Tetrahedron Letters No.9, pp. 1113-1114, 1968. Pergamon Press. Printed in Great Britain.

STEROIDS CCCXXXVI.[1]

SYNTHETIC STUDIES ON INSECT HORMONES, PART VI.[2]

THE SYNTHESIS OF PONASTERONE A AND ITS STEREOCHEMICAL IDENTITY WITH CRUSTECDYSONE

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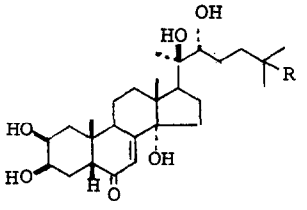
(Received in Japan 15 November 1967)

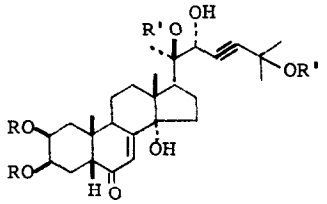
We wish to report the synthesis of ponasterone A (I), a natural product of Podocarpus Nakaii Hay[4], by a method which allows stereochemical correlation with the insect and crustacean moulting hormone crustecdysone[5] (II).

The synthesis of crustecdysone reported in a previous communication[2] from this laboratory involved hydrogenation of the protected acetylenic intermediate (III) followed by hydrolysis of the product to afford crustecdysone (II).



I R = H

II R = OH



III R = acetonide
R'= tetrahydropyran-2-yloxy

IV R = R' = H

Prior removal of the protecting groups of (III) with N/20 hydrochloric acid in 10% aqueous tetrahydrofuran gave cleanly the free hexa-hydroxy acetylene (IV), which was not resolvable from crustecdysone by silica thin layer chromatography but differed in color reactions.

Hydrogenation of (IV) in ethanol solution with 5% palladium on carbon catalyst gave crustecdysone (II) (85%), identified by comparison with an

authentic sample[6], together with a less polar hydrogenolysis product (I). With platinum as catalyst, hydrogenolysis predominated to afford ponasterone A (I) [m.p. 251-5° (dec.); λ_{max}^{EtOH} 242 mμ (ε = 12,200), ν_{max}^{KBr} 1650 cm^{-1}. N.m.r. (perdeuteriopyridine) 0.83 d, J = 6 (26- and 27-H), 1.05 (19-H), 1.19 (18-H), 1.53 (21-H), and 6.21 (7-H) p.p.m.] A mixture m.p. of the synthetic material with authentic ponasterone A[6] m.p. 255-9° showed no depression, and the compounds were identical in chromatographic behavior and color reactions on silica gel impregnated with boric acid.

The stereochemical identity of ponasterone A with crustecdysone at all asymmetric centers is consequently established. Since the tetracycle corresponding to crustecdysone (II) has been shown[7] to be identical with that of ecdysone whose structure was elucidated by X-ray diffraction studies[8], it follows that ponasterone A has the nuclear configurations depicted in I.

References

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6. We thank Dr. D. H. S. Horn for a sample of crustecdysone and Dr. K. Nakanishi for a sample of ponasterone A.
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