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Volatiles of avocado fruit

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Volatile constituents of avocado mesocarp were isolated by concurrent steam distillation/solvent extraction in the Likens–Nickerson apparatus using pentane–ether as solvent. The extracts which resulted were concentrated in a Kuderna–Danish concentrator and analysed using gas chromatography and linked gas chromatography-mass spectroscopy (GC-MS) employing capillary columns of contrasting polarity. Hydrocarbons (mainly sesquiterpenes) and alkanals were the predominant constituents present. In the immediate extract of the avocado mesocarp, β-caryophyllene (60%) was the main sesquiterpene, followed by α-humulene (5.9%), caryophyllene oxide (4.8%), α-copaene (4.5%) and α-cubebene as the main hydrocarbons; alkanals were present, but only in low concentrations. In the extract prepared following storage (2 h) of the mesocarp at room temperature, β-caryophylene (28.8%) was the main sesquiterpene, followed by α-copaene (10.7%), a cadinene isomer (8.5%), α- and β-cubebene (7.7%), α-farnesene (5.3%) and octane (4.8%) as principal hydrocarbons; decenal (6.3%) and heptenal (3.2%) were the main aldehydes. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

The avocado (*Persea Americana mill.*) belongs to the Lauraceae, a family of mainly (sub)tropical trees and shrubs; other well-known members are laurel, cinnamon, saffras and green-heart (a timber of the Guianas). The English name derives from the Spanish word abogada, an adaptation of an Aztec word 'ahuacatl' which became avocat in French (Samson, 1980).

The chemical composition of the edible portion of the flesh is water 65–80%; protein 1–4%; sugar about 1%; oil 3–30%. It is rich in vitamin B and moderately so in vitamins A and D. The oil, which is similar in composition to olive oil, is highly digestible. Because of the high oil content, avocados have the highest energy value of any fruit. The high oil content also contributes to the consistency and the special taste of the fruit (Purseglove, 1969; Hurne, 1971; Lötschert, 1981).

The avocado has been for thousands of years, and still is, a popular food in Central America. It is a nutritious fruit but the sugar content is low; therefore, it can be recommended as a high energy food for the diabetic (Samson, 1980; Swisher, 1988). The high oil content of the fruit has attracted special attention with respect to its composition but relatively little work (Kikuta and Erickson, 1968; Tango *et al.*, 1970; Abou-Aziz *et al.*, 1973, Itoh *et al.*, 1975; Iglesias *et al.*, 1976; Swarts, 1976; Sciancalepore and de Dorbesscan, 1981; Turratti *et al.*, 1985; Oleata *et al.*, 1987; Gaydou *et al.*, 1987; Torres *et al.*, 1987; Whitfield *et al.*, 1980) has been done on the composition of the volatile components of avocado fruit and the present study, therefore, was undertaken to increase knowledge of the volatiles.

MATERIALS AND METHODS

Materials

Fruit and chemicals

Avocado fruit from Israel was purchased from supermarkets in Leeds. The water used was purified by extraction with pentane (24 h), followed by ether (24 h) in a Likens–Nickerson distillation/solvent extraction apparatus. Each solvent was distilled through a fractionating column containing Fenske helices before use. Alkane standards (n-C_7 to n-C_{26}) were used in the measurement of retention indices of standards and components separated from the avocado extracts.

Pyridine, toluene, citral, heptanoic acid, cyclohexane, hexanoic acid, ethanol, ethyl acetate, 2,3-butanedione and anhydrous sodium sulfate were obtained from BDH Chemicals Ltd, Poole, England, and hexanal, sabinene, myrcene, α-pinene, β-pinene, benzaldehyde,

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caryophyllene oxide, nonanal, furfural, hexyl acetate, xylene, hex-2-enal, pentylfuran and terpinen-4-ol from Aldrich Chemical Co. Ltd, Dorset, England. β-Caryophyllene, α-humulene (α-caryophyllene), car-3-ene, camphene, α-cubebene, α-copaene, limonene and but-3-en-2-ol were purchased from Fluka Chemicals, Glossop, England and heptanal and oct-2-ene from Lancaster Synthesis, Morecambe, England.

