284. Solanum *Alkaloids. Part XII.* Solasodamine, a New Tetrasaccharide Derivative of Solasodine, from* S. auriculatum, S. sodomaeum, *and* S. marginatum.

By LINDSAY H. BRIGGS and E. G. BROOKER.

A new tetrasaccharide derivative of solasodine, named solasodamine, has been isolated from the green fruit of *S. auriculatum*, *S. sodomaeum*, and *S. marginatum* by an improved extraction procedure. The carbohydrate component is formed from glucose (1 mol.), galactose (1 mol.), and rhamnose (2 mols.).

IN a further attempt to obtain the glycosidic alkaloid solauricine [1] from *S. auriculatum*, a product contaminated with partially hydrolysed glycosides was obtained. The berries extracted had been minced, dried, and stored for several years and it appeared that enzymic hydrolysis occurred during storage. Hence another extraction procedure was developed to obviate enzymic hydrolysis.

Fresh green berries were cut in halves and immediately placed in boiling methanol, and after extraction the glycosidic alkaloid was precipitated in the presence of methanol. Thus a new glycosidic alkaloid, m. p. 298—300°, named solasodamine, was isolated. Hydrolysis with 5% hydrochloric acid in ethanol gave solasodine and a mixture of sugars, shown to be glucose, galactose, and rhamnose by paper chromatography. Analyses of the glycoside and its picrate and picrolonate agree for the formula, $C_{51}H_{83}O_{20}N$, in accordance with the combination of solasodine with glucose, galactose, and two mols. of rhamnose. Quantitative separation of rhamnose, on a cellulose column, from the sugars obtained on hydrolysis, confirmed the presence of 2 mols. of rhamnose. Further work to elucidate the structure of the glycosidic moiety is in progress.

By the new technique, solasodamine has also been obtained from the fresh green fruits of *S. sodomaeum* and *S. marginatum*. The melting points of the glycosides and those of their picrates and picrolonates were similar. There were no differences in infrared spectra, *X*-ray powder photographs, pK_b values, and specific optical rotations of the three glycosides and they behaved identically on hydrolysis and on periodate oxidation (production of 2 mols. of formic acid and consumption of 6 mols.).

However, the new technique afforded only solasonine from fresh green berries of *S. aviculare*, and only solanine from those of *S. tuberosum*.

The isolation of solasodamine from *S. sodomaeum* suggested that in the earlier isolation of solasonine [2] hydrolysis had occurred with removal of a rhamnose group. That this assumption is not necessarily correct, however, was shown by the isolation of both solasodamine and solamargine from *S. marginatum* by the new procedure. Solasodamine was obtained from green fruit collected in August and solamargine from green fruit collected in April. Enzymic hydrolysis of rhamnose from solasodamine could not yield solamargine. Hydrolysis of pure solamargine affords only glucose and rhamnose as well as solasodine. However, when unpurified samples of solamargine (obtained by the earlier procedure [3]) were hydrolysed, traces of galactose appeared in chromatograms of the sugar mixtures, along with glucose and rhamnose. It appears, therefore, that trisaccharide and tetrasaccharide derivatives of solasodine may co-exist in the plant and that the combination of sugars is not static.

---

* Part XI, *J.*, 1953, 2833.

[1] Bell, Briggs, and Carroll, *J.*, 1942, 12.

[2] Briggs, Newbold, and Stace, *J.*, 1942, 3.

[3] Briggs, Brooker, Harvey, and Odell, *J.*, 1952, 3587.

EXPERIMENTAL

M. p.s marked * were taken in evacuated capillaries. Rotations were determined for MeOH solutions. The infrared spectra were measured with a Beckman IR.2 spectrophotometer. Paper chromatography of sugar solutions was carried out by the descending method on Whatman No. 1 paper with butan-1-ol–pyridine–water (3 : 1 : 1) as developing solvent and aniline hydrogen phthalate solution as spray reagent. Microanalyses are by Dr. A. D. Campbell, University of Otago. Compounds were dried overnight at 100° *in vacuo* over P_2O_5 before analysis.

Isolation of Solasodamine.—(a) *From* S. auriculatum. Fresh green berries, collected at Auckland in June, were coarsely minced and immediately extracted with boiling methanol for 2 hr. The filtered extract was concentrated under reduced pressure under an anti-foaming device and completely dissolved in 3% aqueous acetic acid. Concentrated aqueous ammonia was added to the boiling solution, and the coagulated precipitate collected after cooling. The almost colourless precipitate was redissolved in 3% aqueous acetic acid and again precipitated with ammonia. Repeated crystallisation from aqueous methanol (50%) gave colourless, rectangular plates of *solasodamine*, m. p. 298—300°* (decomp.), $[\alpha]_D^{20}$ −71·6° (*c* 0·447), pK_b 6·23 [4] (Found: C, 59·7; H, 8·4; N, 1·5. $C_{51}H_{83}O_{20}N$ requires C, 59·5; H, 8·1; N, 1·4%). The *picrate*, prepared in and recrystallised from aqueous ethanol (30%) in the presence of a slight excess of picric acid, formed yellow needles, m. p. 205°* (decomp.) (Found: C, 54·0; H, 7·2; N, 4·0. $C_{51}H_{83}O_{20}N,C_6H_3O_7N_3$ requires C, 54·4; H, 6·9; N, 4·4%). The *picrolonate*, prepared in and recrystallised from aqueous ethanol (80%), formed yellow, rectangular plates, m. p. 229—230°* (decomp.) (Found: C, 56·2; H, 6·9; N, 5·7. $C_{51}H_{83}O_{20}N,C_{10}H_8O_5N_4$ requires C, 56·6; H, 7·1; N, 5·4%).

