908. Solanum *Alkaloids. Part XV.*[1] *The Constituents of Some* Solanum *Species and a Reassessment of Solasodamine and Solauricine.*

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The glycosidic alkaloids of the fruit of eight members of the morellae section, and four others, of the *Solanum* species, have been shown by paper chromatography to contain solasonine and solamargine. Diosgenin has been isolated from the fruit of *S. auriculatum* Ait.

Further work has shown that solasodamine is solasonine monohydrate, solauricine is a mixture of solasonine and solamargine, and that solauricidine is probably a complex of solasodine and its galactoside.

The pigments of the ripe fruit of four *Solanum* species and the flowers of one have been identified as petanin and delphanin.

IN a continuation of our investigations of the glycosidic alkaloid constituents of *Solanum* species[2] the green berries of eight plants belonging to the section morellae have been examined by paper chromatography with Paseshnichenko and Guseva's solvent system.[3] The results are reported in Table 1.

The yield of crude alkaloid varied considerably but the major constituents in each case

TABLE 1.

(A) = Solamargine; (B) = solasonine; (C) = β- and (D) = α-"solanigrine." Relative strengths of spots estimated visually on a weak (+) to strong (+++) basis. $R_{\alpha s} = R$ for α-solanine.

Species	Source	Herbarium no.*	Yield (%)	(A) $R_{\alpha s}$ 2·5	(B) $R_{\alpha s}$ 1·3	(C) $R_{\alpha s}$ 0·5	(D) $R_{\alpha s}$ 0·2
Section: morellae							
S. americanum Mill.	U.S.A.	69,340	0·3	+++	+++	+	+
S. furcatum L.	Chile	69,338	0·6	+++	+++	+	+
S. "*gsoba*"	Unknown	69,343	0·6	+++	+++	+	+
S. interandinum Bitt. ...	Ecuador	69,341	0·2	+++	+++	+	+
S. melanocerasum All. ...	Denmark	69,345	0·1	+++	+++	(+)	(+)
S. nigrum L.	New Zealand	—	0·4	+++	+++	++	+
S. roxburghii Dun..........	India	69,346	0·7	+++	+++	++	+
S. sarachoides Sendtner...	U.S.A.	69,344	0·5	+++	+++	++	+
S. villosum Dun.	Denmark	69,342	0·1	+++	+++	+	+
S. aviculare Forst..........	New Zealand	—	0·6	+++	+++	+	
S. ciliatum Lam.	Costa Rica	69,347	0·3	+++	+++		
S. integrifolium Poir	Unknown	—	0·2	+++	+++	+	
S. rostratum Dun.	U.S.A.	69,339	0·1	++	++		
S. vescum F. Muell.	Australia	—	0·9	+++	+++		

* No. of a leaf sample lodged in the herbarium of the Auckland Institute and Museum.

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[1] Part XIV, Briggs, Colebrook, Miller, and Sato, *J.*, 1960, 3417.

[2] Briggs and Cambie, *J.*, 1958, 1422, and preceding papers.

[3] Paseshnichenko and Guseva, *Biokhimiya*, 1956, **21**, 585.

were shown to be solasonine and solamargine by chromatographic comparison with authentic samples. The same alkaloids were also shown to be present in four species belonging to other sections and their presence confirmed in the previously investigated species, *S. nigrum* L.[2,4,5] and *S. aviculare* Forst.[2,6] The presence of the principal alkaloid solasonine in *S. vescum* was confirmed by isolation, analysis, and hydrolysis to solasodine.

In addition to those corresponding to solasonine and solamargine weak spots corresponding to α- and β-" solanigrines," isolated from some species of the *S. nigrum* group by Schreiber,[5] were often observed and are probably due to the presence of different tetrasaccharides of solasodine. Although all berries were extracted by the improved method in which enzymic hydrolysis has been minimised,[7] with a few species traces of faster-moving spots were detected which could possibly correspond to fragments of enzymically hydrolysed solasonine or solamargine.

