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NERIIFOLIOL : A NEW PENTACYCLIC TRITERPENE ALCOHOL FROM OLEANDRA NERIIFOLIA

G. N. Pandey and C. R. Mitra
Utilization Research Laboratory,
National Botanic Gardens, Lucknow, India.

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The ferns of the genus Oleandra grow in the marshy hill slopes of the Eastern Himalayas as well as in the Khasia and Jayantia ranges. With a view to assess the economic importance of certain Pteridophytic flora, systematic chemical examination of the Oleandra genus has been carried out. The isolation and characterization of a new triterpene alcohol, provisionally named neriifoliol, from *Oleandra neriifolia* rhizomes (recently suggested, *O. pistillaris* (Sw) c. chr.), is reported here.

The benzene extractive of the shade-dried rhizones (coarsely powdered) when subjected to chromatography over alumina, the *n*-hexane-benzene eluent fraction yielded neriifoliol.

Neriifoliol, $C_{30}H_{52}O$, m.p. 242-244°, $(\alpha)_D$ +35° (mol. wt. 428, mass spectra) gives positive Liebermann-Burchard and Noller's tests and the TNM test with it is negative. It is optically transparent in the ultraviolet region and exhibits in its infrared spectra a peak at 3330 cm^{-1} (OH) with a supporting band at 1050 cm^{-1} indicating the hydroxyl function to be primary. The combination peaks at 1390 and 1370 cm^{-1} are indicative of *gem*-dimethyl. The

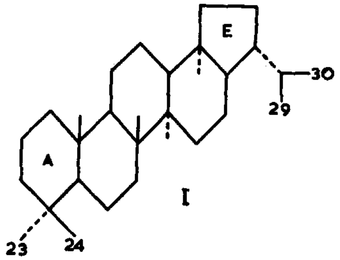
NMR spectra of the alcohol shows methyl signals at 44 (3H), 49.50 (6H), 51.5 (6H) and 58 (6H)cps., all corresponding to methyl groups.

Neriifoliol gives an acetate (acetic anhydride-pyridine) $C_{32}H_{54}O_2$, m.p. 195-96°, $(\alpha)_D$ +20°; ν_{max}^{KBr} 1730, 1235 cm^{-1} (acetate). When the alcohol is oxidised with chromium trioxide-pyridine slurry (1) at room temperature it gives an aldehyde, neriifolial, $C_{30}H_{50}O$, m.p. 76°, ν_{max}^{KBr} 1730 cm^{-1} and with chromium trioxide in acetic acid and benzene, it yields the corresponding acid, neriifolic acid, $C_{30}H_{50}O_2$, m.p. 270-74°; $(\alpha)_D$ +16°; ν_{max}^{KBr} 1730 cm^{-1} with an indefinite shoulder in the region 3571 to 3077 cm^{-1}. Neriifolial when oxidised with chromium trioxide in acetic acid and benzene also gives neriifolic acid. Methyl neriifoliate, $C_{31}H_{52}O_2$, m.p. 242-244°; $(\alpha)_D$ +8°; ν_{max}^{KBr} 1730 cm^{-1}; prepared with diazomethane when reduced with LAH in tetrahydrofuran, yielded the parent alcohol, neriifoliol.

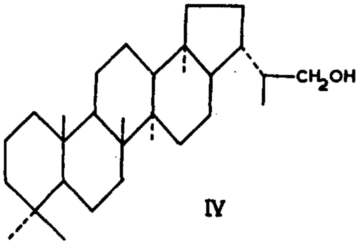
The above findings along with the biogenetic and chemotaxonomic considerations (2) suggested neriifoliol to be a pentacyclic triterpene alcohol having a hopane or modified hopane skeleton with a primary hydroxyl group. The presence of a primary hydroxyl group is also evidenced by the NMR spectra of neriifoliol. The appearance of a broad signal at τ 6.4 corresponding to two protons is attributed to the two protons of $-C\underline{H}_2-OH$. This signal was further resolved in two AB-quartets (J=11 cps.) indicating that the carbon atom to which CH_2OH is bonded, is assymetric.

Neriifoliol when subjected to Huang-Minlon modification (3) of Wolff-Kishner reduction gives the hydrocarbon, hopane (I),

$C_{30}H_{52}$, m.p. 190-192°; $(\alpha)_D$ +36°; identified by its superimposable IR spectra (4). Thus the carbon skeleton of neriifoliol is same



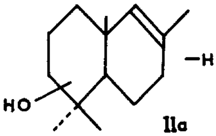
I



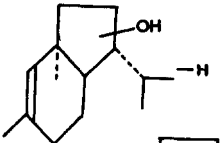
IV

as that of hopane. The nature of the hydroxyl group (primary) indicates it to be attached either to the gem-dimethyl or angular methyl groups or side chain. The relative ease with which methyl neriifoliate is hydrolysed (8 per cent alcoholic KOH for 6 hrs.) excludes any of the angular positions as the possible site for the carboxyl group in neriifolic acid as there is no activating group present in the molecule. Evidently C-23, 29 or 30 can be the possible positions for the carboxyl group as in case of medicagenic and desoxoglycyrrhetic acids (5,6). The position C-24 (axial) is also excluded as the methyl ester will then be saponified with great difficulty (cf. β-boswellic acid). It is, therefore, concluded that the primary hydroxyl group in neriifoliol is attached to C-23, C-29 or C-30.

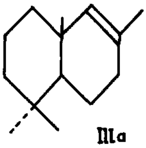
However, a study of the cracking pattern in the mass spectra of neriifoliol, reveals that the primary hydroxyl group is situated in the isopropyl side chain. The mass spectra gives molecular ion peak, M^+ at m/e 428. The peaks m/e 413 and 369 are due to the fragments formed from the molecular ion by the loss of 15 and 59 mass units which corresponds to the loss of a methyl (CH_3) and the isopropyl side chain carrying the primary hydroxyl function (C_3H_7O) and as there is no loss of 31 mass units (CH_2OH) to start with, the mass spectra firmly excludes the possibility of the hydroxyl being attached to the C-23 or C-24 or any other angular methyls and confirms its situation at C-29 or C-30. The splitting of ring C gives rise to the fragments having m/e 207 and 191. The peak m/e 207 may belong either to the left or right side of the molecule having oxygen in ring A (IIa) or ring E (IIb) or side chain as shown above. Similarly the peak m/e 191 may belong to the left or right side of the molecule (IIIa, IIIb). That the succeeding lower mass peak m/e 149 arises from the fragment m/e 207 with the loss of 58 mass units, is confirmed by the appearance of a metastable peak at m/e 107.2 (calculated value 107.3), which may be attributed to the loss of C_3H_6O unit, that is, the isopropyl side chain having the hydroxyl function, under transfer of one hydrogen. Thus the mass spectra of neriifoliol strongly favours the position C-29 (or C-30) for the primary hydroxyl function in a hopane nucleus and hence neriifoliol is assigned the structure IV.



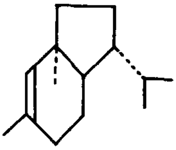
IIa



IIb



IIIa



IIIb

It is interesting that most of the triterpenes isolated from the ferns have hopane or modified hopane skeleton. A number of triterpenes having hopane nucleus have recently been isolated from lichens (7) as well as from higher plants. Neriifoliol however, appears to be the first triterpene alcohol with a primary hydroxyl function, isolated from a fern.

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