birch sap as such has a very mild, slightly wooden aroma, and the optimal birch syrup aroma was thought to have developed as a result of volatiles formed through Maillard reaction and caramelization. Samples of optimal overall quality had a total soluble solids content of 70–75° Brix.

It is possible to reach the desired quality of the syrup by optimizing the heat flow of the evaporating process without any additional heating of the finished product. In the case of birch syrup we cannot, however, use open atmospheric boiling (Kok et al., 1978) following the reverse osmosis concentrating as done in the maple syrup industry.

Registry No. GABA, 56-12-2; Gln, 56-85-9; Glu, 56-86-0; Asn, 70-47-3; Ile, 73-32-5; Phe, 63-91-2; Val, 72-18-4; Tyr, 60-18-4; Thr, 72-19-5; Asp, 56-84-8; Pro, 147-85-3; Leu, 61-90-5; Ser, 56-45-1; N_2, 7727-37-9; malic acid, 6915-15-7; phosphoric acid, 7664-38-2; succinic acid, 110-15-6; citric acid, 77-92-9; fructose, 57-48-7; glucose, 50-99-7; galactose, 59-23-4; sucrose, 57-50-1; inositol, 87-89-8; citrulline, 372-75-8.

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Received for review February 17, 1988. Revised manuscript received March 15, 1988. Accepted June 27, 1988.

Occurrence of 2-(4-Methoxyphenoxy)propanoic Acid in Roasted Coffee Beans: Analysis by Gas–Liquid Chromatography and by High-Performance Liquid Chromatography

Elner B. Rathbone,*[1] Gita D. Patel, Ronald W. Butters, Derek Cookson, and Jane L. Robinson[2]

Aqueous extracts of roasted Colombian Arabica coffee beans were fractionated by solvent extraction and preparative-layer silica gel chromatography and analyzed by gas–liquid chromatography–mass spectrometry (GC–MS) equipped with BP5 or BP20 fused silica capillary columns (25 m × 0.3 mm (i.d.)) and by high-performance liquid chromatography (HPLC) equipped with a Chromspher C_{18} reversed-phase column (250 × 4.6 mm (i.d.)) and a diode array UV detector. The fractionated aqueous extract was shown by HPLC to contain 2-(4-methoxyphenoxy)propanoic acid. Its methyl ester, methyl 2-(4-methoxyphenoxy)propanoate, was found to be more amenable to analysis by GC–MS (greater volatility) and by HPLC (better resolution) than the acid. The purified extract was therefore methylated, and the presence of methyl 2-(4-methoxyphenoxy)propanoate was confirmed by GC–MS and HPLC analysis. The concentration of 2-(4-methoxyphenoxy)propanoic acid in roasted coffee beans was found to be 0.55–1.2 ppm.

2-(4-Methoxyphenoxy)propanoic acid is a new flavoring and a subject of Tate & Lyle PLC's British Patent Application No. 2157148A and corresponding patent applications worldwide (Lindley and Rathbone, 1985). Although it is poorly volatile and has little intrinsic flavor other than an acid taste, it may prove to be an important component for some formulated flavors. Of particular interest is the use of 2-(4-methoxyphenoxy)propanoic acid in formulated sweet products where its ability to modulate high sweetness could be applied to advantage. Structural analogues of 2-(4-methoxyphenoxy)propanoic acid are reported to occur naturally in foods (Van Straten and Maarse, 1983), for example 2-phenylpropanoic acid (wine and beer), 3-phenylpropanoic acid (wine, grape, strawberry, and soya bean), 4-methoxyphenylacetic acid (cocoa), phenylacetic acid (grape, strawberry, beer, cocoa, wine, and honey), 4-methoxybenzoic acid (currants, cocoa, and aniseed), and 3-(2-methoxyphenyl)propanoic acid (cinnamon).

A preliminary investigation by reversed-phase high-performance liquid chromatography (HPLC) led to the conclusion that the acid might be present in green Guatemalan Arabica coffee beans, based on similarity in chromatographic retention time under a number of different elution conditions and similarity in peak height behavior over a limited UV detector wavelength range

Tate & Lyle Research & Technology, P.O. Box 68, Reading, Berkshire RG6 2BX, U.K.
[1] Present address: Sigma Chemical Co. Ltd., Fancy Rd., Poole, Dorset BH17 7NH, U.K.
[2] Present address: Pharmaceutical Department, ICI Pharmaceuticals, Hurdsfield Industrial Estate, Macclesfield, Cheshire SK10 2NA, U.K.

