Available online at www.sciencedirect.com
SCIENCE DIRECT®
Phytochemistry 65 (2004) 2163–2166
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Volatile constituents of *Capillipedium parviflorum* ☆

Umar Mahmood, Vijay K. Kaul *, Ruchi Acharya

Department of Natural Plant Products, Institute of Himalayan Bioresource Technology, P.O. Box No. 6, Palampur 176 061 (HP), India

Received 9 October 2003; received in revised form 17 March 2004
Available online 6 May 2004

Abstract

The essential oil of aerial parts of *Capillipedium parviflorum* (family Poaceae) was obtained by hydrodistillation in 0.4% yield on dry weight basis. The oil was analysed by capillary GC and GC–MS techniques. Two new compounds from plant source 4-nonanol 51.7% and 4-undecanone 23.5% predominated in the essential oil and were separated by column chromatography, identified and confirmed by ^{1}H and ^{13}C NMR. Thirty one compounds were identified from the essential oil accounting for 96% of total identifications.

Keywords: *Capillipedium parviflorum*; Poaceae; Essential oil composition; GC; GC–MS; 4-Nonanol; 4-Undecanone; 4-Decanol; 4-Undecanol

1. Introduction

Capillipedium, a genus of about 14 species, is distributed in tropical and subtropical world and six species are found in India (Shreekumar and Nair, 1991). *Capillipedium parviflorum* is a grass of some economic importance (Watson and Dallwitz, 1994). Since no chemical investigation on the essential oil of this plant or any other species is reported, a detail investigation was undertaken and 31 compounds were identified in which two unusual naturally occurring major compounds **15** and **16** were isolated and their structures confirmed by ^{1}H and ^{13}C NMR (1D and 2D) and MS. A comparative study of GC–MS results of this essential oil on polar and non-polar columns are also reported here.

2. Results and discussion

GC–MS analysis of the essential oil of *C. parviflorum* led to the identification of 31 compounds on a polar column and 24 compounds on a non-polar column; Table 1 lists the compounds in their elution order on Innowax and HP-5 capillary columns. The composition of the oil was interesting because aliphatic compounds accounted for 93.6% of the total oil ranging from C-6 to C-11 alcohols in addition to esters, ketones and aldehydes. Monoterpenes accounted only for 0.7% and sesquiterpenes are represented only by 1.9%. Two unusual major non-terpene constituents identified as 4-nonanol (**15**) 51.7% and 45.5% on HP-5 and Innowax GC columns, respectively, and 4-undecanone (**16**) 23.5% and 24.4% on HP-5 and Innowax GC columns, respectively, were separated by column chromatography. Undecanol 11.1% on innowax and 10.6% on HP-5 and 4-nonanone 6.9% were other major compounds. β-Pinene, heptanal, β-caryophyllene, 11-methyl-4-dodecanone, 1,10-diepicubenol and α-cadinol were not identified on non-polar column while *n*-heptanol was not identified on polar column.

2.1. 4-Nonanol (*15*)

Compound **15** was assigned molecular formula $C_9H_{20}O$ on the basis of its MS ($M^+ - 1$ at m/z 143) and ^{13}C NMR where nine carbons were clearly observed as $2 \times CH_3$, $6 \times CH_2$ and $1 \times CH$ as determined by DEPT experiment. The signal at δ 72.1 for CH confirmed it to be a secondary alcohol. Its ^{1}H NMR showed two triplets ($J = 6.5$ Hz) for 3H each at δ 0.92 and δ 0.87 for

☆ IHBT Communication No. 0315.

* Corresponding author. Tel.: +91-1894-30426; fax: +91-1894-30433.
E-mail address: vkaul2002@yahoo.co.in (V.K. Kaul).

0031-9422/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2004.04.003

Table 1
Composition of the essential oil from the aerial parts of *C. parviflorum*

