

Volatile Components of Roasted Peanuts: Neutral Fraction

Bobby R. Johnson,¹ George R. Waller,* and Rodger L. Foltz²

The volatile components of roasted peanuts were obtained by vacuum degassing of freshly pressed oil from the peanuts. The aqueous condensate was separated into basic and neutral fractions by methylene chloride extraction at high and low pH's. The neutral fraction was analyzed on a Carbowax 1540 500-ft \times 0.02-in. i.d. open tubular column coupled to both high- and low-resolution mass spectrometers.

Identification of 24 compounds not previously reported in roasted peanut volatiles was accomplished by comparison of their mass spectra to reference spectra. Relative retention indices from the open tubular column were used to confirm identifications. The identified compounds include seven furans, six pyrroles, three 2-phenyl-2-alkenals, two thiophenes, and some miscellaneous compounds.

Many of the important volatile components of roasted peanuts have been reported recently by this laboratory. Mason *et al.* (1966) first identified pyrazines as basic constituents of roasted peanut aroma. Later, the same group (Mason *et al.*, 1967) identified the major carbonyls of roasted peanut aroma. Brown *et al.* (1968) reported 12 acids and a few miscellaneous compounds. In a preceding paper by Johnson *et al.* (1971), the most detailed study yet published on the basic fraction of the volatile components of roasted peanuts has been discussed. These data on the minor constituents were obtained through new mass spectrometric techniques employing both high- and low-resolution mass spectrometers coupled to open tubular glc columns. This paper is devoted to identifying the volatile compounds of the neutral fraction and describing companion techniques to those reported in a previous paper (Johnson *et al.*, 1971).

EXPERIMENTAL

Materials. Authentic reference compounds were obtained from reliable commercial sources or were gifts from International Flavors & Fragrances, Inc., and Corporate Research Department of the Coca-Cola Co. Locally obtained high quality Spanish peanuts were utilized.

Isolation and Fractionation of the Volatiles. The oil from whole roasted peanuts was pressed and passed through a vacuum degassing system to collect the volatiles. The condensed volatiles were then fractionated into basic and neutral fractions as outlined by Johnson *et al.* (1971).

Glc Analysis. Glc retention time indices were calculated as I_E values as outlined by Johnson *et al.* (1971). The dilute neutral fraction was reduced to 1-ml volume on a rotatory evaporator keeping the solution temperature near 0° C. A portion of this was then placed in a tapered glass tube prepared by sealing the small end of a disposable Pasteur pipette. This was reduced in volume to 1–2 μ l by using a gentle stream of nitrogen gas. This concentration technique was found necessary to concentrate the complex neutral fraction sufficiently to analyze most components simultaneously. The majority of the more volatile components were lost during

this concentration procedure, but many have been previously identified (Mason *et al.*, 1967).

Headspace analysis was performed to detect the more volatile aroma components. This was accomplished by placing the aroma condensate obtained from the traps of the vacuum degassing system into an 8-mm i.d. 15-cm tube sealed at one end and fitted with a gas-tight septum at the other end. The vapors above the condensate (1–2 ml) were removed with a gas syringe and analyzed by gas chromatography-mass spectrometry (gc-ms).

Capillary Gas Chromatography-Mass Spectral Analysis. Gc-ms analyses on the neutral fraction were obtained by utilizing a 0.02-in. i.d. \times 500-ft stainless steel capillary operated in a prototype of the LKB 9000 gc-ms (Waller, 1967). The column was coated with Carbowax 1540 containing 1% KOH. The column was operated at 40° C initially and manually increased at various intervals to a maximum of 170° C, with a helium flow rate of 3 ml/min and a postcolumn gas adder at 20 ml/min (Johnson *et al.*, 1971).

High-resolution mass spectra (hrms) were obtained for some of the components by connecting the above described capillary column to an AEI MS-902 double focusing mass spectrometer. The adaptation was accomplished by passing the last 3 ft of the column out of the detector box of an adjacent gas chromatograph over to an on-off valve mounted near the ion source of the mass spectrometer. The valve was connected directly to the ion source by a glass line. The portion of the column utilized in the interface was heated by electrical resistance, and it and all other points between the column and ion source were maintained at 200° C or slightly above. The total ion current output of the mass spectrometer was monitored by a recorder to obtain a tracing of the components eluting from the capillary column. This arrangement allowed the direct introduction of all of the column effluent into the mass spectrometer. The column was programmed from 65 to 175° C at 2°/min with a helium flow of approximately 1 ml/min. High-resolution mass spectra were recorded on magnetic tape; later they were analyzed and plotted. Preliminary information was obtained from a similar system described by Johnson *et al.* (1971).