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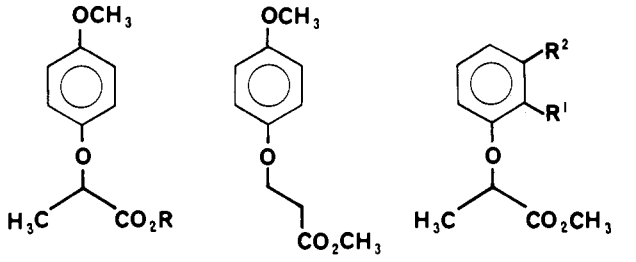
(286–330 nm) when compared with authentic 2-(4-methoxyphenoxy)propanoic acid. The investigation was therefore extended to confirm the presence of 2-(4-methoxyphenoxy)propanoic acid in coffee beans. Colombian Arabica coffee beans were used since the stock of the Guatemalan variety was exhausted in the preliminary study.

MATERIALS AND METHODS

Materials. (±)-2-(4-Methoxyphenoxy)propanoic acid (1) was synthesized from 4-methoxyphenol and 2-bromopropanoic acid according to literature procedures (Koelsch, 1931); the product had physical constants in agreement with published values (Fredga and Avalaht, 1965). Methyl 2-(4-methoxyphenoxy)propanoate (2) was prepared by treatment of 1 with methanol–HCl; the ester had physical constants in agreement with literature values (Hayashi et al., 1983). Analogues of 1, namely 3-(4-methoxyphenoxy)propanoic acid (Gresham et al., 1949), 2-(2-methoxyphenoxy)propanoic acid (Fredga et al., 1966), and 2-(3-methoxyphenoxy)propanoic acid (Fredga et al., 1966), were prepared according to published methods and converted to their respective methyl esters, methyl 3-(4-methoxyphenoxy)propanoate (3), methyl 2-(2-methoxyphenoxy)propanoate (4), and methyl 2-(3-methoxyphenoxy)propanoate (5) for analysis.



1, R = H

2, R = CH_3

3

4, $R^1 = OCH_3$, $R^2 = H$

5, $R^1 = H$, $R^2 = OCH_3$

Colombian Arabica coffee beans were obtained from commercial sources. HPLC-grade solvents were used throughout. Solvent-resistant filters (0.45 μm) were purchased from Schleicher and Schuell (West Germany).

Extraction of Coffee Beans. Preliminary experiments showed that there was less interference from other peaks in chromatograms obtained from extracts made from whole rather than ground coffee beans. Roasted Colombian Arabica coffee beans (40 g) were stirred in hot water (250 mL, 90 °C) for 4 h. The mixture was cooled and filtered and the filtrate extracted with dichloromethane (3 × 150 mL). The combined dichloromethane extract was evaporated to dryness at 40 °C under vacuum. The residue was dissolved in diethyl ether (2 mL) and chromatographed on a preparative-layer silica gel plate (Merck 60 5745, 200 × 200 × 2 mm) with diethyl ether–petroleum ether (40–60 °C)–acetic acid (60:40:1). The band corresponding to the R_f of 2-(4-methoxyphenoxy)propanoic acid (R_f 0.2–0.4) was collected and extracted with acetone (3 × 50 mL) and the acetone solution filtered and evaporated to dryness. The residue (extract A) was dissolved in acetone (1 mL) and filtered through a solvent-resistant filter prior to analysis.

Methylation of Coffee Extract. Aliquots (2 × 100 μL) of the acetone solution of extract A were evaporated to dryness, dissolved in methanolic HCl (1%, 100 μL), and kept at 60 °C for 0.5 h. The resulting solutions (extracts B and C) were analyzed directly by GC–MS and by HPLC.

