m/e (%): 276, M(70); 246, M–CH_2O (62); 206 (40); 205, III (95); 204, IV (100); 191 (33); 189 (92); 176, III–COH (95); 175, IV–COH (94); 161 (30); 148 (23); 147 (47); 146 (52); 78 (21); 73 (24); 71 (20); 43 (47). PMR spectrum, δ, ppm (paramagnetic shift)*: 1.34 s, $3H^a$ (Δ 20 Hz); 1.41, s, 3 H^b (Δ 31 Hz); 2.90, d, H^c, J_{ce} = 3 Hz (Δ 43 Hz); 3.65, s, OCH_3 (Δ 10 Hz); 3.84, m, H^d (Δ 70 Hz); 4.50, d, H^e, J_{ce} = 3 Hz (Δ 54 Hz); 6.09, two d, H^f, J_{fi} = 10 Hz (Δ 11 Hz); 6.69, two d, H^g, J_{gh} = 9 Hz (Δ 10 Hz); 7.15, tr, H^h (Δ 5 Hz), 7.49, two d, H^i, J_{if} = 10 Hz (Δ5 Hz).

Isophlojodicarpin (II), $C_{15}H_{16}O_5$, mp 132-134°C, $[\alpha]_D^{25}$ – 102.5° (methanol), M 276. UV spectrum, λ_{max} (log ε, nm): 260 (3.87); 328 (4.25). IR spectrum, cm^{-1}: 3430, 3000, 1246, 930, 860. 1714, 1610, 835. PMR spectrum, δ, ppm: 1.31, m, 6 H^a; 3.68, s, OCH ; 3.80, d, H^b, J_{bc} = 5 Hz; 4.11, s, H^d; 4.55, d, H^c, J_{bc} = 5 Hz; 6.11, d, H^f, J_{fi} = 10 Hz; 6.61, d, H^g, J_{gh} = 8 Hz; 7.34, d, H^h, J_{gh} = 8 Hz; 7.73, d, H^i, J_{fi} = 10 Hz.

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*The chemical shifts are given for a solution in deuterochloroform at 20°C, and the spin–spin coupling constants are taken from the spectrum recorded with the addition of $Eu(dpm)_3$ at 60°C.

ESSENTIAL OIL OF *Blumea mollis*

Arvind Geda, M. M. Bokadia,
and K. L. Dhar

UDC 665.3/35:665.1.03

The alkanes n-triacontane and n-hentriacontane, 2,3-dimethoxy-p-cymene, chrysanthanone, 2,4,5-trimethoxyallylbenzene, methyl 5-isopropyl-2-methylcyclopentenecarboxylate, and caryophyllene oxide have been isolated from the essential oil of *Blumea mollis* by chromatographic methods. The identities of these terpenoids have been established by physicochemical and spectral methods.

Blumea mollis DC [1] (family Compositae) is a common weed growing in India and Sri Lanka. Its leaves are used in Indian medicine [2]. The antimicrobial activity of the oil of the plant has been investigated [3]. Related species of plants have been studied previously [4, 5], but there is no information on the essential oil of *Blumea mollis* in the literature. This induced us to begin a chemical study of the plant the results of which are given below.

From the essential oil of *Blumea mollis* by chromatographic methods we have isolated the alkanes n-triacontane and n-hentriacontane, 2,3-dimethoxy-p-cymene, chrysanthanone, 2,4,5-trimethoxyallylbenzene, methyl 5-isopropyl-2-methylcyclopentenecarboxylate, and caryophyllene oxide. The identities of these terpenoids have been established by physicochemical and spectral methods.

Chemical Division, Vikram University, Ujjain, India. Regional Scientific-Research Laboratory, Jammu-Tawi, India. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 50-52, January-February, 1981. Original article submitted June 18, 1980.