(b) *From* S. sodomaeum. Fresh green berries, collected at Mt. Wellington, near Auckland, in August and extracted as in (a), gave rectangular plates, m. p. 302°* (decomp.), $[\alpha]_D^{20}$ −72·8° (*c* 0·194), pK_b 6·32 (Found: C, 59·8, 59·8; H, 8·2, 8·2; N, 1·1%). The picrate had m. p. 209° (decomp.) (Found: C, 55·0, 55·0; H, 6·95, 6·9; N, 4·6%) and the picrolonate, m. p. 237—238° (decomp.) (Found: C, 56·6, 56·9; H, 7·3, 7·2; N, 5·8%).

(c) *From* S. marginatum. Fresh green berries, collected at Mt. Wellington in August, on extraction gave rectangular plates, m. p. 301—302°* (decomp.), $[\alpha]_D^{20}$ −71·7° (*c* 0·446), pK_b 6·18 (Found: C, 60·5, 60·55; H, 8·0, 8·4; N, 1·4%). The picrate had m. p. 203° (decomp.) (Found: C, 54·4; H, 6·95; N, 4·85%) and the picrolonate, m. p. 235° (decomp.) (Found: C, 56·9; H, 7·3; N, 5·2%).

The infrared absorption spectra (Nujol mull) of solasodamine from the three species were identical: bands (in KBr) at 3472, 2941, 2890(i), 1684, 1656, 1631, 1458, 1437(i), 1377, 1342, 1309, 1292, 1245, 1190, 1170, 1139, 1088, 1056, 1019, 1003, 978, 965, 931, 896, 882, 837, 808(i), 792, and 755 cm.$^{-1}$ (i = inflexion).

X-Ray powder photographs of the glycosidic alkaloid from each species (8 hr.; copper *K*; sin θ observed up to 45°) were indistinguishable.

Hydrolysis of Solasodamine. Solasodamine (1 g.; from each species in separate experiments) was refluxed in concentrated hydrochloric acid (2 c.c.) and ethanol (20 c.c.) for 2 hr. at 100°. Colourless needles of solasodine hydrochloride were formed after 1½ hr. The mixture was heated with excess of ammonia solution at 100° for 1 hr.; the solid product, on repeated crystallisation from methanol and finally acetone, gave solasodine as colourless hexagonal plates, m. p. and mixed m. p. 200—201°*, infrared bands (in KBr) at 3472, 2941, 2890(i), 1684, 1656, 1631, 1458, 1437(i), 1377, 1342, 1309, 1292, 1245, 1190, 1170, 1139, 1088, 1056, 1019, 1003, 978, 965, 931, 896, 882, 837, 808(i), 792, and 755 cm.$^{-1}$. The picrate had m. p. and mixed m. p. 144—145° (decomp.).

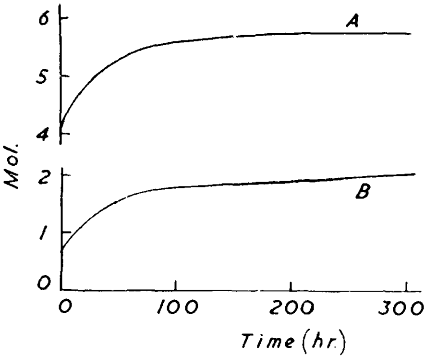
In a simliar experiment, the hydrochloride was removed and washed with water. The combined filtrate and washings were heated for a further hour at 100°, the ethanol being allowed to evaporate, and after removal of a further crop of hydrochloride the filtrate was neutralised (Amberlite I.R.A.-400 ion-exchange resin) and concentrated *in vacuo* at room temperature to *ca.* 1 c.c. Paper chromatography of this solution showed the presence of glucose, galactose, and rhamnose.

Periodate Oxidation of Solasodamine.—Solasodamine (0·5230 g.), previously dried at 110° for 43 hr. *in vacuo* over magnesium perchlorate, was dissolved in 0·0238N-formic acid (30 c.c.; 1·4 mol.), 0·034M-sodium metaperiodate (150 c.c., 10 mol.) added, and the volume made up to

500 c.c. with water. All solutions were held overnight at 25° before mixing. The final solution was held at 25° and the periodate consumed and formic acid produced were determined in aliquot parts at intervals.[5, 6] Results (see p. 1419) were identical with material from each source.

