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## 1. *Solanum Alkaloids. Part I. The Alkaloid from the Fruit of Solanum aviculare.*

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The alkaloid from the green fruit of *Solanum aviculare*, previously regarded as a distinct alkaloid "purapurine," has now been shown to be identical with solasonine.

THE fruit from *Solanum aviculare* (Maori name "poro-poro") has already been investigated by Levi (*J. Soc. Chem. Ind.*, 1930, **49**, 395 r), who isolated a glucosidic alkaloid, m. p. 220—230°, yielding a sugar-free base on hydrolysis. Both compounds were obtained only as green amorphous powders and, of a number of derivatives prepared from the glycoside, only the thiocyanate was obtained crystalline. Since both compounds appeared to possess properties different from those of known compounds in this series, he named these compounds purapurine and purapuridine respectively, probably under the mistaken impression that the Maori name for this plant was "pura-pura." On the basis of analysis, formulæ  $C_{48}H_{78}O_{18}N_2$  and  $C_{37}H_{57}O_6N_2$  were suggested for the glucosidic alkaloid and the free base respectively. Both formulæ contain odd valencies and are therefore incorrect. The difference between the formulæ is  $C_{11}H_{16}O_{12}$ , which by addition of OH should give the sugar produced on hydrolysis. Such a compound,  $C_{11}H_{17}O_{13}$ , also contains odd valencies and even if it were  $C_{11}H_{16}O_{13}$  or  $C_{11}H_{18}O_{13}$  it still does not represent a normal carbohydrate.

The green berries of the shrub have now been reinvestigated. By working up the extract obtained by means of hot alcohol, a colourless crystalline alkaloid, m. p. 284—285° (decomp.), has been obtained in good yield; this is hydrolysed by 3% hydrochloric acid to the free base, m. p. 197·5—198·5°. From both the glycoside and the free base a number of crystalline salts have been prepared. The melting points of all these compounds agree with those of solanine-s and its corresponding free base, solanidine-s (now named solasonine and solasodine respectively; see following paper), from *S. sodomæum*.

To make a more complete comparison, authentic solasonine has been extracted from the green berries of *S. sodomæum*, and the same series of derivatives prepared from the pure alkaloid. In order to avoid differences in the melting and especially the decomposition points of such compounds due to different rates of heating (cf. Briggs, *J. Amer. Chem. Soc.*, 1937, **59**, 1404) the melting points of both sets of compounds and their mixtures have been observed simultaneously in the same melting point apparatus (electrically heated copper block). The melting points are set out in the following table.

| Derivative.         | Alkaloid from <i>S. aviculare</i> , m. p. | Solasonine, m. p. | Mixed m. p. |
|---------------------|---|-------------------|-------------|
| Glucoside .....     | 276—277°                                  | 275—276°          | 275—276°    |
| Picrate .....       | 200·5—201                                 | 199—199·5         | 200—200·5   |
| Picrolonate .....   | 231                                       | 230               | 230         |
| Free base .....     | 197·5—198·5                               | 197·5—198·5       | 197·5—198·5 |
| Picrate .....       | 144                                       | 143·5             | 144—144·5   |
| Picrolonate .....   | 234                                       | 233               | 234         |
| Hydrochloride ..... | 314                                       | 312               | 312·5       |
| Hydriodide .....    | 293                                       | 291               | 291·5       |
| Tartrate .....      | 222                                       | 222               | 221         |
| Oxalate .....       | 248                                       | 249               | 248         |

(All the above compounds melt with decomposition except the free bases.)

It is possible in the *Solanum* alkaloids that the same base can be united to different sugars, giving rise to different glycosidic alkaloids. The melting points, however, of the glycosides and their salts, previously unprepared, as well as the mixed melting points, indicate that both the glycosides and the free bases are identical. It is therefore not necessary to go to the more laborious procedure of identifying the glycoside through the sugars produced on hydrolysis (see Part IV; this vol., p. 17).

Further, crystal measurements of the hydrochloride of the free base are also in complete agreement with those of an authentic specimen. There can be no doubt, therefore, that the alkaloid from *S. aviculare* is identical with solasonine in all respects. The use of the names "purapurine" and "purapuridine" for these compounds should therefore be discontinued.

Solasonine has also been identified from the fruit of *S. xanthocarpum* (Saiyed and Kanga, *Proc. Indian Acad. Sci.*, 1936, 4, A, 255; Gupta and Dutt, *J. Indian Chem. Soc.*, 1938, 15, 95; cf. Briggs, *J. Amer. Chem. Soc.*, 1937, 59, 1404, 2467) and Anderson and Briggs (J., 1937, 1036) have reported its occurrence in the green berries of *S. auriculatum* (see Part III, this vol., p. 12, for further observations on the alkaloids from this source).

