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Short communication

Headspace volatiles of the edible fruit pulp of *Parinari curatellifolia* growing in Malawi using solid phase microextraction

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ABSTRACT

Head-space volatiles of the edible pulp of the mobola plum (*Parinari curatellifolia*) were extracted using solid phase microextraction (SPME), and their identities determined by GC–FID and GC–MS systems. The SPME method extracted eleven major compounds accounting for 99.0% of the volatile constituents. The volatiles were ethyl butyrate, 28.7%; ethyl isovalerate, 19.3%; ethyl valerate, 12.4%; ethyl hexanoate, 3.7%; ethyl benzoate, 2.5%; isoamyl isovalerate, 0.3%; phenol, 10.5%; α-bergamotene, 1.1%; β-farnesene, 3.0%; 2,6-diterbutyl-4-methyl-phenol, 3.1% and phenylacetonitrile, 14.4%. Thus, the valerate and butyrate esters are the most abundant volatiles in the head-space of the edible pulp of the ripe fruit using the SPME method. The compounds, ethyl isovalerate, ethyl valerate, isoamyl isovalerate, phenol, 2,6-diterbutyl-4-methyl-phenol, phenylacetonitrile, α-bergamotene and β-farnesene were identified for the first time in the head-space of this fruit.

1. Introduction

Indigenous fruit trees contribute to the food and nutritional requirements of people in sub-Saharan Africa by providing essential nutrients such as vitamins and minerals (Chirwa and Akinnifesi, 2008). *Parinari curatellifolia* Chrysobalanaceae (Mobola plum) fruit is found in Miombo woodlands of Southern Africa (Joulain et al., 2004). The Mobola plum is an evergreen tree growing up to 20 m with a distinct mushroom shape and yields exceptional large quantities of reddish-yellow fruits, mottled with grey (National Research Council, 2008). The fruits have a sweet and strong pineapple smell (Williamson, 1975). Joulain et al. (2004) isolated 88 volatile flavour components from the *P. curatellifolia* obtained from Venda, South Africa using a vacuum headspace concentration method, which was coupled to hyphenated gas chromatographic mass-spectrometric techniques. About 13.6% of the compounds contained nitrogen, and 2-aminobenzaldehyde and phenyl acetaldoxime were reported for the first time in the edible pulp of the fruit. The optically active 2-nitrobutylbenzene, a new natural product, was also identified. The esters represented about 25% of the volatile fraction.

Indigenous fruit species of Miombo such as Mobola plum are becoming increasingly important food sources for many rural communities, and this fruit is regarded as one of the best wild fruits in Malawi (National Research Council, 2008). In Malawi, the fruit is eaten directly as a snack, and its pulp is made into porridge, juices and or fritters for feeding young children and also used to make alcoholic drinks (Saka et al., 1994). It has been previously revealed that environmental conditions influence volatile formation (Vichi et al., 2003). Until now, the compounds constituting the volatile fraction of the fruit pulp of *P. curatellifolia* from Malawi remain unknown. Volatiles were isolated by using the SPME method which integrates sampling, extraction, concentration into a single solvent free step (Vas and Vekey, 2004). This paper presents the identity and relative abundance of flavour compounds extracted from the head-space of mobola plum using SPME.

2. Materials and methods

2.1. Collection and treatment of fruits

Ripe fruits of *P. curatellifolia* were collected from 10 trees within a radius of 700 m, from Sanga in Nkhata Bay, Malawi in September 2009. Samples were cleaned, packed in polythene bags and refrigerated at −20 °C to minimize changes in flavour.

Abbreviations: FID, flame ionisation detection; GC–FID, gas chromatography–flame ionisation detection; GC–MS, gas chromatography–mass spectrometry; PDMS, polydimethylsiloxane; RI, retention indices; SPME, solid phase microextraction.

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2.2. Extraction and determination of volatiles

2.2.1. Solid phase microextraction (SPME)

An SPME (SUPELCO) device consisting of a fused silica fibre, coated with 100 μm polydimethylsiloxane (PDMS) polymeric adsorbent was used. Ten fruits from each tree were peeled, and the fruit pulp from all fruits collected was mixed to a fine consistency for analysis. A sample (30 g) of the composite pulp was placed in a 100 ml vial and tightly closed. The SPME fibre (5 mm) was inserted into the headspace of the vial for 20 min at room temperature, and then directly inserted into the injection port for 5 min for desorption (Viljoen et al., 2008). This process was repeated twice.