" *Solasodamine.*"—The green berries of *S. auriculatum*, *S. sodomaeum*, and *S. marginatum* were earlier reported[7] to contain solasodamine, a tetrasaccharide of solasodine, the glycosidic moiety of which contained glucose (1 mol.), galactose (1 mol.), and rhamnose (2 mols.), but repeated attempts to isolate further solasodamine from *S. auriculatum* gave solasonine as the major alkaloid with solamargine shown also to be present by paper chromatography. Paseshnichenko and Guseva's solvent system,[3] which was only available after the completion of the earlier work, was here used and in our experience is capable of differentiating mono-, di-, and tri-saccharides in this series. As these have decreasing R_F values, a tetrasaccharide would be expected to have an even lower R_F value. Solasodamine, however, has an R_F value identical with that of solasonine while solasonine, solamargine, and solanine (all with trisaccharide moieties) were readily resolved.

Re-examination (see Experimental section) has now convinced us that solasodamine is solasonine monohydrate and its name should, therefore, be discontinued.

" *Solauricine* " *and* " *Solauricidine.*"—Earlier, the isolation of a supposedly new glycoalkaloid, solauricine, from the dried berries of *S. auriculatum*, was reported.[8] Solauricine differed significantly from solasonine only in that the melting point (222—223°) of the derived alkamine, solauricidine, was higher than that of solasodine (200·5—202·5°). Attempts to reisolate solauricine and solauricidine from dried or fresh berries from monthly samples have been unsuccessful but samples of solauricidine regenerated from its salts still had m. p. 216—219°.

Re-examination of the original small samples by paper chromatography now indicates (see Experimental section) that " solauricidine " was a mixture of solasodine and its galactoside.

In addition, diosgenin has been isolated from the green berries. This has previously been reported from *S. xanthocarpum*[9] and *S. aviculare.*[10]

Pigments.—Two pigments from the ripe berries of *S.* " *gsoba* " were investigated by chromatographic methods.[11] R_F values in four solvent systems and the ultraviolet spectra were identical with those recorded for petanin and delphanin.[11] That the pigments were acylated followed from the chromatographic behaviour; a peak in the ultraviolet spectrum at 310 mμ indicated that the acyl component was *p*-coumaric acid (*p*-hydroxycinnamic acid).[12] Acid hydrolysis of the purified pigments and chromatography gave petunidin as the major anthocyanidin and smaller amounts of delphinidin, *p*-coumaric acid, glucose, and rhamnose, the former sugar occurring in double the concentration of

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[4] Boll, *Acta Chem. Scand.*, 1958, **12**, 358.

[5] Schreiber, *Planta Med.*, 1958, **6**, 435.

[6] Kuhn, Löw, and Trischmann, *Chem. Ber.*, 1955, **88**, 289.

[7] Briggs and Brooker, *J.*, 1958, 1419.

[8] Anderson and Briggs, *J.*, 1937, 1036; Bell, Briggs, and Carroll, *J.*, 1942, 12.

[9] Sato and Latham, *J. Amer. Chem. Soc.*, 1953, **75**, 6067.

[10] Schreiber, " Sonderabduck aus Abhandlungen der deutschen Akademie der Wissenschaften zu Berlin," 1957, October.

[11] Harborne, *Biochem. J.*, 1960, **74**, 262 and preceding papers; *J. Chromat.*, 1958, **1**, 473.

