

Composition of Coriander Leaf Volatiles

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Volatiles were recovered from the fresh green leaves of coriander by steam codistillation with pentane and analyzed by capillary gas chromatography-mass spectrometry. A total of 41 compounds were detected. Constituents identified included alkenals in the C₉-C₁₆ range, C₇-C₁₇ alkanals, C₁₀-C₁₂ primary alkenols and alkanols, and nonane. The estimated mass of volatiles recovered was 4 mg/g (wet weight of leaves) with aldehydes accounting for 82.6% and alcohols 16.6% of the compounds detected. Of the 37 compounds identified, 23 are reported in coriander leaf volatiles for the first time.

INTRODUCTION

Coriander (*Coriandrum sativum* L.) is a hardy annual member of the Umbelliferae family indigenous to the Near East and Mediterranean regions. It has been cultivated since ancient times and was one of the first herbs imported and cultivated in the Massachusetts Bay Colony (Farrel, 1985; Rogers and Fishchetti, 1980). Today, its commercial cultivation and use are nearly worldwide.

This culinary herb is best known for the pungent and aromatic powders and oils produced from its dried ripe fruit. Volatile components of the fruit oil include *d*-linalool as the principal constituent. Other constituents include α - and β -pinene, diterpene, *p*-cymene, and decylaldehyde (Farrel, 1985; Rogers and Fishchetti, 1980).

The fresh green leaves of the plant, commonly known as cilantro or Chinese parsley, also have wide culinary use. They are highly regarded in the cuisines of China, Mexico, South America, India, and Southeast Asia. Their volatile constituents, however, have not been well studied. Only three published works were identified that describe the volatile constituents of coriander leaf volatiles. Further, these works appear to be in conflict with regard to the principal constituents reported. Carblom (1936) reported that decanal, 2-decenal, and 8-methyl-2-nonenal were the major constituents of coriander leaf oils, whereas MacLeod and Islam (1976) have reported a series of saturated and unsaturated aldehydes in the C₈-C₁₅ range. Notably, they reported no 2-alkenals. In contrast, Mookherjee et al. (1989) have reported the detection of 2-alkenals in the C₁₀-C₁₄ range. In addition, they have reported a homologous series of alkanals (C₁₀-C₁₄), related primary alkenols and alkanols, and nonane.

In the current work, we report alkanals and 2-alkenals in the C₉-C₁₆ range, C₁₀-C₁₄ 2-alkenols, 17 related aliphatic aldehydes and alcohols, nonane, and 4 unknowns.

EXPERIMENTAL PROCEDURES

Sample Preparation. Coriander plants were cultivated from seeds (contained in the dried fruit) in a vegetable garden in Orange, MA. The fruits were obtained commercially from Johnny's Selected Seeds (Albion, ME). The variety is unknown. Whole plants were harvested by uprooting at the blooming stage.

Isolation of Volatiles. Leaves (42 g) were removed from the fresh plants with stainless steel tweezers and transferred to a 1-L distillation flask containing 500 mL of distilled deionized water. The flask was then spiked with 0.5 mg each of toluene-*d*₈ and naphthalene-*d*₈ by using acetone as a carrier. Extraction was carried out with 50 mL of *n*-pentane using a modified Likens-Nickerson apparatus (Schultz et al., 1977). Dis-

tillation was allowed to continue for 4 h. The pentane was recovered and concentrated under a stream of dry nitrogen to 1 mL. The extract was stored at -20 °C prior to GC/MS analysis. All solvents and standards were obtained from commercial sources and were used without further purification.

Identical extraction conditions were used for a blank (500-mL water sample spiked with the same quantity of perdeuterated toluene and naphthalene) and 500 mL of water spiked with 0.5 mg each of C₇-C₁₄ *n*-aldehydes, toluene-*d*₈, and naphthalene-*d*₈.

GC/MS Analysis. A Hewlett-Packard 5985B GC/MS system equipped with a 60 m × 0.33 mm (i.d.) DB-5 (J&W Scientific; bonded phase methyl silicone-5% phenyl; 0.25- μ m film) was used for all analyses. The oven temperature program was as follows: 40 °C (hold 1 min) to 220 °C at 2 °C/min. Ultra-high pure helium was used as the carrier gas with a flow rate of 24 cm/s at 40 °C. Injection was in the Grob splitless mode at 250 °C. The outlet end of the column was interfaced to the mass spectrometer through an open-split interface (Scientific Glass Engineering) maintained at 250 °C. Mass spectra were obtained in the electron impact (70 eV) and isobutane chemical ionization modes. Chemical ionization conditions included a source pressure of 0.2 Torr of isobutane and a source temperature of 100 °C. A 20-fold dilution of the leaf extract in pentane was made prior to GC/MS analysis.

