Principal Volatile Components of Raw, Roasted, and Fried Argentinean Peanut Flavors

Laura V. Burroni,*,† Nelson R. Grosso,‡ and Carlos A. Guzmán†

Instituto de Ciencias y Tecnología de los Alimentos (ICTA), Facultad de Ciencias Exactas, Físicas y Naturales, UNC, IMBIV-CONICET, Avenida Vélez Sársfield 299, 5000 Córdoba, Argentina, and Química Biológica, Facultad de Ciencias Agropecuarias, Avenida Valparaíso s/n, CC 509, 5000 Córdoba, Argentina

Volatile components of raw, roasted, and fried Runner peanut seeds from Córdoba (Argentina) were analyzed. The extraction of volatile compounds was performed according to the headspace method. They were separated and identified by GC/MS. Hexanal, 1-methylpyrrole, cyclobutanol, 4-ethyl-2,5-dimethylisoxazolidine, 2,6-dimethylpyrazine, 1-hexanol, and acetic acid were detected. Hexanal and 1-methylpyrrole showed higher concentrations followed by acetic acid. 2,6-Dimethylpyrazine was not found in raw peanuts. Cyclobutanol and 1-hexanol were detected in trace levels in roasted and fried peanuts, respectively. 2,6-Dimethylpyrazine was found in roasted and fried peanuts.

Keywords: *Arachis hypogaea; volatile components; flavor; peanut; Argentina*

INTRODUCTION

Runner peanut is the principal cultivar used in Argentina, which produces and exports great quantities of this peanut (Grosso et al., 1994; Grosso and Guzmán, 1995).

The chemical quality of peanuts determined by chemical composition and flavor is very important to their acceptability and nutritional and health benefits to consumers (Bett et al., 1994).

Mason and Johnson (1966) investigated the flavors of peanut and detected heterocycles, for example, pyrazines and pyrroles. Walradt et al. (1971) identified other heterocyclic and sulfur compounds, phenols, ketones, esters, alcohols, and hydrocarbons among volatile components of roasted peanuts. Oxazoles, thiazoles, and oxazolines were also detected (Lee et al., 1981). Oxidized compounds generated during storage are important to the overall flavor and aroma of roasted peanuts (Ahmed and Young, 1982). The final quality of peanut flavor is strongly influenced by oil stability; the polyunsaturated fatty acids are susceptible to lipid oxidation (Vercellotti et al., 1992a; Braddock et al., 1995). The fatty acids of the peanut produced in Argentina are more unsaturated than those of peanuts produced in other countries (Grosso et al., 1994).

The objective of this study was to characterize volatile compounds of raw, roasted, and fried peanut seeds from Córdoba, Argentina.

MATERIALS AND METHODS

Peanut Seeds. Sound and mature seeds (Runner type, size 50/60) from 1995 crop year were used. Roasted peanuts were prepared in a conventional oven at 170−180 °C during 30 min. After roasting, the peanuts were cooled at room temperature (Hashim et al., 1993). Fried peanuts were obtained by using sunflower oil. They were fried for 4 min.

Extraction of Headspace Volatiles. Peanut seeds were ground for approximately 1 min in a coffee mill. This ground sample was placed in a 10 mL headspace glass tube (Teflon top). The tube was heated at 120 °C for 30 min [Young and Hovis, 1990 (modified)].

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. One milliliter of headspace gas was injected into a Hewlett-Packard Trio-2 VS MASSLAB gas chromatograph/mass spectrometer. A Carbowax 20M capillary column (30 m × 0.25 mm i.d. × 0.25 mm film) was used. Column temperature was programmed from 50 °C (held for 6 min) to 220 °C (30 °C/min). Injector temperature was 240 °C. The carrier (helium) had a flow rate of 1 mL/min. Mass spectra were generated at 70 eV. The mass spectrometer was scanned from *m/z* 30 to 350 at 1 scan/s. The identification of headspace volatile peaks was performed by fragmentation patterns of GC/MS and compared with LAB-BASE (GC/MS Data System). Volatile component levels were estimated on the basis of peak areas (Vercellotti et al., 1992b).

RESULTS AND DISCUSSION

Hexanal, 1-methylpyrrole, cyclobutanol, 4-ethyl-2,5-dimethylisoxazolidine, 1-hexanol, 2,6-dimethylpyrazine, and acetic acid were the principal volatile components identified tentatively in the peanut samples studied in this work. The mass spectral data of these components are presented in Table 1.

