longueur 5 m dia 2 mm. Conditions: isotherme à 120°. Débit d'azote 40 ml/min; temps de rétention: **10**: 2.88 min; **17**: 6.55 min; **14**: 3.58 min; **19**: 9.32 min; **20**: 11.90 min.

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BIBLIOGRAPHIE

1. Fenical, W. (1975) *J. Phycol.* **11**, 245.
2. McConnell, O. et Fenical, W. (1977) *Phytochemistry* **16**, 367.
3. Burreson, B. J. et Moore, R. E. (1975) *Tetrahedron Letters* 473.
4. Burreson B. J., Moore, R. E. et Roller, P. P. (1976) *J. Agric. Food Chem.* **24** (4), 856.
5. Moore, R. E. (1977) *Accounts of Chemical Research* **10**, 40.
6. Fenical, W. (1974) *Tetrahedron Letters*, 4463.
7. Woolard, F. X., Moore, R. E. et Roller, P. P. (1976) *Tetrahedron* **32**, 2843.
8. Codomier, L., Bruneau, Y., Combaut, G. et Teste, J. (1977) *C. R. Acad. Sci. Paris, Série D* **284**, 1163.
9. Codomier, L., Segot, M., Bruneau, Y., Combaut, G. et Teste, J. Manuscrit en préparation.
10. Rappe, C. (1963) *Ark. Kemi* **21**, 503.
11. Chihara, M. *Science Reports of the Tokyo Kyoiku Daigaku 1961, Section B* **10**, 145.
12. Chihara, M. *Science reports of the Tokyo Kyoiku Daigaku 1961, Section B* **10**, 1.

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UMBELACTONE (4-HYDROXYMETHYL-3-METHYL-BUT-2-ENE-4,1-OLIDE) NEW CONSTITUENT OF *MEMYCELON UMBELATUM**

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(*Received* 29 *November* 1977)

Key Word Index—*Memycelon umbelatum*; Melastomaceae; umbelactone; β-amyrin, sitosterol; oleanolic acid; ursolic acid; sitosterol-β- D-glucoside.

INTRODUCTION

Memycelon umbelatum Burm. is reported to be effective in various ailments [1]. The crude plant extract showed activity against Ranikhe disease virus and exhibited spasmolytic and antiamphetamine activities [2]. This communication describes the results of a detailed chemical examination on this plant.

RESULTS AND DISCUSSION

The alcoholic extract of *M. umbelatum* was defatted with petrol and the residual portion was fractionated into $CHCl_3$ and BuOH-soluble fractions. Purification of the petrol and the $CHCl_3$ soluble fractions by various chromatographic procedures led to the isolation of substances A, B, C, D, E and F. The new substance E has been named as umbelactone.

Umbelactone, mp 65°, $C_6H_8O_3$, $(\alpha)_D$ + 5.2° was very hygroscopic and gave a positive colour test for α, β-unsaturated lactone. The absorption bands at both 3435 and 1745 cm^{-1} in the IR spectrum of umbelactone indicated the presence of OH and a five membered lactone ring in the molecule respectively. The PMR spectrum showed signals at δ 2.08 for a vinylic Me, a broad singlet at 3.38 (D_2O exchangeable) for one OH proton, an octet at 3.80 (J_{gem} = 21, J_{vic} (*trans*) = 12.5 and J_{vic} (*cis*) = 3.5 Hz) for a methylene bearing oxygen function, and a multiplet centred at 5.84 ppm for an olefinic proton. The vinylic nature of the Me was confirmed by the solvent-induced upfield shift of the signal in benzene-d_6.

The ^{13}C NMR spectrum of umbelactone indicated six single lines for six carbons at 14.0, 63.6, 90.5, 123.5 176.5 and 183.5 ppm. The intensities of the last two of these lines were much reduced due to lack of NOE. The off resonance ^{13}C NMR spectrum showed a quartet due to a Me, a triplet for a methylene group, two pairs of doublets for two methine groups and two singlets for two quaternary carbons. The quaternary carbons could be assigned readily as the one at lowest field position (183.5) belonging to the lactone carbonyl and that at 176.5 ppm to the vinylic methyl bearing carbon of an α, β-unsaturated lactone system.

