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A FERNANE-TYPE TRITERPENE FROM *SERICOSTOMA PAUCIFLORUM*

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**ABSTRACT.**—Phytochemical studies on *Sericostoma pauciflorum* stocks provided  $\alpha$ -amyrin,  $\beta$ -amyrin,  $\beta$ -amyrin acetate, and sericostinyl acetate [**1**], a new fernane-type triterpene, whose structure has been elucidated as ferna-7,9(11)-dien-20 $\beta$ -yl acetate on the basis of spectroscopic studies including 2D nmr.

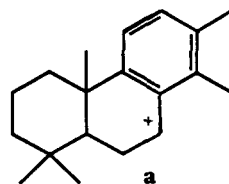
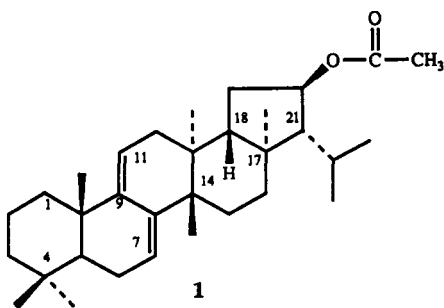
So far, no report of chemical work on species of the genus *Sericostoma* (Boraginaceae) has appeared. Some *Sericostoma* spp. have close morphological resemblance to *Heliotropium* spp., which are reputed to possess antitumor, carcinogenic, diuretic, laxative, and emetic activities (1,2). The genus comprises eight species distributed through the tropical east and northeast of Africa to northwest India. In Pakistan there is only one species, *Sericostoma pauciflorum* stocks ex Wight, a short straggling undershrub. We have isolated four crystalline compounds identified as triterpenes from the petroleum ether extract. Three were found to be  $\alpha$ -amyrin,  $\beta$ -amyrin, and  $\beta$ -amyrin acetate, while the fourth was sericostinyl acetate [**1**], a new triterpene of the fernane (migrated hopane) series.

Sericostinyl acetate [**1**] gave a tetranitromethane color reaction for unsaturation, and the molecular ion peak at  $m/z$  466.3799 (hrms) corresponded to the molecular formula  $C_{32}H_{50}O_2$  (calcd 466.3798). The ir spectrum showed the

presence of an ester (bands at 1710 and 1220  $cm^{-1}$ ), a conjugated trisubstituted  $C=C$  (1660  $cm^{-1}$ ), and a *gem*-dimethyl group (1325 and 1310  $cm^{-1}$ ).

Uv maxima were characteristic for 7,9(11)-dienes with 13 $\alpha$ , 14 $\beta$  methyl groups (3). The  $^1H$ -nmr spectrum revealed two trisubstituted double bonds (dds at  $\delta$  6.17 and 5.45), an acetate group (s at  $\delta$  2.04), a proton geminal to the acetoxy group (q at  $\delta$  4.49), two secondary methyl groups (doublets at  $\delta$  0.85 and 0.94), and six tertiary methyl groups. The  $^{13}C$ -nmr spectrum indicated the presence of 32 carbon atoms; their multiplicities were determined by DEPT experiments keeping the last pulse angle  $\theta = 45^\circ, 90^\circ, \text{an } 135^\circ$  (4,5). Compound **1** showed the presence of nine methyl, eight methylene, and seven methine carbons.

The hrms showed diagnostic fragments at  $m/z$  451.3501 [ $C_{32}H_{50}O_2 - Me$ ] $^+$ , 406.3625 [ $C_{32}H_{50}O_2 - C_2H_4O_2$ ] $^+$ , and 423.3291 [ $C_{32}H_{50}O_2 - C_3H_7$ ] $^+$ , resulting from loss of a methyl group, an ace-



tic acid, and an isopropyl moiety, respectively. Another ion at  $m/z$  391.3353 represented simultaneous loss of a methyl group and acetic acid. The base peak at  $m/z$  255.2115 ( $C_{19}H_{27}$ ) was due to ion **a**, characteristic of ferna-7,9(11)-diene or arboradiene carrying an acetoxy group in rings D/E (3). The presence of an isopropyl group, however, allowed us to assign the fernane type skeleton to **1**, the only problem remaining being the allocation of the acetoxy group. A careful comparison of the  $^1H$ -nmr spectrum of **1** with that of ferna-7,9(11)-diene (6) showed that, of the eight methyl signals in the two compounds, five at 4, 4, 10, 13, and 14 have good agreement, revealing similarity in structure and stereochemistry of rings A–D. The downfield shift of three other methyl signals at 17, 22, 22 in the case of **1** should be due to the influence of the acetoxy group in ring E. Such downfield shifts of these methyl groups have already been reported for fern-9(11)-en-20- $\beta$ -ol (7).