RESULTS AND DISCUSSION

The neutral fraction of roasted peanut volatiles had a very intense roasted peanut aroma, but when highly concentrated the aroma was more "burnt" or coffee-like.

A typical total ion current tracing of a capillary gc-ms

Biochemistry Department, Agricultural Experiment Station, Oklahoma State University, Stillwater, Oklahoma 74074

¹ Department of Food Science, North Carolina State University, Raleigh, North Carolina 27607

² Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201

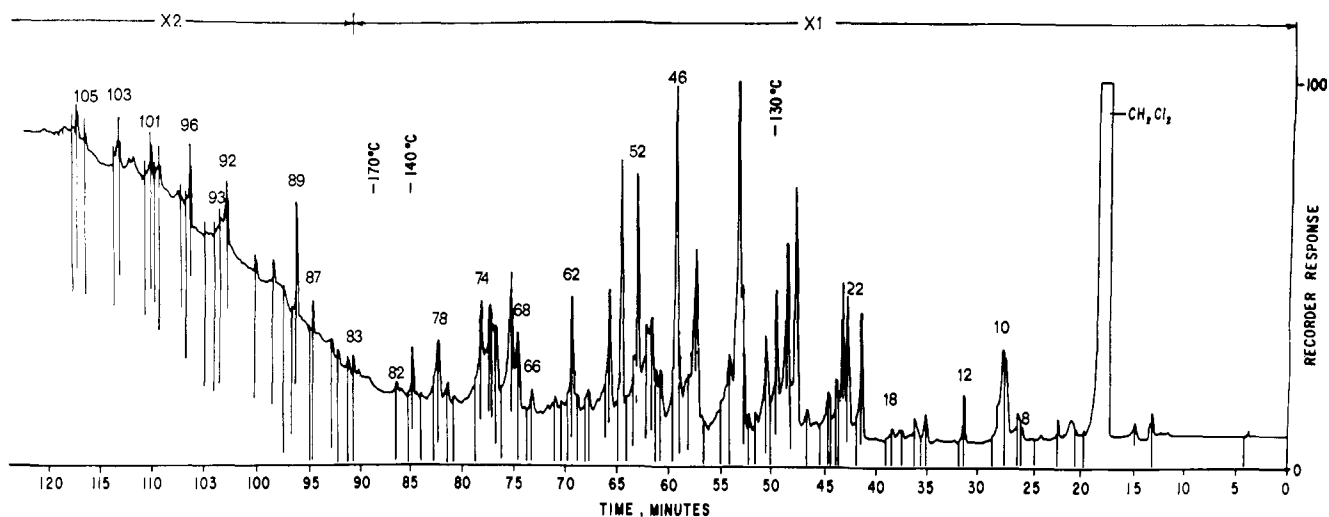


Figure 1. Typical capillary gc-ms analysis of the neutral fraction of roasted peanut volatiles. 0.3 ml injection of concentrated basic fraction of roasted peanut volatiles on a 500-ft \times 0.02-in. i.d. stainless steel capillary coated with Carbowax 1540 containing 1% KOH. Temperature was initially 40° C and was manually increased at frequent intervals up to 170° C and held. Flow rate was 3 ml/min with a postcolumn gas adder at 20 ml/min