Umbelactone formed a monoacetate as a viscous oil, $C_8H_{10}O_4$ (M^+, *m/e* 170), whose PMR spectrum displayed signals for one acetoxy Me at 2.07 ppm. The spectrum further exhibited the octet shifted downfield at 4.4 ppm confirming the presence of a primary OH in the molecule. Catalytic hydrogenation of umbelactone gave a dihydro product which although TLC pure, was indicated by its PMR spectrum to be a mixture of two isomers.

Thus, the structure of umbelactone has been assigned as 4-hydroxymethyl-3-methyl-but-2-ene-4,1-olide (**1**).

Substance A was obtained as colourless needles, mp 196–198° and identified as β-amyrin (mp, mmp, TLC, IR, PMR).

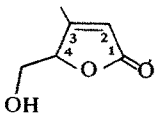
* CDRI Communication No. 2373.

Substance B was identified as sitosterol, mp 136°; $(\alpha)_D$ −39° (*c*, 2.0 $CHCl_3$); Acetyl derivative mp 128°.

Substance C was shown to be oleanolic acid, mp 307–309°. Methyl ester, mp 223–224° (mmp, TLC, IR, PMR).

Substance D was ursolic acid, mp 290–291°; Methyl ester acetate mp 245–247° (mmp, TLC, IR, PMR).

Substance F was sitosterol-β-D-glucoside, mp 227–228°; $(\alpha)_D$ −46°, positive Fiegel test. On hydrolysis, it gave an aglycone, mp 136° identified as sitosterol and the aqueous portion was shown to contain glucose.



1

EXPERIMENTAL

Mps are uncorrected. PMR spectra were recorded in $CDCl_3$ unless otherwise stated.

The powdered aerial part of the plant (7.5 kg) was extracted with EtOH (66%, 180 l.) at room temp. The total EtOH extract was conc. under red. press. to a dark green viscous mass (750 g) which was successively macerated with C_6H_{14}, $CHCl_3$ and *n*-BuOH. A portion of the hexane fraction (10 g) was chromatographed on neutral alumina (activity 2.5, 300 g), the C_6H_6–C_6H_{14} (1:1) eluate gave colourless needles from EtOH of substance A, mp 196–198°, 50 mg. The residue from the C_6H_6 eluate afforded colourless needles from EtOH of substance B, mp 136°, 200 mg.

The dark green $CHCl_3$-soluble fraction (110 g) was treated with charcoal, filtered and conc. to a viscous residue (68 g). It was chromatographed over Si gel (1.5 kg) the C_6H_6-MeOH (3–5%) eluates gave colourless needles from EtOH of substance C mp 307–309°, 400 mg and substance D, mp 290–291°, 230 mg. The successive elution of the column with EtOAc yielded a fraction (6.9 g) containing substance E and with EtOAc–MeOH (5:95) was obtained substance F (1.0 g) which crystallised from EtOH, mp 277–278°. The fraction containing substance E was rechromatographed over Si gel (300 g), the C_6H_6–EtOAc (1:1) eluates gave 2.0 g substance E (umbelactone) as light cream needles from C_6H_6, mp 65°.

