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VOLATILE FLAVOUR CONSTITUENTS IN THE SKIN OIL FROM *FEIJOA SELLOWIANA*

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Key Word Index—*Feijoa sellowiana*; Myrtaceae; fruit peel; essential oil; (*Z*)-hex-3-en-1-ol; linalool; methyl benzoate.

Abstract—The volatile flavour constituents is peel oil from feijoa fruit (*Feijoa sellowiana*) have been analysed by capillary GC and GC-MS. Of the 34 constituents identified, 14 are reported for the first time. (*Z*)-3-Hexen-1-ol, linalool and methyl benzoate made up 53% of the oil.

INTRODUCTION

Feijoa sellowiana Berg. cv mammoth is an evergreen shrub of the Myrtaceae and is closely related to the guava (*Psidium guajava* L.). The plant is native to South America and is found in the high altitude areas of Paraguay, Brazil, Uraguay and Argentina. Because the feijoa plant can tolerate a wide range of climatic and soil conditions, it is grown either as an ornamental or exploited commercially in warm temperate areas of the world.

The volatile flavour constituents of feijoa have been the subject of several GC-MS studies. Hardy and Michael [1] positively identified 16 constituents from a steam distillate of whole fruit, of which ethyl and methyl benzoate constituted 90 area % of the GC trace. In a subsequent study, Shiota and co-workers [2] identified 57 compounds, of which octan-3-one, methyl benzoate, ethyl benzoate and linalool accounted for 70 area % of the GC profile. As part of an investigation to characterise the distribution of flavour constituents throughout the fruit, Shaw *et al.* [3] examined the composition of volatile constituents in the headspace surrounding intact fruit at different stages of ripeness. More recently, the volatile flavour fraction associated with the fruit flesh has been reported [4].

In this communication we report on the isolation and characterization of the principal volatile flavour constituents associated with the skin oil.

RESULTS AND DISCUSSION

The volatile flavour constituents from feijoa skin oil were isolated by low temperature vacuum steam distillation and subsequent liquid–liquid extraction of the essence to give a concentrated extract with an odour reminiscent of fresh feijoa. The extract was examined by capillary GC using a Carbowax 20 M liquid phase and by GC-MS. The composition of the oil is shown in Table 1, together with GC retention data and relative abundances as determined by integration of GC peak areas. Analysis of the GC traces from each of three samples showed that peak areas varied by only 5%. The constituents listed were characterized by GC-MS and where possible these identifications were confirmed by co-chromatography with authentic standards. To assist in the characterisation of the extract, a small sample was fractionated into a hydrocarbon and oxygenated fractions. Each fraction was analysed qualitatively.

Of the 34 constituents identified in this study, 14 have not been previously identified in feijoa. As expected, there were significant quantitative differences in the chemical composition of the headspace emanation, flesh fraction and skin oil. The skin oil is the most complex. Notable in the peel oil was the quantitative dominance of (*Z*)-hex-3-en-1-ol, linalool and methyl benzoate, which collectively made up 53% of the profile. The high concentration of (*Z*)-hex-3-en-1-ol together with other C-5–C-8 alcohols and associated acetates strongly contribute to the 'greenish' odour evident in the peel oil concentrate [6]. From a biosynthetic point of view [7], it is interesting that although C-6 saturated and unsaturated aldehydes were found in the headspace emanation and in the flesh, there was none identified in the skin oil fraction. On the other hand, the occurrence of C-6 alcohols and associated hex-3-enyl acetate, butanoate and benzoate esters suggests that any aldehydes formed from the metabolism of linolenic and linoleic acids are probably rapidly reduced.

In comparison with previous reports, [3, 4], it appears that linalool is localized in the skin of feijoa. The relatively high concentration of this constituent and octan-3-one found in the present study is consistent with that reported by Shiota *et al.* [2]. In contrast, the other major and organoleptically important constituent, ethyl benzoate, which was a feature of the analysis the earlier report [2] was found in relatively low abundance in the present study. This difference is probably a reflection of fruit used in the two studies being at different stages of ripeness. Previous work [3, 4] suggests that high levels of ethyl benzoate in the volatile flavour fraction is closely associated with over-ripe fruit.

