Available online at www.sciencedirect.com
ScienceDirect
South African Journal of Botany 74 (2008) 768–770
SOUTH AFRICAN JOURNAL OF BOTANY
www.elsevier.com/locate/sajb

Short communication

Head-space volatiles of *Gethyllis afra* and *G. ciliaris* fruits ("kukumakranka")

G.P.P. Kamatou [a], A.M. Viljoen [a,*], T. Őzek [b], K.H.C. Başer [b]

[a] *Department of Pharmaceutical Sciences, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa*
[b] *Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, 26470-Eskişehir, Turkey*

Received 25 March 2008; received in revised form 19 June 2008; accepted 7 July 2008

Abstract

The head-space volatiles of *Gethyllis afra* and *G. ciliaris* fruits collected in the South Western Cape Province of South Africa were analysed by solid phase micro-extraction (SPME) followed by gas chromatography coupled to mass spectrometry (GC-MS). Twenty-nine compounds were characterized in the fruit of *G. ciliaris* representing 96.5% of the total composition. Major compounds include pentacosane (19.2%); ethyl octanoate (18.0%); ethyl isovalerate (11.7%); ethyl hexanoate (9.1%) and ethyl benzoate (7.4%). These compounds may be the major contributors to the fruity-sweet odour of *G. ciliaris*. Forty-three compounds were identified in the fruit of *G. afra* representing 87.9% of the total composition with α-pinene (11.2%), *n*-butyl *n*-butyrate (8.5%), isoamyl acetate (8.1%), β-pinene (6.4%) and 2-methylbutyl butyrate (5.8%) as main constituents. These major constituents may impart the banana/piney/fruity odours associated with the *G. afra*. The compounds identified in the volatiles of the two fruits in amounts greater than 1% include ethyl butyrate, ethyl isovalerate, isobutyl 3-methyl butyrate, ethyl octanoate and ethyl benzoate.

Keywords: Ethyl isovalerate; *Gethyllis ciliaris*; *Gethyllis afra*; Head-space; Isoamyl acetate; Pentacosane; SPME; α-Pinene

1. Introduction

Gethyllis is a genus in the Amaryllidaceae family that is found mostly in the winter rainfall region of southern Africa. The plant has such unusual foliage, flowers and fruits that it ranks as one of the most fascinating groups of bulbous plants in southern Africa. It is a most amazing genus as it produces leaves, flowers and fruit all at different times of the year which never co-occur (Van Wyk and Gericke, 2000). *Gethyllis* flowers in summer and has a subterranean ovary which remains cool and protected underground. The attractive white or pink flowers are followed by fragrant club-shaped berries that emerge in mid-winter, long after the flowers and leaves have wilted (Van Wyk and Gericke, 2000). The genus is considered rare and endangered and comprises about 32 species mostly found in southern Africa (Namibia and South Africa) (Elgorashi and Van staden, 2004; Elgorashi et al., 2007).

In South Africa species such as *G. ciliaris* are used in traditional medicine to treat colic, flatulence and indigestion (Watt and Breyer-Brandwijk, 1962). The fruits of many species of *Gethyllis* are administered as an alcohol infusion or as a brandy to treat stomach disorders.

The fruits are much sought after for their fragrance and reported medicinal properties. The ripe fruits are edible and have a powerful sweet, fruity odour. In the past, the odourous dried fruits were often used to scent handkerchiefs and linen cupboards (Van Wyk and Gericke, 2000). Today the edible fruits of *G. afra* are still used to make "kukumakranka" brandy, a popular remedy for colic and indigestion (Van Wyk and Gericke, 2000). Although there are some reports on the pharmacological properties and some aspects of the chemistry, the volatile compounds of the fruits of *G. afra* and *G. ciliaris* have not previously been reported.

* Corresponding author. Tel.: +27 12 3826360; fax: +27 12 3826243.
E-mail address: viljoenam@tut.ac.za (A.M. Viljoen).

0254-6299/$ - see front matter © 2008 SAAB. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.sajb.2008.07.002

2. Materials and methods

Ripe fruits were obtained from the Darling area in the South Western Cape of South Africa (*Gethyllis afra* W.F. Barker 10817 NBG 94286 (NBG) and *Gethyllis ciliaris* T.T. Barnard s.n. NBG 94983). The SPME analysis is described elsewhere (Viljoen et al., 2008). Briefly, a SPME (SUPELCO) device consisting of a fused silica fiber, coated with 100 µm polydimethylsiloxane polymeric adsorbent was used. The fruits were placed in separate vials and tightly closed. The SPME fiber (5 mm) was inserted into the head-space for 2 min, removed from the vial and directly inserted into the injection port for desorption. This experiment was repeated three times. The head-space volatiles were analysed with a GC-MS system (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 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 composition (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

The chemical composition of the volatiles of the two fruits is presented in Table 1. Quantitative and qualitative variations were observed between the two fruits (Table 1). Twenty-nine compounds were identified in the fruit of *G. ciliaris* representing 96.5% of the total composition. Major compounds include pentacosane (19.1%); ethyl octanoate (18.0%); ethyl isovalerate (11.7%); ethyl hexanoate (9.1%) and ethyl benzoate (7.4%).