Apparatus

Mesocarp of avocado fruit was extracted in the modified Likens–Nickerson (L–N) apparatus described by Nursten and Sheene (1974) and the resulting extracts were concentrated in a Kudema–Danish type concentrator fitted with a 3-cavity Snyder column.

A Carlo Erba HRGC 5160 Mega series gas chromatograph equipped with a flame ionisation detector and a Carlo Erba Mega series integrator were utilised in routine gas chromatographic analysis. Two types of bonded-phase open tubular fused silica capillary columns (SGE) were employed (25 m × 0.32 mm i.d.) containing BP1 (analogue of dimethylsilane) and a 25 m × 0.32 mm i.d. column containing BP20 (analogue of polyethylene glycol); the outside of each column was polyimide- or aluminium-coated for protection. A Kratos MS 80 RFA mass spectrometer with a DS90 data system directly coupled to a Carlo Erba 4200 series gas chromatograph fitted with either a BP1 (25 m × 0.32 mm i.d.) or a BP20 (25 m × 0.32 mm i.d.) fused silica capillary column was used for mass spectral analysis. The ion source was heated to 150°C, 70 eV was used as the ionisation voltage and ions were collected over the range m/z 400–17 at 1 s decade^{-1}. Chemical ionization mass spectra were produced using isobutane as reagent gas and 20 eV ionization voltage.

Isolation of volatiles

Avocado fruit was cleaned, peeled and the seeds removed, then the pulpy, edible part (mesocarp) was cut into small pieces and treated in one of the two ways: (i) The small pieces (ca. 770 g) and purified water (1.5 litre) were extracted using the modified Likens–Nickerson distillation/solvent extraction apparatus. The contents of the flask were heated under boiling for 4 h while simultaneously the condensing vapours were extracted with pentane (50 ml), after which extraction was carried out for 4 hr using ether. (ii) The cut pieces of avocado mesocarp (ca. 650 g) were allowed to stand at room temperature (20°C) for 2 h before being treated as in (i).

In each case, the ether extract from the Likens–Nickerson distillation/solvent extraction was dried with anhydrous sodium sulphate and pooled with the corresponding pentane extract before concentration in a Kuderna–Danish concentrator to ca. 300 μl. In each approach, the concentrated extract was subjected to gas–liquid chromatography (glc) and gas–liquid-chromatography-mass spectometry (GIC–MS) for identification of components.

Gas chromatographic analysis of volatiles

Concentrated extracts of volatiles, stored in sealed capillary tubes at −20°C until analysis, were subjected to gas chromatographic analyses using a fused silica BP1 and BP20 columns (SGE, Milton Keynes, UK). The oven temperature was held at 5°C for 5 min and programmed linearly at 5°C min^{-1} and was held at 210°C (BP20) or 250°C (BP1) for between 20 and 30 min. Other operating conditions were: injector and detector temperatures 200°C and 250°C, respectively; helium carrier flow, 2 ml min^{-1}. The samples were injected (ca. 0.3 μl) using the split mode with a split ratio of 30:1. Peak measurements were performed using a Carlo Erba Mega integrator and chromatograms were also recorded using a B.B.C. SE 120 chart recorder. Linear retention indices for the volatile components on each column were calculated by chromatographing n-alkanes (C_7 to C_{26}) mixed with the samples (Majlát *et al.*, 1974). Linear retention indices for authentic aroma compounds were similarly determined.

