol, dimethyl disulfide, methyl propyl disulfide, methyl propenyl disulfide, dimethyl trisulfide, dipropyl disulfide, methyl propyl trisulfide, and 2,5-dihydro-3,4-dimethylthiophen-2-one. However, only small quantities of the three dimethylthiophene isomers are found with the headspace condensation method (H.S.C.) in contrast to the large amount of 3,4-dimethylthiophene found by steam distillation (Boelens and Brandsma, 1972). Allyl methyl sulfide, allyl methyl disulfide, and the traces of methylthiophene isomers from the steam distillation are no longer present in the headspace condensate; on the other hand we notice the presence of three propenyl propyl disulfide isomers and of dipropyl trisulfide which were absent in the steam distillation, the latter probably being decomposed.

Products which are believed to result from Maillard reactions, such as 2-furyl alcohol, 2-furaldehyde, and ethyl furyl ketone, are completely absent in the headspace condensate. The two alkyl-substituted 2,3-dihydro-5-methylfuran-2-ones are found in the H.S.C., which suggests that they are not formed via Maillard reactions. The lower concentrations can be explained by a lower evaporation ratio at 30 °C instead of 104 °C as is the case in steam distillation.

A large number of saturated alcohols are isolated with both methods, such as propanol, butanol, pentanol, 2-butanol, 3-methylbutanol, 2-methylpentanol, hexanol, benzyl alcohol, 2-phenylethanol, and 3-hydroxy-2-butanone. 3-Octanol is only present in the H.S.C.

Comparing the unsaturated alcohols of both methods shows us that only *trans*-3-hexen-1-ol is present in both of them.

The H.S.C. shows two pentenol isomers, 3-octen-1-ol and the very important hexenol isomers 3-hexen-1-ol (cis and trans) and 2-hexen-1-ol (trans) which are present in relatively large concentrations. They have a great influence on the overall natural aroma of leek as will be clearly shown in the aromagram. From the pyrazines, dimethylpyrazine is found with both methods while methylpyrazine is only found in the steam distillate. New identified products in the headspace condensate are methyl and ethyl cinnamate, and two lactones.

From the aldehydes propanol and 2-methyl-2-pentenal are easily recognized in both methods, while 3-methylbutanal and 2-methylpentanal occur only in the steam distillate.

cis-3-Hexenal and *trans*-2-hexenal are only found in the headspace condensate and contribute highly to the "green" flavor, together with the hexenols.

Aromagram results of the analyzed leek oil are illustrated in Figure 3 and Table I where odor descriptions are

Table I. Identification of Volatile Components Found in Leek by Headspace Condensation