0009-3130/81/1701-0043$07.50

EXPERIMENTAL

The plant, collected in the flowering period (February-April), was subjected to steam distillation [6]. This gave a dark brown oil (0.034%) with a characteristic sweet smell and the following physical constants: n_D^{29} 1.44, $[\alpha]_D^{29}+ 0°$, d_4^{29} 0.98, acid No. 054, ester No. 596, distillation temperature 87-220°C/4 mm Hg.

The oil was separated into acidic and neutral fractions by washing with 5% NaOH. The acid fraction has not been considered because of its insignificant amount.

The neutral fraction (14 g) was chromatographed on Al_2O_3 (activity grade II) [7] (1:30). Elution with petroleum ether (40-60°C), benzene, and ether yielded three main fractions. Thin-layer chromatography of the petroleum fraction (8 g) on silica gel impregnated with $AgNO_3$ (15%) [8] revealed six spots. The fraction was rechromatographed on active silica gel (1:40) impregnated with $AgNO_3$ (7.5%).

Elution with petroleum ether yielded the chromatographically pure compounds A, B, C, and D.

Compound A: bp 200-225°C/4 mm Hg, M^+ 422, corresponding to the composition $C_{30}H_{62}$. On cooling with ice it solidified in the form of a white mass (0.80 g). The IR spectrum contained absorption bands at 2920 and 2850 cm^{-1} (C–H stretching vibrations), 1460 and 1375 cm^{-1} (deformation vibrations of $-CH_3$), and 720 cm^{-1} (deformation vibrations of $(CH_2)_n$). The NMR spectrum (CCl_4, δ) showed signals at 0.78 ppm (6 H, two methyl groups) and a narrow signal at 1.12 ppm (methylene, $(CH_2)_n$). The compound was identified as n-triacontane [9].

Compound B: bp 180-220°C/4 mm Hg, M^+ 436, corresponding to the composition $C_{31}H_{64}$. It was crystallized from ethyl acetate. mp 64-65°C, yield 0.63 g. It consists of a long-chain aliphatic hydrocarbon. The IR spectrum contained absorption bands at 2900, 1470, 1380, 728, and 713 cm^{-1}. The NMR spectrum showed signals at 0.85 and 1.21 ppm. On the basis of its spectral characteristics, the compound was identified as n-hentriacontane [11, 12].

Compound C: bp 80-85°C/0.5 mm Hg, n_D^{29} 1.478, $[\alpha]_D^{20} \pm 0°$, composition $C_{12}H_{18}O_2$ (two methoxy groups) (M^+ m/e 194), yield 1.50 g. The IR spectrum showed absorption bands at 2900 cm^{-1} (C–H stretching vibrations) 1379, 1362, and 1178 cm^{-1} (isopropyl group), 1210, 1157, and 1065 cm^{-1} (phenolic ether), 860 cm^{-1} (two free adjacent hydrogen atoms in an aromatic ring), and 810 cm^{-1} (1,2,3,4-tetrasubstituted benzene) [13]. The NMR spectrum (CCl_4) contained signals at 1.01 and 1.12 ppm (6 H, s, two methyl groups of an isopropyl grouping), 2.05 ppm (3 H, s, one methyl group), 6.41 ppm (2 H, d, aromatic protons), 3.67 ppm (6 H, d, two methoxy groups), and 3.15–3.29 ppm (1 H, m, benzyl proton). The NMR spectrum of the compound agrees well with that of p-cymene, with the exception of the signals at 3.67 ppm due to methoxy groups.

Thus, on the basis of a comparison of the results obtained with those given in the literature, it was concluded that the compound was 2,3-dimethoxy-p-cymene.

Compound D: bp 70-75°C/0.6 mm Hg, n_D^{25} 1.4729, $[\alpha]_D^{26}$ −87°, composition $C_{10}H_{14}O$ (M^+ 150). The IR spectrum had adsorption bands at 2900 cm^{-1} (C–H stretching vibrations), 1780 cm^{-1} ($>C=$ groups possibly present in a cyclobutane ring), 1670 and 821 cm^{-1} (trisubstituted alkene $-C=CH$), 1450 cm^{-1} (deformation $-CH_3$ vibration), and 1380 and 1340 cm^{-1} (isopropyl group).