Reference Compounds. Reference compounds were obtained commercially and by donation from Bedoukian Fine Chemicals and Takasago Inc. In addition, 9-decenal was prepared by oxidation of 9-decen-1-ol following procedures outlined by Hanesian et al. (1981). The purity of all reference compounds was concluded to be greater than 90% on the basis of GC/MS data and infrared spectra.

RESULTS AND DISCUSSION

The total ion current chromatogram of the coriander leaf volatiles is shown in Figure 1 with peak identifications provided in Table I. Compounds identified included homologous series of saturated and monounsaturated aldehydes and alcohols in the C₇-C₁₇ range.

Where indicated in Table I, reference compounds were analyzed under identical conditions for compound confirmation. This included 20 of the compounds identified. Structural assignments for other compounds were based on retention indices and interpretation of electron impact and chemical ionization mass spectra. It was possible, particularly from the isobutane chemical ionization spectra, to differentiate between saturated and unsaturated aldehydes and alcohols. Prominent peaks in the aldehyde spectra were *M* + 1, *M* + 1 - 18, and *M* + 57, while alcohols exhibited peaks at *M* - 1, *M* - 17, and *M* + 57 - 18. In addition, the relative intensity of these ions in the monounsaturated compounds studied was dependent on the position of the double bond. A detailed

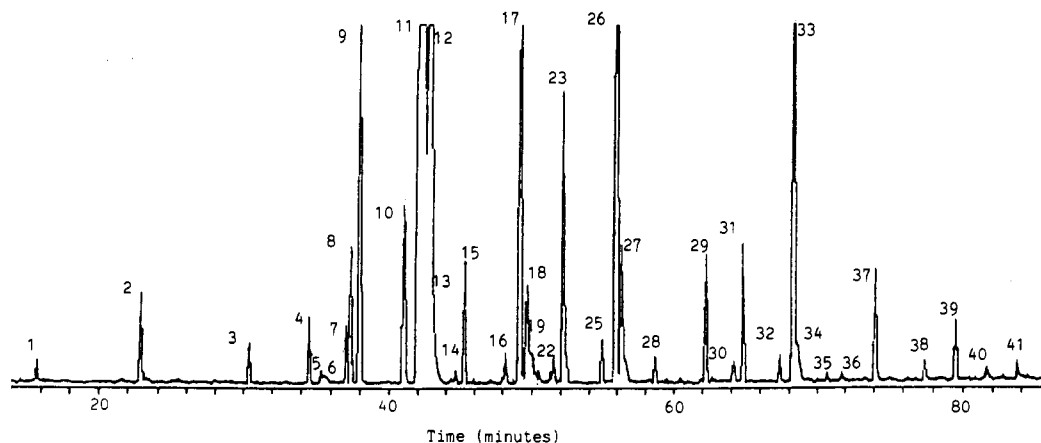


Figure 1. Total ion current chromatogram of coriander leaf volatiles.

Table I. Coriander Leaf Volatiles Identified

peak	compd	retention index ^a	confirm ^b	% TIC ^c
1	nonane	<700	Y	0.2
2	octanal	800	Y	0.5
3	nonanal	900	Y	0.2
4	(E)-2-nonenal	958	Y	0.3
5	C ₁₀ -enal (branched)	968		0.3
6	C ₁₀ -enal (branched)	973		0.2
7	(Z)-4-decenal	990	Y	0.3
8	9-decenal	993	Y	0.8
9	decanal	1000	Y	4.4
10	8-methyl-2-nonenal	1046		1.3
11	(E)-2-decenal	1058	Y	46.1
12	2-decen-1-ol	1070		9.2
13	1-decanol	1072	Y	4.3
14	10-undecenal	1093	Y	0.1
15	undecanal	1100	Y	0.5
16	9-methyl-2-decenal	1145		0.1
17	(E)-2-undecenal	1160	Y	5.6
18	2-undecen-1-ol	1167		0.9
19	1-undecanol	1171	Y	0.2
20	C ₁₂ -enal (branched)	1173		0.1
21	4-dodecenal	1188		0.1
22	11-dodecenal	1191		0.2
23	dodecanal	1200	Y	1.6
24	unknown	1205		0.2
25	10-methyl-2-undecenal	1245		0.3
26	(E)-2-dodecenal	1262	Y	10.3
27	2-dodecen-1-ol	1266		1.4
28	tridecanal	1300	Y	0.1
29	(E)-2-tridecenal	1361	Y	0.7
30	13-tetradecenal	1391		0.1
31	tetradecanal	1400	Y	0.7
32	12-methyl-2-tridecenal	1445		0.2
33	(E)-2-tetradecenal	1463	Y	5.8
34	2-tetradecen-1-ol	1466		0.6
35	pentadecanal	1500	Y	0.1
36	unknown	(71.72)		0.2
37	2-pentadecenal	(74.02)		0.7
38	unknown	(77.43)		0.1
39	2-hexadecenal	(79.50)		0.4
40	heptadecanal	(81.58)		0.3
41	unknown	(83.67)		0.3

