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THE STRUCTURE OF THE C-NOR-D-HOMO ENDOCYCLIC OLEFIN DERIVED FROM HECOGENIN

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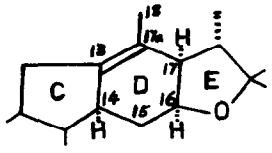
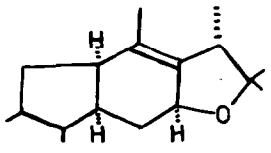
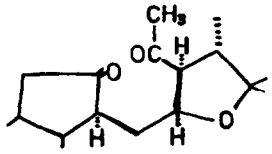
The alkali-catalysed decomposition of hecogenin toluene-p-sulphonylhydrazone proceeds with rearrangement to give mainly the C-nor-D-homo-$\Delta^{13(17a)}$-olefin (I), and not the $\Delta^{17(17a)}$-isomer (II) which was preferred by the original authors.[1,2]



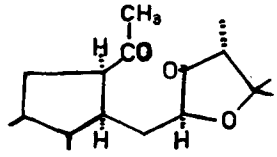
I



II



III



IV

Evidence in favour of the $\Delta^{13(17a)}$-structure was first obtained from the NMR spectrum* of the olefin (I), in which the

* Determined at 60 mc in $CDCl_3$, with $CHCl_3$ and $(CH_3)_4Si$ as internal standards.

16α-proton signal appeared as a multiplet (probably an octet) of total width 25 c/s centred at τ5.82. The chemical shift of the 16α-proton signal agrees closely with data which we have collected for related spirostan derivatives, including the C-nor-D-homo-$\Delta^{17a(18)}$-exocyclic olefin,[1] and the multiplicity can best be explained as the result of spin-spin coupling of the 16α-proton with <u>three</u> adjacent protons, namely those at 15α, 15β, and 17α in the $\Delta^{13(17a)}$-structure (I).

Additional support for structure (I) was adduced from the NMR spectrum of the diketone[2] derived by cleavage of the olefin with osmic acid followed by periodic acid. A low-field signal equivalent to one proton, at τ5.43, was assigned to the 16α-proton in the 13,17a-seco structure (III), for spin-spin coupling with adjacent protons again split the signal into a multiplet (sextet or octet) of total width 23.5 c/s. The alternative structure (IV) for the diketone could only give rise to a quadruplet for the 16α-proton.

Treatment of the diketone (III) with toluene-<u>p</u>-sulphonic acid in refluxing acetic acid, followed by alkaline hydrolysis, gave an amorphous product which still exhibited the IR absorption band at 1740 cm^{-1} due to the 5-membered ring ketone, although the bands associated with the spiroketal system were no longer present. This is consistent only with formulation (III) for the diketone, as the 17-keto function in the alternative 17,17a-seco diketone (IV) would not retain its IR characteristics after rupture of the spiroketal system.

Finally the α-epoxide[3] derived from the endocyclic

olefin afforded hecogenin acetate (25% yield) on rearrangement with boron trifluoride in benzene. This can only be explained in terms of a 13,17a-epoxy structure, which suffers cleavage at C-17a with migration of the 13,14-bond to regenerate the normal steroid skeleton.

A full account of this and related work will be published elsewhere.

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