[12] Harborne, *Biochem. J.*, 1958, **70**, 22.

the latter. A small spot corresponding to arabinose was also observed but Harborne and Sherratt[13] have pointed out that paper chromatography with solvents containing hydrochloric acid can produce arabinose as an artifact. The report that petanin, accompanied by traces of delphanin, is of widespread occurrence in plants of the Solanaceæ[11] supports the identification of the pigments in the present case. A similar investigation showed that the same pigments are present in the ripe berries of *S. americanum, S. interandinum,* and *S. intrusum,* and the flowers of *S. auriculatum.*

EXPERIMENTAL

Analyses are by Dr. A. D. Campbell, University of Otago, New Zealand, samples being dried at 100° to constant weight. *X*-Ray powder photographs were measured by using Pyrex capillaries and copper-*K* radiation. The crude alkaloids were isolated from green berries as previously described.[2] The species examined were germinated from seed in sterilised soil at 70° F and grown under controlled conditions.

Chromatography of Solanum *Alkaloids.*—Whatman's No. 1 paper, equilibrated for 12 hr., was used throughout with the following solvent systems: A (for glycosides), ethyl acetate–acetic acid–water (11 : 2 : 1·85; to give a homogeneous mixture; cf. ref. 3). In addition the system ethyl acetate–pyridine–water (3 : 1 : 3) was employed for comparison of $R_{\alpha s}$ values with those obtained by Schreiber for α- and β-" solanigrine ";[5] B (for alkamines), benzene–chloroform (1 : 2) saturated with formamide (stabilised with 1% v/v of light petroleum) on paper impregnated with formamide–acetone (3 : 7).[14] Iodine in light petroleum solution and a 25% solution of antimony trichloride in chloroform were used as sprays. With solvent A the following $R_{\alpha s}$ values were recorded: solanine 1·0; solasonine 1·3; solamargine 2·3; solasodine glucosylgalactoside * 2·5; solasodine rhamnosylglucoside 5·0;[15] solasodine glucoside 10·0, R_F 0·40; solasodine 15·0; R_F 0·76; solanidine 14·0, R_F 0·73. With solvent B the following R_F values were recorded: solasodine 0·5; solanidine 0·3; solasodine glucoside and solasonine 0·0.

The sugars from hydrolysis were examined as previously described.[2,7]

S. vescum.—*Isolation of solasonine.* The crude alkaloid (4·2 g.) from green berries (464 g.) was purified by repeated precipitation from boiling 3% acetic acid solution with ammonia. Repeated crystallisation from aqueous methanol (50%) gave needles, m. p. 298—302° (decomp.), which gave a single spot on the chromatogram corresponding to solasonine (Found: C, 61·3; H, 8·65; N, 1·7. Calc. for $C_{45}H_{73}NO_{16}$: C, 61·1; H, 8·3; N, 1·6%) [picrolonate, needles, m. p. 234° (decomp.) (Found: C, 57·1; H, 7·2; N, 6·2. Calc. for $C_{45}H_{73}NO_{16},C_{10}H_8N_4O_5$: C, 57·5; H, 7·1; N, 6·1%)].

Hydrolysis of solasonine in the usual manner[2] gave solasodine, m. p. and mixed m. p. 199—200°. Comparative paper chromatography of the concentrated sugar solution showed the presence of galactose, glucose, and rhamnose.

S. auriculatum.—*Isolation of diosgenin.* The mixed glycosides (10 g.) from green berries (4·5 kg.), containing solasonine, solamargine, and a trace of a further alkaloid ($R_{\alpha s}$ 0·5), were hydrolysed in the usual manner, and the precipitated solasodine hydrochloride was washed with water and ether. Ether removed from the aqueous filtrate a gum which was chromatographed in chloroform on alumina (Spence and Co., grade H). Crystallisation of fractions eluted with chloroform gave diosgenin (40 mg.) which separated from acetone as needles, m. p. and mixed m. p. 203—206° (Found: C, 77·9; H, 10·1. Calc. for $C_{27}H_{42}O_3$: C, 78·2; H, 10·2%) (correct infrared spectrum). The acetate crystallised from acetone in rods, m. p. and mixed m. p. 197—198·5° (Found: C, 75·9; H, 9·8; Ac, 9·6. Calc. for $C_{29}H_{44}O_4$: C, 76·3; H, 9·7; Ac, 9·4%).

