

## CHEMICAL EXAMINATION OF *SOLANUM TRILOBATUM*

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*Solanum trilobatum* L. is a very prickly trailing or climbing undershrub.<sup>1</sup> Its shoots are stellate and pubescent with ovate leaves. The corolla is blue and the berry,  $\frac{1}{4}$ – $\frac{1}{3}$  in. in diameter is globular. The plant is prescribed in the *Siddha*† system of medicine, for its cardiac, tonic, and carminative properties.<sup>2</sup>

Extraction of the plant with 2% acetic acid yielded a mixture of glyco alkaloids which was difficult to purify by crystallization.<sup>3</sup> 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.<sup>4</sup>

The base readily yielded a digitonide. Catalytic hydrogenation of the base in the presence of Pd–CaCO<sub>3</sub> 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 alkalamines. Our base therefore should be tomatid-5-en-3 $\beta$ -ol, and had constants comparable to the tomatid-5-en-3 $\beta$ -ol [(25*S*)-22 $\beta$ *N*-spirosol-5-en-3 $\beta$ -ol] isolated from *S. dulcumara* 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 an 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.

<sup>1</sup> Gamble, J. S., "Flora of the Presidency of Madras." Vol. II, p. 659. (Botanical Survey of India: Calcutta 1957.)

<sup>2</sup> Nadkarni, K. M., "Indian Materia Medica." 3rd Edn, Vol. II, pp. 1153–4. (Popular Book Depot: Bombay 1954.)

<sup>3</sup> Prelog, V., and Jeger, O., "The Alkaloids." (Ed. by R. H. F. Manske.) Vol. II, p. 343. (Academic Press: New York 1960.)

<sup>4</sup> Schreiber, K., "The Alkaloids." (Ed. by R. H. F. Manske.) Vol. X, p. 42. (Academic Press: New York 1968.)

*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  $C_{27}H_{44}ClNO_2$ : C, 72.15; H, 9.9%).

*Isolation of the Base*

The pure base liberated from the hydrochloride was crystallized from alcohol, m.p. 226–228° (Found: C, 78.15; H, 10.4; N, 3.4. Calc. for  $C_{27}H_{43}NO_2$ : C, 78.4; H, 10.4; N, 3.4%).  $[\alpha]_D^{30} -38.3$  (c, 2 in  $CHCl_3$ ).

*Picrate*

The picrate obtained by the usual procedure had m.p. 183–186° (Found: C, 61.4; H, 7.0. Calc. for  $C_{33}H_{46}NO_9$ : 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  $C_{28}H_{45}NO_3$ : C, 76.4; H, 9.9%).

From the hexane-soluble fraction, a diacetate was obtained identical with that of tomatidin-5-en-3 $\beta$ -ol, m.p. and mixed m.p. 164–165° (Found: C, 74.9; H, 9.6. Calc. for  $C_{31}H_{47}NO_4$ : C, 74.8; H, 9.5%).

*Hydrogenation*

Catalytic hydrogenation of the base (150 mg) in alcohol (20 ml) in the presence of Pd–CaCO<sub>3</sub> 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  $C_{27}H_{45}NO_2$ : C, 78.0; H, 10.9%).

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