Serial no.	Constituents	KI	Innowax column polar %	Constituents	KI	HP-5 column (non-polar) %
1	α-Pinene	1036	t	*n*-Hexanal	780	t
2	*n*-Hexanal	1084	t	2-Hexenal	832	t
3	β-Pinene	1120	t	2-Hexen-1-ol	854	t
4	4-Heptanone	–	t	4-Heptanone	860	t
5	Heptanal	1186	t	4-Heptanol	879	t
6	2-Hexenal	1207	t	*n*-Heptanol	883	0.1
7	4-Heptanol	1250	0.1	α-Pinene	942	t
8	*n*-Hexenyl acetate	1300	t	Octanol	985	–
9	*Trans*-2-hexenyl acetate	1315	0.7	*n*-Hexenyl acetate	987	t
10	2-Hexen-1-ol	1368	t	*Trans*-2-Hexenyl acetate	997	0.5
11	*n*-Nonanal	1382	0.1	4-Nonanone	1030	6.9
12	3-Octanol	1386	t	4-Nonanol	1078	51.7
13	4-Nonanone	–	7.1	*n*-Nonanal	1087	0.5
14	*Trans*-2-hexenyl butyrate	1461	1.1	Linalool	1092	0.1
15	4-Nonanol	1467	45.5	4-Decanol	1098	t
16	4-Undecanone	1476	24.4	*Trans*-2-hexenyl butyrate	1180	0.8
17	Decanal	1485	1.0	Decanal	1188	0.3
18	Linalool	1506	t	4-Undecanone	1208	23.5
19	Octanol	1519	t	4-Undecanol	1281	10.6
20	β-Caryophyllene	1617	0.4	α-Caryophyllene	1428	t
21	4-Undecanol	1672	11.1	4-Tridecanone	–	1.1
22	Germacrene-D	1712	0.2	Germacrene-D	1468	t
23	4-Decanol	–	t	γ-Muurolene	1586	t
24	γ-Muurolene	1725	1.3	Caryophyllene oxide	1837	t
25	α-Muurolene	1750	t			
26	α-Caryophyllene	–	t			
27	4-Tridecanone	–	1.6			
28	Caryophyllene oxide	2000	0.1			
29	11-Methyl-4-dodecanone	–	0.1			
30	1,10-Diepi-cubenol	–	t			
31	α-Cadinol	2224	0.3			

KI, Kovats index.

terminal methyl groups (Me-1 and Me-9). The multiplet centered at 1.43 (8H) was accounted for 2, 6, 7 and 8 methylenes while other multiplet at δ 1.62 was assigned for 3 and 5 methylene groups. A pentet at δ 3.61 was observed for methine proton at 4 position. These assignments were further confirmed by HMBC. The position of hydroxyl group was further confirmed by its mass spectral fragmentation pattern (Fig. 1) MS of this compound also matched with the reported fragmentation pattern of 4-nonanol (McLafferty, 1988). The above data confirms peak **15** in GC–MS as 4-nonanol. To the best of our knowledge this compound has not been reported previously from plants. As this compound is a major compound (51.7%) of essential oil of *C. parviflorum*, this plant can be a good source of this compound for commercial application.

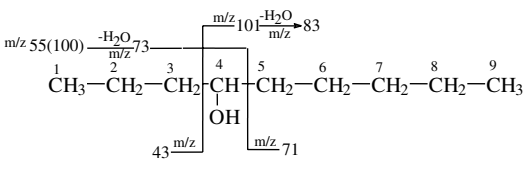

Fig. 1. Important mass fragmentation of **15**.

2.2. 4-Undecanone (*16*)

Compound **16** was assigned molecular formula $C_{11}H_{22}O$ on basis of its MS (m/z 170) and ^{13}C NMR which clearly showed 11-carbons, $2 \times CH_3$, $8 \times CH_2$ and $1 \times C{=}O$ as determined by DEPT experiment. Its ^1H NMR spectrum displayed two triplets ($J = 6$, Hz, 3H each) at δ 0.90 and δ 0.87 for 1 and 11 terminal methyls. Two triplets at δ 2.37 and δ 2.38 ($J = 6.5$ Hz) were observed for the methylene at 3 and 5 positions adjacent to carbonyl group, a multiplet for C-2 and C-6 methylenes was observed at δ 1.58 while the methylenes at C-7 to C-10 were observed as broad singlet at δ 1.26. These observations were further confirmed by HMBC experiments alongwith its mass spectral fragmentation which gives α and β-fission involving H transfer from γ-position (Silversein and Webster, 2002) as shown in Fig. 2. The above data fully confirms the structure of **16** as 4-undecanone. To the best of our knowledge this is a new naturally occurring compound.

Compound **21** and **23** have been synthesised and reported earlier (McLafferty, 1988; Stephen, 1998). We are reporting these two compounds for the first time from natural source.