GC–MS. GC–MS analysis was performed on a Kratos MS80RF/DS55 mass spectrometer and data system, directly coupled to either of two bonded-phase fused silica columns, supplied by Scientific Glass Engineering Ltd. Column A: Nonpolar (5% methylphenylsiloxane type) BP5 (50 m × 0.33 mm (i.d.)) temperature programmed 1 min at 120 °C, 16 °C/min to 250 °C, 10 min at 250 °C. Helium at 0.36 kg/cm^2 used as carrier gas. Column B: Polar (polyethylene glycol type) BP20 (25 m × 0.33 mm (i.d.)), temperature programmed 1 min at 70 °C, 8 °C/min to 220 °C, 15 min at 220 °C. Helium carrier gas at 0.36 kg/cm^2. Other conditions: helium flow rate into source, equivalent to 1–2 mL/min at atmospheric pressure; injection volumes, 1 μL, injected cold on column; MS scan rate, 1 s/decade, interscan time 1 s, range m/z 30–800. Quantitative measurements for compound 2 in the extracts were made by comparison of peak areas and heights with those of standard solutions.

HPLC Analysis. An LKB HPLC system was used, fitted with two 2150 pumps, an LC 2152 controller, and a rapid spectral detector (2140), scanning 190–370 nm. A Chrompak Chromspher C_{18} HPLC column (250 × 4.6 mm (i.d.)) was used at room temperature. Elution was programmed as follows: (a) initial composition of chloride buffer–methanol (70:30, v/v) changing linearly over 25 min to 45:55 (v/v), (b) the buffer to methanol ratio (45:55, v/v) maintained for 10 min, (c) composition changed to 20:80 buffer–methanol (v/v) over 1 min, and (d) the latter composition maintained for 9 min to the end of the run (run time 45 min). The gradient was changed to achieve the initial composition (70:30, v/v) over 1 min, which was maintained for a further 9 min prior to the next injection (total cycle time 55 min). Chloride buffer composition: NaCl (5.74 g) dissolved in 0.002 M HCl (1 L) and diluted with methanol (10% v/v in the buffer solution). Injection volume was 20 μL via a Rheodyne injector loop, and a flow rate of 1 mL/min was maintained throughout. Data were processed on a Wang professional computer with IBM PC emulation option (version 3.2) using LKB Wavescan system 2140-250 (version 1.08) and Nelson chromatography system 2145-200 software. Background absorption and noise variation were minimized by use of the LKB wavescan arithmetic subtraction routine [$F(t) = A(225\text{ nm}) - 0.9A(245\text{ nm})$] with which irrelevant absorptions (245 nm) are subtracted from those of interest (225 nm). Concentrations of compounds 1 and 2 in extracts were determined by comparison of peak areas with those of standard solutions.

RESULTS AND DISCUSSION

GC–MS Analysis. The relatively low volatility of 2-(4-methoxyphenoxy)propanoic acid makes it unsuitable for direct analysis by capillary column GC. Injection of standard solutions of compound 1 (156–625 ppm, 1 μL) gave very broad peaks under the standard GC conditions (columns A and B). Analysis of extract A by GC–MS (column B) gave inconclusive results for the presence of 2-(4-methoxyphenoxy)propanoic acid.

To increase the volatility of 2-(4-methoxyphenoxy)-propanoic acid, GC–MS analyses were performed on the methyl ester (2) and the methylated extracts (extracts B and C), initially using column B. The GC trace of methyl 2-(4-methoxyphenoxy)propanoate (2; 50 ppm) showed a sharp peak with retention time 13.09 min. The mass spectrum obtained for this peak is presented in Figure 1a and shows characteristic principal ions at m/z 210 (M), 151 (M – CO_2Me), 123 (151 – $CHCH_3$, 100%), and 109 (123 – CH_2).

The GC trace of extract B, monitored at m/z 210 and at the total ion current, shows a sharp peak (Figure 2) at the same retention time as compound 2 (13.09 min). The

Table I. GC Retention Times and Principal MS Ions for Methyl 2-(4-Methoxyphenoxy)propanoate (2) and Analogues

compd	ret time,[a] min	principal ions (m/z)[b]							
		210	151	124	123	109	95	87	77
2	13.09	35	10	30	100	21	<10	<10	<10
3	15.55	76	<10	67	78	42	17	100	<10
4	11.86	100	94	86	67	71	47	<10	55
5	12.88	41	100	27	<10	<10	11	<10	15

[a] Column B. [b] Intensities (%) relative to base peak (100%).