Hexanal and 1-methylpyrrole showed higher concentrations followed by acetic acid in raw, roasted, and fried peanuts (Table 2). The cyclobutanol and 4-ethyl-2,5-dimethylisoxazolidine were detected for the first time. The mass spectra of these components are shown in Figure 1. Thermal degradation of sugars and amino acids could produce oxazoles and oxazolines (Lee et al., 1981). However, this nucleus was not found in natural products (Gilchrist, 1995). The isoxazolidinone is the active principle of a herbicide used in peanut cultivation (CASAFE, 1995). This compound could be accumulated and later appear in the seeds. The 2,5-dimethylisoxazolidine could probably also have some of these origins. Alcohols including some cyclic alcohols, for example, cyclohexanol, were found in the volatile flavors of the peanut and were derived by lipid oxidative processes (Walradt et al., 1971; St. Angelo et al., 1984). The cyclobutanol could have a similar origin.

Cyclobutanol and 1-hexanol were detected in trace levels in roasted and fried peanuts, respectively. An-

* Author to whom correspondence should be addressed.
† Instituto de Ciencias y Tecnología de los Alimentos.
‡ Facultad de Ciencias Agropecuarias.

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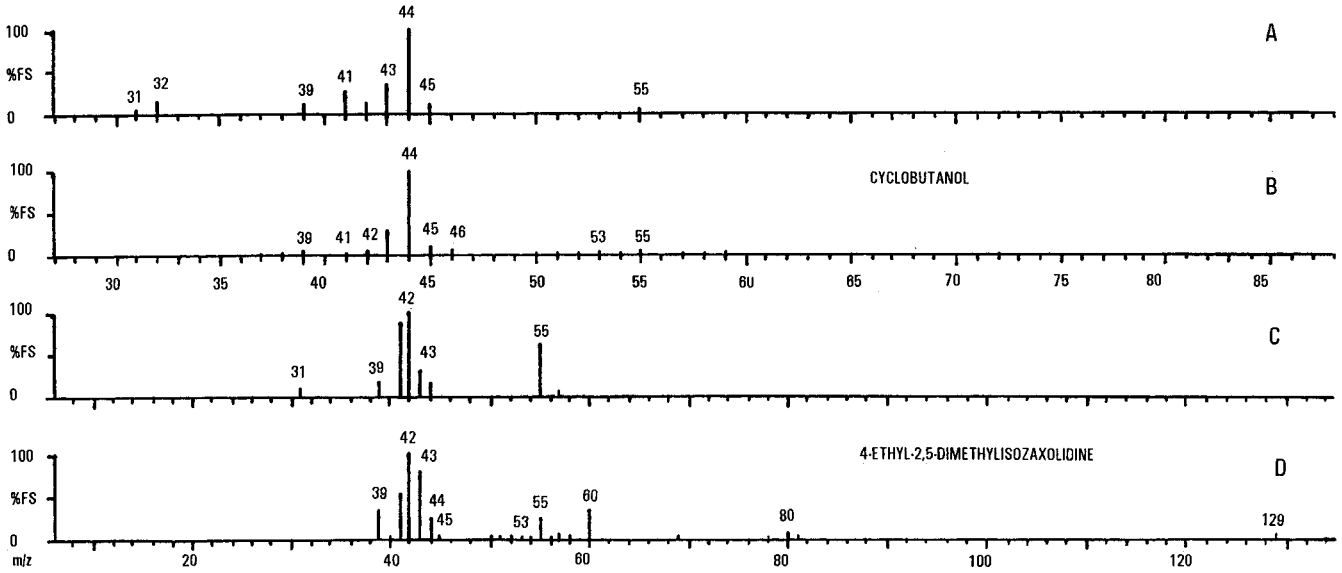

Figure 1. Mass spectra of unknown compounds (A and C) and cyclobutanol and 4-ethyl-2,5-dimethylisoxazolidine (B and D, respectively).

