280. *The Occurrence of Solanidine in Sprouting Potatoes.*

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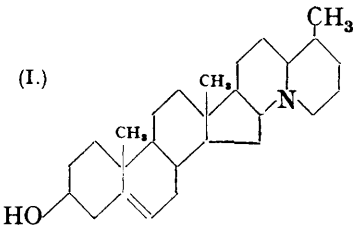
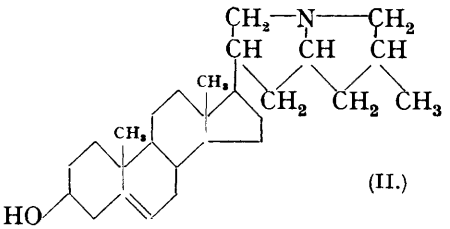
IN the course of a survey now being undertaken, we examined the shoots of potatoes, and in view of the publication of Soltys and Wallenfels (*Ber.*, 1936, **69**, 811) it appears desirable to place our results on record. Besides the alkaloidal glucoside, solanine, we have found that in some varieties the aglucone solanidine is present, presumably in the free state, as it can be readily extracted by ether. Thus, from the British Queen we obtained solanidine equivalent to 0·04% of the weight of the fresh undried colourless shoots, and about the same proportion is present in Kerr's Pink and the Bishop. Very little was found in shoots of the Majestic, and none in those of Arran Banner, at any rate at the season at which we examined them, but on then extracting the same Arran Banner shoots with 2% acetic acid, as used by Soltys and Wallenfels, we obtained 0·04% of their weight of solanine. The examination of many varieties of potatoes has shown that solanidine is only to be found in the eyes or shoots and not in the body or eye-free skin of either normal mature or quite young tubers. The identity of the solanidine was established by its m. p. and specific rotation, and the preparation of an acetyl and a dihydro-derivative, whose properties are in agreement with those recorded by Soltys (*Ber.*, 1933, **66**, 762). It is not affected by treatment with methyl-alcoholic potash or sodium amalgam, and shows only weak general absorption in the ultra-violet.

Soltys and Wallenfels, on the grounds of the formation of Diels's hydrocarbon by the selenium treatment of solanidine, suggest for it formula (I), containing fused sterol and lupinane nuclei. We consider, however, that selenium dehydrogenation would be unlikely

(I.)





(II.)

to split out the lupinane nucleus entirely from such a system. Such a formula would be derived from a C_{27} sterol. The well-characterised phytosterols contain 28 or 29 carbon atoms, but our analyses as well of those of Soltys are in better agreement with C_{27} for solanidine. At present, the well-characterised C_{27} sterols are the zoosterols cholesterol and coprosterol. Preservation of the established side chain in these leads to formula (II), which we suggest may represent solanidine rather than (I). This structure, in which the remaining 8 carbon atoms are attached only to carbon atom 17 of the sterol nucleus, would more readily explain the formation of Diels's hydrocarbon, and further, 5-membered heterocyclic rings attached to C_{17} occur in the cardiac glucosides such as strophanthin.

Menschikoff (*Ber.*, 1936, **69**, 1802) suggests that a methyldipyrrole system such as forms part of (II) is also the parent substance of the basic part of the alkaloid helotrine, from *Heliotropium lasiocarpium*, but his work cannot yet be regarded as conclusive.

Work on this interesting problem is being continued.

EXPERIMENTAL.

The fresh shoots were minced, covered with ether, and left for 48 hours. The ether was dried (sodium sulphate) and evaporated, and the resulting solanidine (m. p. 213° alone or mixed with a specimen prepared from Merck's solanine; Soltys gives m. p. 219°) recrystallised from light petroleum (b. p. 80—100°) (Found: C, 81·2, 81·2, 81·3; H, 10·8, 11·1, 11·4. Calc. for $C_{27}H_{43}ON$: C, 81·0; H, 11·0%); $\alpha_D^{21°}$ in alcohol (l = 2, c = 0·3668) — 0·209°, $[\alpha]_D^{21°}$ — 28·5°.

The dihydro-derivative was formed when solanidine (30 mg.) in alcohol (30 c.c.) was shaken with platinum oxide (150 mg.) in hydrogen at 100 lb./in.^{2}. After removal of the catalyst and alcohol, the residue crystallised from light petroleum in colourless needles (11·3 mg., m. p. 214°;

Soltys gives 222°) (Found : C, 81·1, 81·4; H, 11·5, 11·7. Calc. for $C_{27}H_{45}ON$: C, 81·2; H, 11·3%).

The acetyl derivative was obtained by heating solanidine (12 mg.) with acetic anhydride (10 drops) for 10 minutes. Water and sodium carbonate solution were added, and the acetyl derivative collected. It crystallised from alcohol in needles (11 mg., m. p. 203°; Soltys gives 204°) (Found : C, 79·3; H, 10·1. Calc. for $C_{29}H_{45}O_2N$: C, 79·2; H, 10·3%).

The shoots, after the ether extraction, were extracted for solanine as recommended by Soltys.

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