(acetoxy carbonyl), 1385, 875 (terminal methylene). NMR, δ 4.30 (2H, *d*, *cis* olefinic protons at C-6 and C-7, 4.21 (2H, *s*, terminate methylene protons at C-24), 4.15–3.75 (1H, *br*, H-3), 1.69 (3H, *s*, acetoxy methyl), 1.1–1.55 (22H, complex, *m*, ring methylene protons, side chain methylene protons and methine protons at C-9, C-13, C-17 and C-25), 0.70 (6H, *s*, gem dimethyl at C-26 and C-27), 0.83 (3H, *s*, Me-18), 0.9 (3H, *s*, deshielded tertiary methyl protons at C_{21}), 0.45 (3H, *s*, Me-19). (Found: C, 79.28, H, 10.24. $C_{30}H_{46}O_3$ requires: C, 79.25; H, 10.20%.)

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REFERENCES

1. Takemoto, T., Ogawa, S., Mishimoto, N., Yen, K. Y., Abe, K., Sato, T. and Takashi, M. (1967) *Yakugaku Zasshi* **87**, 1521.
2. Takemoto, T., Hikino, Y. and Mishimoto, N. (1967) *Yakugaku Zasshi* **87**, 325.
3. Takemoto, T., Nomoto, N. and Himino, H. (1968) *Tetrahedron Letters*. 4953.
4. Galbraith, M. N., Horn, D. H. S., Middleton, E. J. and Hackney, R. J. (1968) *Chem. Commum*. 466.
5. Bhacca, S. N. and Williams, D. H. (1964) in *Application of NMR Spectroscopy in Organic Chemistry*. Holden-Day, San Francisco.
6. Cohen, C. F., Louloudes, S. J. and Thompson, M. J. (1967) *Steroids* **9**, 591.

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A DAMMARANE TRITERPENE FROM *COMMELINA UNDULATA**

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Key Word Index—*Commelina undulata*; Commelinaceae; dammarane triterpene; dammar-12, 25-dien-3β-acetate.

Abstract—The chemical investigation of *Commelina undulata* afforded, in addition to 2-heneicosanone, *n*-octacosanol, sitosterol and sitosterol-β-D-glucoside, a new triterpene characterized as dammar-12,25-dien-3β-acetate.

INTRODUCTION

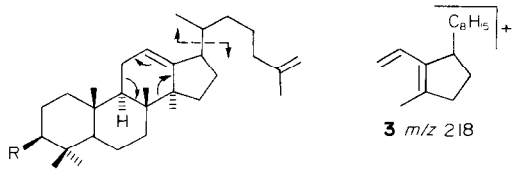
In the course of our search for anti-cancer constituents in Indian plants, we have examined *Commelina undulata* which possessed anti-cancer activity against lymphoid leukaemia in mice (PS 388) in the screening programme of NIH. A new triterpene (**1**) of the dammarane series was isolated together with 2-heneicosanone, *n*-octacosanol, sitosterol and sitosterol-β-D-glucoside.

RESULTS AND DISCUSSION

Systematic fractionations of an alcoholic extract of the plant was carried out with hexane, benzene, ethyl acetate and *n*-butanol. The crystalline compound **1** was isolated by CC from the hexane fraction over Si gel.

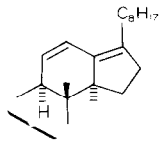
The IR spectrum of compound **1** had absorption bands at 1740 (C = O); 1384, 1370 (gem methyls); 1245 (C–O–C), 1660, 1640, 985 and 885 cm^{-1} (C=CH and C=CH_2). The UV spectrum had λ_{max} at 240 nm (ϵ = 523). The compound exhibited a positive Liebermann–Burchardt test and gave a yellow colouration with tetranitromethane. The ^1H NMR spectrum showed five tertiary methyl signals at δ 0.73, 0.8, 0.82 (6H) and 0.88 and a signal at 0.95 (3H, *d*, J = 7 Hz), assigned to Me-20[1]. The methylene and methine protons were in the range δ1.55–1.08. A vinylic methyl appeared at 1.6 (3H, *s*) and an acetoxyl methyl singlet was at δ1.95. A multiplet was centered at 2.25 (4H, H-11 and H-24) and the signals at 4.6 and 4.48 (*d*, J = 2 Hz) were assigned to the C-26 methylene protons. The signal at 4.36 (1H, *dd*, $J_{ax,ax}$ = 10 Hz, $J_{ax,eq}$ = 6.5 Hz,) was assigned to the C-3α proton and an olefinic proton was observed at 5.1 (1H, *m*, H-12). The mass spectrum of this compound had the M^+ at *m/z* 468 and other ions at *m/z* 453 $[M-Me]^+$, 425 $[M-\overset{O}{\overset{\|}{C}}-Me]^+$ and 408 $[M-MeCO_2H]^+$. The presence of side chain and C-12 double bonds in the molecule was evident from the ion peak at *m/z*

