4. Solanum *Alkaloids. Part IV. The Glycosidic Moiety of Solauricine.*

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The glycosidic moiety of solauricine is shown to consist of glucose, rhamnose, and galactose. The trisaccharide portion of the molecule is therefore probably the same as that occurring in solanine and solasonine.

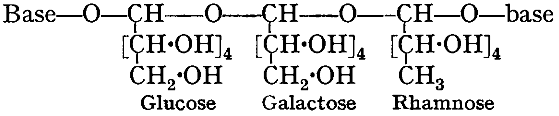
In Part III (preceding paper) evidence has been given that the glucosidic alkaloid solauricine isolated from *Solanum auriculatum* and its aglycone, solauricidine, are isomeric with but different from the corresponding bases solasonine and solasodine from *S. sodomæum.* The possibility that the aglycone solauricidine is combined in the glucosidic alkaloid with a trisaccharide different from that occurring in both solanine and solasonine (Zemplén and Gerecs, *Ber.*, 1928, **61**, 2294; Oddo and Caronna, *ibid.*, 1934, **67**, 444; cf. also Part II, this vol., p. 3) has been tested experimentally and in the sugar solution obtained on hydrolysis the presence of galactose, rhamnose, and glucose has been established. The galactose was identified as its *o*-tolylhydrazone by treatment with *o*-tolylhydrazine, which does not yield a solid derivative with glucose or rhamnose (van der Haar, *Rec. Trav. chim.*, 1917, **37**, 108).

Treatment of the sugar solution with phenylhydrazine gave a mixture of osazones from which glucosazone was isolated by fractional crystallisation, and after evaporation of another portion almost to dryness, followed by treatment with absolute alcohol, rhamnose separated in a pure form and was identified as its *p*-nitrophenylhydrazone. The deposition of rhamnose from the sugar solution before glucose or galactose agrees with the experiments of Zeisel and Wittmann (*Ber.*, 1903, **36**, 3554), but according to Hudson and Tanovsky (*J. Amer. Chem. Soc.*, 1917, **39**, 1013) rhamnose is much more soluble than either glucose or galactose in aqueous alcoholic solution.

Since these sugars from solauricine also form the trisaccharide moiety of solanine and solasonine, on phytochemical grounds all three trisaccharides are probably identical. Zemplén and Gerecs do not indicate whether glucosidic or ether linkages are present in the sugars, but Oddo and Caronna suggest the following general formula for solanine :

$$\underset{\text{Rhamnose}}{C_6H_{11}O_4}\text{—O—}\underset{\text{Galactose}}{C_6H_{10}O_4}\text{—O—}\underset{\text{Glucose}}{C_6H_{10}O_4}\text{—O—}\underset{\text{Solanidine}}{\text{base}}$$

and an unusual type of linkage for solasonine (cf. also Oddo and Cesaris, *Gazzetta*, 1914, **44**, ii, 182)



$$\begin{array}{cccc} \text{Base—O—} & \text{CH——O——} & \text{CH——O——} & \text{CH—O—base} \\ & [\text{CH·OH}]_4 & [\text{CH·OH}]_4 & [\text{CH·OH}]_4 \\ & CH_2\text{·OH} & CH_2\text{·OH} & CH_3 \\ & \text{Glucose} & \text{Galactose} & \text{Rhamnose} \end{array}$$

or

$$\text{base—O—}C_6H_{12}O_5\text{—O—}C_6H_{12}O_5\text{—O—}C_6H_{12}O_4\text{—O—base}$$

Apart from the fact that it has been shown in Part II that only one molecule of solasodine is joined to the trisaccharide and not two as suggested by Oddo, by comparison of the above formulæ it is seen that the sugar units of solasonine contain one molecule of water more than the corresponding sugars in solanine. Since a trisaccharide containing glucose, galactose, and rhamnose units does not occur to the authors' knowledge elsewhere in the plant kingdom other than in the *Solanum* genus, it seems most unlikely that the sugar units in solanine and solasonine differ in the way indicated by Oddo and co-workers. The partial formula given for solanine agrees for normal pyranose (or furanose) structures for each sugar unit, so solasonine and solauricine should be similarly formulated. Oddo and Cesaris (*loc. cit.*) have reported that solasonine fails to react with phenylhydrazine and it can thus be concluded that the sugars are united to each other through their potential aldehyde structures.

