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PARTHENOLIDE AND A NEW GERMACRANOLIDE, 11,13-DEHYDROLANUGINOLIDE, FROM *MICHELIA LANUGINOSA*

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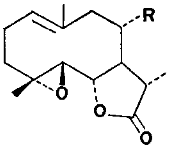
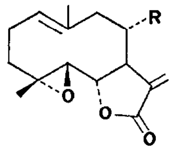
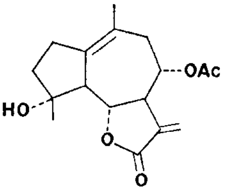
Michelia lanuginosa Wall (Magnoliaceae, tribe Magnolieae), one of the nine Indian *Michelia* species, is a small or large tree growing in the temperate Himalayas at an altitude of 1500–2500 m, from Nepal to Bhotan and in the Khasia hills.[1] The structural elucidation of a new oxoaporphine lanuginosine[2] and two germacranolides, dihydroparthenolide (I)[3] and lanuginolide (II),[3] from the mature trunk bark of this plant collected from Darjeeling district, had been reported by us earlier. From the less mature trunk bark collected in the same region, two other germacranolides having quite different R_fs, have been isolated from the $CHCl_3$ extract at room temp. by exhaustive chromatographic separation over silica gel. One of them, $C_{15}H_{20}O_3$ (M^+248), m.p. 115°, $[\alpha]_D$ −88° ($CHCl_3$, *c* 0·54) is identical (m.m.p., TLC, IR) with parthenolide (III)[4] isolated from *Michelia champaca* L. We wish to present here spectroscopic and chemical evidence in support of structure IV for the second compound, designated 11,13-dehydrolanuginolide.



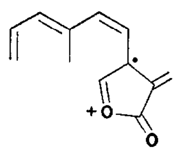
(I) R = H
(II) R = OAc



(III) R = H
(IV) R = OAc



(V)



a, *m/e* 188 (100%)

11,13-Dehydrolanuginolide (IV), a new thermally somewhat unstable germacranolide, $C_{17}H_{22}O_5$ (M^+306), crystallizes from $CHCl_3$–petrol. in flakes, m.p. 168°(d), $[\alpha]_D$ −96·5° ($CHCl_3$, *c* 0·74). It contains an α,β-unsaturated γ-lactone moiety [λ_{max} (ETOH) 215 nm (log ϵ, 3·82); ν_{max}(KBr) 1779 and 1647 cm^{-1}]. The IR spectrum also displayed characteristic bands at 1733 and 1233 (–OAc), 901 and 806 (epoxy ring), and 855 and 822 cm^{-1} (trisubstituted double bond). A careful analysis of its PMR spectrum (60 MHz, $CDCl_3$, TMS internal standard) and its comparison with that of lanuginolide (II)[3] permit its complete

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[1] HOOKER, J. D. (1875) *Flora of British India*, Vol. 1, p. 43, L. Reeve, London.

[2] TALAPATRA, S. K., PATRA, A. and TALAPATRA, B. (1969) *Chem. Ind.* (*London*) 1056.

[3] TALAPATRA, S. K., PATRA, A. and TALAPATRA, B. (1970) *Chem. Commun.* 1534.

[4] GOVINDACHARI, T. R., KAMAT, V. N. and JOSHI, B. S. (1965) *Tetrahedron* **21**, 1509.

structural elaboration. The appearance of the characteristic pair of doublets (slightly broad) at 5·75 ppm (1H, J 3 Hz) and 6·37 ppm (1H, J 3 Hz) in the PMR spectrum of IV in association with its UV and IR spectal characteristics suggested the presence of an exocyclic methylene group conjugated with the γ-lactone carbonyl function in it. These signals are absent from and are replaced by the secondary methyl doublet at 1·41 ppm (J 6 Hz) in the spectrum of lanuginolide (II).[3] The spectrum of IV also shows a set of signals at 1·28 (3H, *s*), 1·81 (3H, *s*), 2·0 (3H, *s*), 2·63 (1H, *d*, J 9·5 Hz) and 5·30 ppm (1H, *m*) similar to that of II, assignable to an epoxy methyl (4–Me), vinyl methyl (10–Me), acetate methyl (8–OCOMe), epoxy proton (H–5) and the vinyl proton (H–1) respectively. An important feature which deserves special mention is that the lactonic methine proton at C-6 appears as a double doublet at 4·25 ppm ($J_{6,5}$ 9·5 Hz, $J_{6,7}$ 7·5 Hz) and not as a triplet (J 9 Hz) as in the cases of I, II and III, thus strongly suggesting that in the preferred conformation of IV the dihedral angles HC_6-C_5H and HC_6-C_7H are significantly different[5,6] due to the combined influence of the $\Delta^{11,13}$ bond and the 8-α-acetoxy function, in contrast to the conformations of I, II and III, in each of which the said dihedral angles are expected to be nearly same.[5,6] IV also exhibited signals at 3·27 ppm (1H, *m*, H-7) and 4·59 ppm (1H, *m*, the acetoxy methine H-8).

The dihydroderivative of IV formed by its controlled hydrogenation (15 min) in EtOH solution in presence of Pd–C (10%) was found to be identical with lanuginolide (II) by direct comparison (TLC, m.m.p. and IR) thus confirming the structure and stereochemistry of IV. As in the cases of lanuginolide[3] and dihydroparthenolide[4] transannular cyclisation of IV, catalysed by BF_3 in Et_2O in N_2 atmosphere afforded the *t*-alcohol V, $C_{17}H_{22}O_5$ (M^+ 306), m.p. 200°, $[\alpha]_D$ +14° ($CHCl_3$, *c* 0·59); IR: ν_{max} (KBr) 3510 (–OH, broad), 1735 and 1242 (–OAc), 1777 and 1650 (α,β-unsaturated γ-lactone); peaks for epoxy ring and trisubstituted double bond absent. V remained unchanged after Ac_2O–py treatment and showed yellow colour with TNM.

The MS fragmentation of 11,13-dehydrolanuginolide (IV) is also consistent with its structure. The most important fragmentation involved the facile loss of the elements of HOAc from the very weak parent ion (0·5%) generating the ion with *m/e* 246 (65%) having a 7,8 or 8,9 double bond; subsequent cleavages of 3,4 and 5,6 bonds and expulsion of H-2 and H-9 (or H-7) led to the base peak at *m/e* 188 due to the resonance stablized radical ion *a*. The ion with *m/e* 246 underwent successive losses of the epoxy Me and the lactonic CO giving rise to peaks at *m/e* 231 (5%) and 203 (22%).

The occurrence of I and II in the mature trunk bark of *M. lanuginosa* collected earlier and of only III and IV in the trunk bark of the less mature plant might be biogenetically quite significant. It appears that the hydrogenation of 11,13-double bond of II and IV takes place only when the plant attains certain maturity. A voucher specimen No. M.1.2/71 has been preserved in this laboratory.

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[5] KARPLUS, M. (1959) *J. Chem. Phys.* **30**, 11.

[6] CONROY, H. (1960) in *Advances in Organic Chemistry* (RAPHAEL, R. A., TAYLOR, E. C. and WYNBERG, H., eds.), Vol. 2, p. 285, Interscience, New York.