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VOLATILE CONSTITUENTS OF PEONY FLOWERS*

NARENDRA KUMAR and MICHAEL G. MOTTO

Fritzsche Dodge and Olcott Inc., Chemical Research Laboratories, 76 Ninth Avenue, New York, NY 10011, U.S.A.

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Key Word Index—*Peony albiflora*; Paeoniaceae; flower odour; monoterpenoids; sesquiterpenoids; aromatics; aliphatics.

Abstract—Fragrance components of fresh peony flower include oxygenated mono- and sesqui-terpenes and a number of aliphatic and aromatic aldehydes, esters and alcohols. 3-Oxo-1,8-cineole is a new natural product.

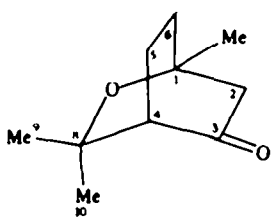
INTRODUCTION

Peony albiflora (syn. *P. lactiflora*) is a herbaceous perennial desirable as an ornamental and for the sweet fragrance of its flowers. Previous investigations of *P. albiflora* have been on the roots and leaves which are known to possess medicinal properties and resulted in the isolation of mainly flavonoid and monoterpene glycosides [1–5]. The roots and root-bark of *P. lactiflora* and *P. suffructicosa* have also been used in skin cosmetics [6]. Despite the attractive olfactory value of the flowers, no detailed study on the odour constituents has appeared in the literature. The only report [17] on *P. albiflora* flowers described the isolation of sitosterol, methyl tetradecanoic acid and pentacosane, none of which contributes to their odour. We have now carried out a detailed investigation on the fragrant constituents of these flowers and report here the volatile components.

RESULTS AND DISCUSSION

A pentane extract of the fresh petals was fractionated by Kugelrohr distillation to obtain a low boiling fraction. This distillate had a strong green-spicy odour and was found (by GC-MS and GC-FTIR†) to contain aromatic as well as aliphatic oxygenated compounds (Table 1). Substances 1–16, 32–43, 53–64 and 26 were identified in this manner. The residue from the Kugelrohr distillation was chromatographed on silica gel to yield ten fractions. The first nonpolar fraction consisted of waxes (45%) and had no odour value. The remaining nine fractions had varying odour properties and were, therefore, examined extensively. Since these fractions were also accompanied by large amounts of high boiling fatty acids, esters and stearoptenes, they were first subfractionated by HPLC, preparative GC and vacuum distillation. These subfractions were then analysed by GC-MS. Substances which could not be identified by GC-MS and GC-FTIR were isolated and studied by ^{1}H NMR and ^{13}C NMR. Table 1 lists all the 70 components, 66 of which we have identified, arranged according to their structural class.

The substance (compound 17) shown to be a monoterpene ketone by GC-MS (*m/z* 168 $[M]^+$, *m/z* 140 $[M-C{=}O]^+$) and GC-FTIR (1749 cm^{-1}) was isolated by preparative GC as a colourless liquid. Analysis of the ^{1}H NMR spectrum showed the presence of three singlets at δ1.15 (3H), 1.23 (3H) and 1.31 (3H), indicating the presence of methyl groups attached to the oxygen bearing carbon atoms. Examination of the IR spectrum indicated no hydroxyl absorption, and the presence of a band at 1144 cm^{-1} suggested an ether linkage. The IR band at 1383 cm^{-1} indicated that the ether was associated with a *gem*-dimethyl group. ^{1}H NMR further showed an 'AB' pattern composed of a downfield doublet of doublets at δ2.39 (J = 20, 3 Hz) and its higher field component doublet at δ2.25 (J = 20 Hz) and showed the presence of a methylene attached to the carbonyl function. A narrow triplet at δ2.16 (J = 2.5 Hz) suggested that the carbonyl was flanked on the other side by a methine proton which was adjacent to a methylene group. These features could be satisfactorily accounted for by 3-oxo-1,8-cineole structure, **1**. The small coupling (3 Hz) observed for the signal at δ2.39, assigned to the 2-*endo*-proton, is due to the *W*-coupling involving the 6-*endo*-proton. This could be demonstrated by decoupling experiments which also allowed the assignment of the signal at δ1.89 (*m*) to this 6-*endo*-proton. Comparison of the ^{1}H NMR with that reported for synthetic [8] and microbially [9] derived substance confirmed its structure. To our knowledge, this



*Dedicated to Professor Werner Herz on his 65th birthday.

†GC-FTIR data was obtained through the courtesy of BASF A.G., Ludwigshafen, Germany.

