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SHORT COMMUNICATION

SAPONINS AND SAPOGENINS—XXIX*

THE SAPOGENIN OF *SOLANUM NIGRUM* L. BERRIES

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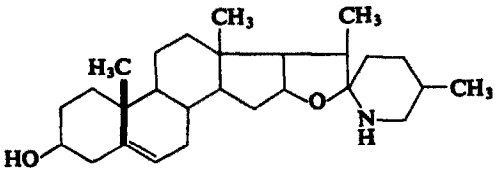
Abstract—The berries of *Solanum nigrum* L. have been found to contain a saturated steroidal genin which has been identified as tigogenin by mixed melting point and i.r. spectroscopy.

MEMBERS of the *Solanum* species (family Solanaceae) have been studied in the past and found to be a rich source of the steroidal alkaloids, solanine, solamargine, solasonine, and α- and β-solanigrine.[1,2] One of the species, *Solanum nigrum*, grows wild in India and is known as "makoi" in Hindustani. It is extensively used in Indian medicine.[3,4]

The berries of *Solanum nigrum* from New Zealand have recently been studied and found to contain four steroidal alkaloid glycosides, solamargine, solasonine, α- and β-solanigrine, all of which yield solasodine (I) as the aglycone.[2]



(I)

Though the presence of saponins in some Solanum species has been reported[5,6] no work seems to have been done so far on the saponin and sapogenin contents of *Solanum nigrum*.

The dried, powdered berries of this plant were defatted and extracted with ethanol; concentration of the extract and subsequent treatment give a mixture of saponins. Hydrolysis

* Part XXVIII, *Tetrahedron Lett.* No. 17, 1187 (1965).

[1] H. BRIGGS and R. C. CAMBIE, *J. Chem. Soc.* 1422, (1958); L. J. HAYNES and C. E. SEAFORTH, *J. Chem. Soc.* 745 (1963); S. B. CHAUDHARI and P. R. RAO, *Ind. J. Chem.* 2, 424 (1964).

[2] H. BRIGGS, R. C. CAMBIE and J. L. HOARE, *J. Chem. Soc.* 4645 (1961).

[3] M. K. NADKARNI and A. K. NADKARNI, *Indian Materia Medica*, Vol. 1, p. 1152, Popular Book Depot, Bombay (1954).

[4] R. N. CHOPRA, I. C. CHOPRA, K. L. HANDA and L. D. KAPOOR, *Indigenous Drugs of India*, p. 885 and 524, Dhar and Sons, Calcutta (1958).

[5] M. ROBERG, *Arch. Pharm.* 275, 145 (1937); *Chem. Abstr.* 31, 4052 (1937).

[6] R. E. MARKER, R. B. WAGNER, P. R. ULSHAFER, E. L. WITTBECKER, D. P. J. GOLDSMITH and C. HUOF, *J. Am. Chem. Soc.* 69, 1199 (1943).

of the saponins with sulphuric acid gave a mixture of genins which was separated into acid and neutral fractions. The neutral genin on crystallization from methanol had m.p. 206–208°,* acetate m.p. 200–202° (cf. tigogenin m.p. 206–207°, acetate m.p. 200–202°). It gave tests for the steroidal genin, and did not give any colour with tetranitromethane. The genin has been positively identified as tigogenin by mixed melting points of the genin and its acetate, and by the comparison of its i.r. spectra with authentic samples of tigogenin and its acetate prepared by the catalytic reduction of diosgenin obtained from *Balanitus roxburghii*.[7]

EXPERIMENTAL

Extraction of the saponin. Well-dried finely-powdered berries (1 kg) were defatted with light petrol., 40–60°, and then exhaustively extracted with ethanol. Removal of the ethanol left a dark brown syrupy mass which was treated with petrol, ether, carbon tetrachloride, chloroform and finally acetone. The light brown residue thus obtained was dissolved in a little alcohol and precipitated a number of times with ether–acetone. The light yellow powder thus obtained gave a copious foam when shaken with water.

Hydrolysis of the saponin. The saponin (6·0 g) was dissolved in water (3 l.) and hydrolysed with 8–10% H_2SO_4 at 100° for 1 hr followed by 30 min heating under reflux. The solid which separated was filtered, washed free of acid and dried.

Separation of the acid and the neutral genins. The crude genin mixture (2·0 g) was refluxed with 10% methanolic KOH on a water bath for 30 min, half the methanol was removed and the mixture was poured into a large volume of water which was then extracted with ether four times. The combined ethereal extracts were washed free of alkali and on removal of the solvent gave a crude yellowish neutral genin (600 mg). The alkaline solution left over after ether extraction was acidified with hydrochloric acid which precipitated the acid genin as a brownish precipitate. This was filtered and washed free of acid (500 mg).

Purification of neutral genin. The neutral genin obtained from the ethereal extracts was crystallized a number of times from methanol as colourless needles and had m.p. 206–208°.

Acetylation of the neutral genin. The neutral genin (200 mg) was acetylated with pyridine and acetic anhydride in cold in the usual manner. The acetate was crystallized from methanol as colourless needles m.p. 200–202°. It did not give any yellow colour with tetranitromethane (cf. tigogenin acetate m.p. 200–202°). Mixed m.p. with authentic tigogenin acetate showed no depression and i.r. spectra was superimposable. (Found: C, 76·15; H, 10·1. Calc. for $C_{29}H_{46}O_4$: C, 75·9; H, 10·1%).

Deacetylation of acetate. The neutral genin acetate was deacetylated by refluxing with 10% methanolic KOH. The genin after crystallization had m.p. 206–208° and showed no unsaturation with tetranitromethane. It gave no depression in m.p. when mixed with authentic sample of tigogenin (m.p. 206–207°).

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* All melting points are corrected.

[7] I. P. VARSHNEY and K. M. SHAMSUDDIN, *Arch. Pharm.* **295**, 401 (1962).