

**SYNTHESIS OF RUBROSTERONE,  
A METABOLITE OF INSECT-MOULTING SUBSTANCES FROM ACHYRANTHES RUBROFUSCA**

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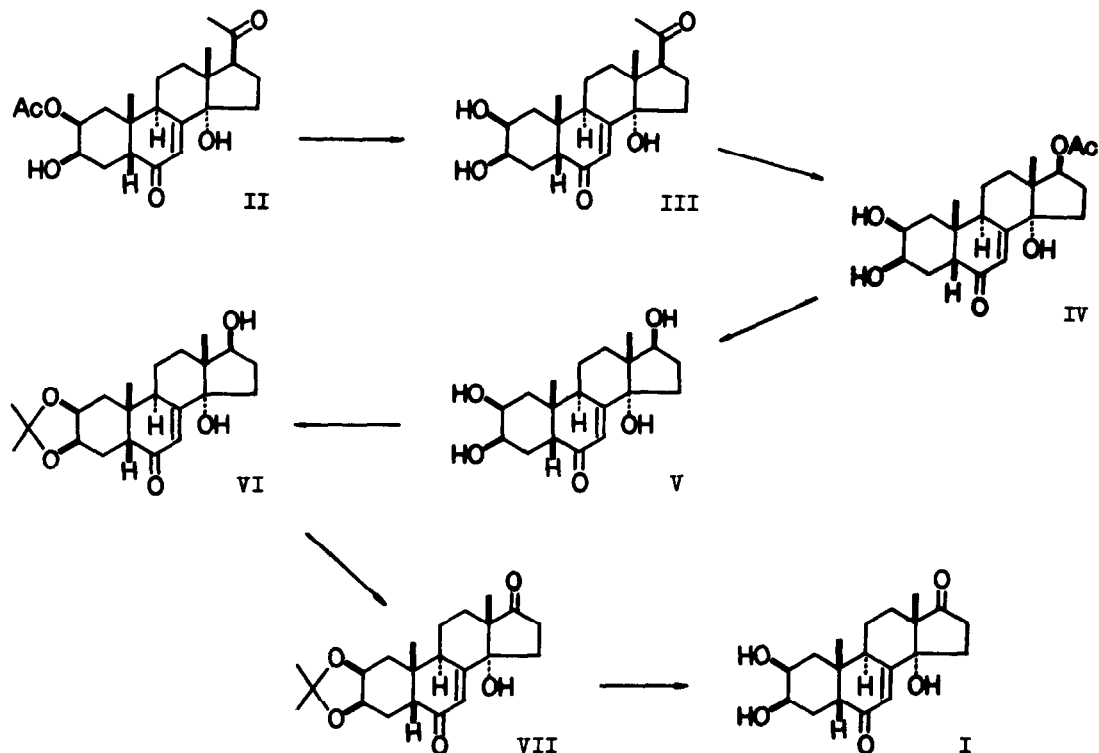
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Rubrosterone (I)<sup>1)</sup> is the novel steroid which has been isolated first from Achyranthes rubrofusca Wight<sup>2)</sup> and later from A. fauriei Léveillé et Vaniot<sup>3)</sup> (Amaranthaceae). Since these plants also contain the insect-moulting substances, ecdysterone and inokosterone,<sup>2-4)</sup> rubrosterone is considered to be most probably a metabolite of these steroids in the plants. Of interest biologically is that rubrosterone shows little insect-moulting hormone activity, while it still exhibits high stimulating effect on protein synthesis in mouse. A synthesis confirming both structure and absolute configuration is now presented.

2 $\beta$ -Acetoxy-3 $\beta$ ,14 $\alpha$ -dihydroxy-5 $\beta$ -pregn-7-ene-6,20-dione (II), derived from ecdysterone<sup>5)</sup> which has already been synthesized,<sup>6)</sup> was hydrolyzed to give the known methyl ketone (III)<sup>7)</sup> which on pertrifluoroacetic acid oxidation afforded the acetate (IV), m.p. 226-228°,  $\nu_{\max}$  3420 (hydroxyl), 1727, 1242 (acetoxy), and 1645 cm<sup>-1</sup> (cyclohexenone)\*. Hydrolysis of the acetate (IV) with potassium carbonate in aqueous methanol yielded the tetra-ol (V), m.p. 268-270°,  $\nu_{\max}$  3340 (hydroxyl) and 1648 cm<sup>-1</sup> (cyclohexenone). When the corresponding acetonide (VI), m.p. 246-248°,  $\nu_{\max}$  3360 (hydroxyl) and 1645 cm<sup>-1</sup> (cyclohexenone), prepared with acetone in the presence of *p*-toluenesulfonic acid, was oxidised with chromium trioxide-pyridine complex the ketone (VII), m.p. 247-248.5°,  $\nu_{\max}$  3400 (hydroxyl), 1731 (cyclopentanone), and 1677 cm<sup>-1</sup> (cyclohexenone), was obtained. Treatment of the acetonide (VII) with aqueous ethanol under reflux furnished the diketo-triol, m.p. 246-248° (decomp.),  $\nu_{\max}$  3410 (hydroxyl), 1741 (cyclopentanone), and 1641 cm<sup>-1</sup> (cyclohexenone), which was identified as the natural rubrosterone (I).

Preparation of these intermediates (II-VII) with a variety of structural modifications led us to examine their biological activities. In the Sarcophaga test, however, none of them gave positive responses when injected in a dosage of 1  $\mu$ g per isolated larval abdomen. On the other hand, the methyl ketone (III) induced enhancement of protein anabolism in mouse liver, though the



other analogues (II, IV-VII) showed no activity. These data will contribute to the structure-activity correlation study on the ecdysone derivatives.

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#### FOOTNOTE AND REFERENCES

\* Melting points are uncorrected. IR spectra were determined in KBr disk.

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