Table I. Compounds Identified in the Neutral Fraction of Peanut Volatiles

Compound	Mass spectrum number (Figure 1)	Modes of analysis	ms Identification	ms Reference
2-Butanone		hrms (C ₄ H ₈ O)	Tentative	Stoll <i>et al.</i> , 1967
Toluene	8	hrms (C ₇ H ₈)	+	Stoll <i>et al.</i> , 1967
Methyl disulfide	9	hrms (C ₂ H ₆ S ₂)	+	Cornu and Massot, 1966
<i>n</i> -Hexanal	10	hrms (C ₆ H ₁₂ O)	+	Cornu and Massot, 1966
4-Methyl-3-penten-2-one	12	ms	Tentative	Stoll <i>et al.</i> , 1967
2-Amylfuran	18	hrms (C ₉ H ₁₄ O)	Tentative	Stoll <i>et al.</i> , 1967
2-Methyltetrahydrofuran-3-one	22	hrms (C ₆ H ₈ O ₂), rt	+	Viani <i>et al.</i> , 1965
2-Furfural	46	hrms (C ₅ H ₄ O ₂), rt	+	Cornu and Massot, 1966
2-Acetylfuran	52	ms	Tentative	Cornu and Massot, 1966
5-Methylfurfural	62	hrms (C ₆ H ₆ O ₂), rt	+	Cornu and Massot, 1966
<i>N</i> -Ethylpyrrole-2-carboxaldehyde	66	hrms (C ₇ H ₉ NO)	Tentative	Tatum <i>et al.</i> , 1967
<i>N</i> -Methylpyrrole-2-carboxaldehyde	68	ms	Tentative	Stoll <i>et al.</i> , 1967
Furfuryl alcohol	74	hrms (C ₅ H ₆ O ₂)	+	Cornu and Massot, 1966
Thiophene-2-carboxaldehyde	78	ms, rt	Tentative	Stoll <i>et al.</i> , 1967
Naphthalene	82	hrms (C ₁₀ H ₈), rt	+	Stoll <i>et al.</i> , 1967
Acetyl-2-thiophene	83	hrms (C ₆ H ₆ OS), rt	+	Stoll <i>et al.</i> , 1967
<i>N</i> -(2-furfuryl)pyrrole	87	ms, rt	+	Stoll <i>et al.</i> , 1967
Phenyl-3-furan	89	hrms (C ₁₀ H ₈ O)	+	Stoll <i>et al.</i> , 1967
2-Phenyl-2-butenal	92	ms, rt	+	van Praag <i>et al.</i> , 1968
4-Methyl-2-phenyl-2-pentenal	93	ms	Tentative	van Praag <i>et al.</i> , 1968
2-Acetylpyrrole	96	ms, rt	+	Budzikiewicz <i>et al.</i> , 1967
Pyrrole-2-carboxaldehyde	101	ms, rt	+	Budzikiewicz <i>et al.</i> , 1967
5-Methyl-2-phenyl-2-hexenal	103	ms, rt	+	van Praag <i>et al.</i> , 1968
5-Methyl-2-pyrrolaldehyde	105	ms	Tentative	Tatum <i>et al.</i> , 1967

analysis of the neutral fraction is shown in Figure 1. The vertical slash marks are points where mass spectra scans were taken. A list of the compounds identified in the neutral fraction, along with the modes of analyses used, is shown in Table I. Identifications were accomplished by comparison of mass spectra to those of authentic compounds and by comparison of relative retention time indices (I_E). In some cases additional confirmation of identity was obtained from high-resolution mass spectra. The elemental composition of the molecular ion is included when high-resolution mass spectrometric data were obtained. Tentative identifications are reported when mass spectral data were inconclusive due to mixtures, high column background, or lack of appropriate reference materials.

The following compounds are reported for the first time in

the volatiles of roasted peanuts: toluene, methyl disulfide, *n*-hexanal, 2-methyltetrahydrofuran-3-one, furfural, 5-methylfurfural, furfuryl alcohol, naphthalene, acetyl-2-thiophene, *N*-(2-furfuryl)pyrrole, phenyl-3-furan, 2-phenyl-2-butenal, 2-acetylpyrrole, pyrrole-2-carboxaldehyde, and 5-methyl-2-2-hexenal.

2-Butanone, 4-methyl-3-penten-2-one, 2-amylfuran, methyl furyl ketone, *N*-ethylpyrrole-2-carboxaldehyde, *N*-methylpyrrole-2-carboxaldehyde, thiophene-2-carboxaldehyde, 4-methyl-2-phenyl-2-pentenal, and 5-methyl-2-pyrrolaldehyde are tentatively reported.