Examination of the Green Berries of S. marginatum *collected at a Different Season.*—Fresh green berries, collected at Mt. Wellington in April, were extracted by the above procedure. The product, after five recrystallisations from aqueous ammonia–ethanol (50%), yielded colourless pointed plates of solamargine, m. p. 302°* (decomp.), $[\alpha]_D^{17}$ −104° (*c* 1·561) (lit.,[3] m. p. 301°, $[\alpha]_D$ −105°) (Found: C, 62·2, 62·4; H, 8·6, 8·5; N, 1·6. Calc. for $C_{45}H_{73}O_{15}N$: C, 62·3; H, 8·5; N, 1·6%). The infrared spectrum could not be distinguished from that of solasodamine. The picrate formed rectangular yellow plates, m. p. 185°* (decomp.) (lit.,[3] m. p. 188—189°) (Found: C, 55·7; H, 6·6. Calc. for $C_{45}H_{73}O_{15}N,C_6H_3O_7N_3$: C, 55·8; H, 6·9%). The picrolonate formed yellow needles, m. p. 199—200°* (decomp.) (lit.,[3] m. p. 204—205°) (Found: C, 58·3; H, 6·9. Calc. for $C_{45}H_{73}O_{15}N,C_{10}H_8O_5N_4$: C, 58·3; H, 7·2%).

Hydrolysis of the glycoside with ethanolic hydrochloric acid (10%) for 3 hr. at 100° afforded solasodine, m. p. and mixed m. p. 201—202°*, and paper chromatography of the neutralised sugar solution showed the presence of glucose and rhamnose.



A, Periodate consumed;
B, formic acid produced.

Examination of the Green Berries of S. aviculare.—Extraction of fresh green berries collected in Auckland in February gave solasonine (0·75%) which crystallised from aqueous methanol as colourless rectangular plates, m. p. 300—301°* (decomp.) (lit.,[7] 284—285°) (Found: C, 61·1; 61·1, 61·25; H, 8·4, 8·4, 8·4. Calc. for $C_{46}H_{73}O_{16}N$: C, 61·1; H, 8·3%). The picrate formed yellow plates, m. p. 203°* (decomp.) (lit.,[7] m. p. 200·5—201°) (Found: C, 55·4; H, 6·8; N, 5·2. Calc. for $C_{45}H_{73}O_{16},C_6H_3O_7N_3$: C, 55·0; H, 6·9; N, 5·0%). The picrolonate formed yellow plates, m. p. 234°* (decomp.) (lit.,[7] m. p. 231°) (Found: C, 57·7; H, 7·0; N, 5·8. Calc. for $C_{45}H_{73}O_{16}N,C_{10}H_8O_5N_4$: C, 57·5; H, 7·1; N, 6·1%). The infrared spectrum could not be distinguished from that of solasodamine.

Examination of the Green Berries of S. tuberosum.—Extraction of fresh green berries of *S. tuberosum* var. "Chippewa" ("potato apples") collected at Ashburton in January, and separation from considerable inorganic material containing aluminium compounds, gave solanine as colourless needles, m. p. 290°* (decomp.) (lit.,[8] m. p. 285°) (Found: C, 62·2, 62·5; H, 8·3, 8·4; N, 1·5. Calc. for $C_{45}H_{75}O_{15}N$: C, 62·3; H, 8·5; N, 1·6%). The infrared spectrum (KBr) had bands at 3448, 2985, 1460, 1437, 1422, 1370, 1346(i), 1323, 1241, 1202, 1147, 1080, 990(i), 916, 989(i), 826, 777, and 738(i) cm.$^{-1}$.

We are greatly indebted to Dr. H. Bloom for pK_b measurements, Dr. L. D. Calvert for *X*-ray powder photographs, and Dr. B. Cleverly and Mr. L. D. Colebrook for infrared measurements. We gratefully acknowledge financial assistance from the Chemical Society, The Rockefeller Foundation of New York, the Australian and New Zealand Association for the Advancement of Science, the Royal Society of New Zealand, and the Grants Committee of the University of New Zealand, and gifts of chemicals from Messrs. Rohm and Haas Company, Philadelphia. One of us (E. G. B.) is also indebted for a University Research Fund Fellowship.

UNIVERSITY OF AUCKLAND, AUCKLAND, NEW ZEALAND. [*Received, October 29th,* 1957.]

---

[4] Bloom and Briggs, *J.*, 1952, 3591.
[5] Briggs and Vining, *J.*, 1953, 2809.
[6] Briggs and Brooker, *J.*, 1953, 2833.
[7] Bell and Briggs, *J.*, 1942, 1.
[8] Soltys and Wallenfels, *Ber.*, 1936, **69**, 811.