Treatment of an aqueous suspension of solasodine hydrochloride with aqueous ammonia (*d* 0·88) for 1 hr. at 100° gave solasodine, which on crystallisation from methanol had m. p. and mixed m. p. 199—201°.

The basified mother-liquors (600 c.c.) were extracted with chloroform and the extracts

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* Unpublished work.

[13] Harborne and Sherratt, *Experientia*, 1957, **13**, 486.

[14] Tuzson, *Naturwiss.*, 1956, **43**, 198.

[15] Briggs, Tagungsberichte der Internationales Symposium über Chemie und Biochemie der Solanum-Alkaloide, Berlin, June 1959.

washed, dried, and concentrated to dryness *in vacuo*. The amorphous residue was chromatographed in chloroform on activated alumina, 100-c.c. fractions being eluted with chloroform. The combined residues from fractions 3—6 were washed with a little benzene and recrystallised from acetone, to give solasodiene (140 mg.) as rectangular plates, m. p. and mixed m. p. 177—178° (Found: C, 82·0; H, 10·6; N, 3·3. Calc. for $C_{27}H_{41}NO$: C, 82·0; H, 10·45; N, 3·5%). The hydrochloride prepared by passing hydrogen chloride into an 80% aqueous ethanol solution had m. p. 318—320° (decomp.) [lit.,[16] m. p. 318° (decomp.)] (Found: C, 75·1; H, 10·2. Calc. for $C_{27}H_{41}NO,HCl$: C, 75·0; H, 9·8%).

Leaves of S. auriculatum.—Fresh green leaves (820 g.) worked up in the usual manner gave crude mixed alkaloids (5·0 g.) containing solasonine ($R_{\alpha s}$ 1·3) and solamargine ($R_{\alpha s}$ 2·5).

Berries of S. auriculatum.—(*a*) The alkaloids (7·5 g.) isolated in the normal manner from dried berries (1·65 kg.) contained solasonine ($R_{\alpha s}$ 1·3, strong), solamargine ($R_{\alpha s}$ 2·5, strong), and two alkaloids ($R_{\alpha s}$ 0·5, weak; and 5·8, strong).

(*b*) Ripe yellow berries (2·6 kg.) were coarsely crushed, made into a slurry with water, covered with toluene, and left to ferment for 4 months. The slurry was mixed with Celite and filtered. Precipitation of the alkaloids with ammonia and working up in the usual manner with separation from considerable inorganic matter gave crude bases, containing solasonine ($R_{\alpha s}$ 1·3, very weak) and an alkaloid ($R_{\alpha s}$ 0·5, very weak).

Re-examination of " Solasodamine."—No significant difference exists between the recorded physical properties of solasodamine and solasonine or of their respective derivatives. The analytical requirements for solasodamine (Calc. for $C_{51}H_{83}NO_{20}$: C, 59·5; H, 8·1; N, 1·4%) are very similar to those for solasonine monohydrate (Calc. for $C_{45}H_{73}NO_{16},H_2O$: C, 59·9; H, 8·4; N, 1·55%); the same applies to the picrates and picrolonates. The original samples of solasodamine for analysis were dried overnight at 100° over phosphorus pentoxide. Samples of solasodamine dried to constant weight at 100° have now given analytical figures in agreement with those for solasonine (Found: C, 61·3; H, 8·3; N, 1·4. Calc. for $C_{45}H_{73}NO_{16}$: C, 61·15; H, 8·3; N, 1·6%).

Solasodamine was found earlier on periodate oxidation to consume 6 mol./mol. and to produce 2 mol. of formic acid. When the calculations are re-interpreted on the basis of the molecular weight of solasonine (the samples oxidised were dried at 110° for 43 hr. *in vacuo* over magnesium perchlorate), the values become 5·0 and 1·8, respectively, in agreement with those found for solasonine.[17]

In the quantitative separation of the sugars liberated on hydrolysis of solasodamine it was reported that 2 mol. of rhamnose were produced. The rhamnose, eluted as the initial product from a cellulose column, was obtained only as a syrup which was dried to constant weight at 40° over magnesium perchlorate. Although the rhamnose was uncontaminated with other sugars it appears that significant amounts of impurity could have been eluted from the column or that the material was insufficiently dried. In subsequent experiments involving the chromatography of sugars on cellulose columns we found that impurities are still eluted from columns which had been pre-washed before use.