^a Retention index values are Kovats indices based on the retention times of the saturated *n*-aldehydes. Numbers reported in parentheses are uncorrected retention times in minutes. ^b "Y" in the confirm column indicates that identification was based on the GC/MS analysis of a reference compound. ^c Percent TIC (total ion current) values are expressed as the relative percent of the total area of all peaks detected.

discussion of the isobutane chemical ionization mass spectra of monounsaturated primary alcohols and aldehydes will be published elsewhere. In related work Munson et al. (1986) have shown that such spectra can be useful for double-bond location in monounsaturated aliphatic alcohols.

The percent recovery of the surrogate standards, toluene-

*d*₈ and naphthalene-*d*₈, in the coriander extraction was 48 and 91%, respectively. This compared favorably with percent recoveries for these compounds from the blank and from the water spiked with C₇-C₁₄ aldehydes. Note that for the aldehydes recoveries ranged from 91 to 32%, with recovery decreasing with increasing carbon number.

On the basis of an assumed equivalent total ion current response [to (E)-2-decenal] for all compounds detected, the total mass of volatiles recovered was estimated to be 4 mg/g (wet weight) of leaves. The relative distribution of the compounds is expressed as a percent of the total ion current in Table I. Alcohols accounted for 16.6% and aldehydes 82.6% of the compounds detected.

The presumed source of the aldehydes and alcohols in coriander leaf volatiles is peroxidation of unsaturated fatty acids in the C₁₂-C₁₈ range and/or transamination and decarboxylation of amino acids. Croteau and Karp (1990) have provided detailed discussions of the biogenesis of aldehydes and alcohols in plants via these mechanisms and report that 2-alkenals often predominate. These compounds present the most stable configuration of monounsaturated aldehydes since the olefinic and carbonyl double bonds are conjugated. In this study, such aldehydes accounted for 69.2% of the total ion current and 84% of the aldehydes detected.

The occurrence of relatively large amounts of volatile aldehydes and alcohols in coriander leaf volatiles is presumably responsible for the unique flavor characteristics of this herb. Many of the same compounds have been detected in volatiles of various plants, butter oils, and cooked meats and have been used to formulate artificial chicken and other "meatlike" flavors (Boelens et al., 1987; Begeman and Harkes, 1974).

Another feature of these compounds is that many are strong irritants, in particular 2-decenal (Sax and Lewis, 1979). In addition, at least one, 1-decanol, has been reported to have carcinogenic potential (Sax, 1981).

The occurrence of the unsaturated aldehydes in coriander leaf volatiles also suggests some potentially interesting plant-insect and plant-microbe interactions. For example, 10-undecenal is classed as a topical antifungal and is used for this purpose commercially (Anonymous, 1983). Other coriander volatiles with reported antifungal activity include 2-nonenal, 2-decenal, and 2-undecenal (Iriye et al., 1988). Various 2-alkenals have also been detected in cotton leaf volatiles, which when bubbled through *Aspergillus flavus* cultures inhibited growth (Zeringue and McCormick, 1989). Among the coriander leaf volatiles with reported insect repellent activity are 2-nonenal (Ryan and Guerin, 1989; Meloan, 1982). Insect

repellant activity for 2-decenal can also be inferred since it is one of the major components of the defensive secretions of two *Thaumestella* spp (Jacobs et al., 1989).