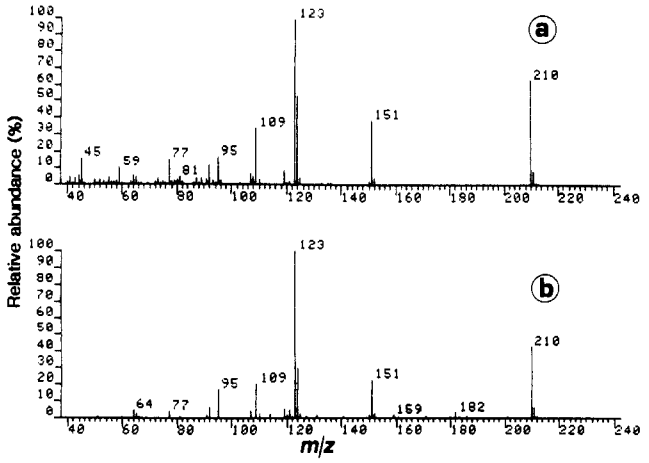


Figure 1. Mass spectra: (a) GC peak of methyl 2-(4-methoxyphenoxy)propanoate (2) standard; (b) GC peak with the same retention time as compound 2 in coffee extract B.

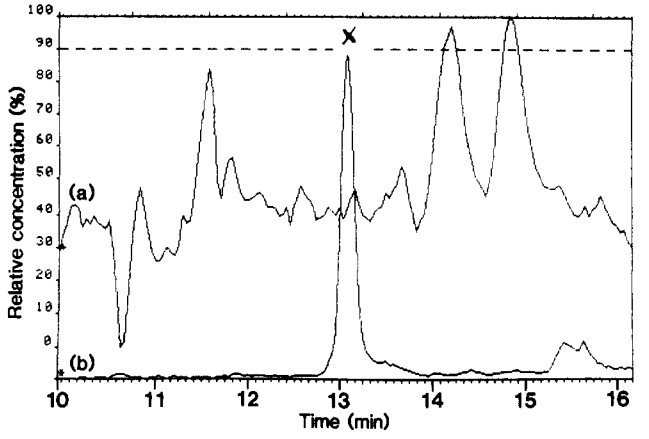


Figure 2. GC (column B) of coffee extract B, monitored at (a) the total ion current and (b) m/z 210. The peak at X (13.09 min) corresponds to that of standard methyl 2-(4-methoxyphenoxy)-propanoate under the same conditions.

fragmentation pattern of the mass spectrum corresponding to this peak (Figure 1b) is essentially the same as that of methyl 2-(4-methoxyphenoxy)propanoate (Figure 1a), showing characteristic ions at m/z 210, 151, 123, and 109. Similar results were obtained for extract C.

The GC–MS characteristics of compound **2** were compared with those of a number of closely related analogues, namely methyl 3-(4-methoxyphenoxy)propanoate (**3**), methyl 2-(2-methoxyphenoxy)propanoate (**4**), and methyl 2-(3-methoxyphenoxy)propanoate (**5**). Compound **3** was recently identified in the culture broth of *Irpex lacteus* (Hayashi et al., 1981).

The GC retention times and major MS fragments for compounds **2–5** are presented in Table I and show the differences in parameters within this series of analogues, making it possible to distinguish between the four compounds.

The amount of methyl 2-(4-methoxyphenoxy)-propanoate present in extracts B and C as analyzed by GC–MS was quantified; the results are presented in Table II. There is good agreement between results based on measurement of peak area for the two extracts (41, 48 ppm); quantification by peak height gave slightly lower values (32, 38 ppm).

Table II. Concentrations of Methyl 2-(4-Methoxyphenoxy)propanoate (2) in Extracts B and C and 2-(4-Methoxyphenoxy)propanoic Acid (1) in Extract A

extract	method	compd	concn, ppm
B	GC–MS[a]	2	41 ± 1
B	GC–MS[b]	2	32 ± 7
C	GC–MS[a]	2	48 ± 2
C	GC–MS[b]	2	38 ± 8
B + C	HPLC[a]	2	50 ± 5
A	HPLC[a]	1	22 ± 5

[a] Based on peak area measurements. [b] Based on peak height measurements.

