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# SYNTHESES BASED ON STROPHANTHIDIN

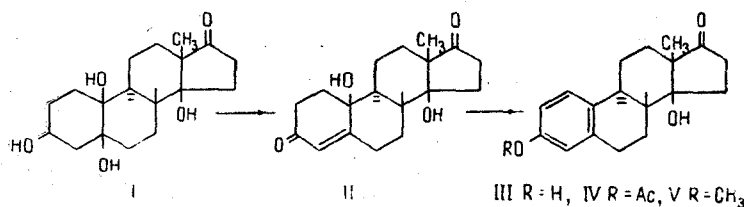
## III. Synthesis of 14 $\beta$ -Hydroxyestrone

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The catalytic dehydrogenation with platinum in aqueous acetone and in an atmosphere of oxygen [1] of 3 $\beta$ , 5 $\beta$ , 10 $\beta$ , 14 $\beta$ -tetrahydroxy-19-nor-androstan-17-one (I), obtained previously by the degradation of strophanthidin [2], has led to a product which migrated on a thin-layer chromatogram [ $\text{Al}_2\text{O}_3$ , benzene-methanol (10:1); revealing agent  $\text{SbCl}_3$ ] at the level of the initial 3-hydroxy ketone [1]. Subsequent evaporation of the solution in vacuum (50°-60° C) gave 10 $\beta$ , 14 $\beta$ -dihydroxy-18-nor-androst-4-en-3, 17-dione (II) with mp 238°-239° C (from acetone),  $[\alpha]_D^{20} + 80.0^\circ$  (c 0.81; methanol). Yield 67.4%. UV spectrum:  $\lambda_{\text{max}}$  (in alcohol) 234, 303 m $\mu$  (log  $\epsilon$  4.20, 1.90). IR spectrum: 3485 (OH), 1730 (17, C=O), 1676 (3, C=O), 1635 (C=C)  $\text{cm}^{-1}$ .

A solution of the unsaturated dione (II) in glacial acetic acid was heated at 118° C in a gentle current of nitrogen for 6 hr, which gave a mixture of substances. The latter was chromatographed on a column of alumina. The fractions eluted with chloroform-alcohol (50:1) contained 14 $\beta$ -hydroxyestrone (III) with mp 227° C [chloroform-alcohol (5:1)],  $[\alpha]_D^{20} + 94.9^\circ$  (c 0.57; methanol). Yield 79.8%. UV spectrum:  $\lambda_{\text{max}}$  (in alcohol) 281 m $\mu$  (log  $\epsilon$  3.40). IR spectrum: 3500 (OH), 3340-3260 (OH), 1734 (17, C=O), 1615, 1510 (Ar)  $\text{cm}^{-1}$ . The hydroxyestrone (III) was also obtained by shaking (for 25 min at room temperature) a solution of the dione (II) in glacial acetic acid containing 1 vol. % of concentrated hydrochloric acid. Yield 64.3%.



14 $\beta$ -Hydroxyestrone 3-acetate (VI) had mp 202°-203° C from chloroform,  $[\alpha]_D^{20} + 107.6^\circ$  (c 0.50; chloroform). UV spectrum:  $\lambda_{\text{max}}$  (in alcohol) 264, 275 m $\mu$  (log  $\epsilon$  3.14, 3.06). IR spectrum: 3515 (OH), 1750 (C=O), 1225 (C-O-C), 1610, 1590, 1500 (Ar)  $\text{cm}^{-1}$ .

The methyl ether of 14 $\beta$ -hydroxyestrone (V) was obtained with mp 162°-163° C (from benzene),  $[\alpha]_D^{20} + 88.3^\circ$  (c 0.41; chloroform). UV spectrum:  $\lambda_{\text{max}}$  (in alcohol) 280, 285 m $\mu$  (log  $\epsilon$  3.39, 3.34). IR spectrum: 3505 (OH), 1736 (C=O at C-17), 1620, 1590, 1516, (Ar), 1245, 1197, 1143 (Ar-O-C)  $\text{cm}^{-1}$ . Substance (V) possesses the natural 8 $\beta$ , 9 $\alpha$  configuration and differs in its constants from the 8 $\alpha$ , 9 $\alpha$ - and 8 $\alpha$ , 9 $\beta$ -isomers of 14 $\beta$ -hydroxyestrone that have been synthesized [3].

## REFERENCES

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