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OCCURRENCE OF 31-NORCYCLOARTANOL IN *SMILAX ASPERA* LINN.

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This communication deals with the isolation and characterisation of 31-norcycloartanol from the roots of *Smilax aspera* Linn. The powdered roots were extracted with hot ethanol and the extract concentrated under reduced pressure. The solvent-free residue was repeatedly extracted with ether. The combined ether solution was shaken with aqueous alkali, then washed neutral with water, dried and evaporated. The residue which on TLC showed the presence of two major and a minor component was chromatographed over neutral alumina. Petroleum ether-benzene (1:1) eluted a substance (referred to as A for convenience) which was identified as 31-norcycloartanol as described below. Benzene and benzene-chloroform (9:1) eluted a mixture of two substances. By fractionally crystallising it from chloroform-methanol it was possible to obtain the more soluble component in the pure state. It was identified as β-sitosterol $[\alpha]_D$ -42.3°, m.p. and m.m.p. 138°, and co-TLC with authentic specimen, confirmed by the preparation of its acetate m.p. and m.m.p. 127-128° and co-TLC with authentic specimen. The other component was isolated in pure form by preparatory TLC of the less soluble portion of the mixture. It was identified as sarsasapogenin (m.p., m.m.p. 200-203° and co-TLC with authentic sample). It has to be mentioned here that sarsasapogenin was present in the plant material under investigation (roots of *Smilax aspera*) in large quantities in combination with sugars as saponin.

The substance A crystallised as colourless plates from methanol or acetone, m.p. 132°, $[\alpha]_D^*$ +42° and analysed** for $C_{29}H_{50}O$. Liebermann-Burchard and TNM reactions positive. It formed an acetate (Py/Ac_2O, 38°, 24 hrs.) $C_{31}H_{52}O_2$, m.p. 102-103°, $[\alpha]_D$ +54.4°, and a benzoate (C_6H_5COCl/Py, 120°, 3 hrs.) $C_{36}H_{54}O_2$, m.p. 122-124°, $[\alpha]_D$ +65.1°. Oxidation of A with $K_2Cr_2O_7/H_2SO_4$ in acetone medium yielded a ketone $C_{29}H_{48}O$, m.p.104-106°, $[\alpha]_D$ +52.5°, which gave a positive Zimmermann colour reaction[1]. The NMR spectrum*** of A showed signals mainly in the alkyl region. Conspicuous were the methyl signals integrating to 18 protons and signals at δ 0.45 (doublet, J = 4 cps) integrating to one proton and at δ 0.2 (doublet, J = 4 cps) also integrating to one proton. In the acetate of A the last two signals were seen at δ 0.5 (doublet, J = 4 cps) and δ 0.2 (doublet, J = 4 cps). These high field signals indicate the presence of a cyclopropane ring in the molecule[2] and their actual values indicate that C_4 carries only one methyl group[3]. The elementary composition and properties of A and its derivatives indicated that the parent compound might be 31-norcycloartanol (see Fig.). This substance first prepared synthetically[4], has so far been isolated from only one natural source, namely the fern Polypodium vulgare Linn.[5] The identity was confirmed by direct comparison with an authentic sample kindly provided by Professor G. Berti (mixed m.p., TLC and superimposable IR spectra). It is interesting to note that Polypodium vulgare is a cryptogam and Smilax aspera is a phanerogam.

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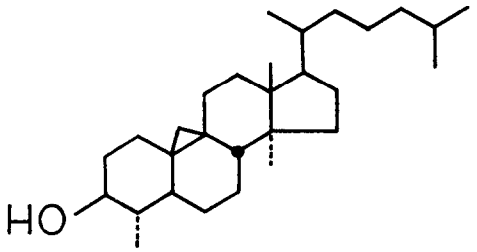
* All rotations were taken in chloroform solution.

** All the compounds whose formulae are given in this communication analysed correctly for C & H.

*** NMR spectra were recorded in $CDCl_3$ solution on a Varian A-60 instrument with TMS as internal standard.

As a result of their findings in tobacco tissue culture experiments, Benveniste et al.[6] suggested that in these cultures cycloartenol may replace lanosterol as an intermediate in the biosynthesis of phytosterols. Berti et al.[5] who isolated cycloartanol, 31-norcycloartanol, cycloleudenol and 31-norcycloleudenol from Polypodium vulgare suggested that these could constitute metabolic intermediates for the transformation of a common precursor, probably cycloartenol, into steroid compounds. The occurrence reported in the present communication of 31-norcycloartanol along with β-sitosterol and steroid sapogenins [sarsasapogenin and two others (unpublished work of the authors)] in the same plant seems to support the above suggestions.



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REFERENCES

1. D.H.R. Barton and P. de Mayo, J. Chem. Soc. 1964, 890.
2. R. Mc Crindle and C. Djerassi, Chemistry and Industry, 1961, 1311.
3. G. Berti, F. Bottari, B. Macchia, A. Marsili, G. Ourisson and H. Piotrowska, Bull. Soc. Chim. France, 1964, 2359.
4. J.S.G. Cox, F.E. King and T.J. King, J. Chem. Soc., 1956, 1384.
5. G. Berti, F. Bottari, A. Marsili, I. Morelli and M. Polvani, Tetrahedron Letters, 1967, 125.
6. P. Benveniste, L. Hirth and G. Ourisson, Phytochemistry, 5, 45 (1966).