*CDRI communication no. 3058.



1 R = OAc
2 R = OH

3 *m/z* 218



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357 $[M-C_8H_{15}]^+$ and the prominent fragment at *m/z* 218 (3) formed through retro Diels–Alder fission of ring C.

From the above spectral data it is evident that the compound belongs to the dammarane series [1, 2] with an acetoxyl group at C-3 and two double bonds, one in the C-ring and the other in the side chain. The presence of the side chain double bond was further confirmed through catalytic hydrogenation of compound **1** which gave a dihydro product, dammarenyl acetate, mp 197° (MeOH), $C_{32}H_{54}O_2$ (M^+470). The signal at 0.85 (6H, *d*, $J = 7$ Hz) and the absence of a vinylic methyl and methylene proton signals in the ^{1}H NMR spectrum of the dihydo product established the presence of a terminal isopropyl group in the molecule.

Alkaline hydrolysis of compound **1** yielded the deacetylated product **2**, mp 182–184° (MeOH), $[\alpha]_D$ + 116° ($CHCl_3$; *c* 0.82), $C_{30}H_{50}O$(M^+426). Its IR spectrum had a band at 3400 cm^{-1} (–OH). The ^{1}H NMR spectrum had signals at δ3.36 (1H, *dd*, $J_{ax,ax} = 10$ Hz, $J_{ax,eq} = 6$ Hz) which were assigned to the secondary carbinol proton at C-3, which was deshielded by δ1.0 on acetylation.

The major product isolated after selenium dioxide oxidation of dammarenyl acetate was the heteroannular diene, **4** [3], mp 163–164° (MeOH), (M^+468). The UV spectrum of compound **4** had three λ_{max} at 242 ($\epsilon = 6598$) 250 ($\epsilon = 32\,090$) and 260 nm [4–6] and the IR spectrum had a C–H deformation band at 975 cm^{-1}, characteristic for a *trans*-diene. The ^{1}H NMR spectrum of compound **4** displayed one of the ethylenic protons at δ5.4 (*dd*, $J = 10$, 1.5 Hz, H-12) and the other at 6.25 (*dd*, $J = 10$, 3.2 Hz, H-11).

Column chromatography of the benzene fraction over Si gel yielded a minor compound **2** $C_{30}H_{50}O$ (M^+426), mp 182–83° (MeOH), which was found to be identical in all respects (mmp, IR, NMR, MS and co-TLC) with the compound obtained through the alkali treatment of dammar-12, 25-dien-3β-acetate (**1**).

EXPERIMENTAL

Mps are uncorr.

Isolation of dammaradienyl acetate (**1**). The air-dried powdered herb (10 kg) was extracted with EtOH. The residue obtained was fractionated successively with C_6H_{14} (5 × 2 l.), C_6H_6 (3 × 1 l.), EtOAc (3 × 1 l.) and *n*-BuOH (2 × 1 l.). The C_6H_{14} extract (238 g) was concd and chromatographed over Si gel. Elution with C_6H_{14}–C_6H_6 (1:1) yielded dammaradienyl acetate (**1**) crystallized from MeOH (0.5 g) mp 177–178°; $[\alpha]_D$ + 113° (pyridine *c* 0.7). (Found: C, 81.55; H, 10.69; Calc. for $C_{32}H_{52}O_2$, C, 82.05; H, 11.11%.)