2.2.2. Determination of volatiles

The volatiles were analysed by the GC–MS Agilent 6890N GC system coupled directly to a 5973 MS (Viljoen et al., 2008). The splitless injection was carried out manually at 24.79 psi and an inlet temperature of 250 °C. The GC system was equipped with a HP-Innowax polyethylene glycol column (60 m × 250 μm i.d., 0.25 μm film thickness). The oven temperature programme was set at 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. The flame ionisation detection (FID) was kept at 250 °C. Helium was used as a carrier gas at a constant flow rate of 1.2 ml/min. The percentage peak areas of the individual components were calculated from the total FID response. Spectra were obtained on electron impact at 70 eV, scanning from 35 to 550 *m/z*. In calculating the percentages, the same response for all compounds was assumed.

The *n*-alkanes (C6–C24) were used as reference points in the calculation of retention indices (RI). Compounds were identified by comparison with the mass spectra and retention indices found in the literature using NIST®, MassFinder®, Flavour and the Baser library of essential oil constituents (Viljoen et al., 2008).

3. Results and discussion

The identity and chemical composition of the major volatile constituents of the headspace of the edible pulp of ripe *P. curatellifolia* using SPME method are provided in Table 1. The results revealed that eleven most abundant volatiles accounted for 99.0% of the FID response.

Table 1
Identity and relative abundance of headspace volatiles from ripe *P. curatellifolia fruits* using SPME (Mean ± SD, n = 2).

RI	Compounds	MW (g/mol)	B.P (°C)	Peak area(%)
Esters				
1051	Ethyl butyrate	116.16	120–121	28.7 ± 0.6
1066	Ethyl isovalerate	130.19	131–133	19.3 ± 0.3
1142	Ethyl valerate	130.19	144–145	12.4 ± 0.2
1228	Ethyl hexanoate	144.21	166–168	3.7 ± 0.2
1670	Ethyl benzoate	150.18	211–213	2.5 ± 0.4
1298	Isoamyl isovalerate	172.26	192–193	0.3 ± 0.3
Sesquiterpenes				
1570	α-Bergamotene	204.35	259–260	1.1 ± 0.1
1665	β-Farnesene	204.35	206.0	3.0 ± 0.4
Phenols				
1915	2,6-Di-ter butyl-4-methyl-phenol	220.35	265	3.1 ± 0.3
Alcohols				
1917	Phenol	108.14	205	10.5 ± 0.4
Heteroatoms				
1940	Phenyl acetonitrile	117.15	234	14.4 ± 0.5
	Total			99.0

RI, relative retention indices calculated relative to n-alkanes.

Esters (66.9%) were more abundant than alcohols (10.5%), heteroatoms (14.4%), sesquiterpenes (4.1%) and phenols (3.1%). Hence, esters appear to contribute much more significantly to the total volatiles of the fruit pulp. The most abundant ester, ethyl butyrate (28.7%) was the third most abundant compound obtained in the *P. curatellifolia* from Thohoyandu, Venda South Africa using a different method, namely vacuum headspace concentration (Joulain et al., 2004). In the earlier study, 2-phenylethanol and ethyl pentanoate were the most abundant. Ethyl butyrate has also been determined among the volatile components of Oiti fruit (*Licania tomentosa* Benth.), *Gethyllis afra* and *Gethyllis ciliaris* fruits (Kamatou et al., 2008). Ethyl valerate also known as the green apple flavour is well known for its wide uses in the areas of food, pharmaceuticals and cosmetics industries (Raghavendra et al., 2010). Ethyl valerate and ethyl butyrate were identified in headspace volatiles of *Scutellaria californica* A. Gray flowers (Takeoka et al., 2008).

The extraction methods significantly determine the range and type of extracted compounds, evidently, dynamic extraction has greater sensitivity than a static equilibrium process (Joulain et al., 2004). This work has thus expanded the range of volatiles obtainable from the headspace of the fruit: ethyl isovalerate, ethyl valerate, isoamyl isovalerate, phenol, 2,6-diter butyl-4-methyl-phenol, phenylacetonitrile, α-bergamotene and β-farnesene. The PDMS fibre used on the SPME was responsible for the sample-headspace-fibre equilibrium; this probably accounted for the type of compounds extracted. The results also seem to show that lower molecular weight esters were easier to extract using the SPME than higher molecular weight esters. For example, ethyl hexanoate (144.21 g/mol), ethyl benzoate (150.18 g/mol) and isoamyl isovalerate (172.26 g/mol) accounted for 3.7%, 2.5% and 0.3% respectively. Ethyl butyrate, having the lowest molecular weight (116.16 g/mol) was the most abundant ester extracted. Further, ethyl isovalerate (boiling point of 131 °C–133 °C) is more volatile than ethyl valerate (144 °C–145 °C). Consequently, ethyl isovalerate gave a larger peak area (19.3%) than ethyl valerate (12.4%). Furthermore, the real relative abundances of the volatiles played a very important role in their extraction. The present results will inform future work on establishing the effect of provenance on the headspace volatiles of the pulp.

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