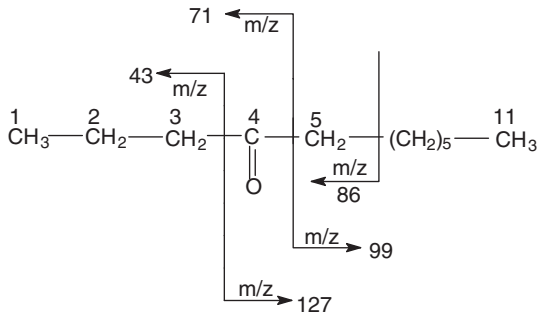

Fig. 2. Important mass fragmentation of **16**.

n-Nonanol and 2-nonanol are found in some essential oils in minor quantities and 1-, 2- and 3-nonanols are used in low concentrations in different perfume compositions (Arctander, 1994). 1-Nonanol contributes freshness to rose and a trace of this alcohol is used in flavours like peach, pineapple and lime. 2-Nonanol also finds use in perfume compositions mainly as top note complex in green floral bases such as gardenia and carnation, while 3-nonanol, isolated from scotch spearmint oil, has herbaceous, mild spicy and earthy odour and is used in perfume formulations because of its low cost (Anon, 1998). It also serves as an intermediate in the preparation of number of new perfumery compounds including hydroxylated alcohols for lavender and jasmine type odour (Arctander, 1994). 4-Nonanol which can be obtained from *C. parviflorum* in appreciable quantities could be used for producing medium grade perfumes or utilised as an intermediate for synthesis of perfumery compounds such as made from 3-nonanol. 2- and 3-Nonanols and 2-undecanol are reported to have pheromone activity (Anon, 1998), it is also likely that 4-nonanol and 4-undecanol can have such activity, although 4-methyl-5-nonanol occurs in the sex pheromone of weevil *Metamasius hemipterus* (Perez et al., 1997; Oeshlschlager et al., 2002).

3. Experimental

3.1. Plant Material

Aerial parts of *C. parviflorum* at flowering stage were collected during mid September 2002 form chambalhar area in Palampur. A voucher specimen of the plant has been deposited in the herbarium of our institute (Voucher specimen No. VKK 3436).

3.2. Oil isolation and analysis

Aerial parts of the plant (2 kg) were air dried, chopped and hydrodistilled for 3 h in a Clevenger type apparatus. The oil content was 0.4% (v/w), on fresh weight basis. The oil was analysed by GC–MS on 6890 Agilant gas chromatograph equipped with fused silica polar (Innowax) and non-polar (HP-5) capillary columns. Analysis was carried out first by using an Innowax column (30 m×0.25 mm, i.d.; film thickness 0.25 μm). The operating conditions were as follows: Injector and detector temperatures, 230 and 250 °C, respectively; carrier gas, He; oven, temperature isothermal at 40 °C, then increase at 5°/min to 190 °C and finally held isothermal for 5 min. Analysis was repeated on a non-polar column, HP-5 (30 m × 0.25 mm i.d.; film thickness 0.25 μm). The operating conditions were as follows: Injector and detector temperature, 250 and 250 °C, respectively; carrier gas, He; flow rate 1 ml/min oven temperature programme, 5 min isothermal at 50 °C, then 3 °C/min to 240 °C and finally held at 280° for 25 min, transfer line temperature 290 °C, mass scan range 30–600 amu, sample solvent ratio 1:10, injection volume 0.2 μl ionisation voltage 70 eV.

Compound identification is based on computer matching of mass spectra. Using library search system HP-5872 (Hewlett–Packard), we consulted the following data bases: Wiley 275 and NBS 75K libraries (McLafferty, 1988) NIST 98 (Stephen, 1998) and compilation by Adam (1995). Wherever necessary we used the Kovats retention index reported in literature (Adam, 1995; Jennings and Shibamato, 1980) for confirmations.

The structures of major constituents of the oil were confirmed by NMR. NMR spectra (^{1}H, ^{13}C, 1D, 2D) were recorded in $CDCl_3$ on Bruker DRX-300 and 75 MHz (^{13}C) instrument using TMS as internal standard and the chemical shifts are reported in δ (ppm) units relative to TMS signal and coupling constants (J) in Hz.

3.3. Isolation of major compounds

Two hundred and fifty milligrams oil was subjected to column chromatography on silica gel and eluted with *n*-hexane containing increasing amounts of EtOAc (to 5%) to give nine fractions. The first six fractions (17 mg) (hexane:EtOAc, 100–98:0–2) containing mixture of non-polar compounds were rejected. Fraction seven (95 mg) (hexane:EtOAc, 97:3) were found to contain major constituent, i.e. 4-nonanol. Fraction nine (wt 25 mg) (hexane:EtOAc, 95:5) was found to contain 4-undecanone whereas fraction eight (65 mg) was mixture of several compounds.