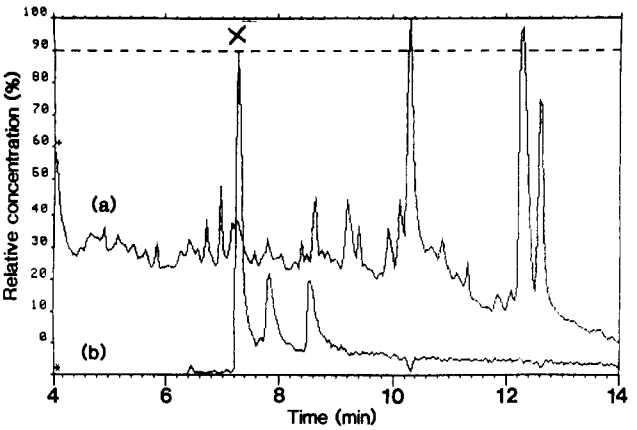


Figure 3. GC (column A) of coffee extract B, monitored at (a) the total ion current and (b) m/z 210. The peak at X (7.22 min) corresponds to that of methyl 2-(4-methoxyphenoxy)propanoate under the same conditions.

Analysis of extracts B and C on column A again showed the presence of a peak at the same retention time (7.22 min) and with a mass spectrum similar to those obtained for methyl 2-(4-methoxyphenoxy)propanoate. The GC trace for extract B on column A is shown in Figure 3.

HPLC Analysis. 2-(4-Methoxyphenoxy)propanoic acid (**1**) and its methyl ester (**2**) are well separated under the HPLC conditions used, retention times being 15.05 and 21.28 min, respectively (Figure 4a). The UV spectra corresponding to the two standards were obtained from peaks X and Y on the chromatogram and are shown in Figure 5 parts a and b, respectively.

Extract A was analyzed by HPLC for the presence of acid **1**. The retention time of peak X in the chromatogram of extract A (Figure 4b) coincided with that of standard acid **1**; the UV spectrum of the peak (Figure 5c) was similar to that of **1**. The concentration of 2-(4-methoxyphenoxy)propanoic acid in extract A was quantified, and the result is given in Table II.

The methylated extracts (B and C) from the GC–MS analysis were combined for examination by HPLC. The HPLC chromatogram of the combined extracts showed a