Peak no.	Component	Ip[c]	Identification[a]	Description (intensity)[b]
1	Methanethiol[d]		MS, RT, A	Rotten (M)
2	Ethanol[d]		MS, RT, A	
3	Propanol[d]		MS, RT, A	
4	Dichloromethane (s)		MS, RT, A	Dichloromethane (M)
5	Carbon disulfide (s)		MS, RT, A	
6	Dichloroethylene (s)		MS, RT, A	
7	1-Propanol[d]		MS, RT, A	
8	1-Propanethiol[d]		MS, RT	Chopped leek, onion (S)
9	Trichloromethane (s)		MS, RT, A	
10	Ethyl acetate[d]	603	MS, RT, A	Pleasant, aromatic (S)
11	2-Methylpropanol[d]	627	MS, RT, A	
12	Benzene[d]	648	MS, RT, A	Characteristic (W)
13	Carbon tetrachloride (s)	652	MS, RT, A	
14	1-Butanol[d]	666	MS, RT	
15	1-Penten-3-ol	672	MS, T	Pleasant, pungent (W)
		676		Alcoholic (W)
16	Trichloroethylene (s)	687	MS, RT, A	
17	2-Hydroxy-3-butanone[d]	689	MS, RT, A	Buttery (S)
18	Dimethyl disulfide[d]	726	MS, RT	Bad smell, onion (M)
19	3-Methylbutanol[d]	728	MS, RT	Alcoholic, bad (M)
20	Toluene[d]	754	MS, RT, A	
21	1-Pentanol[d]	763	MS, RT, A	Alcoholic (W)
22	Pentenol isomer	768	MS, T	Alcoholic, charact. (W)
23	*cis*-3-Hexenal	778	MS, T	Green (S)
24	Ethyl butyrate	785	MS, RT	Pleasant (M)
25	Tetrachloroethylene (s)	796	MS, RT, A	
		798		Musty (M)
26	2-Methylpent-2-enal[d]	811	MS, RT	Pleasant, almonds (S)
		815		Rotten, stinking (S)
		820		Leek (W)
27	Mixture of 3-methylpentanol + 2-methylpentanol[d]	826	MS, RT, A	Unpleasant, pungent rotten apples (M)
28	*trans*-2-Hexenal	830	MS, RT	Green (S)
		839		Unpleasant (S)
29	*trans*-3-Hexen-1-ol[d]	845	MS, RT	Green, flowers (VS)
30	*cis*-3-Hexen-1-ol	848	MS, RT, A	Green (VS)
31	Unknown	854	U	Green (S)
32	*trans*-2-Hexen-1-ol	858	MS, T	Green (S)
33	1-Hexanol[d]	861	MS, RT, A	Green, aromatic (S)
34	3,4-Dimethylthiophene[d]	888	MS, RT	Burnt onion, potatoes (S)
35	Dimethylpyrazine (isom.)	892	MS, T	
		908		Characteristic (W)
36	Methyl propyl disulfide[d]	914	MS, RT	Leek (S)
37	Methyl propenyl disulfide[d]	921	MS, RT	Onion, *Allium sativum* (M)
38	Unknown	926	U	Burnt onion (M)
39	Benzaldehyde[d]	935	MS, RT, A	
40	Dimethyl trisulfide[d]	950	MS, RT	Pungent (M)
41	Unknown	958	U	
42	1-Octen-3-ol	970	MS, T	Pleasant (W)
43	3-Octanol	986	MS, T	Alcoholic, pungent (M)
		1010		Onion (M)
44	Benzyl alcohol[d]	1014	MS, RT, A	
		1037		Bad smell (M)
45	Unknown	1062	U	Aromatic (W)
46	Unknown	1071	U	Peas (S)
47	Propenyl propyl disulfide	1079	MS, RT	Leek (W)
48	Dipropyl disulfide[d]	1095	MS, RT, A	Onion (VS)
49	2-Phenylethanol[d]	1096	MS, RT, A	
50	Propenyl propyl disulfide (isomer)	1100	MS, RT	Leek (W)
		1110		Hay, coumarine (M)
51	Propenyl propyl disulfide (isomer)	1112	MS, RT	
52	1,2-Dimethoxybenzene[d]	1117	MS, RT, A	
		1128		Pungent (S)
53	Propenyl propyl disulfide (isomer)	1132	MS, RT	
54	Methyl propyl trisulfide[d]	1137	MS, RT	Pungent, leek (S)
		1153		Burnt potatoes (M)
		1182		Bad, musty (M)
55	*O*-Methoxyphenyl acetate	1195	MS, T	
56	2,5-Dihydro-3,4-dimethylthiophen-2-one[d]	1200	MS, RT	
		1207		Rubbery (S)
57	γ-Hexanolacetone	1227	MS, T	
58	Unknown	1234	U	
59	Unknown	1243	U	Cinnamon (W)
60	Unknown	1247	U	Leek (S)
61	2-Undecanone	1274	MS, RT	
		1284		Bad smell (M)
62	Dipropyl trisulfide	1314	MS, RT	Onion, leek, pungent (VS)

Table I. (*Continued*)

Peak no.	Component	Ip[c]	Identification[a]	Description (intensity)[b]
63	Propenyl propyl trisulfide[d]	1322	MS, RT	Rotten, leek (M)
64	γ-Heptanolacetone	1328	MS, T	Characteristic (S)
		1338		Carrots (W)
65	Methyl cinnamate	1363	MS, T	
66	Unknown	1370	U	Pungent, leek (VS)
67	Unknown	1388	U	Pungent (S)
68	2,3-Dihydro-5-methyl-2-*n*-hexylfuran-3-one[d]	1413	MS, RT	
		1435		Onion (M)
69	Ethyl cinnamate	1462	MS, T	
70	2-Tridecanone[d]	1475	MS, RT	
		1479		Onion (S)
		1561		Onion (S)
71	2,3-Dihydro-5-methyl-2-*n*-octylfuran-3-one[d]	1622	MS, RT	

[a] MS, mass spectrometry; RT, retention index; A, comparison with authentic product; for suppliers see Schreyen et al., 1976; T, tentative; U, unidentified. [b] W, weak; V, very; M, medium; S. strong. [c] Retention index on OV 1 between C_6 and C_{17} with linear temperature programming. [d] Also present in leek essential oil obtained by steam distillation; s, solvent or solvent impurity.

listed together with the corresponding odor intensities. Strong "green" smells are produced by *trans*-3-hexen-1-ol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol, *cis*-3-hexenal, and *trans*-2-hexenal. Identified products which are believed to contribute to leek flavor are the sulfur components propanethiol, dimethyl disulfide, methyl propyl disulfide, dipropyl disulfide, dimethyl trisulfide, methyl propyl trisulfide, dipropyl trisulfide, methyl propenyl disulfide, propenyl propyl disulfide (three isomers), propenyl propyl trisulfide, dimethylthiophene isomers, and some unidentified products of which no interpretable mass spectrum could be taken. About 11 leek-like odors are noticed in the aromagram in addition to numerous pronounced onion odors (Boelens et al., 1971). Two interesting unidentified products with strong leek odor are peaks 60 and 66 in Figure 2. Their mass spectra are listed in Table II.