Table 1

	Component	Approximate concentration*	Structural evidence†	Reference
Oxygenated monoterpenes				
1	Methyl heptenone	m	MS, IR	NC
2	1,8-Cineole	m	MS, IR	NC
3	Linalol	m	MS, IR	NC
4	*cis*-Linalol oxide	t	MS, IR	NC
5	*trans*-Linalol oxide	t	MS, IR	NC
6	*cis*-Rose oxide	t	MS, IR	NC
7	α-Terpineol	m	MS, IR	NC
8	Citronellol	h	MS, IR, NMR, RT	NC
9	Citronellal	m	MS, IR	NC
10	Geraniol	m	MS, IR	NC
11	Geranial	t	MS, IR	NC
12	Neral	t	MS, IR	NC
13	Unknown, $[M]^+$ 138	t		
14	Unknown, $[M]^+$ 172	t		
15	Unknown, $[M]^+$ 154	t		
16	Citronellyl acetate	t	MS, IR	NC
17	3-oxo-1,8-Cineole[a]	t	MS, IR, ^{1}H-NMR	NNC [8, 9]
18	*trans*-Rose oxide	t	MS	NC
19	Nerol	t	MS	NC
20	Myrtenal	t	MS	NC
21	*trans*-Myrtanol	t	MS, ^{1}H NMR, ^{13}C NMR	
22	*cis*-Myrtanol	t	MS, synthesis [10]	NC
23	Carvacrol	t	MS, RT	[5]
24	*cis*-Jasmone	t	MS	NC
25	Terpinen-4-ol	t	MS	NC
Sesquiterpenes				
26	β-Caryophyllene	l	MS, IR	NC
27	Farnesol	m	MS	NC
28	2,3-Dihydrofarnesol	m	MS, synthesis	NC
29	*trans*-β-Farnesene	t	MS	NC
30	*trans*-Nerolidol	m	MS, ^{1}H NMR, ^{13}C NMR	NC
31	Unidentified, $[M]^+$ 220	t	MS	NC
Aromatics				
32	Benzaldehyde	m	MS, IR	[5], NF
33	Benzyl alcohol	l	MS, IR	[5], NF
34	Phenyl acetaldehyde	l	MS, IR	[5], NF
35	Salicylaldehyde	l	MS, IR	NC
36	Methyl benzoate	l	MS, IR	[5], NF
37	Guaicol	m	MS, IR	NC
38	β-Phenylethyl alcohol	h	MS, IR, RT	[5], NF
39	*o*-Dimethoxybenzene	l	MS, IR	NC
40	Dimethyl hydroquinone	m	MS, IR	NC
41	Methyl salicylate	l	MS, IR	[5], NF
42	Ethyl benzoate	l	MS, IR	NC
43	Phenyl ethyl acetate	l	MS, IR	NC
44	Methyl *o*-methoxybenzoate	t	MS	NC
45	Methyl cinnamate	l	MS	NC
46	Ethyl salicylate	t	MS	[5], NF
47	Methyl anisate	t	MS	NC
48	Eugenol	l	MS	NC
49	Methyl eugenol	l	MS	NC
50	Benzyl benzoate	t	MS	NC
51	Benzoic acid	t	MS	[5, 11]
52	Elemicin	t	^{1}H NMR, ^{13}C NMR	NC
Aliphatic hydrocarbons and oxygenated compounds				
53	*n*-Amyl alcohol	t	MS, IR	NC
54	Isoamyl alcohol	t	MS, IR	NC
55	*n*-Butanol	t	MS, IR	[5], NF
56	2-Methylbutanol	t	MS, IR	NC
57	Hexanol	l	MS, IR	NC

Table 1 (*Continued*)

	Component	Approximate concentration*	Structural evidence†	Reference
58	Hexanal	l	MS, IR	NC
59	*trans*-2-Hexenal	l	MS, IR	NC
60	*trans*-2-Hexenol	l	MS, IR	NC
61	*cis*-3-Hexenal	l	MS, IR	NC
62	*cis*-3-Hexenol	l	MS, IR	NC
63	*cis*-3-Hexenyl acetate	t	MS, IR	NC
64	*n*-Hexyl acetate	l	MS, IR	NC
65	Decenal	t	MS	NC
66	Decanal	t	MS	NC
67	Decane	t	MS	NC
68	*n*-Hexane	t	MS	NC
Fatty acids				
69	Palmitic acid	h	MS	NC
70	Oleic acid	h	MS	NC

*h = High (> 1%); m = medium (0.5%–1%); l = low (0.1–5%); t = trace (< 0.1%) referred to the concrete; NC = new component; NNC = new natural component; NF = new in flowers; a = isolated and characterized.

†Identication methods: MS, library match of component from GC-MS; library match of component from GC-FTIR; synthesis, material was synthesized using literature procedure and directly compared; RT, identity established by co-injection of authentic sample.

is the first instance of its isolation from a natural source.

Phenyl ethyl alcohol and citronellol are the major volatile constituents of peony flowers which give the 'rosy' character to their fragrance. The low boiling fraction consisting of hexenal and hexenol isomers is responsible for the 'green' odour character. The extract lacked monoterpene hydrocarbons, but contains large amounts of waxes, stearoptenes and fatty acids and esters.

EXPERIMENTAL

Material. Peony flowers (*ca* 3000 full blooms), white, pink and violet, were collected in June in Connecticut. The petals were carefully separated from the sepal, pistil and stamen and 45 kg extracted in 3 × cold distilled HPLC grade pentane (35 l.). All extractions were started within 4 hr of picking the flowers. The pentane was removed by careful distillation, using a Vigreaux column in the final stages of solvent removal to obtain the 'concrete', 20 g.

