

SYNTHESIS OF THE STEROIDAL ALKALOID SOLANOCAPSINE*

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For solanocapsine the structure 3 β -amino-22.26-epimino-16 α .23-epoxy-5 α .22 α H.25 β H-cholestan-23 β -ol (XII) has been proven by degradation (1), synthetic investigation (2), NMR spectroscopy (2), and X-ray crystal analysis (3). In the following we describe the synthesis of this alkaloid, starting with solafloridine ((25R)-22.26-epimino-5 α -cholest-22(N)-en-3 β .16 α -diol, I (1)) obtained by formal total synthesis (1).

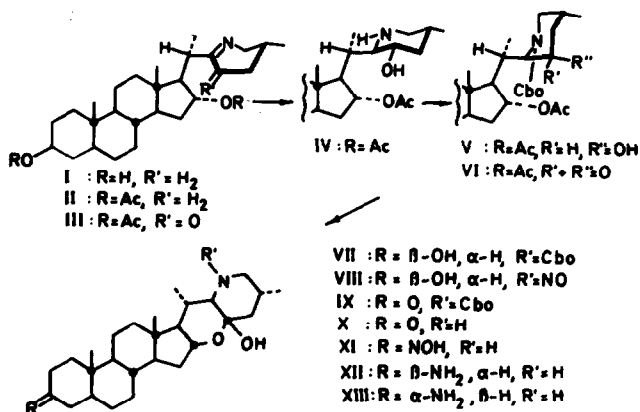
Acetylation of I with acetic anhydride-zinc chloride-acetic acid furnished the diacetate II in 83 % yield (m.p. 182-183 $^{\circ}$, $[\alpha]_D^{25}$ -53.3 $^{\circ}$ in CHCl₃). Subsequent oxidation with manganese dioxide in CHCl₃ at room temperature (4) yielded the azomethineketone III, which without purification was reduced with sodium borohydride to the piperidinol IV (m.p. 179-180 $^{\circ}$, $[\alpha]_D^{25}$ -53.7 $^{\circ}$ †, yield, from II, 57 %). Reaction of IV with benzylchloroformate afforded the N-benzylloxycarbonyl derivative V in 60 % yield (m.p. 177-178 $^{\circ}$, $[\alpha]_D^{25}$ -25.5 $^{\circ}$), which was oxidized by chromium trioxide-sulphuric acid in acetone to the amorphous ketone VI ($[\alpha]_D^{25}$ -11.8 $^{\circ}$, yield 90 %). Partial hydrolysis with methanolic KOH and spontaneous hemiketal formation gave VII in 75 % yield (m.p. 218-220 $^{\circ}$, $[\alpha]_D^{25}$ +78.0 $^{\circ}$), which was shown to be

*Solanum Alkaloids. Part XCI.- Part XC of this series of. ref. 3. Part of the Thesis F.-J. Sych, Univ. Halle 1971. Regarding the programme of this synthesis cf. K. Schreiber, Pure and Applied Chemistry **21**, 131 (1970).

**Dedicated to Professor Dr. Dr. h. c. mult. K. Mothes on the occasion of his 70th birthday.

†Specific rotations in pyridine unless otherwise stated.

identical with VII obtained from N-nitroso-3-deamino-3 β -hydroxy-solanocapsine (VIII; 1) by hydrogenolytic cleavage of the nitroso group by means of alkaline Raney nickel and subsequent reaction with benzylchloroformate (35 % yield). VII was oxidized with chromium trioxide in pyridine to the ketone IX in 68 % yield (m.p. 211-213°, $[\alpha]_D +45.4^\circ$). Cleavage of the carbobenzoxy residue by hydrogen bromide-acetic acid afforded the basic ketone X (m.p. 208-210°, $[\alpha]_D +26.6^\circ$, yield 72 %). Reaction of X with hydroxylamine furnished the oxime XI (m.p. 225-228° (dec.), $[\alpha]_D +24.8^\circ$, yield 78 %), the catalytic hydrogenation of which in the presence of platinum in acetic acid solution yielded solanocapsine (XII, m.p. 202-211° (dec.), $[\alpha]_D +27.8^\circ$, yield 20 %) as well as the 3-epimeric amine XIII (m.p. 180-185°/208-214° (dec.), $[\alpha]_D +27.2^\circ$, yield 18 %).



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