Our main purpose was to isolate volatile components from leek in mild conditions in order to obtain a natural leek flavor with a minimum of artefacts. Since direct headspace analysis on open tubular columns is a problem without enrichment, due to the small concentrations of available products, we checked a modified technique whereby the headspace was condensed on a cold finger. This method can also be considered as a steam distillation at ambient temperature. The flavor obtained by headspace condensation is somewhat less complex than that obtained by steam distillation. We found that for optimum flavor isolation, without risk of producing off-flavors, the condensate of 250 ml should be obtained within 24 h with a maximum temperature of 30 °C under the cover. Changes in flavor were sometimes noticed after a longer sampling period. Only in the case of tomato samples a mycelium formation was noticed after a few hours due to optimum conditions for mold growth. This can be avoided by adding 1 g of potassium sorbate to the chopped tissue prior to sampling. From the analysis results it is clear that the isolation technique is very mild since only very small amounts of dimethylthiophene isomers are formed due to heating of unsaturated disulfides (Boelens et al., 1971). Those products are present in large quantities in the steam distillation procedure. In addition, three propenyl propyl disulfides are identified in the headspace condensate. They are probably not present in the steam distillate because of decomposition or rearrangement to dimethylthiophenes.

Quantitative results were difficult to obtain because of a varying degree of solvent concentration between samples. To make quantitative results comparable we added an internal standard of dodecane to the condensate, prior to extraction, so the degree of concentration could be easily determined.

Table II. Mass Spectral Data of Constituents of Leek Oil

trans-2-Hexenal: 41 (100), 42 (65), 27 (50), 39 (47), 29 (47), 83 (40), 69 (39), 55 (37), 98 (30), 70 (13), 97 (9)
trans-3-Hexen-1-ol: 41 (100), 67 (42), 69 (40), 82 (35), 55 (33), 42 (22), 39 (18), 29 (18), 31 (16), 57 (13), 70 (12), 43 (12), 53 (9), 45 (8), 68 (7), 100 (2)
cis-3-Hexen-1-ol: 41 (100), 67 (56), 55 (36), 82 (35), 42 (27), 69 (26), 39 (23), 31 (25), 29 (16), 27 (21), 57 (12), 43 (11), 70 (10), 53 (9), 100 (2)
trans-2-Hexen-1-ol: 57 (100), 41 (48), 27 (20), 67 (19), 44 (18), 82 (17), 39 (16), 29 (14), 43 (12), 42 (10), 71 (9), 31 (8), 69 (4), 72 (3), 100 (2)
cis-2-Hexen-1-ol: 57 (100), 41 (45), 82 (30), 67 (30), 29 (25)
1-Octen-3-ol: 57 (100), 43 (22), 41 (21), 29 (15), 55 (14), 72 (12), 27 (12), 85 (6), 81 (6), 31 (5), 99 (3)
3-Octanol: 59 (100), 55 (90), 41 (54), 29 (48), 43 (42), 83 (40), 27 (26), 31 (19), 39 (18), 101 (16)
O-Methoxyphenyl acetate: 124 (100), 109 (68), 43 (47), 81 (11), 166 (15), 77 (10)
γ-Hexanolacetone: 85 (100), 29 (56), all other peaks less than 10%
Unknown, peak no. 60: 43 (100), 41 (82), 42 (50), 59 (40), 29 (39), 47 (38), 39 (38), 45 (37), 76 (33), 166 (10, mol wt), 46 (19), 106 (15), 108 (14), 89 (8), 90 (10), 91 (9), 168 (3)
Dipropyl trisulfide: 43 (100), 41 (56), 75 (41), 182 (27), 29 (27), 42 (22), 39 (18), 47 (16), 76 (13), 45 (11), 108 (6), 105 (5), 184 (3), 140 (2), 147 (2), 98 (1)
γ-Heptanolacetone: Weak spectrum, base peak 85
Methyl cinnamate: 131 (100), 103 (53), 162 (45), 77 (35), 161 (23), 51 (12), 102 (6), 65.5, 51.5
Unknown, peaks no. 66 and 67: 69 (100), 129 (82), 176 (34, with ident. MS mol wt), 41 (33), 45 (21), 61 (18), 67 (16), 59 (10), 128 (9), 47 (8), 178 (3, 7, sulfur isotope, 2 sulfur atoms)
Ethyl cinnamate: 131 (100), 103 (43), 176 (32), 77 (30), 148 (15), 51 (15), 104 (11), 132 (11), 147 (10), 65.5, 51.5
3-Methylbutanal: 44 (100), 41 (98), 43 (66), 58 (54), 39 (36), 27 (29), 20 (28), 57 (19), 71 (16), 86 (2)

CONCLUSION

Leek essential oil has been isolated by headspace condensation and dichloromethane extraction. The isolated oil had a pleasant natural leek flavor which differed

remarkably from that obtained by steam distillation. Even higher boiling products with a retention index up to 1700 can be isolated by this method which proves to be very mild and produces practically no artefacts. It has been applied successfully to leek, apples (Dirinck et al., 1975), and tomatoes (Dirinck et al., 1976) and can be used in evaluating natural flavor quality of fruits and vegetables.