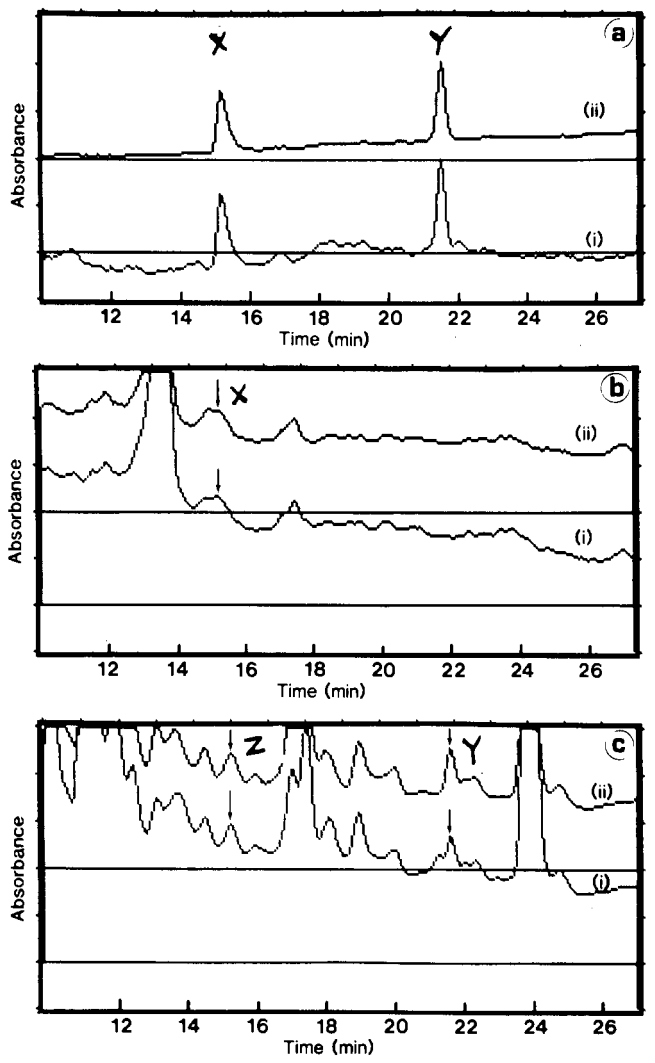


Figure 4. HPLC traces: (a) standard solution containing equal concentrations (20 ppm) of compound 1 (peak X) and compound **2** (peak Y); (b) coffee extract A, showing the peak (X) with retention time the same as that of acid 1; (c) coffee extract B, showing the peak (Y) with the same retention time as that of methyl ester **2**. In each figure the lower trace (i) was monitored at 225 nm, whereas the upper trace (ii) is the background-subtracted chromatogram (see text).

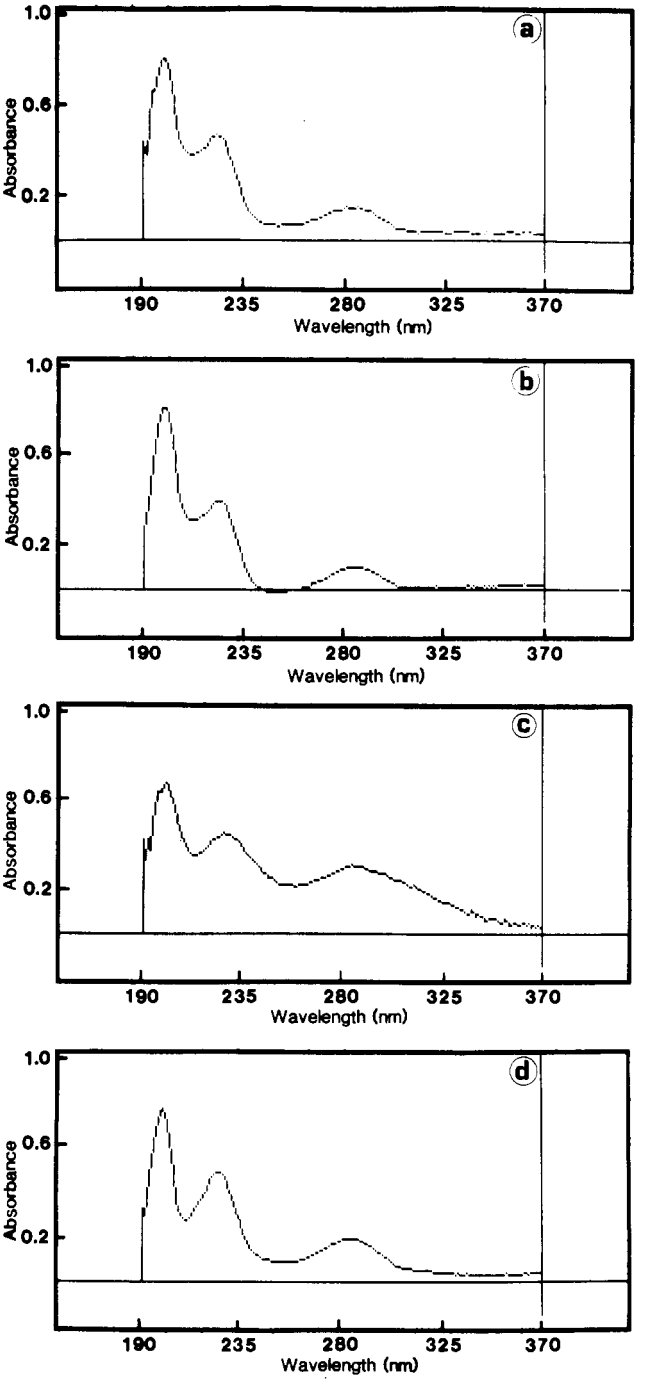


Figure 5. UV spectra (190–370 nm) of HPLC peaks: (a) 2-(4-methoxyphenoxy)propanoic acid (1) standard; (b) methyl 2-(4-methoxyphenoxy)propanoate (**2**) standard; (c) peak with the same retention time as compound 1 in extract A; (d) peak with the same retention time as **2** in extract B.