Dammarenyl acetate. A soln of **1** (50 mg) in EtOAc was hydrogenated with PtO_2 for 3 hr. The product was crystallized from MeOH, mp 197°; $[M]^+$ at *m/z* 470 ($C_{32}H_{54}O_2$); IR ν_{max}^{KBr} cm^{-1}: 2925, 1735, 1450, 1380, 1365, 1245, 1100, 1025 and 800; ^{1}H NMR (90 MH_3, $CDCl_3$): δ0.75 (3H, *s*), 0.78 (3H, *s*), 0.82 (6H, *s*), 0.84 (3H, *s*), 0.85 (6H, *d*, $J = 7$ Hz), 0.99 (3H, *d*, $J = 7$ Hz), 1.1–1.8 (23H, *m*), 0.95 (3H, *s*, –C(=O)–Me), 2.64 (2H, *m*), 4.4 (1H, *dd*, $J = 10$, 6 Hz) and 5.04 (1H, *m*).

Selenium dioxide oxidation. A soln of the dammarenyl acetate (30 mg) in AcOH (5 ml) and H_2O (2 ml) was refluxed with freshly sublimed SeO_2 (60 mg) for 10 hr. After adding NaOAc it was again refluxed for another 2 hr. The reaction mixture was poured into 50 ml H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with $NaHCO_3$ and then with H_2O and finally dried over Na_2SO_4. The products were separated by prep. TLC on Si gel. The major product was a heteroannular diene (**4**), mp 163° (MeOH) IR ν_{max}^{KBr} cm^{-1}: 2900, 1730, 1700 (sh), 1460, 1380, 1365, 1250, 1025, 980 and 800; UV λ_{max}^{MeOH} nm: 242 ($\epsilon = 6598$), 250 ($\epsilon = 32\,090$) and 260 nm; ^{1}H NMR ($CDCl_3$): δ0.7 (3H, *s*), 0.78 (3H, *s*), 0.8 (6H, *s*), 0.85 (3H, *s*), 0.85 (6H, *d*, $J = 7$ Hz), 0.95 (3H, *d*, $J = 7$ Hz), 1.0–1.85 (20H, *m*), 1.98 (3H, *s*), 2.1–2.7 (4H, *m*), 4.4 (1H, *dd*, $J = 10$, 6 Hz), 5.4 (*dd*, $J = 10$, 1.5 Hz, H-12) and 6.25 (*dd*, $J = 10$, 3.2 Hz, H-11); MS, *m/z*: 468 $[M]^+$, 451, 410, 406, 271, 229, 218 (100%), 203, 189, 133, 135, 121, 119, 113, 111 and 107.

Alkaline hydrolysis of. A soln of **1** in 5% methanolic KOH was refluxed for 4 hr to give dammaradienol (**2**) mp 182–83° (MeOH), $[\alpha]_D$ + 116° ($CHCl_3$; *c* 0.82), IR, ν_{max}^{KBr} cm^{-1}: 3350, 1660 (sh), 1640, 1460, 1380, 1360, 1180, 1140, 1100, 1030, 990, 880 and 760 ^{1}H NMR($CDCl_3$): 0.7, 0.72, 0.75, 0.88, 0.9 (each singlet equivalent to 3H), 0.95 (3H, *d*, $J = 6$ Hz) 1.3–1.5 (1H, *m*, OH), 3.35 (1H, *dd*, $J = 10$, 6 Hz), 4.48, 4.6 (each equivalent to 1H, both *d*, $J = 2$ Hz, H-26H) and 5.2 (1H, *m*); MS, *m/z*: 426 $[M]^+$, 411, 408 $[M-H_2O]^+$, 393, 315, 313, 218 (100%), 203, 189, 175, 161, 149, 147, 135, 123, 121, 111, 109, 107 and 97.

REFERENCES

1. Barnes, C. S., Galbraith, M. N., Ritchie, E. and Taylor, W. C. (1965) *Aust. J. Chem.* **18**, 1411.
2. Talpatra, S. K., Bhar, D. S. and Talapatra, B. (1974) *Aust. J. Chem.* **27**, 1137.
3. Budziarek, R., Manson, W. and Spring, F. S. (1951) *J. Chem. Soc.* 3336.
4. Scott, A. I. (1964) *Interpretation of the Ultraviolet Spectra of Natural Products* Vol. 7, p. 51.
5. Fischer, G. F. and Seiler, N. (1961) *Ann. Chem.* **644**, 162.
6. Arigoni, von D., Jeger, O. and Ruzicka, L. (1955) *Helv. Chim. Acta* **38**, 222.