Gas chromatographic-mass spectrometric analysis of volatiles

Capillary gas chromatography-mass spectrometry was carried out using a Kratos MS80 RFA with a DS-90 data system directly coupled to a Carlo Erba 4200 gas chromatograph fitted with a BP1 or BP20 fused silica column (SGE). The temperature programme was 5 min at 50°C increasing at 5°C min^{-1} to 250°C for the apolar column or to 210°C for the polar column. The operating parameters on the mass spectrometer were: ionisation potential, 70 eV; ion source temperature, 150°C, scan speed, 1 s decade^{-1}. Scan range, m/z 400–17 mass units. Both electron impact (E.I.) and (in some cases) chemical ionisation (C.I.) techniques were used to obtain mass spectra of the volatiles. The corrected electron impact mass spectra of the separated components were used in automatic searches of the data system; other mass spectral libraries were consulted as appropriate. Where available, compounds provisionally identified using this approach were obtained and the mass spectra and retention index of each determined. The mass spectra and retention indexes of compounds which were not available, were matched, where possible, with values recorded in the literature. Chemical ionisation mass spectra were used to indicate the likely molecular mass of compounds which could not readily be identified.

RESULTS AND DISCUSSION

Volatile components in the direct extract of Israeli avocado mesocarp

Identified components with their retention indices on an apolar column are given in Table 1. The main component is the sesquiterpene, β-caryophyllene. This extract is characterised by appreciable amounts of terpene hydrocarbons which, in total, form about 80% of the extract. As expected, lipid breakdown volatiles, e.g. hexanal, heptanal and decadienal, are clearly evident together with heptyl- and pentyl-furan, which are also lipid-derived; on a polar column, 18 compounds were identified compared to the 25 found on the apolar column. Other sesquiterpenes found include cubebenes, copaene and cadinenes, but only three monoterpenes, myrcene, camphene and limonene.

Alcohols are fewer in number than those found by Yamaguchi *et al.* (1983) in their work on avocado volatiles.

Volatile components in the extract of Israeli avocado mesocarp left at room temperature for two hours before (L–N) extraction

Finely-cut avocado mesocarp was left at room temperature (20°C) for 2 h to allow formation of enzyme-generated volatiles before extraction. Results showed that the main sesquiterpene was still β-caryophyllene followed by other sesquiterpenes α-copaene, α-cubebene and a cadinene isomer (see Table 2). Other sesquiterpenes observed were bergomotene, farnesene and elemene, which were not present in the direct extract of the mesocarp.

The other noticeable effect of enzymatic action was to increase the number of alkanals present; hexanal, octanal, decadienals and tetradecanal were present after enzymic action had been allowed to occur. In addition, there was a noticeable increase in the number of hydrocarbons detected; thus in the direct extract 10 hydrocarbons were found, whilst in the extract stored at room-temperature, 20 hydrocarbons were identified, and among these were several sesquiterpenes not seen on immediate extraction, thus implying that enzyme action led to liberation or formation of these terpenes.

Table 1. Volatile components, isolated using the Likens–Nickerson apparatus, of avocado mesocarp extracted immediately after removal of the pericarp

Compound	% Total peak area[a]	Retention index (BP1)	Reliability of identification[b]
Pyridine	0.1	772	+ + +
Hexanal	0.3	776	+ + +
Furfural	<0.1	802	+ + +
Hexanol	<0.1	849	+ + +
Hept-2(E)-enal	0.1	932	+ + +
Camphene	<0.1	945	+ + +
2-Pentylfuran	0.6	981	+ + +
Myrcene	0.1	982	+ + +
Limonene	<0.1	1031	+ + +
Non-2-(E)-enal	<0.1	1134	+ + +
Dec-4-enal	<0.1	1171	+ +
2-Heptylfuran	0.1	1182	+ + +
Deca-2(E),4(Z)-dienal	0.5	1272	+ + +
Deca-2(E),4(E)-enal	1.5	1293	+ + +
α-Cubebene	3.6	1356	+ + +
α-Copaene	4.5	1384	+ + +
β-Caryophyllene	60.2	1426	+ + +
α-Humulene	5.9	1463	+ + +
α-Cadinene	1.1	1525	+ +
Cadinene isomer	0.1	1530	+ + +
Caryophyllene oxide	4.8	1573	+ +
Tridecenal	0.1	1610	+
Heptadecane	0.1	1700	+ + +
Farnesyl acetate	<0.1	2000	+ + +
Phytol	0.1	2070	+ + +

[a] Based on response to the flame ionization detector.

[b] + + + Retention index and mass spectrum identical to those of an authentic sample.

