

SYNTHETIC STUDIES IN STEROIDAL ALKALOIDS AND SAPOGENINS.VII

SYNTHESIS OF SOLANIDINE

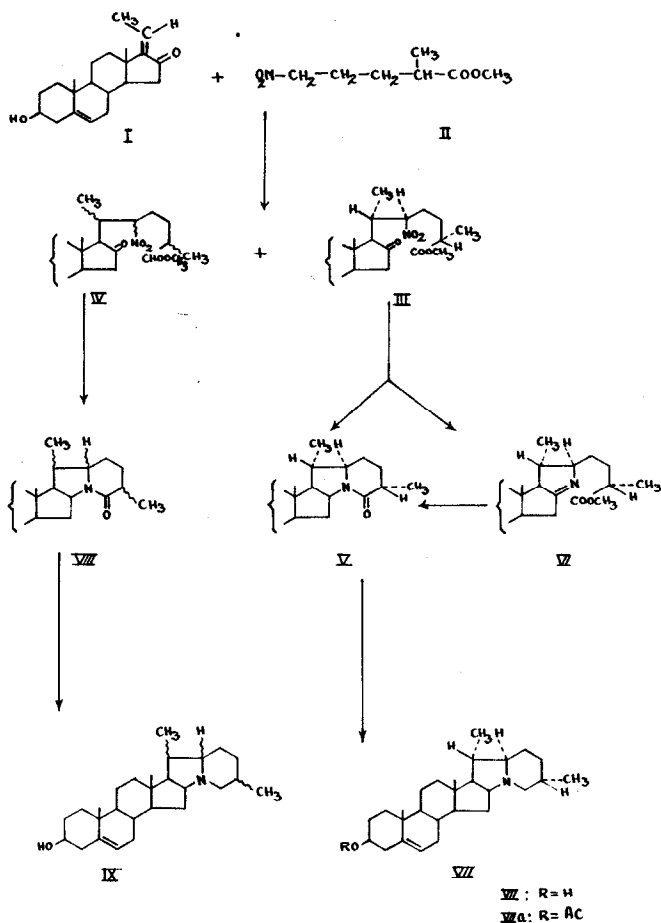
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Using the general approach to steroidal alkaloids and sapogenins developed in these laboratories¹, a direct² formal total synthesis of solanidine has been achieved.

The nitro ester II ($C_7H_{13}NO_4$, b.p. $87-90^\circ/1$ mm., $[\alpha]_D^{30} + 16^\circ$, $n_D^{29} 1.444$) was obtained from S-2-allylpropionic acid³ in four steps. Its Michael reaction with unsaturated ketone I afforded a mixture which was separated into adducts III ($C_{28}H_{43}NO_6$, m.p. $163-164^\circ$, $[\alpha]_D^{20} - 125^\circ$) and IV ($C_{28}H_{43}NO_6$, m.p. $160-161^\circ$, $[\alpha]_D^{20} - 132^\circ$) by thick layer chromatography. The nitro ketone III was reduced with zinc and acetic acid and the product was separated into neutral and basic fractions. The neutral portion on chromatography furnished amide V ($C_{27}H_{41}NO_2$, m.p. $222-224^\circ$, $[\alpha]_D^{17} - 26^\circ$) and its 3β -acetate ($C_{29}H_{43}NO_3$, m.p. $230-232^\circ$). The basic fraction VI (ν_{max} . $1550, 1610, 1725$ cm^{-1}) also lead to amide V through sodium borohydride reduction and cyclisation. Treatment of V with lithium aluminium hydride gave base VII ($C_{27}H_{43}NO$, m.p. $212-214^\circ$, $[\alpha]_D - 25^\circ$) which was found to be identical with natural solanidine⁴ by mixed melting point, IR and TLC. Its acetate VIIa, m.p. $200-201^\circ$, was also identical with that of the natural compound.



The nitro ketone IV by a series of similar steps afforded an isomeric base IX (m.p. 180-183^o) stereochemistry of which is under investigation.

REFERENCES

1. S.V. Kessar, Y.P. Gupta and A.L. Rampal, Tetrahedron letters, 4318 (1966).
2. K.Schreiber and H. Rönisch, Ber., 97, 2362 (1964).
3. G.Ställberg, Acta Chem.Scand., 11, 1430 (1967).
4. We are grateful to Prof. Schreiber of Gaterslaben for a sample of natural solanidine.