Further, as previously reported,[7] the infrared spectra of solasodamine and solasonine are indistinguishable but further measurements now show a slight difference between those of solasonine and solamargine. Finally, *X*-ray powder photographs of solasodamine and solasonine are identical but that of solamargine is different.

Solasonine " solasodamine " (5·1 g.), dried over magnesium perchlorate at 110°/0·01 mm. for 3 days, was heated under reflux with acetic anhydride (83 c.c.) and pyridine (1 c.c.) for 2 hr. The solution was concentrated to 25 c.c. *in vacuo* and treated with ice. The oil produced slowly solidified. Purification by repeated precipitation from alcohol with water, followed by repeated crystallisation from moist benzene, gave hygroscopic prisms of *deca-acetylsolasonine* (6·67 g.), m. p. 159·5—163° (decomp.) with sintering at 125° (Found: C, 60·0; H, 7·4; N, 1·0; Ac, 32·9. $C_{65}H_{93}NO_{26}$ requires C, 60·0; H, 7·2; N, 1·1; 10Ac, 33·0%).

Re-examination of " Solauricine " and " Solauricidine."—Solauricine gave a major spot identical with that of solasonine and a minor spot corresponding to solamargine, a compound now shown to co-exist in the berries. Reversed-phase paper chromatography of analytical samples of solauricidine showed a major spot corresponding to solasodine, and a spot at the origin corresponding to glycosidic material. When a solvent system capable of resolving

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

[17] Briggs and Vining, *J.*, 1953, 2809.

glycosides was used this impurity appeared as a spot corresponding to a solasodine monosaccharide. This was then shown to be solasodine galactoside since hydrolysis of the sample and chromatographic examination of the sugars showed a faint spot corresponding to galactose (it will be shown later that in solasonine galactose is directly joined to the alkamine, as in solanine). Single crystals of solauricidine, however, on the micro-stage showed no sign of melting around 200° (the m. p. of solasodine), but softened and gradually shrank above 212° with melting at 218—222°, varying somewhat from crystal to crystal. Although insufficient material remains to resolve the problem unambiguously it appears that solauricidine is a complex of solasodine and solasodine galactoside resulting from incomplete hydrolysis.

Examination of the Anthocyanins.—The general method of isolation, separation, and purification of pigments, and the conditions used for spectroscopy and paper chromatography, were those recorded by Harborne for petanin and delphanin.

To isolate the pigments from *S.* "*gsoba*" chromatography was initially carried out in Harborne's solvent A,[11] followed by rechromatography in Harborne's solvents B and C,[11] on Whatman No. 3MM paper until the pigments were free from visible impurities and substances fluorescing in ultraviolet light. At each purification the pigments were eluted from the paper with acetic acid–methanol–water (5 : 70 : 25) in Canny's apparatus,[18] and the resulting extracts were concentrated *in vacuo* at room temperature.

After acid hydrolysis [11] of the pigments, comparative paper chromatography and spectroscopic examination showed the presence of petunidin, delphinidin [Harborne's solvent B,[11] and formic acid–concentrated hydrochloric acid–water (5 : 2 : 3)], and glucose, rhamnose, and arabinose [butan-1-ol–pyridine–water (3 : 1 : 5, upper phase with 1 vol. of pyridine)].

Alkaline hydrolysis [11] and comparative chromatography showed the presence of *p*-coumaric acid (Harborne's solvent B).

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[18] Canny, *J. Chromat.*, 1960, **3**, 496.