+ + Retention index and mass spectrum agree with the published data of Moshonas and Lund (1970), Jennings and Shibamoto (1980), Whitfield *et al.* (1980), Vernin *et al.* (1990), Binder *et al.* (1990), Chen and Ho (1988), Wylie *et al.* (1990).

+ Tentative, based on mass spectrum only.

Table 2. Volatile components, isolated using the Likens–Nickerson apparatus, of avocado mesocarp extracted after removal of the pericarp, tissue disruption and standing for 2 h at room temperature

Compound	% Peak area[a]	Retention index (BP1)	Reliability of identification[b]
Heptane	0.1	700	+ + +
Hexanal	0.1	770	+ + +
Octane	4.8	800	+ + +
Oct-2(E)-ene	0.2	810	+ + +
o-Xylene	0.1	876	+ + +
Hept-2(E)-enal	3.2	931	+ + +
Oct-3-en-1-ol	<0.1	954	+
Octanal	0.3	979	+ + +
Phenylacetaldehyde	0.11	1008	+ + +
Limonene	1.5	1032	+ + +
Nonanal	0.1	1082	+ + +
Non-2-(E)-enal	0.1	1134	+ + +
Dec-4-enal	0.2	1172	+ +
Dec-2(E)-enal	6.3	1242	+ + +
Deca-2(E),4(Z)-dienal	0.3	1273	+ + +
Deca-2(E),4(E)-dienal	0.7	1293	+ + +
δ-Elemene	0.2	1339	+
α-Cubebene	7.7	1356	+ + +
Elemene isomer	2.3	1376	+ + +
α-Copaene	10.7	1383	+ + +
β-Cubebene	7.7	1391	+ + +
β-Caryophyllene	28.8	1426	+ + +
Bergamotene	<0.1	1439	+ +
Bisabolene	0.3	1443	+
α-Farnesene	5.3	1452	+ +
α-Humulene	0.3	1462	+ + +
Cadinene isomer	0.2	1473	+
Cadinene isomer	8.5	1484	+
Elemene (and another compound)	1.8	1494	+
Isomer of α-Farnesene	0.1	1500	+ +
α-Cadinene	2.4	1521	+
Cadinene isomer	0.1	1531	+
Caryophyllene oxide	1.1	1573	+ + +
Tetradecanal	0.2	1593	+ +
Hexadecane	0.1	1600	+ + +
α-Cadinol	0.1	1664	+
Farnesyl acetate	0.1	1804	+ + +

Abbreviations as for Table 1.