The variety of aliphatic and aromatic esters in the peel oil was similar to that found in other parts of the fruit [3, 4]. Methyl benzoate, the constituent most closely associated with the characteristic 'sweet' notes of fresh feijoa constituted 15% of the total oil. In contrast to the volatile flavour constituents found in the headspace

Table 1. Volatile flavour constituents identified in the peel oil from *Feijoa sellowiana* Berg cv mammoth

Constituent	Retention time (min) CW20M	Relative abundance (%)
Diethyl ether	4.36	—
Acetaldehyde	4.42	3.05
Methyl acetate	5.63	0.60
Ethyl acetate	6.36	2.60
Ethanol	7.01	3.70
Ethyl propanoate	7.45	0.80
Ethyl butanoate	9.11	0.16
Myrcene	12.10	0.13
Heptan-2-one	12.90	0.51
Pentanol	13.78	0.37
Hexan-3-ol	14.06	0.28
Octan-3-one	14.08	5.80
(*Z*)-*β*-Ocimene	14.28	0.13
(*E*)-*β*-Ocimene	14.84	0.21
(*Z*)-Hex-3-enyl acetate	15.79	0.32
(*E*)-3-Hexenyl acetate	16.54	0.28
Hexan-1-ol	17.32	0.48
(*Z*)-Hex-3-en-1-ol	18.29	20.00
Octan-3-ol	18.41	6.45
(*Z*)-Hex-3-enyl butanoate	20.60	1.44
Linalool	22.69	18.08
α-Copaene	22.83	0.14
Undecan-2-one	24.39	0.18
β-Elemene	24.48	0.52
Methyl benzoate	24.93	14.50
β-Caryophyllene	25.27	3.40
β-Farnescene	26.03	0.14
Ethyl benzoate	26.42	0.83
α-Humulene	26.84	1.25
Germacrene-D	27.82	6.10
Unknown sesquiterpene	28.43	0.28
Geraniol	30.39	0.80
Calamenene	30.80	0.41
Methyl anisate	38.38	2.10
(*Z*)-Hex-3-enyl benzoate	39.85	2.50
Butyl anisate	44.13	1.46

emanation and the flesh fraction, the skin oil was rich in terpenoid constituents, making up *ca* 32% of the extract. Myrcene, (*Z*)-*β*-ocimene, *α*-copaene, *β*-caryophyllene, *β*-farnesene, *α*-humulene, germacrene-D and calamenene have not been reported in feijoa previously.

EXPERIMENTAL

Plant material. Feijoa fruit (*Feijoa sellowiana* Berg. cv mammoth) were obtained from a local commercial orchard. Naturally abscised fruit were collected over a 24 hr period and then ripened for 7 days at ambient temperatures (18–20°), at which point the fruit were judged to be at optimum eating and flavour quality [4].

Peel oil extraction. Three representative 1 kg samples of unblemished fruit were peeled to a depth of approximately 3 mm and then pureed in 2 l H_2O using a Waring blender. The mixture was vacuum steam-dist. for 3 hr at 30–35° using an apparatus similar to that described in ref. [5]. The essence was collected in a 2 l receiver flask cooled in a solid CO_2 isopropanol bath. The essence was slowly warmed to ambient temp. and then saturated with NaCl before continuously extracting the flavour volatiles with 3 × 200 ml portions of double-distilled Et_2O. The extracts were combined, dried ($MgSO_4$) and concd to 1–2 ml using a low hold-up vigreux distillation column. Samples were stored at −70°, in small vials fitted with teflon lined caps, until required.

Fractionation of skin oil. A portion of the skin oil concentrate (0.5 ml) was taken up in hexane and placed onto a small column of silica gel (Mallinckrodt Silic AR CC-7). A hydrocarbon fraction was eluted with hexane (50 ml) and the oxygenated fraction eluted with Et_2O (50 ml). Each fraction was carefully concd down to *ca* 1 ml as described above.

Gas chromatography. Preliminary GC analysis of the volatile flavour constituents from peel oil was performed on a Hewlett-Packard model 5840A capillary GC equipped with a Grob split/splitless injector and FID detector and fitted with a 50 m × 0.2 mm Carbowax 20 M WCOT glass capillary column. Operating conditions: linear temperature programme, 150 to 240° at 5°/min; injector, 240°; detector, 250°; N_2 carrier gas, 30 cm^3/sec. Splitless injection.

Gas chromatography-electron impact mass spectrometry. Low resolution GC-MS was performed on a Pye model 104 GC interfaced via an all glass single stage jet separator to a Kratos MS 30. GC separations were carried out on a 2.5 m × 4 mm glass column packed with 3% Carbowax 20 M on 100–120 mesh Gas Chrom. Q. Samples were chromatographed using a linear temperature programme from 50 to 180° at 2°/min. Injector and detector temps were 250 and 260°, respectively. He carrier flow rate was 40 cm^3/min. Mass spectra were recorded at 70 eV. The GC-MS interface was held at 230°. Scan speed was 3 sec/decade.

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