

Übereinstimmung ist sehr gut.

3-Epigigitoxigenin und 3-Epioleandrogenin zeigten wie 3-Epidigitoxigenin und 3-Epitanghinigenin keine nachweisbare Toxizität. Für die charakteristische Digitalis-wirkung scheint demnach die  $3\beta$ -Oxy-Konfiguration mindestens in der Reihe von Digitoxigenin (A/B: *cis*) unentbehrlich zu sein.

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### A Synthetic Method for $\Delta^{1,4}$ -3-Ketosteroids

In the course of santonin synthesis in this laboratory,<sup>1)</sup> application of selenium dioxide to the dehydrogenation of monoenone ring compounds was introduced as a new synthetic reaction to obtain cross-conjugated dienone ring compounds.

The authors thereafter found that the reaction proceeds smoothly in steroids as expected and have applied for a patent<sup>2)</sup> on this reaction as a synthetic method for  $\Delta^{1,4}$ -3-ketosteroids.

Recently, three papers<sup>3~5)</sup> concerning the same reaction have been published independently in foreign countries, so the authors wish to present here the syntheses of the following two compounds which have not appeared in the foreign reports.

Reaction of  $\Delta^4$ -tigogenone with selenium dioxide in benzene yielded an oil, which was treated with methanol to afford  $\Delta^{1,4}$ -tigogenone as colorless plates, m.p. 186° (*Anal.* Calcd. for  $C_{27}H_{38}O_3$ : C, 78.98; H, 9.33. Found: C, 79.12; H, 9.63);  $\lambda_{max}^{Nujol}$  6.00, 6.14, 6.22  $\mu$  ( $\Delta^{1,4}$ -3-ketone).

When the acetate of 16,17-epoxy- $\Delta^4$ -pregnen-21-ol-3,20-dione was treated with selenium dioxide in *tert*-butanol-acetic acid and the product was submitted to chromatography on alumina, the acetate of 16,17-epoxy- $\Delta^{1,4}$ -pregnadien-21-ol-3,20-dione was obtained as colorless prisms, m.p. 199° (*Anal.* Calcd. for  $C_{23}H_{28}O_3$ : C, 71.85; H, 7.34. Found: C, 71.58; H, 7.23);  $\lambda_{max}^{Nujol}$  5.97, 6.14, 6.22  $\mu$  ( $\Delta^{1,4}$ -3-ketone).

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