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SOME DERIVATIVES OF A/B-CIS-SPIROSOLAN

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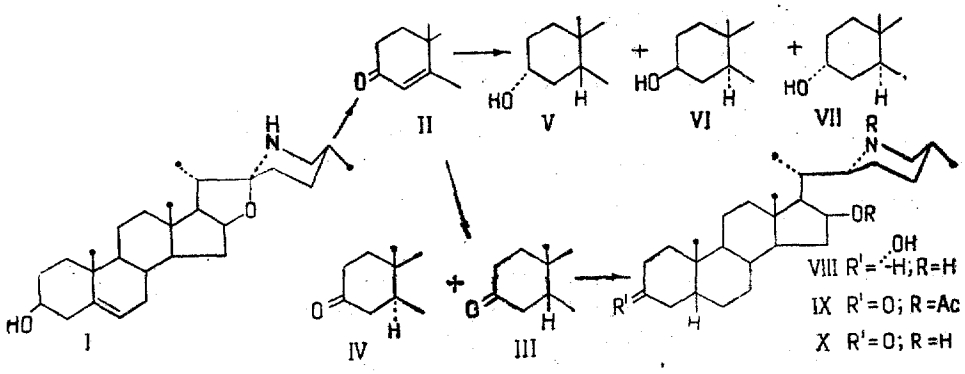
In the series of steroid alkaloids of Solanum, A/B-cis compounds are known only for derivatives of solanidine [1].

In the present paper we describe A/B-cis-spirosolans obtained from solasodine, which have not been previously studied. When solasodine (I) was oxidized by the Oppenauer method (toluene, cyclohexanone, aluminum isopropoxide), the reaction mixture gave a 70% yield of solasodenone (II), mp 183-184° C; $\lambda_{max}^{C_2H_5OH}$ 242 and 304 mμ (log ε 4.24, 2.02). The hydrogenation of II on $Pd/CaCO_3$ in ethanol led to two solasodanones, whose configurations were established from their optical rotatory dispersion curves. A/B-cis-solasodanone (III) with mp 164-175° C, $\lambda_{max}^{C_2H_5OH}$ 280 mμ (log ε 1.45) has a dispersion curve with a valley at about 310 mμ which is characteristic for 5β-3-ketosteroids [2]; the second ketone has the 5α-configuration (IV) mp 204-205° C, $\lambda_{max}^{C_2H_5OH}$ 280 mμ (log ε 1.38) $[\alpha]_{310}$ +2800° (peak).

The hydrogenation of II over $Pd/CaCO_3$ in pyridine took place stereoselectively giving, as was to be expected [3], the ketone III in quantitative yield. When II was hydrogenated over Raney nickel in ethanol, a mixture of four alcohols was formed from which were isolated the known 5α-solasodan-3β-ol (VI) with mp 209-210° C and the unknown 5β-solasodan-3α-ol (V) with mp 206-207° C, and also 5α-solasodan-3α-ol (VII) with mp 199-199.5° C. On reduction with potassium borohydride in methanol at 0° C, the ketone III was easily converted into the alcohol V. The reduction of III with lithium aluminum hydride in ether and benzene or with potassium borohydride in boiling methanol led to the opening of the spiroaminoketal ring and to the formation of 20α-(5'-methylpiperidino) pregnan-3α, 16β-diol (VIII) with a yield of 80-85%, mp 214-215° C. The oxidation of the N,16-diacetate of the diol VIII gave the 3-ketone (IX) (R = Ac) with mp 184-186° C, which was readily saponified on being boiled with 3% methanolic caustic potash to the ketone (X) (R = H) with mp 169-170.5° C.



The results of elemental analysis were satisfactory for all the compounds described. The purity of the compounds was checked by thin-layer chromatography.

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