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CYANOMACLURIN

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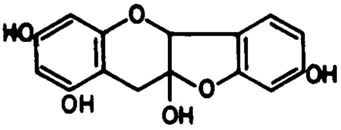
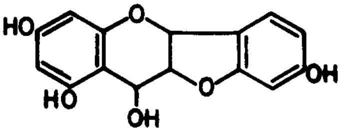
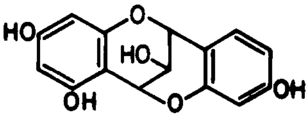
THE Appel-Robinson structure I and the structure II for cyanomaclurin based on a flavan-3,4-diol have been discussed recently.[1,2] Chakravarty and Seshadri[1] support II because a benzylic methylene group is absent in the NMR spectra of cyanomaclurin and its trimethyl ether, and cyanomaclurin acetate does not react with N-bromosuccinimide,


I


II


III

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[1] G. Chakravarty and T. R. Seshadri, Tetrahedron Letters No.18, 787 (1962).

[2] J. W. Clark-Lewis in The Chemistry of Flavonoid Compounds p. 220, 228. Pergamon, Oxford (1962).

in contrast with catechin and its acetate; according to Clark-Lewis[2] "all the available evidence is consistent with" II. We suggest that cyanomaclurin has the structure III.

After treatment of cyanomaclurin trimethyl ether with manganese dioxide in boiling benzene or chromium trioxide in dimethylformamide at 100° for several hours, the infrared spectrum remains unchanged and shows no carbonyl absorption. After treatment of cyanomaclurin with ten times its weight of Raney nickel in boiling ethanol, the characteristic blue colour with alkali persists.[3] Such inertness is difficult to reconcile with the presence of a benzylic secondary hydroxyl group as in II. We have therefore considered the alternative structure III, which also is in good agreement with the NMR data[1] for cyanomaclurin and its trimethyl ether. The single proton resonances at τ = 4.61 and 4.88 in the NMR spectrum of cyanomaclurin trimethyl ether, corresponding to those at 4.67 and 4.92 for the parent compound, are assigned to the protons on the benzylic carbon atoms which are bound to oxygen.[1,4] The proton in the 3-position, which is non-benzylic, absorbs at 5.67 in the trimethyl ether; acylation of the alcoholic hydroxyl group should not cause any major shift in the position of this absorption if structure II is correct, but the signal for one of the

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[3] K. G. Dave, Ph.D. Thesis, University of Bombay (1956).

[4] (a) J. J. Gordon, L. M. Jackman, W. D. Ollis and I. O. Sutherland, Tetrahedron Letters No.8, 28 (1960).
(b) J. B. Bredenberg and J. N. Shoolery, Ibid. No.9, 285 (1961).
(c) E. J. Corey, E. M. Philbin and T. S. Wheeler, Ibid. No.13, 429 (1961).

benzylic protons should shift down-field[5] by 1 ppm or more. On the other hand if III is correct, the absorption centered at 5.67 representing the proton in position 3 of cyanomaclurin trimethyl ether should shift down to the region of the benzylic protons when the hydroxyl group is acylated. The spectrum of cyanomaclurin trimethyl ether acetate (Fig. 1) shows a three-proton absorption in the region between 4.4 and 4.7. It is evident that the hydroxyl group in cyanomaclurin trimethyl ether is attached to 3-C as in III, and not to 4-C as in II. The benzylic proton resonances at 4.61 and 4.88 in the spectrum of the trimethyl ether may be assigned to H_a and H_c of the formula in Fig. 1, since H_c is adjacent to the phloroglucinol part of the molecule. In

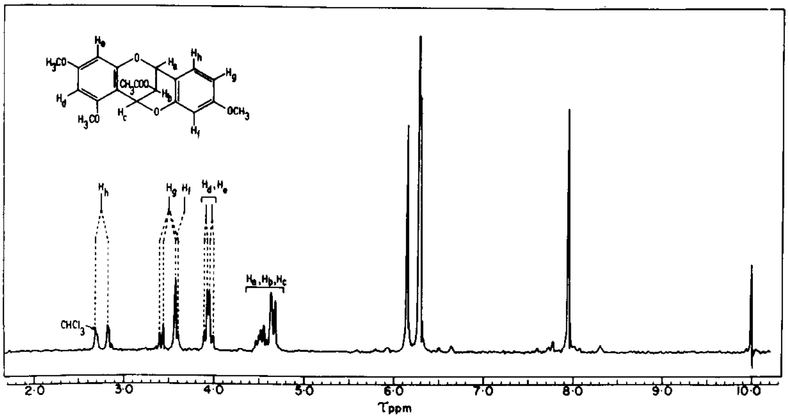

FIG.1. NMR spectrum of cyanomaclurin trimethyl ether acetate

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[5] (a) J. N. Shoolery and M. T. Rogers, *J. Amer. Chem. Soc.* **80**, 5121 (1958).

(b) L. M. Jackman, *Applications of NMR Spectroscopy in Organic Chemistry* p. 55. Pergamon, London (1959).

flavan-3,4-diols $J_{3,4}$ (ax-eq) is 6 to 7 cps.[6] Such a coupling is not observed in the spectrum, indicating that H_b is trans to H_a and H_c which have to be cis and equatorial in structure III.

We are indebted to Dr. C. S. Barnes, Division of Organic Chemistry, CSIRO Chemical Research Laboratories, Melbourne, for determining the NMR spectrum of cyanomaclurin trimethyl ether acetate.

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[6] J. W. Clark-Lewis and L. M. Jackman, Proc. Chem. Soc. 165 (1961).