

Short communication

Head-space volatiles of marula (*Sclerocarya birrea* subsp. *caffra*)

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Abstract

Head-space volatiles of the fruit pulp and the whole fruits (skin volatiles) were investigated using solid phase micro-extraction (SPME) and GC–MS. The two major compounds in the fruit pulp were β -caryophyllene (91.3%) and α -humulene (8.3%). Thirty volatiles representing 88.7% of the total composition were identified in the head-space of the whole fruits. Heptadecene (16.1%); benzyl 4-methylpentanoate (8.8%), benzyl butyrate (6.7%), (*Z*)-13-octadecenal (6.2%) and cyclo-pentadecane (5.7%) were present in levels higher than 5%. The major alcohol detected in the head-space of the whole intact fruits was (*Z*)-3-decen-1-ol (8.4%).

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1. Introduction

The marula tree (*Sclerocarya birrea*, A. Rich.; Hoscht subspecies *caffra*, Sond) is a member of the Anacardiaceae which encompasses 73 genera and 600 species (Pretorius et al., 1985). This tree is distributed throughout Africa with its southern most location in the lowlands of KwaZulu-Natal (South Africa) from where it extends northwards through tropical Africa into Ethiopia and Sudan (Van Wyk, 1974). Of all fruit trees indigenous to South Africa, the marula has received most attention in terms of domestication and commercialization (Shackleton, 1996). Several products such as beer, juice, jam and jelly have been developed from the mesocarp and successfully marketed, the most recent being a marula liqueur (Burger et al., 1987). Despite the traditional and commercial uses, the flavour constituents remain poorly studied, especially for the pericarp. Ripe marula fruit can be consumed by biting or cutting through the thick leathery skin and sucking the juice or chewing the mucilaginous flesh after removal of the skin. The ripe fruit has an average vitamin C content of 168 mg/100 g which is approximately three times that of oranges and comparable to the amounts present in guavas (Wilson, 1980).

Bark and leaf infusions are often used to treat boils, malaria and diarrhoea (Shone, 1979). The seed oil is used as cosmetic and to preserve meat (Shone, 1979).

Despite the several commercial uses of marula, the volatile constituents of the fruits are poorly studied. As part of the investigation on South African fruit flavours, we reported here the volatile constituents of the marula fruit pulp and the intact whole fruit volatiles.

2. Materials and methods

Ripe fruits were obtained from trees grown in the Limpopo Province, South Africa. Head-space analysis was carried out on the intact fruits and pulp. A SPME (SUPELCO) device consisting of a fused silica fiber, coated with 100 μ m polydimethylsiloxane polymeric adsorbent was used. The intact fruits and pulp were placed in separate vials and tightly closed. The SPME fiber (5 mm) was inserted into the head-space for 2 min. The fiber was removed from the vial and directly inserted into the injection port for desorption. This experiment was repeated in triplicate.

The head-space volatiles were analysed by GC–MS (Agilent 6890N GC system coupled directly to a 5973 MS). The splitless injection was carried out manually at 24.79 psi and an inlet temperature of 250 °C. The GC

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Table 1
Percentage area (mean ± SD; $n=3$) of the volatile compounds identified by head-space SPME and GC–MS of marula

