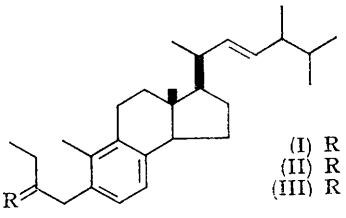
# An Unusual Aromatic Seco-steroid[1]

By P. J. FLANAGAN and J. B. THOMSON
(*Department of Chemistry, University College, Dublin, Ireland*)

PYROLYSIS of bisergostatrienol[2] has been reported[3] to yield, in addition to the well-known neoergosterol, an isomer of dehydroergosterol. A re-examination of this reaction has now shown that the major, crystalline by-product is the novel 1,10-seco-steroid (I), m.p. 75—76°, $[\alpha]_D^{21}$ + 39°, (*c* 1·0 in chloroform).

That ring-B is aromatic is demonstrated by the formation of a styrene system, $\lambda_{max}$ (methanol) 269 mμ (ε 20,000), on dehydration of the alcohol with phosphorus pentoxide. The n.m.r. spectrum of the acetate (II), m.p. 68—70°, $[\alpha]_D^{32}$ + 34° (*c* 1·1 in chloroform), shows the characteristic multiplet, at τ 4·8, for the olefinic protons in the side chain, the C-18 proton signal at τ 9·42, the C-19 proton signal at τ 7·82 (methyl group on an aromatic ring), and an AB quartet centred at τ 3·27 ($J$ = 8 c./sec.) for the aromatic protons. In the mass spectrum* of the ketone (III), m.p. 97—100°, $[\alpha]_D^{21}$ + 22° (*c* 0·9 in chloroform), the molecular ion (base peak) occurs at *m/e* 394 ($C_{28}H_{42}O$), indicating that the molecule is tricyclic. The most abundant fragment ion, at *m/e* 337, corresponds to loss of $C_3H_5O$ from $M^+$ which immediately suggests the 1,10-seco-structure (III). Clear confirmation of this structure is obtained from the 100 Mc./sec. n.m.r. spectrum† of the ketone (III) which shows the expected $A_2X_3$ system for the $CH_3{\cdot}CH_2{\cdot}CO$ group as a quartet at τ 7·59 ($J$ = 7 c./sec.) and a triplet at τ 8·89 ($J$ = 7 c./sec.). The C-4 proton signal appears as a barely resolved AB quartet at τ 6·33 ($J$ = −16 c./sec.).

Other spectroscopic and analytical data are consistent with the suggested structures.




(I) R = H, OH
(II) R = H, OAc
(III) R = O

(*Received, February 8th*, 1967; *Com.* 120.)

[1] Previous paper: P. J. Flanagan and J. B. Thomson, *Tetrahedron Letters*, 1965, 1671.
[2] L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, 1959, p. 104.
[3] T. Ando, *Bull. Chem. Soc. Japan*, 1938, **13**, 371; 1939, **14**, 169.
* Recorded by Drs. A. R. West and R. L. Erskine (British Petroleum) on an A.E.I. MS-9 instrument.
† Recorded by Dr. L. J. Durham (Stanford) on a Varian HR-100 instrument.