Table 1. Mass Spectral Data of Volatile Compounds Identified in Argentinean Peanut Flavor

compound[a]	MS data, *m/z* (relative intensity)
hexanal	31 (1.85), 32 (4.96), 39 (31.53), 40 (4.24), 41 (80.90), 42 (14.32), 43 (60.30), 44 (100.00), 45 (26.38), 46 (2.80), 55 (15.20), 56 (61.81), 57 (45.73), 58 (3.99), 67 (5.03), 71 (4.24), 72 (9.80), 79 (5.62), 82 (4.46), 94 (9.55)
1-methylpyrrole	37 (3.17), 38 (11.94), 39 (55.22), 40 (13.81), 41 (6.02), 42 (48.51), 44 (3.26), 50 (6.16), 51 (8.96), 52 (5.27), 53 (41.42), 54 (14.93), 55 (21.83), 78 (4.10), 80 (67.16), 81 (100.00)
cyclobutanol	31 (4.89), 32 (16.64), 39 (11.68), 41 (25.82), 42 (16.03), 43 (37.50), 44 (100.00), 45 (10.87), 55 (5.71)
4-ethyl-2,5-dimethyl-isoxazolidine	31 (45.39), 39 (27.30), 41 (87.23), 42 (100.00), 43 (26.06), 44 (11.08), 55 (55.32), 57 (6.83)
2,6-dimethylpyrazine	38 (6.25), 39 (48.11), 40 (22.82), 41 (6.72), 42 (100.00), 43 (30.30), 108 (13.64)
1-hexanol	31 (26.39), 39 (32.87), 41 (88.43), 42 (59.72), 43 (100.00), 44 (11.46), 55 (60.65), 56 (98.15), 69 (7.99)
acetic acid	41 (4.41), 42 (14.75), 43 (100.00), 44 (7.84), 45 (82.79), 60 (26.23)

[a] Tentative identification.

Table 2. Volatile Components in Raw, Roasted, and Fried Peanuts

	relative peak areas (%)		
compound	raw	roasted	fried
hexanal	38.9 (a−c)[a]	38.4 (d−j)	71.3
1-methylpyrrole	36.9 (a, c)	35.6 (d, g−i, k)	13.4
cyclobutanol	7.5	tr[b]	5.3
4-ethyl-2,5-dimethyl-isoxazolidine	2.3	3.5	2.3
2,6-dimethylpyrazine		3.5 (d, g, h, j, l, m)	1.2
1-hexanol	4.1 (a, c)	4.0 (d, g, h)	tr
acetic acid	10.2	17.3 (f)	6.6

[a] Compound confirmed in peanut volatiles by other investigators: a, Lovegren et al. (1982); b, Singleton et al. (1971); c, St. Angelo et al. (1984); d, Walradt et al. (1971); e, Johnson et al. (1971a); f, Braddock et al. (1995); g, Vercellotti et al. (1992a); h, Vercellotti et al. (1992b); i, Coleman (1992); j, Coleman et al. (1994); k, Mason et al. (1966); l, Johnson et al. (1971b); m, Bett et al. (1994). [b] tr, value <0.5%.

other four to six peaks were found as trace levels (<0.5%) in the chromatogram and were not identified. They could be some components of the peanut flavors previously reported by other investigators (Lee et al., 1981; Young and Hovis, 1990; Braddock et al., 1995).

2,6-Dimethylpyrazine, a compound of roasted peanut flavor, was found in roasted and fried peanuts. The alkylpyrazines are present in volatiles of different feeds. They are derived from thermal treatment during industrialization (Mason and Johnson, 1966; Braddock et al., 1995).

Heterocyclic compounds are responsible for much of the roasted nut flavor of the peanut. Trained flavor profile panelists detected a limited rancid aroma when the samples contained a high level of 1-methylpyrrole (Young and Hovis, 1990). The samples showed an important level of this component (Table 2).

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LITERATURE CITED

Ahmed, E. M.; Young, C. T. Composition, nutrition, quality of peanuts. In *Peanut Science and Technology*; Pattee, H. E., Young, C. T., Eds.; American Peanut Research and Education Society: Yoakum, TX, 1982; pp 655−687.

Bett, K. L.; Vercellotti, J. R.; Lovegren, N. V.; Sanders, T. H.; Hinsch, R. T.; Rasmussen, G. K. A comparison of the flavor and compositional quality of peanuts from several origins. *Food Chem.* **1994**, *51*, 21−27.

Braddock, J. C.; Sims, C. A.; O'Keefe, S. F. Flavor and oxidative stability of roasted high oleic acid peanuts. *J. Food Sci.* **1995**, *60*, 489−493.