RRI	Compounds (% area)	Fruit pulp	Intact fruits
1079	Ethyl isovalerate	–	1.8±0.7
1250	Ethyl hexanoate	–	0.3±0.1
1444	Ethyl octanoate	–	0.4±0.2
1468	Isoamyl hexanoate	–	0.5±0.2
1473	Ethyl <i>cis</i> -4-octenoate ^a	–	0.7±0.3
1500	Pentadecane	–	4.0±0.4
1519	Cyclo-pentadecane	–	5.7±0.6
1612	β-Caryophyllene	91.3±0.3	3.0±1.1
1654	Hexadecene	–	0.1±0.0
1664	Isoamyl octanoate	–	0.4±0.0
1687	α-Humulene	8.3±0.2	0.3±0.1
1688	Ethyl <i>trans</i> -4-decenoate ^a	–	0.3±0.1
1700	Heptadecane	–	2.3±0.3
1703	(<i>Z</i>)-3-Decenyl acetate ^a	–	0.3±0.0
1718	Heptadecene	–	16.1±2.4
1726	Germacrene D	0.1±0.0	–
1747	Benzyl acetate	–	0.5±0.1
1782	(<i>Z</i>)-3-Decen-1-ol ^a	–	8.4±3.4
1845	1-Octen-3-yl butyrate	–	1.3±0.3
1874	Benzyl butyrate	–	6.7±3.0
1900	Nonadecane	–	1.4±0.2
2004	6-Dodecen-1-ol ^a	–	3.8±0.3
2040	Cyclododecene ^a	–	2.0±0.3
2056	Benzyl metacrylate ^a	–	1.0±0.2
2080	Benzyl 4-methylpentanoate ^a	–	8.8±1.1
2135	Benzyl tiglate	–	1.4±0.1
2136	Hexadecanal	–	2.5±0.5
2170	11-Hexadecanal ^a	–	4.4±0.9
2286	Ethyl 9-hexadecenoate ^a	–	1.5±0.4
2295	Benzyl octanoate	–	2.6±0.5
2384	(<i>Z</i>)-13-Octadecenal	–	6.2±1.6
		99.8	88.7

–: not detected.

RRI = relative retention index.

^a Tentative identification based on MS data only.

system equipped with a HP-Innowax polyethylene glycol column 60 m × 250 μm i.d. × 0.25 μm film thickness was used. The oven temperature program was 60 °C for the first 10 min, rising to 220 °C at a rate of 4 °C/min and held for 10 min and then rising to 240 °C at a rate of 1 °C/min. Helium was used as carrier gas at a constant flow of 1.2 ml/min. Spectra were obtained on electron impact at 70 eV, scanning from 35 to 550 *m/z*. The percentage compositions (mean of three experiments) of the individual components were obtained from electronic integration measurements using flame ionization detection (FID, 250 °C). *n*-Alkanes were used as reference points in the calculation of relative retention indices (RRI). Component identifications were made by comparing mass spectra and retention indices. Library searches were carried out using NIST®, Mass Finder® and the Başer Library of Essential Oil Constituents.

3. Results and discussion

A significant qualitative and quantitative variation was found between the fruit pulp and the intact whole fruits. Thirty compounds representing 88.7% of the total composition were identified in the head-space of the intact fruits (Table 1). Esters and hydrocarbons were the most dominant compounds. The major compounds included heptadecene (16.1%), benzyl 4-methylpentanoate (8.8%), benzyl butyrate (6.7%), (*Z*)-13-octadecenal (6.2%) and cyclo-pentadecane (5.7%). The major alcohol was (*Z*)-3-decen-1-ol (8.4%) and 6-dodecen-1-ol (3.8%), while the major aldehyde was 11-hexadecanal (4.4%). However, the alcohol such as *n*-pentanol, 3-methoxy-2-butanol and 2-methyl-1-pentanol previously reported by Pretorius et al. (1985) were absent.

Only three compounds namely β-caryophyllene (91.3%), α-humulene (8.3%) and germacrene D (0.1%) representing 99.8% of the total compounds were identified in the fruit pulp. Monoterpene hydrocarbons were absent in both the intact and the pulp fruits. The analysis by Pretorius et al. (1985) for marula fruit juice also reported that sesquiterpene hydrocarbons were the most abundant constituents with β-caryophyllene being the major compound while, relatively few monoterpenes (represented only by linalool, furanoid oxide and geraniol) were found. This difference in the composition reported here compared to Pretorius et al. (1985) may be due to the fact that liquid–liquid extraction was employed by Pretorius et al. (1985). Although one should be cautious to quantify using SPME, the emphasis in this study is on the qualitative differences between the intact fruits and the fruit pulp. These results reveal, for the first time, the complex and interesting composition of the skin volatiles. It is well known that the red grape skins contribute largely to the flavour and odour profile of rosé wines. Similarly, production processes should consider the role of marula skin volatiles and optimize contact time of the skin with the fruit pulp to produce products with desirable organoleptic properties.

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