As already reported (Briggs, *Nature*, 1939, 144, 247), analytical data now agree with formulæ  $C_{45}H_{73}O_{16}N$  and  $C_{27}H_{43}O_2N$  for solasonine and solasodine respectively. These formulæ have been confirmed by the analyses of a number of derivatives (see Part II) and also by Rochelmeyer (*Arch. Pharm.*, 1939, 277, 329). Solasonine and solasodine crystallise with four and one molecule of water of crystallisation respectively and in both cases this is only removed with considerable difficulty.

#### EXPERIMENTAL.

*Isolation of Solasonine.*—The dried green berries from shrubs growing in Auckland were exhaustively extracted with alcohol in the apparatus described by Briggs (*Ind. Eng. Chem., [Anal.]*, 1937, 9, 250). When most of the alcohol had been removed from the extract by distillation, excess of 2% aqueous acetic acid was added, and the residual alcohol removed by steam-distillation. The aqueous solution was filtered, the filtrate boiled, and the crude solasonine precipitated in a granular form by the addition of ammonia (precipitation in the cold produces a jelly). The crude alkaloid was purified by solution in dilute acetic acid and reprecipitation with ammonia, followed by repeated crystallisation from 60–80% alcohol and 80% dioxan–water (crystallisation from higher concentrations of alcohol or dioxan produces a jelly) to give colourless pointed plates, m. p. 284–285° (decomp.),  $[\alpha]_D^{25}$  – 68.7° in alcohol ( $l = 2$  dcm.,  $c = 0.2320$ ) (Found: C, 60.5; H, 8.4; N, 1.6. Calc. for  $C_{45}H_{73}O_{16}N \cdot \frac{1}{2}H_2O$ : C, 60.6; H, 8.4; N, 1.6%).

The alkaloid from the green berries of *S. sodomæum* growing in Auckland was similarly extracted and purified;  $[\alpha]_D^{25}$  – 53.0° in alcohol ( $l = 2$  dcm.,  $c = 0.2736$ ) (Found: C, 60.5; H, 8.4; N, 1.6%).

Both compounds gave with concentrated sulphuric acid in the cold an amber-red colour and with concentrated nitric acid a brownish-yellow colour (for further colour reactions, see the following paper).

The picrate and the picrolonate were obtained by mixing the two components in hot alcoholic solution and were twice recrystallised from 60% alcohol.

*Hydrolysis of Solasonine.*—The pure alkaloid was heated with excess of 3% hydrochloric acid at 100° for 3 hours. (Solasodine hydrochloride, in contrast to solasonine hydrochloride, is only slightly soluble in the cold and is precipitated in a crystalline condition even from the hot solution.) After cooling, the hydrochloride was collected, recrystallised twice from 80% alcohol, suspended in hot water, basified with ammonia, and heated at 100° for  $\frac{1}{2}$  hour. The solasodine was collected after cooling and repeatedly crystallised from 80% alcohol, forming hexagonal plates, m. p. 197.5–198.5°,  $[\alpha]_D^{25}$  – 97.1° in methyl alcohol ( $l = 1$  dcm.,  $c = 0.1400$ ) (Found: C, 77.7, 77.7; H, 10.5, 10.6; N, 3.8. Calc. for  $C_{27}H_{43}O_2N$ : C, 78.45; H, 10.4; N, 3.4%). The hydrochloride had  $[\alpha]_D^{25}$  – 68.0° in methyl alcohol ( $l = 1$  dcm.,  $c = 0.4708$ ).

In the same manner solasodine was obtained by the hydrolysis of solasonine from *S. sodomæum*;  $[\alpha]_D^{25}$  – 80.4° in methyl alcohol ( $l = 1$  dcm.,  $c = 0.1984$ ) (Found: C, 77.9, 77.9; H, 10.5, 10.7; N, 3.4, 3.5%).

The colour reactions of both compounds are the same as those of the glycosides.

The salts of both compounds were prepared by addition of the components in hot alcohol and recrystallised in all cases from 80% alcohol. The melting points and mixed melting points are recorded on p. 1.

The hydrochlorides of solasodine from *S. aviculare* and *S. sodomæum* have been examined by Dr. F. J. Turner, Otago University, to whom we are indebted for the following report. (The crystals are too fragile for the crystal angles to be measured, but the optic axes have been measured.)

“Solasodine hydrochloride (*ex S. aviculare*):

$2V$  (the optic axial angle) = 80°, 82°, 82°, 84°, mean  $82^\circ \pm 2^\circ$ .

Optical character positive.

Some crystals are elongated parallel to  $\beta$  with  $\gamma$  nearly perpendicular to the plane of flattening. These have the same axial angle and the shape is due to variation in habit.

Solasodine hydrochloride (*ex S. sodomæum*):

$2V = 80^\circ, 82^\circ, 86^\circ, 90^\circ$ , mean  $85^\circ \pm 5^\circ$ .

Optical character positive.

Also, one measurement,  $2V = 88^\circ$ , optical character negative.

The hydrochlorides appear to be identical as regards habit, orientation and optic axial angle.”

The analyses are by Dr.-Ing. A. Schoeller.

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