Integration of the NMR spectrum showed the presence of 14 protons, demonstrating the bicyclic nature of the molecule at least with one double bond and a keto group in a four-membered ring. The presence of a keto group in a four-membered ring was confirmed by the absorption band of the compound in the IR spectrum at 1780 cm^{-1}. The NMR spectrum contained the following signals: 1.07 ppm (6 H, doublet, gem-dimethyl group), 1.65 ppm (3 H, quartet, allyl methyl group), 5.20 ppm (1 H, s, olefinic proton), and 2.5 ppm (4 H, multiplet, allyl methylene group and two methine protons).

Thus, all the facts given confirm the structure of the compound as 6,7,7-trimethylbicyclo[3,1,1]hept-5-en-2-one (chrysanthanone) [15].

The benzene fraction (3.5 g) was chromatographed on silica gel, and then on silica gel impregnated with $AgNO_2$ (15%). This gave compounds E and F, the purity of which was checked by TLC.

Compound E: bp 140-155°C/2 mm Hg, n_D^{31} 1.5295, d_4^{28} 1.0796, $[\alpha]_D^{30} \pm 0°$, absorption bands due to the stretching vibrations of C–H bonds at 2927, 3080, 1640, 995, and 915 cm^{-1} ($-CH=CH_2$, vinyl double bond), 1460 cm^{-1} (deformation vibrations, $-OCH_3$), 1610, 1508, 860, 850, and 755 cm^{-1} (1,2,4,5-tetrasubstituted benzene), and 1617 and 1220 cm^{-1} and 1205 and 1040 cm^{-1} (phenolic ether).

The integration curve of the NMR spectrum showed the presence of 16 protons.

The NMR spectrum contained signals at 3.61 ppm (9 H, m, 3 OCH_3), 3.10 ppm (2 H, d, benzyl proton), 4.82 ppm (2 H, m, allyl methylene), 5.75 ppm (1 H, m, olefinic methine, $CH{=}CH_2$), and 6.25 and 6.45 ppm (1 H and 1 H, s, aromatic protons).

The spectral characteristics given confirm the structure of the compound as 2,4,5-trimethoxyallylbenzene [18].

Compound F: bp 59-60°C, composition $C_{15}H_{24}O$ (M^+ 220), yield 0.7 g. TLC on silica gel gave a spot which was colored pink by vanillin/sulfuric acid. It was identified as caryophyllene oxide on the basis of the results of a comparison of the IR and NMR spectra of compound F and an authentic sample.

The ethereal fraction, 1.5 g of neutral oil, was chromatographed on a column containing silica gel (1:50). This yielded compound G.

Compound G: bp 170°C/3.5 mm Hg, yield 0.75 g, composition $C_{11}H_{18}O_2$ (M^+ 182).

The IR spectrum contained absorption bands at 2975 and 2930 cm^{-1} (stretching vibrations of C-H bonds), 1730 cm^{-1} (α, β-unsaturated carbonyl with a double bond in a five-membered ring), 1670 cm^{-1} (tetrasubstituted alkene), 1450 (deformation vibrations of an $-OCH_3$ group), 1380 and 1340 cm^{-1} (isopropyl group), and 1320 cm^{-1} (ester carbonyl).

The NMR spectrum showed signals at 1.10 ppm (6 H, d, isopropyl group), 2.1 ppm (3 H, s, methyl group), 1.64 ppm (5 H, t, protons of a cyclopentene ring), 4.45 ppm (1 H, d, benzyl proton), and 5.18 ppm (3 H, m, methyl proton, $-COOCH_3$).

On the basis of the results of elementary analysis and spectral characteristics it was concluded that the compound was methyl 5-isopropyl-2-methylcyclopentenecarboxylate.

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