peak with the same retention time (peak Y, Figure 4c) and UV spectrum (Figure 5d) similar to those of methyl ester **2**. The UV spectrum of peak Z (the retention time of which coincided with that of 2-(4-methoxyphenoxy)-propanoic acid) was different from that of acid 1. An estimation of the concentration of methyl 2-(4-methoxyphenoxy)propanoate present in the combined extracts is given in Table II.

The evidence presented here demonstrates the presence of 2-(4-methoxyphenoxy)propanoic acid in roasted Colombian coffee beans. The apparent difference in quantified levels of the acid in the unmethylated extract and methyl ester in the methylated extract is most likely due to integration errors as a result of incomplete resolution of the acid and ester peaks from other components in the chromatograms of the respective extracts.

Quantification of 1 and 2 in Coffee Beans. There is satisfactory agreement between results obtained by the three techniques, viz. methyl ester GC–MS (32–48 ppm), methyl ester HPLC (50 ppm), and acid HPLC (22 ppm). The measured concentrations (Table II) of 2-(4-methoxyphenoxy)propanoic acid in extract A (22 ppm) and methyl 2-(4-methoxyphenoxy)propanoate in extracts B and C (32–50 ppm) correspond to levels of 0.55–1.2 ppm of 2-(4-methoxyphenoxy)propanoic acid in the coffee beans.

Registry No. 1, 4276-73-7; **2**, 117957-07-0; **3**, 18333-12-5; **4**, 63857-99-8; **5**, 117896-91-0; 3-(4-methoxyphenoxy)propanoic acid, 20811-60-3; 2-(2-methoxyphenoxy)propanoic acid, 7309-51-5; 2-(3-methoxyphenoxy)propanoic acid, 7309-52-6.

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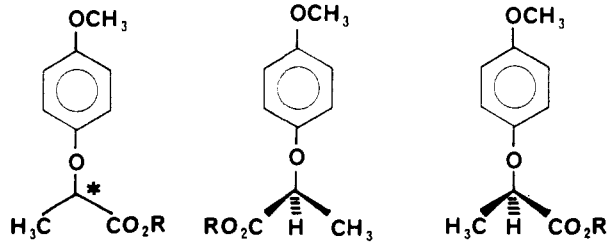
Received for review November 3, 1987. Accepted June 27, 1988.

Chirality of 2-(4-Methoxyphenoxy)propanoic Acid in Roasted Coffee Beans: Analysis of the Methyl Esters by Chiral High-Performance Liquid Chromatography

Elner B. Rathbone,*[1] Ronald W. Butters, Derek Cookson, and Jane L. Robinson[2]

Methyl 2-(4-methoxyphenoxy)propanoate, previously shown to be present in methylated aqueous extracts of roasted Colombian Arabica coffee beans, was purified by reversed-phase high-performance liquid chromatography (HPLC) with a Chromspher C_{18} column (250 × 4.6 mm). The purified extract was analyzed by chiral HPLC with a Chiralcel OK column (250 × 4.6 mm), which provided excellent separation of the two enantiomers of the ester. The methyl 2-(4-methoxyphenoxy)propanoate in the methylated coffee extract was shown to be composed of predominantly (80%) the (*S*)-(−) enantiomer.

A new flavoring, 2-(4-methoxyphenoxy)propanoic acid, which is the subject of Tate & Lyle PLC's British Patent Application No. 2157148A and corresponding patent applications worldwide (Lindley and Rathbone, 1985), has recently been identified in aqueous extracts of roasted Colombian Arabica coffee beans (Rathbone et al., 1989). This flavoring (**1**) has an asymmetric carbon atom and can therefore exist in two enantiomeric forms: (*S*)-(−) and (*R*)-(+) (**3** and **5**, respectively). Sensory evaluation of the individual enantiomers (**3** and **5**) has shown that the important flavoring functionalities (Rathbone et al., 1989) reside solely in the (*S*)-(−) form, the (*R*)-(+) enantiomer being functionally inert. To establish which enantiomer of 2-(4-methoxyphenoxy)propanoic acid occurs in roasted coffee beans, the extracts generated by the previous investigation (Rathbone et al., 1989) were methylated, purified by HPLC, and analyzed by chiral HPLC for the presence of the individual enantiomers of methyl 2-(4-methoxyphenoxy)propanoate.