3.4. 4-Nonanol (*15*)

Colourless oil ^{1}H NMR (300 MHz, $CDCl_3$) 0.87 (3H, *t*, $J = 6.5$ Hz, CH_3-9) 0.92 (3H, *t*, $J = 6.5$ Hz, CH_3-1), 1.43 (8H, *m*, CH_2-2, CH_2-6, CH_2-7, CH_2-8), 1.62 (4H, *m*, CH_2-3, CH_2-5), 3.61 (1H, *p*, CH-4); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) 14.47 (*q*, C-9), 14.53 (*q*, C-1),

19.23 (*t*, C-2) 23.06 (*t*, C-8), 25.74 (*t*, C-6), 32.32 (*t*, C-7), 37.84 (*t*, C-5) 40.03 (*t*, C-3), 72.11 (*d*, C-4); MS (EI, 70 eV) *m*/*z* (rel. int.) 144 (M^+ absent) 143 ($M^+ - 1$) (0.20), 126 (4), 101 (32), 83 (72), 73 (70.01), 55 (100), 43(31).

3.5. 4-Undecanone (**16**)

Colourless oil, ^{1}H NMR (300 MHz, $CDCl_3$) 0.87 (*t*, $J = 6.5$, C-11), 0.90 (*t*, $J = 6.5$ Hz, C-1) 1.26 (8H, *m*, CH_2-7, CH_2-8, CH_2-9 and CH_2-10), 1.58 (4H, *m*, CH_2-2, CH_2-6) 2.37 (2H, *t*, $J = 6.5$, CH_2-5), 2.38 (2H, *t*, $J = 6.5$, CH_2-3); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) 14.06 (*q*, C-11) 14.84 (*q*, C-1), 17.68 (*t*, C-2), 23.01 (*t*, C-10), 24.25 (*t*, C-6) 29.49 (*t*, C-8), 29.62 (*t*, C-7), 32.08 (*t*, C-9) 43.24 (*t*, C-5), 45.09 (*t*, C-3), 212.15 (*s*, C-4) MS (EI, 70 eV) *m*/*z* (rel. int.) 170(M^+)(5), 152 (2), 127 (65) 86 (67), 71 (82), 58 (84), 57 (98), 43 (100).

Acknowledgements

Authors are thankful to Dr. P.S. Ahuja, Director, IHBT for providing necessary facilities and constant encouragement during the course of the work. Authors are also grateful to Dr. S.K. Vats for suggesting the plant for chemical investigation.

References

Adam, R.P., 1995. Identification of Essential oils component by Gas Chromatography/Mass Spectroscopy. Allured Publishing Corporation, Carol Stream, IL.

Anon, 1998. Dictionary of Natural Products (Chemical Data Base). Chapman & Hall, London.

Arctander, S., 1994. In: Perfume and Flavour Chemicals, vols. I and 2. Allured Publishing Corporation, IL, USA.

Jennings, W., Shibamato, T., 1980. Quantitative Analysis of Flavour and Fragrance Volatiles by Glass Capillary Gas Chromatography. Academic Press, New York.

McLafferty, F.W., 1988. Wiley/NBS Registry of Mass Spectral Data, fourth ed. Wiley, New York.

Oeshlschlager, A.C., Lilliana, G., Manuel, G., Carlos, R., Romano, A., 2002. Pheromone-based trapping of West Indian sugarcane weevil in sugarcane plantation. J. Chem. Ecol. 28, 1653–1664.

Perez, A.L., Campos, Y., Chinchilla, C.M., Gries, G., Gries, R., Pierce Jr., H.D., Gonzales, L.M., Oeshlschlager, A.C., Castrillo, R.E., McDonald, R.S., Giblin-Davis, R.M., Pena, J.E., Duncan, R.E., Andrade, R., 1997. Aggregation pheromones and host kairomones of West Indian sugarcane weevil *Metamasius hemipterus*. J. Chem. Ecol. 23, 869–888.

Shreekumar, P.V., Nair, V.J., 1991. Flora of Kerala – Grasses, Botanical Survey of India, Calcutta, p. 55.

Silversein, R.M., Webster, F.X., 2002. Spectroscopic Identification of Organic Compounds. Wiley, New York. p. 22.

Stephen, S., 1998. NIST 98 Mass Spectral Library. The NIST Mass Spectroscopy Data Centre, Gaithersburg, MD.

Watson, L., Dallwitz, M.J., 1994. The Grasses Genera of the World. CAB International Publisher, Willingford. pp. 202–203.