On the matter of the identity of coriander leaf volatiles, we found our study to be in close agreement with that of Carlblom (1936). He reported that steam-distilled leaf oils comprised decanal, 2-decenal, and 8-methyl-2-nonenal. In our work, these compounds accounted for 51.8% of the leaf volatiles. Our work is also in agreement with that of Mookerjee et al. (1989). This agreement, both in the types and relative amounts of various alcohols and aldehydes detected, is notable in that they used room temperature "purge and trap" techniques to recover volatiles from living and fresh picked leaves.

Where our work differs with that of Mookerjee et al. (1989) is in the relative amount of nonane detected and in the number of aldehydes and alcohols detected. With regard to nonane, they report it as a major constituent of the volatiles of living plants with lesser amounts in fresh picked leaves. The relatively low recovery of this compound in our study may be due to losses during extraction. Mookerjee et al. (1989) report that the concentration of this compound is drastically reduced upon picking.

In contrast to our work and the aforementioned studies of Carlblom (1936) and Mookerjee et al. (1989), MacLeod and Islam (1976) did not report the detection of any 2-alkenals. They also reported that 7-dodecenal, 9-tetradecenal, 3,6-undecadienal, 5,8-tridecadienal, 8-tridecanal, and 10-pentadecanal were major constituents. These compounds were not detected in our work or in the published works cited. This suggests substantial variation between coriander varieties.

An alternate explanation is that MacLeod and Islam (1976) misinterpreted their methane chemical ionization mass spectra. They report, for example, that aldehydes gave intense $M + 2$ as well as $M + 1$, $M + 29$, and $M + 41$ peaks. Although not indicated, it is presumed that the intensity of $M + 2$ ions reported was in excess of the expected intensity of the ^{13}C isotope ion associated with the $M + 1$ ions. If this were the case, the reported occurrence of the $M + 2$ ion is unusual and suggests a failure to chromatographically separate corresponding unsaturated aldehydes and alcohols. In work in this laboratory, with methane as a reagent gas for saturated and unsaturated aliphatic aldehydes and alcohols, prominent $M + 1$ ions were observed for aldehydes and $M - 1$ ions for alcohols (Potter, unpublished results). Further, it appears that depending on reagent gas purity and other factors, alcohols may produce M^+ ions by methane chemical ionization. Given this, accurate assessment of the presence or absence of a true $M + 2$ ion for compounds such as 2-decenal requires that it be chromatographically separated from corresponding unsaturated alcohols.

ACKNOWLEDGMENT

We thank Lydia Potter for cultivation of the coriander, Jean Lee for assistance in the early phase of this work, R. Croteau and F. Karp for providing a copy of their manuscript, and R. Maloney of Bedoukian Fine Chemicals and C. Manley of Takasago Inc. for donating many reference compounds. Contribution No. 2994 from the Massachusetts Agricultural Experiment Station.

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Received for review February 8, 1990. Revised manuscript received May 11, 1990. Accepted June 10, 1990.

Registry No. Nonane, 111-84-2; octanal, 124-13-0; nonanal, 124-19-6; (*E*)-2-nonenal, 18829-56-6; (*Z*)-4-decenal, 21662-09-9; 9-decenal, 39770-05-3; decanal, 112-31-2; 8-methyl-2-nonenal, 128926-05-6; (*E*)-2-decenal, 3913-81-3; 2-decen-1-ol, 22104-80-9; 1-decanol, 112-30-1; 10-undecenal, 112-45-8; 9-methyl-2-decenal, 58196-32-0; (*E*)-2-undecenal, 53448-07-0; 2-undecen-1-ol, 37617-03-1; 1-undecanol, 112-42-5; 4-dodecenal, 30390-51-3; 11-dodecenal, 51148-68-6; dodecanal, 112-54-9; undecanal, 112-44-7; 10-methyl-2-undecenal, 128926-06-7; (*E*)-2-dodecenal, 20407-84-5; 2-dodecen-1-ol, 22104-81-0; tridecanal, 10486-19-8; (*E*)-2-tridecenal, 7069-41-2; 13-tetradecenal, 85896-31-7; tetradecanal, 124-25-4; 12-methyl-2-tridecenal, 128926-07-8; (*E*)-2-tetradecenal, 51534-36-2; 2-tetradecen-1-ol, 22104-82-1; pentadecanal, 2765-11-9; 2-pentadecenal, 64462-00-6; 2-hexadecenal, 3163-37-9; heptadecanal, 629-90-3.