Fractionation. The extract (20 g) was distilled in a Kugelrohr apparatus at 30 mm of Hg and 100°. The distillate (0.2 g) was trapped in collection bulbs cooled in dry ice. The residue (19.8 g) was chromatographed over silica gel (200 g, EM reagent) and eluted with hexane. The hexane eluate gave fraction 1 consisting primarily of waxes (7.5 g). Further elution with hexane–EtOAc mixtures gave the odorous fractions 2–10. These fractions were then separated further by prep. HPLC and prep. GC.

Identification. HPLC determinations utilized a DuPont System 8800 Liquid Chromatograph equipped with the four-solvent gradient programmer, a UV spectrophotometer, and an R_i detector.

Analytical work was accomplished using a Rainin SiO_2 Microsorb short-one column (4.6 × 100 mm, 3μ). Preparative separations were done on an Altex SiO_2 semiprep. Column (10 × 250 mm 5μ μ-porasil). Solvents used were HPLC grade and degassed with He before use. Collections were carried out using a Seimens automatic fraction collector operating in the time collection mode.

Analytical GC was performed on either a Perkin–Elmer Sigma 2000 or a Perkin–Elmer Sigma-2 gas chromatograph using DB-1 (J&W Scientific 30 m × 0.32 mm, 1μ film), Carbowax-20M capillary columns (J&W Scientific, 30 m × 0.32 mm) and an SE-30 capillary column (J&W Scientific, 30 m × 0.32 mm) and He as carrier gas. Prep. GC was done on an OV-101 glass column (0.25 in. × 10 ft.) using a Perkin–Elmer, model 900 gas chromatograph in FID mode; split ratio was (9:1). MS and GC-MS were recorded on a Hewlett-Packard model 5985 spectrometer equipped with an H-P gas chromatograph with a DB-1 GC column (J&W Scientific, 30 m × 0.25 mm, 1μ film). NMR spectra were recorded at 250 MHz for proton and 62.9 MHz for carbon. All the spectra were obtained in $CDCl_3$ and were referenced to the solvent peak (^{1}H NMR, 7.25 ppm; ^{13}C NMR, 77.0 ppm).

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(−)-3β-ACETOXYDRIMENIN FROM THE LEAVES OF *DRIMYS WINTERI*

JORGE R. SIERRA, JOSÉ T. LÓPEZ and MANUEL J. CORTÉS

Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago, Chile

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Key Word Index—*Drimys winteri*; Winteraceae; Canelo; leaves; drimane sesquiterpene; (−)-3β-acetoxydrimenin.

Abstract—A new natural product, 3β-acetoxydrimenin was isolated from the petrol extract of the leaves of *Drimys winteri* which also contains the known compounds safrol, drimenol and polygodial. The structure of the new compound was determined by chemical and spectroscopic methods.

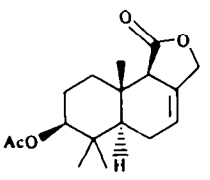
INTRODUCTION

The stem bark of the South American tree *Drimys winteri* Forst has been shown to contain sesquiterpenoids of the drimane type [1, 2]. Further investigation of the leaves afforded cryptomeridiol, cirsimaritin, quercetin, astilbin and quercitrin [3].

We now report the isolation and structure determination of 3β-acetoxydrimenin (**1**), a new drimane sesquiterpene, from leaves of *D. winteri*, together with the previously known compounds safrol [4], drimenol (**2**) [1] and polygodial (**3**) [5]. To the best of our knowledge, only two drimane sesquiterpenes oxygenated at C-3*, have been found in nature. These are iresin (ent-drimane) from *Iresine celosioides* [6, 7] and uvidin B isolated from *Lactarius uvidis* Fries (Basidiomycetes) [8].

RESULTS AND DISCUSSION

The petrol extract of *D. winteri* leaves afforded safrol [4], drimenol (**2**) [1], polygodial (**3**) [5] and a new drimane sesquiterpene identified as 3β-acetoxydrimenin (**1**) on the basis of the following evidence. The formula $C_{17}H_{24}O_4$ for compound **1** is supported by elementary analysis and mass spectral data. Its IR spectrum shows absorption bands at 1760 and 1725 cm^{-1} confirming the presence of saturated γ-lactone and acetoxyl groups. The ^1H NMR spectrum of **1** shows resonances for three tertiary methyl groups at δ0.94 (6H, *s*, 2 × Me) and 1.00 (3H, *s*, Me), and for one acetate group at δ2.1 (3H, *s*). The



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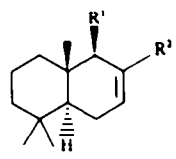
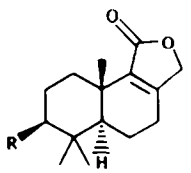
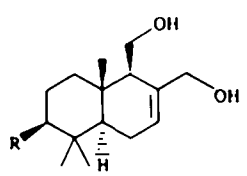


2 R¹ = CH₂OH, R² = Me
3 R¹ = R² = CHO



4 R = OAc
5 R = OH



6 R = OH
7 R = H

*We have numbered the C-atoms according to the usual trivial names.