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ACYCLIC MONOTERPENES FROM THE ESSENTIAL OIL OF *TAGETES MINUTA* FLOWERS

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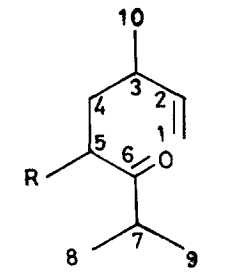
Key Word Index—*Tagetes minuta*; Asteraceae; monoterpenes.

Abstract—The steam-distilled essential oil of *T. minuta* flowers afforded three new acylic monoterpene ketones identified as 3,7-dimethyloct-1-en-6-one, 3,7-dimethyl-5-hydroxyoct-1-en-6-one and 3,7-dimethyloct-1,7-dien-6-one along with major compounds (*Z*)-β-ocimene (38.77%), dihydrotagetone (9.07%), (*Z*)-tagetone (7%), (*Z*)-ocimenone and (*E*)-ocimenone (20%). © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The vast and varied genus *Tagetes* belongs to the family Asteraceae. Some species of *Tagetes* have been examined chemically such as *Tagetes patula*, *T. glandulifera*, *T. erecta*, and *T. riojana*. The essential oil of *T. minuta* L. of Indian origin has been analysed by various workers [1–3]. Ocimenone which is the major constituent of essential oil of *T. minuta* flowers was reported to have mosquito larvicidal activity [4]. The present paper describes the analysis of the steam-distilled oil of *T. minuta* flowers collected from Kahsmir.



1	2	3
R = H	OH	H
		Δ7

RESULTS AND DISCUSSION

On repeated column chromatography over silica gel the essential oil of *T. minuta* flowers yielded three new compounds viz. 3,7-dimethyloct-1-en-6-one (**1**), 3,7-dimethyl-5-hydroxyoct-1-en-6-one (**2**) and 3,7-dimethyloct-1, 7-dien-6-one (**3**). Compound **1**, analysed for molecular formula $C_{10}H_{18}O$ displayed absorption bands for a vinyl group at 995 and 910 cm^{-1}. The sharp band at 1720 cm^{-1} suggested the presence of a carbonyl group. The 400 MHz ^1H NMR spectrum exhibited signals for a terminal vinyl group, an isopropyl group and other signals for methylene, methyl and methines. The above data indicated the presence of a monoterpene with a terminal vinyl group, an isopropyl group, a methyl group and a ketonic group. These groups were also observed in its ^{13}C NMR spectrum. The structure of **1** is proposed for this compound on the basis of comparison of its spectral data with those reported in the literature [5–7] for similar monoterpenoids.

Compound **2** was obtained as viscous mass having the molecular formula $C_{10}H_{18}O_2$ (M^+ at *m/z* 170) indicating two degrees of unsaturation. The IR spectrum exhibited bands for C=O (1725) and the double bond (1630, 995 and 890 cm^{-1}). The absorption band in the IR spectrum at 3460 cm^{-1} and a signal in its ^1H NMR spectrum at δ 4.00 (1H, *dd*, *J* = 6 and 8 Hz) indicated the presence of a hydroxy group. The downfield shift of this carbinyl proton suggested the position of the hydroxy group was adjacent to the oxo group. ^1H NMR signals at δ 4.95, 5.05 and 5.75 further corroborated the presence of a vinyl group. The presence of an isopropyl group was sown by the doublet at δ 0.85 (6H, *d*, *J* = 7 Hz) and a septet at δ 2.65 (1H, *sep*, *J* = 7 Hz) in it ^1H NMR spectrum. The above spectral data led to the structure **2**.

Compound **3** was a viscous oil having the molecular formula $C_{10}H_{16}O$ (M^+ at *m/z* 152), indicating three

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double bond equivalents and displayed absorption bands for a vinyl group at δ 990 and 905 cm^{-1} as well as a carbonyl function at 1725 cm^{-1}. The ^1H NMR spectrum exhibited signals for terminal vinyl and exomethylene groups which were further confirmed by signal in its ^{13}C NMR spectrum. The ^1H NMR spectrum also showed the presence of one secondary and one tertiary methyl group at δ 0.94 (3H, *d*, $J = 7$ Hz) and 1.83 (3H, *s*), respectively. By comparing the spectral data of **3** with those of **1** it was observed that one of the methyl groups of the isopropyl group in **1** was an exomethylene group in **3**. Hence, the above spectral data led to its structure as **3**. Although, this compound has been reported synthetically [7], this is the first report on the isolation of **3** from a natural source.

EXPERIMENTAL

General

^1H NMR: 400 MHz: ^{13}C NMR: 100 MHz in $CDCl_3$ and TMS as int. standard. TLC and CC silica gel (Merck, India).

Plant materials

Tagetes minuta flowers were collected in the Central Institute of Medicinal and Aromatic Plants field station, Pulwama, Kashmir, in October 1994.

Extraction and isolation

The oil (25 ml) was obtained by steam-distillation of the flowers (3.52 kg) and yielded 0.7% (v/w) on fresh weight, d^{18}: 0.9175: n_D^{18} 1.4970: $[\alpha]_D^{18}$: $+5.2°$ (neat).