Most of the newly identified components can be readily attributed to nonenzymatic browning reactions involving carbohydrates, lipids, free amino acids, and proteins. However, the 2-phenyl-2-alkenals do not appear to be formed di-

rectly from these reactions, as reported by van Praag *et al.* (1968). These compounds are dehydrated aldol condensation products between phenylacetaldehyde and acetaldehyde, isobutyraldehyde, or isovaleraldehyde. This seems to be the case in peanuts, since these four aldehydes are present in abundant amounts (Mason *et al.*, 1967).

These newly reported constituents of the neutral fraction of roasted peanut aroma are common to other roasted foods, which include coffee (Stoll *et al.*, 1967; Goldman *et al.*, 1967; Bondarovich *et al.*, 1967; Stoffelsma and Pypker, 1968), potato chips (Mookherjee *et al.*, 1965; Deck, 1968), cocoa (Flament *et al.*, 1967; Marion *et al.*, 1967; Van der Wal *et al.*, 1968; van Praag *et al.*, 1968), and popcorn (Walradt *et al.*, 1970a).

A number of phenols, lactones, and esters have been reported as volatile constituents of roasted peanuts (Walradt *et al.*, 1970b) but were not detected in this study since these classes of compounds would not have survived chromatography on the Carbowax 1540 with 1% KOH open tubular column utilized.

LITERATURE CITED

- Bondarovich, H. A., Friedel, P., Krampl, V., Renner, J. A., Shephard, F. W., Gianturco, M. A., *J. AGR. FOOD CHEM.* **15**, 1093 (1967).
- Brown, B. A., Konigsbacher, K. S., Ellison, F. E., Mann, G. E., *J. Food Sci.* **33**, 595 (1968).
- Budzikiewicz, H., Djerassi, C., Williams, D. H., "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, 1967, pp 602-603.
- Cornu, A., Massot, R., "Compilation of Mass Spectral Data," Heyden and Son, London, 1966.
- Deck, R. E., *Diss. Abstr. B* **29**(6), 2078 (1968).
- Flament, I., Willhalm, B., Stoll, M., *Helv. Chim. Acta* **50**, 2233 (1967).
- Goldman, I. M., Seibl, J., Flament, I., Gautschi, F., Winter, M., Willhalm, B., Stoll, M., *Helv. Chim. Acta* **50**, 694 (1967).
- Johnson, B. R., Waller, G. R., Burlingame, A. L., *J. AGR. FOOD CHEM.* **19**, 1020 (1971).
- Marion, J. P., Müggler-Chavan, F., Viani, R., Bricout, J., Reymond, D., Egli, R. H., *Helv. Chim. Acta* **50**, 1509 (1967).
- Mason, M. E., Johnson, B. R., Hamming, M., *J. AGR. FOOD CHEM.* **14**, 454 (1966).
- Mason, M. E., Johnson, B. R., Hamming, M., *J. AGR. FOOD CHEM.* **15**, 760 (1967).
- Mookherjee, B. D., Deck, R. E., Chang, S. S., *J. AGR. FOOD CHEM.* **13**, 131 (1965).
- Stoffelsma, J., Pypker, J., *Recl. Trav. Chim. Pays-Bas* **87**, 241 (1968).
- Stoll, M., Winter, M., Gautschi, F., Flament, L., Willhalm, B., *Helv. Chim. Acta* **50**, 628 (1967).
- Tatum, J. H., Shaw, P. E., Berry, R. E., *J. AGR. FOOD CHEM.* **15**, 773 (1967).
- Van der Wal, B., Sipma, G., Kettenes, D. K., Semper, A., Th. J., *Recl. Trav. Chim. Pays-Bas* **87**, 241 (1968).
- van Praag, M., Stein, H. S., Tibbetts, M. S., *J. AGR. FOOD CHEM.* **16**, 1005 (1968).
- Viani, R., Müggler-Chavan, F., Reymond, D., Egli, R. H., *Helv. Chim. Acta* **48**, 1809 (1965).
- Waller, G. R., *Proc. Okla. Acad. Sci.* **47**, 271 (1967).
- Walradt, J., Lindsay, R. C., Libbey, L. M., *J. AGR. FOOD CHEM.* **18**, 926 (1970a).
- Walradt, J. P., Pittet, A. O., Kinlin, T. E., Sanderson, A., Abstracts of Papers, 160th ACS National Meeting, Chicago, Ill., September 1970b, AGFD 70.

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