1, R = H **2**, R = CH_3 **3**, R = H **4**, R = CH_3 **5**, R = H **6**, R = CH_3

Tate & Lyle Research & Technology, P.O. Box 68, Reading, Berkshire RG6 2BX, U.K.

[1] Present address: Sigma Chemical Co. Ltd., Fancy Rd., Poole, Dorset BH17 7NH, U.K.

[2] Present address: Pharmaceutical Department, ICI Pharmaceuticals, Hurdsfield Industrial Estate, Macclesfield, Cheshire SK10 2NA, U.K.

MATERIALS AND METHODS

Materials. (*S*)-(−)-2-(4-Methoxyphenoxy)propanoic acid (**3**) was prepared by resolution of the racemic acid (**1**) via its brucine salt (Fredga and Avalaht, 1965): mp 65–66 °C; $[\alpha]^{20}_D$ −42.7° (*c* 0.95, absolute EtOH); lit. (Fredga and Avalaht, 1965) mp 65–66 °C; lit. (Fredga and Avalaht, 1965) $[\alpha]^{20}_D$ −43.1° (*c* 2.17, absolute EtOH).

Methyl (*S*)-(−)-2-(4-methoxyphenoxy)propanoate (**4**) was prepared by treatment of **3** (2.0 g) with methanol–HCl (1%, 6 mL) at 60 °C for 0.5 h. CH_2Cl_2 (50 mL) was added to the cooled solution and the mixture extracted with saturated aqueous $NaHCO_3$ solution (2 × 20 mL). The CH_2Cl_2 layer was washed with water (2 × 20 mL), dried (Na_2SO_4), and concentrated in vacuo to afford the product (**4**) as a pale yellow liquid: 2.0 g; $[\alpha]^{20}_D$ −71.4°, $[\alpha]^{20}_{365}$ −282.8° (*c* 2.3, acetone); EI MS, *m/z* (relative intensity) 210 (M^+, 63), 151 (39), 124 (53), 123 (100), 109 (34), 95 (16), 77 (15); ^{1}H NMR δ 6.82 (4 H, H-2′, 3′, 5′, 6′, unresolved m), 4.67 (1 H, q, H-2, $J_{2,3}$ = 6.8 Hz), 3.752, 3.747, (2 × 3 H, 2 s, CO_2CH_3, 4′-OCH_3), 1.59 (3 H, d, H-3, $J_{3,2}$ = 6.8 Hz); ^{13}C NMR δ 172.7 (C-1), 154.4 (C-1′), 151.5 (C-4′), 116.3 (C-2′, 6′), 114.5 (C-3′, 5′), 73.4 (ester CH_3), 55.4 (4′-OCH_3), 52.1 (C-2), 18.5 (C-3).

Extracts A–C and (*R,S*)-(±)-2-(4-methoxyphenoxy)-propanoic acid (**1**) and its methyl ester (**2**) were obtained as previously described (Rathbone et al., 1989). HPLC-grade solvents were used throughout. Solvent-resistant filters were purchased from Schleicher and Schuell (West Germany).

HPLC Analysis. An LKB HPLC system was used, fitted with two 2150 pumps, an LC 2152 controller, and a rapid spectral detector (2140), scanning 190–370 nm. LKB wavescan (2140-250 version 1.08) and Nelson chromatography (2145-200) software was used to process the data on a Wang PC with IBM PC emulation option (version 3.2). Injection was via Rheodyne injector loops (20 or 250 μL). Either of the following columns was used at room temperature. Column A: Chrompak Chromspher C_{18} HPLC column (250 × 4.6 mm). Elution program: (a)

0021-8561/89/1437-0058$01.50/0