Umbelactone, mp 65°, $(\alpha)_D$ + 5.2°, R_f 0.44 (C_6H_6–EtOAc, 1:1) on $AgNO_3$–Si gel plates. It was soluble in H_2O as well as $CHCl_3$. IR ν_{max}^{KBr} cm^{-1}; 3435, 2920, 2865, 1745 (broad), 1640, 1432, 1305, 1150, 1043, 940 and 855. UV: λ_{max}^{MeOH} 221 nm. PMR: δ 2.08 (3H, *m*, main coupling J = 1.5 Hz, Me), 3.38 (1H, *br s*, OH D_2O exchangeable), 3.80 (2H, *octet*, J = 21, 12.5 and 3.5 Hz, $-CH_2-O-$), 4.91 (1H, *m*, —CHO—) and 5.84 (1H, *m*, olefinic); PMR (C_6D_6): 1.53 (3H, Me), 3.08 (1H, *br s*, OH, D_2O exchangeable), 3.6 (2H, *octet*, J = 21, 12.5, 4 Hz, $-CH_2O-$), 4.4 (1H, *m*, —CHO—) and 5.57 (1H, *m*, olefinic). ^{13}C NMR ($CDCl_3$): δ 14.0 (C-6), 63.6 (C-5), 90.5 (C-2), 123.5 (C-4), 176.5 (C-3), 183.5 (C-1). Off resonance ^{13}C NMR: δ 14.0 (C-6, *q*), 63.6 (C-5, *t*), 90.5 (C-2, *d*), 123.5 (C-4, *d*), 176.5 (C-3, *s*), 183.5 (C-1, *s*). MS: *m/e* 128 (M^+), 97,68. (Found: C, 56.4; H, 6.22 $C_6H_8O_3$ requires C, 56.25; H, 6.25%).

Umbelactone acetate: Umbelactone (100 mg) in dry Py (0.5 ml) was reacted with Ac_2O (0.5 ml) overnight at room temp. Work up as usual gave a yellow oily residue which was chromatographed over Si gel. The elution with C_6H_6–MeOH (97:3) gave umbelactone acetate as a colourless viscous mass (95 mg). IR ν_{max}^{Neat} cm^{-1}: 2920, 1755, 1650, 1450, 1390, 1235, 1160, 1060, 955 and 900. UV: λ_{max}^{MeOH} 212, 258 nm. PMR: δ 2.07 (3H, *s*, —OCOMe), 2.15 (3H, *m*, Me), 4.4 (2H, *octet*, J = 20, 12.5 and 3 Hz, CH_2OAc), 5.09 (1H, *m*, —CHO) and 5.9 (1H, *m*, olefinic); PMR (C_6D_6): δ 1.23 (3H, *m*, Me), 1.48 (3H, *s*, —OCOMe), 3.82 (2H, *octet*; J = 20, 12.5, 3.0 Hz, $-CH_2OAc$), 4.17 (1H, *m*, —CHO—) and 5.32 (1H, *m*, olefinic). (Found: C, 55.02; H, 5.60 $C_8H_{10}O_4$ requires C, 55.29; H, 5.88%).

Dihydroumbelactone: Umbelactone (100 mg), EtOH (5 ml) and Pd/C (10%, 100 mg) were shaken in a H_2 atmosphere for 6 hr at room temp. It was worked up to get an oily mass which was chromatographed over a Si gel column. The C_6H_6–EtOAc (1:1) eluate yielded the hydrogenated product (80 mg) as a colourless liquid, R_f 0.5 (EtOAc–C_6H_6, 1:1). IR ν_{max}^{Neat} cm^{-1} 3370, 2900, 1740, 1430, 1395, 1167, 1092, 1035, 998 and 932.

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REFERENCES

1. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 165. Council of Scientific & Industrial Research, New Delhi.
2. Dhar, M. L., Dhar, M. M., Dhawan, B. N., Mehrotra, B. N. and Ray, C. (1968) *Indian J. Exp. Biol.* **6**, 241.

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ACIDIC COMPONENTS IN ESSENTIAL OILS OF COSTUS ROOT, PATCHOULI AND OLIBANUM

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Key Word Index—*Saussurea lappa*; Compositae; *Pogostemon cablin*; Labiatae; *Boswellia* sp., Burseraceae; essential oils; organic acids; phenols.

We wish to report on our results of the analysis of the acidic fraction of three essential oils in which we found important scent compounds, i.e. olibanum oil, patchouli oil and costus root oil.

Costus root oil (oil from the roots of the Costus plant, *Saussurea lappa* Clarke)

The acidic fraction was isolated by extraction of the oil with an ice cold soln of $NaHCO_3$ (no stronger base was used to avoid cleavage of the abundantly present lactones [1]); the aq. layer was washed several times with Et_2O, acidified at 0° with dil. HCl and subsequently extracted with Et_2O. After evapn of the solvent, the residue was analysed by GC–MS. Compounds remain-