Forty-three compounds were identified in the fruit of *G. afra* representing 87.9% of the total composition. The major compounds identified include α-pinene (11.2%), *n*-butyl *n*-butyrate (8.5%), isoamyl acetate (8.1%), β-pinene (6.4%) and 2-methylbutyl butyrate (5.8%). Pentacosane present in *G. ciliaris* in high amount (19.1%) was only detected in small amount in *G. afra* (0.4%), while the monoterpene α-pinene and β-pinene present in high amount (11.2% and 6.4%, respectively) in *G. afra* were totally absent in *G. ciliaris* (Table 1). The organoleptic properties of fruits may often be due to a single ester, but more often, the flavour or the aroma is due to a complex mixture of compounds. Although the smell of the two fruits were similar, the major esters which may be responsible for the odour were qualitatively and quantitatively different. *Gethyllis afra* were dominated by *n*-butyl *n*-butyrate (8.5%), 2-methylbutyl butyrate (5.8%) and 2-methylbutyl isovalerate (4.7%) and isobutyl butyrate (3.1%). In *G. ciliaris*, the major esters found were ethyl octanoate (18.0), ethyl isovalerate (11.7%), ethyl hexanoate (9.1%) and isobutyl 3-methyl butyrate (3.9%).

Table 1
Chemical composition and relative amounts (% area) of *Gethyllis afra* and *G. ciliaris* fruits

RRI	Compound	*G. afra*	*G. ciliaris*
893	Ethyl acetate	0.7	1.3
975	Isopropyl isobutyrate		2.5
1032	α-Pinene	11.2	
1045	Ethyl butyrate	2.3	3.4
1079	Ethyl isovalerate	2.3	11.7
1100	Isobutyl isobutyrate		0.3
1118	β-Pinene	6.4	
1136	Isoamyl acetate	8.1	
1170	Isobutyl butyrate	3.1	
1174	Myrcene	0.5	
1192	2-Heptanone		0.9
1198	Isobutyl 3-methyl butyrate (=*Isobutyl isovalerate*)	1.2	3.9
1203	Limonene	3.7	
1213	1,8-Cineole	5.0	
1230	*n*-Butyl *n*-butyrate	8.5	
1250	Ethyl hexanoate	3.6	9.1
1275	2-Methylbutyl butyrate	5.8	
1282	Hexyl acetate	2.5	
1299	2-Methylbutyl isovalerate	4.7	1.4
1320	2-Heptanol		0.5
1360	Hexanol	0.2	0.3
1365	Isobutyl caproate	0.7	1.0
1398	2-Nonanone		0.2
1426	Heptyl isobutyrate	1.3	
1427	Butyl hexanoate	0.2	
1444	Ethyl octanoate	2.0	18.0
1457	Hexyl-3-methyl butyrate (=*Hexyl isovalerate*)	0.1	0.7
1468	3-Methyl butyl hexanoate (=*Isoamyl hexanoate*)	1.5	0.5
1483	Octyl acetate	2.7	0.5
1562	Octanol	0.6	7.8
1600	Hexadecane	0.1	
1611	Terpinen-4-ol	0.1	
1617	Hexyl hexanoate	0.1	
1620	Butyl caprylate	0.2	
1623	Octyl butyrate		0.1
1647	Ethyl decanoate		0.8
1654	Octyl 3-methyl butyrate (=*Octyl isovalerate*)	0.2	0.5
1658	Isoamyl octanoate		0.6
1661	*trans*-Pinocarvyl acetate	0.2	
1685	Ethyl benzoate	2.9	7.4
1687	Decyl acetate	0.2	
1704	Myrtenyl acetate	0.1	
1706	α-Terpineol	1.6	0.8
1725	Verbenone	0.1	
1744	Benzyl acetate	0.6	
1772	Neryl isobutyrate	0.6	
1809	Isobutyl benzoate	0.4	0.6
1883	Butyl benzoate	0.2	
1896	Benzylalcohol		1.5
1902	Benzyl isovalerate	0.3	0.8
1927	Isoamyl benzoate	0.7	
1929	2-Methyl butyl benzoate		0.3
2500	Pentacosane	0.4	19.1
	Total	87.9	96.5

RRI — Relative retention indices calculated against *n*-alkanes, % calculated from FID data.

References

Elgorashi, E.E., Van staden, J., 2004. Pharmacological screening of six Amaryllidaceae species. Journal of Ethnopharmacology 90, 27–32.

Elgorashi, E.E., Coombes, P.H., Mulholland, D.A., Van staden, J., 2007. Isoeugenitol, a cyclo-oxygenase-1 inhibitor from *Gethyllis cilliaris*. South African Journal of Botany 73, 156–158.

Van Wyk, B.E., Gericke, N., 2000. People's Plants: a Guide to Useful Plants of Southern Africa, Briza Publications, 1st ed. Pretoria, South Africa.

Viljoen, A.M., Kamatou, G.P.P., Başer, K.H.C., 2008. Head-space volatiles of Marula (*Sclerocarya birrea*, subspecies *caffra*). South African Journal of Botany 74, 325–326.

Watt, J.M., Breyer-Brandwijk, M.G., 1962. The Medicinal and Poisonous Plants of Southern and Eastern Africa, 2nd ed. E and S. Livingstone, Edinburgh.

Edited by AK Jäger