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REINVESTIGATION ON THE FERN OLEANDRA NERIFOLIA : ISOLATION OF A NEW TRITERPENE 29-ETHOXYHOPANE.

A.Goswami*, Asok Dasgupta, A.Nath,
T.K.Roy* and Late H.N.Khastgir,
Department of Chemistry,
North Bengal University,
Dt. Darjeeling, 734430, INDIA.

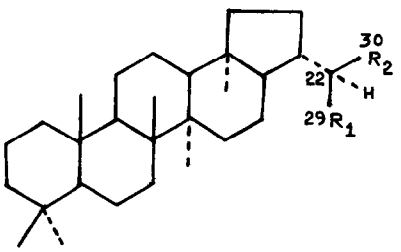
In 1967, Pandey and Mitra reported[1] the isolation of a new triterpene-alcohol, nerifoliol 1 from Oleandra nerifolia. Further investigation of the same source by us led to the isolation of a new triterpene, 29-ethoxyhopane 2, along with filicene, nerifoliol 1 and β-sitosterol.

The neutral part of the benzene extract of the rhizomes of Oleandra nerifolia on extensive chromatography followed by fractional crystallisation afforded the new triterpene 29-ethoxyhopane 2, $C_{32}H_{56}O$, m.p. 179-80°, $(\alpha)_D$ 27.16°, ν_{max}^{nujol} 1105 cm^{-1}, which gave a positive LB but negative TNM test. The PMR spectrum (80 MH_z) showed signals between δ 0.7 to 0.95 (seven CH_3 groups) and a broad multiplet in the region δ 2.8 to 3.6 (4H) indicating the presence of an ether linkage. The mass spectrum of 2 showed prominent peaks at m/e 456(M^+), 441 (M^+-CH_3), 411($M^+-OCH_2CH_3$), 396 ($M^+-CH_3-OCH_2CH_3$), 369 ($M^+-CH<^{CH_2OCH_2CH_3}_{CH_3}$), 235, 204, 191, 175 and 147. On the basis of all the above observations, along with the occurrence of 2 in the plant with 1, it was suggested that 2 contained a hopane type of nucleus with an ethoxy group in the isopropyl side chain.

A detailed study of the PMR spectra (80 MH_z) with plot expansion and decoupling at δ 1.175 ($-OCH_2\underline{CH_3}$) and δ 1.75 (H on C-22) confirmed the presence of the grouping $>CH-CH_2-O-CH_2-CH_3$ in 2.

Nerifoliol 1 on refluxing with potassium metal and ethyl iodide in benzene[2,3] was converted into its ethyl ether 2, identical with the new-triterpene 2 isolated from O. nerifolia. By the way, dryocrassol[4] 3 was similarly converted into its ethyl ether 4, m.p. 148-50°, ν_{max}^{nujol} 1110 cm^{-1} which was

found to be different from 2 isolated from O.nerifolia. Furthermore, the new triterpene 2 on treatment with anhydrous ferric chloride in ethyl acetate-acetic anhydride mixture[5] was converted into nerifoliol acetate 5. The new triterpene 2, being structurally related to nerifoliol 1 (possessing 22-R configuration[4]) possesses 22-R configuration. Thus the structure 2 was proposed for the new triterpene and it was named as 29-ethoxyhopane. Simple ethyl ethers are rare in nature and 2 is the first example of such compounds in ferns.



1, $R_1 = CH_2OH$, $R_2 = CH_3$.
2, $R_1 = CH_2OCH_2CH_3$, $R_2 = CH_3$.
3, $R_1 = CH_3$, $R_2 = CH_2OH$.
4, $R_1 = CH_3$, $R_2 = CH_2OCH_2CH_3$.
5, $R_1 = CH_2OCOCH_3$, $R_2 = CH_3$.

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