CHEMICAL EXAMINATION OF SOLANUM TRILOBATUM

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Solanum trilobatum L. is a very prickly trailing or climbing undershrub.1 Its shoots are stellate and pubescent with ovate leaves. The corolla is blue and the berry, $\frac{1}{2}$ in. in diameter is globular. The plant is prescribed in the Siddha† system of medicine, for its cardiac, tonic, and carminative properties.2

Extraction of the plant with 2% acetic acid yielded a mixture of glyco alkaloids which was difficult to purify by crystallization.3 Acid hydrolysis of this mixture and subsequent basification of the crystalline hydrochloride yielded a single base, m.p. 226–228°, and was analysed for molecular formula $C_{27}H_{45}NO_2$ (M+, 413). The infrared spectrum showed absorption for the presence of hydroxyl (3600 and 1045 cm$^{-1}$) and NH (3310 cm$^{-1}$) which was further confirmed by the preparation of the $N,O$-diacetate, the i.r. spectrum of which did not show any absorption in the 3600–3300 cm$^{-1}$ region. The mass spectrum of the compound showed fragments, m/e 114 and 138, characteristic of the spirosolene structure.4

The base readily yielded a digitonide. Catalytic hydrogenation of the base in the presence of Pd–CaCO$_3$ yielded a dihydro compound identical in all respects with tomatidine. It gave a positive Clark reaction and only one olefinic proton was observable in the n.m.r. spectrum at $\delta 5.33$ p.p.m., as in $\Delta^5$ steroidal alkamines. Our base therefore should be tomatid-5-en-3β-ol, and had constants comparable to the tomatid-5-en-3β-ol [(25S)-22βN-spirosol-5-en-3β-ol] isolated from S. dulcamara with which it was found to be identical by comparison with the free base and the diacetate (m.p., mixed m.p., and t.l.c. in three different solvent systems).

Experimental

All melting points are uncorrected. The n.m.r. spectrum was recorded on a A60 machine and the mass spectrum was taken on a Hitachi Perkin–Elmer RMU-6D spectrometer. The i.r. spectra were recorded on a Perkin–Elmer grating 337 instrument.

Extraction

Dried and powdered plant (4 kg) was extracted with acetic acid (2%; 10 l.; 48 hr) at room temperature. The base was precipitated out at 100°, dried, purified, and crystallized from dioxan (2·8 g), m.p. 276° (sintering at 245°), and was found to be a mixture of three glyco alkaloids by paper chromatography.

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† One of the very ancient systems of medicine followed in India.

Acid Hydrolysis

The glycoside (5 g) was refluxed with alcoholic HCl (100:20; 3 hr) and worked up by the usual procedure to yield the hydrochloride (1.8 g), m.p. 271–273° (dec.) (Found: C, 71.8; H, 9.7. Calc. for C27H44ClNO2: C, 72.15; H, 9.9%).

Isolation of the Base

The pure base liberated from the hydrochloride was crystallized from alcohol, m.p. 228–228° (Found: C, 78.15; H, 10.4; N, 3.4. Calc. for C27H43N02: C, 78.4; H, 10.4; N, 3.4%). [α]D50 = -38.3 (c, 2 in CHCl3).

Picrate

The picrate obtained by the usual procedure had m.p. 183–186° (Found: C, 61.4; H, 7.0. Calc. for C33H46N09: C, 61.65; H, 7.2%).

Digitonide

The base (50 mg) in rectified spirit yielded digitonide (60 mg) by addition of 1% solution of digitonin in rectified spirit (calc. 62 mg).

Acetylation

The product obtained from a mixture of the base (100 mg), pyridine (5 ml), triethylamine (2 ml), and acetic anhydride at room temperature overnight was extracted with hexane. The hexane-insoluble portion was crystallized from ether-hexane mixture to get the hitherto unreported monoacetate, m.p. 202–206° (Found: C, 76.2; H, 10.2. Calc. for C29H48N02: C, 76.4; H, 9.9%).

From the hexane-soluble fraction, a diacetate was obtained identical with that of tomatid-5-en-3β-ol, m.p. and mixed m.p. 164–165° (Found: C, 74.9; H, 9.6. Calc. for C31H47N04: C, 74.8; H, 9.5%).

Hydrogenation

Catalytic hydrogenation of the base (150 mg) in alcohol (20 ml) in the presence of Pd-CaCO3 at atmospheric pressure and temperature yielded tomatidin, which crystallized from hexane-ether (60 mg), m.p. 203–205° (mixed m.p., and t.l.c.) (Found: C, 77.7; H, 11.2. Calc. for C27H45N02: C, 78.0; H, 10.9%).

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