CASAFE (Cámara de Sanidad Agropecuaria y Fertilizantes). *Guía de Productos Fitosanitarios para la República Argentina*, 7th ed.; Cámara de Sanidad Agropecuaria y Fertilizantes: Buenos Aires, Argentina, 1995; p 1343.

Coleman, W. M., III. Automated purge-and-trap-gas chromatography analysis of headspace volatiles from natural products. *J. Chromatogr. Sci.* **1992**, *30*, 159−163.

Coleman, W. M., III; White, J. L.; Perfetti, T. A. A hyphenated GC-based quantitative analysis of volatile materials from natural products. *J. Chromatogr. Sci.* **1994**, *32*, 323−327.

Gilchrist, T. L. *Química Heterocíclica*, 2nd ed.; Addison Wesley Iberoamericana: Wilmington, DE, 1995; pp 285−335.

Grosso, N. R.; Guzmán, C. A. Chemical characteristics of argentinean groundnut cultivars. *Int. Arachis Newsl.* **1995**, *15*, 17−18.

Grosso, N. R.; Lamarque, A. L.; Maestri, D. M.; Zygadlo, J. A.; Guzmán, C. A. Fatty acid variation of runner peanut (*Arachis hypogaea* L.) among geographic localities from Córdoba (Argentina). *J. Am. Oil Chem. Soc.* **1994**, *71*, 541−542.

Hashim, I. B.; Koehler, P. E.; Kvien, C. K. Fatty acid composition, mineral content, and flavor quality of Southern Runner peanuts treated with herbicides and fungicides. *Peanut Sci.* **1993**, *20*, 106−111.

Johnson, B. R.; Waller, G. R.; Burlingame, A. L. Volatile components of roasted peanuts: basic fraction. *J. Agric. Food Chem.* **1971a**, *19*, 1020−1024.

Johnson, B. R.; Waller, G. R.; Foltz, R. L. Volatile components of roasted peanuts: neutral fraction. *J. Agric. Food Chem.* **1971b**, *19*, 1025−1027.

Lee, M. H.; Ho, C. T.; Chang, S. S. Thiazoles, oxazoles and oxazolines identified in the volatile flavor of roasted peanuts. *J. Agric. Food Chem.* **1981**, *29*, 684−686.

Lovegren, N. V.; Vinnett, C. H.; St. Angelo, A. J. Gas chromatographic profile of good quality raw peanuts. *Peanut Sci.* **1982**, *9*, 93−96.

Mason, M. E.; Johnson, B. R. Flavor components of roasted peanuts. Some low molecular weight pyrazines and a pyrrole. *J. Agric. Food Chem.* **1966**, *14*, 455−460.

Singleton, J. A.; Pattee, H. E.; Johns, E. B. Influence of the curing temperature on the volatile components of peanuts. *J. Agric. Food Chem.* **1971**, *19*, 130−133.

St. Angelo, A. J.; Lovegren, N. V.; Vinnett, C. H. Volatile "fingerprint" profile of raw peanuts as an indicator of quality. *Peanut Sci.* **1984**, *11*, 36−40.

Vercellotti, J. R.; Mills, O. E.; Bett, K. L.; Sullen, D. L. Gas chromatographic analyses of lipid oxidation volatiles in foods. In *Lipid Oxidation in Foods*; St. Angelo, Ed.; ACS Symposium Series 500; American Chemical Society: Washington, DC, 1992a; pp 232−265.

Vercellotti, J. R.; Crippen, K. L.; Lovegren, N. V.; Sanders, T. H. Defining roasted peanut flavor quality. Part 1. Correlation of GC volatiles roast color as an estimate of quality. In *Food Science and Human Nutrition*; Charalambous, G., Ed.; Elsevier Science Publishers: Amsterdam, 1992b; pp 183−209.

Walradt, J. P.; Pittet, A. Q.; Kinlin, T. H.; Muralidhara, R.; Sanderson, A. Volatile components of roasted peanuts. *J. Agric. Food Chem.* **1971**, *19*, 972−979.

Young, C. T.; Hovis, A. R. A method for the rapid analysis of headspace volatiles of raw and roasted peanuts. *J. Food Sci.* **1990**, *55*, 279−280.

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