The presence of an acetoxy function in ring E at C-20 in  $\beta$  and equatorial orientation was finally demonstrated by a combination of selective homodecoupling experiments, using  $^1H$ - $^1H$ - and  $^1H$ - $^{13}C$ -correlated spectroscopy. The proton geminal to the acetoxy group at  $\delta$  4.49 showed cross peaks with proton signals at  $\delta$  1.65 and  $\delta$  1.17 in the COSY-45° spectrum. The latter in turn showed cross peaks with carbon signals at  $\delta$  59.30 and 23.56 in the hetero-COSY spectrum; these were found to be methylene and methine carbons by DEPT experiments, thereby confirming the presence of an acetoxy group at position 19/20. Irradiation at either of the methyl doublets simplified the multiplet at  $\delta$  1.19 which could, therefore, be assigned to the methine proton of the isopropyl moiety. On the other hand, irradiation at  $\delta$  1.19 caused the double doublet at  $\delta$  1.17 to collapse into a doublet showing an axial-axial coupling of 6.21 Hz with the neighboring proton. The signal at  $\delta$  1.17 could, there-

fore, be assigned for  $\beta$  and the axial proton at C-21. The connectivity of this proton to the proton geminal to the acetoxy group confirmed the position of the latter at C-20 in  $\beta$  and equatorial orientation. The stereostructure of **1** could, therefore, be suggested as shown.

The fernane-type triterpenes are a rare class of compounds which, to date, have been isolated only from ferns. The present report constitutes the first example of their occurrence in other plants, which may be of chemotaxonomic importance.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The ir spectra were recorded on a JASCO A-302 spectrometer. Hrms and eims were recorded on a Finnigan MAT-312 mass spectrometer connected to a PDP 11/34 (DEC) computer system. The  $^1H$ - and  $^{13}C$ -nmr spectra were recorded on a Bruker AM-400 spectrometer with TMS as internal reference. The DEPT experiments were carried out with last pulse angle  $\theta = 45^\circ, 90^\circ, \text{ and } 135^\circ$ . The quaternary carbons were determined by subtraction of these spectra from the broad-band  $^{13}C$ -nmr spectrum.

PLANT MATERIAL.—The plant material was collected in Karachi, Pakistan and was identified by Prof. Dr. S.I. Ali, Plant Taxonomist, Department of Botany, University of Karachi, where a voucher specimen is deposited.

ISOLATION OF COMPOUNDS.—The freshly collected plant material (20 kg) was chopped in small pieces and then extracted thrice with MeOH (total 60 liters). The residue of the combined MeOH extract was partitioned with  $H_2O$  and petroleum ether. The petroleum ether fraction (10 g) was chromatographed over Si gel (400 g) and successively eluted with increasing polarities of a mixture of hexane and  $CHCl_3$ . The hexane- $CHCl_3$  (9:1 and 8:2) eluates yielded crystalline residues which on repeated crystallization from hexane/ $CHCl_3$  provided  $\beta$ -amyrin acetate (25 mg) and a mixture of triterpenes. The latter could be resolved through flash cc over Si gel using the same solvent system to yield  $\alpha$ -amyrin (12 mg) and  $\beta$ -amyrin (10 mg), respectively. All were identified by comparison of physical and spectral data with those reported in the literature (8,9). The eluate from hexane- $CHCl_3$  (7:3) yielded sericostinylnyl acetate [**1**] (20 mg), which crystallized from hexane/ $CHCl_3$ .

SERICOSTINYLNYL ACETATE [**1**].—Mp 268–270°;  $[\alpha]_D -12.34$  ( $c = 0.12, CHCl_3$ ); ir ( $CHCl_3$ )  $\nu$  max  $cm^{-1}$  1710, 1660, 1325, 1310,

1220; ms  $m/z$  (rel. int. %)  $[M]^+$  ( $C_{32}H_{50}O_2$ ) 466.3799 (90), 451.3501 (20), 423.3291 (22), 406.3625 (18), 391.3353 (12), 255.2115 (100%); uv (MeOH)  $\lambda$  max nm 232, 237, 250, 258;  $^1H$  nmr ( $CDCl_3$ , 400 MHz)  $\delta$  6.17 (1H, dd,  $J = 10.28$  and  $3.12$  Hz, H-7), 5.45 (1H, dd,  $J = 10.47$  and  $1.72$  Hz, H-11), 4.49 (1H, q, H-20), 2.04 (3H, s, Ac), 1.01 (3H, s, Me-25), 0.94 (3H, d,  $J = 6.58$  Hz, Me-30), 0.92 (3H, s, Me-26), 0.91 (3H, s, Me-27), 0.90 (3H, s, Me-28), 0.89 (3H, s, Me-24), 0.85 (3H, d,  $J = 6.10$  Hz, Me-29), 0.72 (3H, s, Me-23);  $^{13}C$  nmr ( $CDCl_3$ , 100.61 MHz)  $\delta$  39.10 (C-1), 18.56 (C-2), 26.46 (C-3), 38.01 (C-4), 55.21 (C-5), 27.95 (C-6), 126.81 (C-7), 131.52 (C-8), 147.03 (C-9), 40.76 (C-10), 123.86 (C-11), 32.91 (C-12), 36.85 (C-13), 33.74 (C-14), 29.71 (C-15), 37.12 (C-16), 43.76 (C-17), 54.12 (C-18), 23.56 (C-19), 80.95 (C-20), 59.30 (C-21), 40.15 (C-22), 27.82 (C-23), 17.58 (C-24), 26.38 (C-25), 18.19 (C-26), 16.17 (C-27), 17.89 (C-28), 21.22 (C-29), 23.00 (C-30), 29.57 ( $H_3CCO$ ), 170.85 ( $COCH_3$ ). The assignments were based on calculated values supported by hetero-COSY.

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