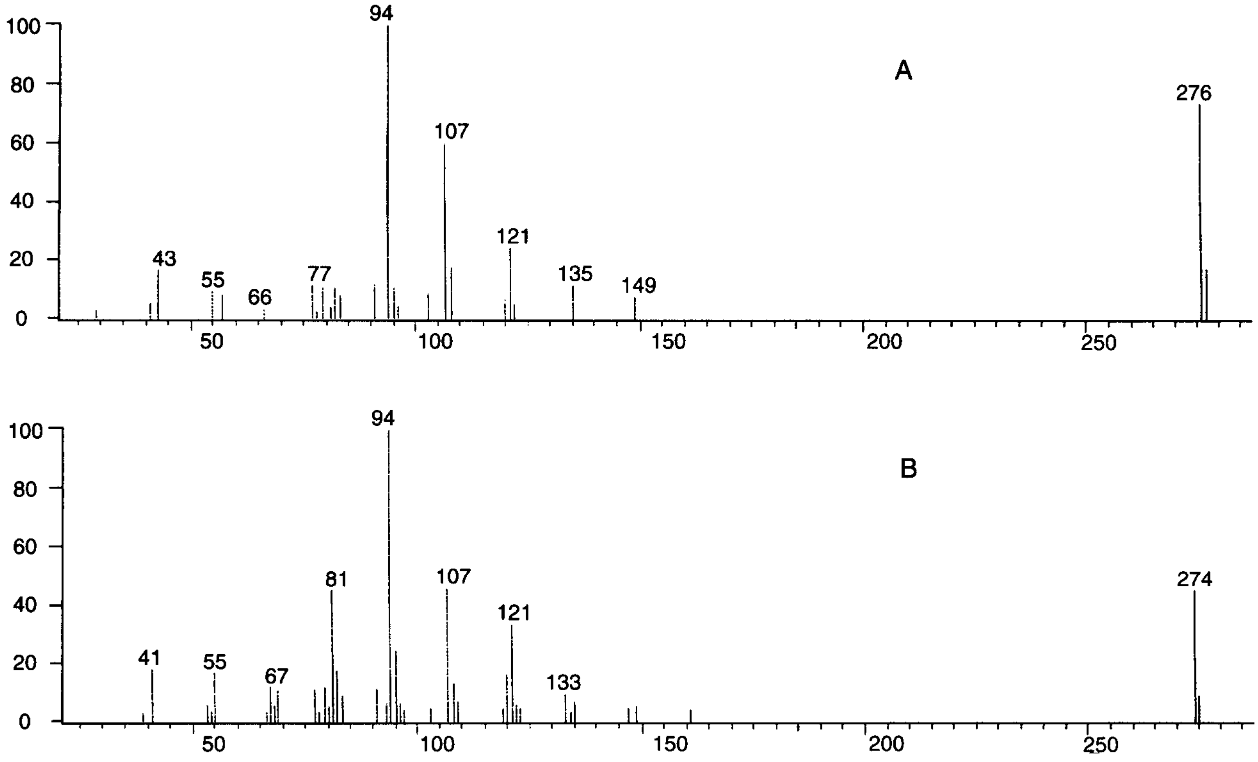

Fig. 1. Mass spectra (E.I.) of unidentified components of avocado. A, molecular weight 276; B, molecular weight 274 (from C.I. mass spectrometry).

In the two extracts, the monoterpene content differed in that the 'stored' mesocarp extract contained only one monoterpene (limonene) whereas the immediate extract showed three (camphene, myrcene and limonene). There was a greater number of aldehydes in the 'stored' avocado mesocarp, eleven compounds compared to seven in the 'unstored' extract.

The major compounds in the direct extract were: *β*-caryophyllene (60%), *α*-humulene (6%), caryophyllene oxide (5%) and *α*-copaene (5%) as revealed on a BP1 column. However, for the extract of 'stored' avocado mesocarp, the major compounds identified were *β*-caryophyllene (29%), *α*-copaene (11%), a cadinene isomer (9%), cubebene (8%) and dec-2-enal (6%). In each case, sesquiterpenes formed the main component of the volatiles. It was also noted that the volatile compounds recognised included more putative cadinene isomers (4) in the extract from the 'stored' avocado mesocarp than in the immediate extract where only one was identified. The furans identified in the extract were not present in the 'stored' extract. Yamaguchi *et al.* (1983) found no sesquiterpenes in avocado mesocarp extracted under reduced pressure, but found 2-methyl-2-butanal, N,N-dimethyl formamide and menthol which were not found in this study.

In this work, as expected, a large number of volatile compounds were obtained in addition to terpenes, especially compounds resulting from degradation processes, for example, lipid degradation products which included aldehydes. Unfortunately, the profiles of compounds obtained by concurrent distillation/solvent extraction did not reflect the true aroma of avocado; due to the terpenoid component, the aroma of the extract could be described as more 'floral or dry wood-like' (Shibamoto and Tang, 1990) than the characteristic avocado aroma as described in sensory tests (Gramshaw and Sinyinda, unpublished). The technique therefore, seems to be unsuitable for obtaining 'true' avocado aroma. In addition to the compounds identified, avocado extracts contained a number of, apparently related, higher molecular weight compounds which are probably esters of substituted phenols; studies to identify these continue. Spectra typical of this group of unknown compounds appear in Fig. 1. Compound A was shown by Chemical Ionization mass spectrometry to have a molecular weight of 276 and compound B a molecular weight of 274. Each shows a fragmentation pattern (El) consistent with that of a substituted phenolic ester.

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