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Nitrosopyrrolidine Formation in Fried Bacon

Lucy Sun Hwang[1] and Joseph D. Rosen*

Experiments involving ^{14}C-labeled amines have shown that proline is more likely to be the precursor of nitrosopyrrolidine formation than either spermidine or putrescine in fried bacon. The data are consistent with a mechanism involving formation of nitrosoproline from sodium nitrite and free proline during processing with subsequent decarboxylation of nitrosoproline during frying.

The existence of the carcinogen, nitrosopyrrolidine (NPYR), in fried bacon is well documented. Crosby et al. (1972) found NPYR in 13 out of 24 samples of fried bacon in concentrations up to 40 ppb. Sen et al. (1973) found NPYR in 8 out of 9 samples of fried bacon in concentrations from 4 to 25 ppb. Higher levels, from 10 to 108 ppb, were reported by Fazio et al. (1973) in eight commercial brands of bacon fried at 350 °F. Nitrosopyrrolidine was not found in raw bacon, indicating that the high temperatures involved in the bacon frying process played a major role in its formation. Another major factor is the amount of sodium nitrite (Sen et al., 1974) added to pork bellies during processing as the reaction of nitrite with some amines is known to produce nitrosamines.

Thus, the amount of NPYR formed can be reduced by the addition of lower quantities of sodium nitrite or by the inclusion of nitrite scavengers such as ascorbic acid (Fiddler et al., 1973) or propyl gallate (Sen et al., 1975). Unfortunately, a combination of improved analytical methodology such as obtained by the use of thermal energy analyzer detectors (Fine et al., 1975) and the apparently unresolvable controversy over whether or not there is a threshold value for carcinogens makes for continuous consumer concern and the possibility of ever more stringent government regulatory action on the use of nitrites. Further reduction in nitrite levels may result in bacon with inferior color and taste as well as bacon with higher amounts of disease-causing microorganisms (Christiansen et al., 1974). As a result, there have been efforts in the recent past to determine what compound(s) react(s) with nitrite to form NPYR so that the mechanism of the reaction could be better understood. With this knowledge, it might be possible to alter processing techniques in order to eliminate NPYR formation without too great a reduction in nitrite.

Bills et al. (1973) found that NPYR was produced from nitrosoproline, pyrrolidine, spermidine, proline, and putrescine in yields of 2.6, 1.0, 1.0, 0.4, and 0.04%, respectively, in a model system containing 1 ml of water in 100 ml of oil heated at 170 °C for 5 min.

Huxel et al. (1974) found that NPYR could arise from heating dry samples of sodium nitrite with the pyrrolidine ring containing compounds: proline, glycylproline, prolylglycine, and pyrrolidine at 170 °C for 2 h. Dry collagen samples formed NPYR when heated with nitrite at 195 °C.

Using a model system similar to that of Bills et al., Gray and Dugan (1975) found that NPYR could be formed as a result of thermal decomposition of collagen to proline with subsequent reaction with nitrite after only 20 min at temperatures as low as 120 °C. Using still another model system, Warthesen et al. (1975) found that putrescine dihydrochloride and ornithine hydrochloride produced NPYR in 22.8 and 1.2% theoretical yields, respectively. Model systems, while useful, do not adequately reflect actual conditions. Our approach, therefore, involved spiking bacon with known amounts of ^{14}C-labeled precursors and determining the yield of NPYR formed after frying.

EXPERIMENTAL SECTION

Apparatus. *Liquid Scintillation Counter.* A Beckman LS-233 scintillation counter equipped with an external standardization system was used. Readings (in counts per minute) were obtained from a full channel (0–1000) window.

GC–MS. A DuPont 21-490 mass spectrometer equipped with mass fragmentography accessory (Pareles and Rosen, 1974) and interfaced to a Varian 2740 gas chromatograph was used. The column was a 3 ft × $^1/_8$ in. i.d. 1% OV-17 on HP Chromosorb W, 80–100 mesh. At column, injector, and detector temperatures of 90, 100, and 225 °C, respectively, and a helium flow rate of 30 cm^3/min, NPYR had a retention time of 4.5 min. Mass fragmentography

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