The oil (25 ml) was chromatographed over a silica column eluting with hexane, various proportions of hexane and Et_2O yielding 10 frs of 250 ml each. Similar frs were combined on the basis of TLC analysis. Out of the 5 frs thus obtained, rechromatography of the first 4 frs resulted in the isolation of (*Z*)-β-ocimene (38.72%), dihydrotagetone (9.07%), (*Z*)-tagetone (7%), (*Z*)-ocimenone (7%) and (*E*)-ocimenone (13%) which constituted about 75% of the oil. An additional fr. V (2 gm) was rechromatographed to provide compounds **1** 20 mg, **2** 40 mg, **3** 25 mg having R_f values 0.75, 0.55 and 0.62 ($CHCl_3$), respectively.

3,7-*dimethyloct*-1-*en*-6-*one* (**1**). Viscous mass (20 mg), TLC (system $CHCl_3$) R_f 0.75; $[\alpha]_D^{18}$ $+2.7°$ ($CHCl_3$; *c* 0.27); IR ν_{max}^{neat} cm^{-1}: 2950, 2940, 2880, 1720, 1640, 1400, 1370, 995, 910. ^1H NMR: δ 5.70 (1H, *ddd*, $J = 18$, 10, 10 Hz), 4.98 (1H, *d*, $J = 18$ Hz), 4.90 (1H, *d*, $J = 10$ Hz), 2.70 (1H, *sep*, $J = 7$ Hz), 2.15–2.35 (4H, *m*), 2.10 (1H, *m*), 0.92 (3H, *d*, $J = 7$ Hz), 0.90 (6H, *d*, $J = 7$ Hz). ^{13}C NMR: δ 112.20 (C-1), 141.8 (C-2), 31.4 (C-3), 33.4 (C-4), 43.00 (C-5), 209.40 (C-6), 51.25 (C-7), 21.4 (C-8), 20.20 (C-9), 22.40 (C-10). MS *m/z* (rel. int.): 154 $[M]^+$ (5) 111(40), 85(72), 71(35), 69(52), 55(40), 43(100), 41(65), (Found: C, 76.94: H, 11.52 Calc. for $C_{10}H_{18}O$ C, 77.93, H, 11.69).

3,7-*dimethyl*-5-*hydroxyoct*-1-*en*-6-*one* (**2**). Viscous mass, TLC (system $CHCl_3$). R_f 0.55; $[\alpha]_D^{18}$ $+35.5°$ ($CHCl_3$; *c* 1.0); IR ν_{max}^{neat} cm^{-1} 3460, 2950, 2940, 2860, 1725, 1630, 1460, 1375, 995, 890. ^1H NMR: δ 5.75 (1H, *ddd*, $J = 18$, 10 and 10 Hz), 5.05 (1H, *d*, $J = 18$ Hz), 4.95 (1H, *d*, $J = 10$ Hz), 4.00 (1H, *dd*, $J = 6$, 8 Hz), 2.65 (1H, *sep*, $J = 7$ Hz), 1.85–2.30 (3H, *m*), 0.95 (3H, *d*, $J = 7$ Hz), 0.85 (6H, *d*, $J = 7$ Hz). ^{13}C NMR: δ 112.5 (C-1), 142.8 (C-2), 32.7 (C-3), 41.00 (C-4), 68.5 (C-5), 207.7 (C-6), 53.05 (C-7), 22.00 (C-8), 19.00 (C-9), 24.00 (C-10). MS *m/z* (rel. int.): 170 $[M]^+$ (8), 152 $(M-H_2O)^+$ (3), 127(80), 113(50), 109(30), 85(74), 83(35), 71(35), 69(42), 55(27), 43(100), 41(85).

3,7-*dimethyloct*-1,7-*dien*-6-*one* (**3**). Viscous oil, TLC (system $CHCl_3$). R_f 0.62; $[\alpha]_D^{18}$ $-17.5°$ ($CHCl_3$, *c* 0.75); UV λ_{max} [MeOH] 224 nm ($\varepsilon = 9700$) IR ν_{max}^{neat} cm^{-1}: 2960, 2935, 2850, 1725, 1635, 1465, 990 and 905. ^1H NMR: δ 5.85 (1H, *s*), 5.80 (1H, *s*), 5.70 (1H, *ddd*, $J = 18$, 10, 10 Hz), 5.20 (1H, *d*, $J = 18$ Hz), δ 5.04 (1H, *d*, $J = 10$ Hz), 2.65 (1H, *ddd*, $J = 18$, 10, 5 Hz), 2.80 (1H, *ddd*, $J = 18$, 10, 5 Hz), 1.95–2.35 (3H, *m*), δ 1.83 (3H, *s* H-9), δ 0.94 (3H, *d*, $J = 7$ Hz). ^{13}C NMR: 112.50 (C-1), 141.20 (C-2), 32.84 (C-3), 33.80 (C-4), 44.40 (C-5), 205.43 (C-6), 143.50 (C-7), 123.40 (C-8), 17.50 (C-9), 21.40 (C-10). MS *m/z* (rel. int.) 152 $[M]^+$ (5) for $C_{10}H_{16}O$.

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