On the above formulation both solanine and solasonine should yield an acetate containing nine acetyl groups (all combined with sugar hydroxyl groups). This is not, however, in accordance with the results of previous workers on both solanine (Hilger, *Annalen*, 1879, **195**, 321; Heiduschka and Sieger, *Arch. Pharm.*, 1917, **255**, 18; Zemplén and Gerecs, *loc. cit.*; Oddo and Caronna, *loc. cit.*; Heiduschka and Philippi, *Ber.*, 1935, **68**, 669) and solasonine (Oddo and Caronna, *loc. cit.*).

Since these previous results, however, are not concordant in themselves, our conclusions for the formulation of the trisaccharide moiety are not thereby invalidated.

EXPERIMENTAL.

Solauricine, m. p. 270—271° (decomp.), was obtained by working up the alcoholic extract of the dried green berries of *S. auriculatum* as described in Parts I and III.

Solauricine (20 g.) was hydrolysed by heating with 2% sulphuric acid (4 c.c. of concentrated acid in 400 c.c. of water) on the water-bath for 3 hours. After cooling, the precipitate of solauricidine sulphate was removed, and the filtrate heated for 2 hours to complete the hydrolysis and again filtered. The sulphate, when treated in aqueous suspension with ammonia, afforded material, m. p. 218—220°, which after repeated crystallisation from 80% alcohol (charcoal) formed colourless plates of solauricidine, m. p. 219°.

The combined filtrates from the hydrolysis were shaken with excess of barium carbonate and kept for 24 hours, and the insoluble material removed. The neutral filtrate was concentrated in a vacuum to a fifth of its volume with the use of an anti-foaming device. After filtration from a small amount of solid matter a clear, almost colourless solution of the sugars was obtained.

Identification of Galactose.—An aliquot portion (13·5 c.c.) of the sugar solution was mixed with freshly distilled *o*-tolylhydrazine (0·61 g.) and dissolved in the minimum amount of alcohol. After ½ hour's heating at 100° and cooling, colourless needles formed, which were collected and washed with 50% alcohol. The crystals then had m. p. 173° (decomp.), undepressed by authentic galactose-*o*-tolylhydrazone prepared in a similar manner. Van der Haar (*loc. cit.*) gives m. p. 176° (decomp.).

Identification of Rhamnose.—An aliquot portion of the sugar solution (13·5 c.c.) was evaporated almost to dryness on a water-bath, triturated with absolute alcohol, and kept for some days. Large, colourless, homogeneous crystals had then separated which, after being washed with 50% alcohol and dried, had m. p. 90—91°, undepressed by a commercial sample of rhamnose of the same m. p.

The above material (100 mg.), m. p. 90—91°, and *p*-nitrophenylhydrazine (100 mg.) were dissolved in alcohol (15—20 c.c.), boiled for a few minutes, and allowed to cool. The yellow needles which separated, after being washed with 50% alcohol and dried, had m. p. 191°, undepressed by authentic rhamnose-*p*-nitrophenylhydrazone similarly prepared. Butler and Cretcher (*J. Amer. Chem. Soc.*, 1931, **53**, 4363) record m. p. 190—191°.

Identification of Glucose.—A further portion of the original sugar solution (15 c.c.) was heated with freshly distilled phenylhydrazine (4·85 g.), glacial acetic acid (7·5 c.c.), and water (30 c.c.) on the water-bath for ½ hour; more water (2 c.c.) was then added, and heating continued for ½ hour. During the first heating and afterwards the characteristic sheaf-like needles of glucosazone could be detected in the reaction mixture. The product, after being washed with 2% acetic acid, had m. p. 176—187° (decomp.), but after successive trituration with ether, acetone and boiling acetone the m. p. rose to 197—199° (decomp.). The crystals were then dissolved in a large quantity of boiling acetone, and the solution concentrated to half volume and allowed to cool. Glucosazone separated, m. p. 209—209·5°, undepressed by an authentic specimen.

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