RE-EXAMINATION OF THE ALKALOIDS OF THE FRUITS OF SOLANUM XANTHOCARPUM*

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*Solanum xanthocarpum was first examined by Dymock.¹ He found that its fruits gave alkaloidal reactions corresponding to those of Solanine. Pendse and Dutt² detected the presence of very small quantities of alkaloids in the fruits.

Saied and Kanga³ reported the isolation from the seeds of a glucos-alkaloid, m.p. 245°C. In addition to this they also obtained from the alcoholic extract, two more basic substances melting at 265°C. and 196°C. The same authors have given a detailed account of their studies in a later communication.⁴ They named the gluco-alkaloid, ‘Solanarpine’, C_{44}H_{77}O_{19}N, m.p. 288–89°C. (decomp.), and the agluco-alkaloid, ‘Solarcarmidine’, C_{28}H_{43}O_{3}N, m.p., 197–98°C. On the hydrolysis of the gluco-alkaloid they obtained glucose, rhamnose and another hexose and suggested that the third sugar was probably galactose.

Briggs⁵ has proved by the method of mixed melting point, the identity of Solanacarpine with ‘Solanine–S’, m.p. 272°C., from Solanum sodamæum,⁶ and Solanum auriculatum.⁷

Gupta and Dutt⁸ on the other hand claim to have isolated from the seeds of Solanum xanthocarpum a gluco-alkaloid, ‘Solanacarpine’, C_{44}H_{74}O_{11}N_{2}, m.p. 272°C., which on hydrolysis gave an agluco-alkaloid ‘Solanacarpigenin’, C_{32}H_{54}O_{2}N_{2}, m.p. 196°C., together with glucose and rhamnose only.

In view of the discrepancies observed above a re-examination of the alkaloidal constituents of the fruits of Solanum xanthocarpum was undertaken. The gluco-alkaloid, Solanine–S was found to melt at 279°C. and decompose at 290°C. and had the formula C_{44}H_{77}O_{19}N. The agluco-alkaloid, Solanidine-S, C_{28}H_{43}O_{3}N, melted at 197.5°C. The tribenzoyl and the tri-O-methyl-N-methyl methiodide of the agluco-alkaloid have been prepared and analysed. Among the sugars formed by the hydrolysis of the gluco-alkaloid, glucose, rhamnose, and galactose have been identified.

* From the thesis submitted by M. S. for the M.Sc. degree of the University of Mysore.
Experimental

Isolation of the gluco-alkaloid Solanine-S

19 Kg. of the finely powdered dry fruits were defatted by means of petroleum ether and then extracted with alcohol. The viscous residue obtained after distilling off alcohol was exhaustively extracted with water (Solution A). The water insoluble portion was extracted with 2% hydrochloric acid (Solution B).

From Solution A proteins and tannins were precipitated by the addition of basic lead acetate and excess of lead was removed by H2S. The solution was then concentrated and treated with dilute ammonia when a dirty yellow solid separated. This was filtered, washed with a small quantity of water, dried, and dissolved in hot 95% alcohol. The solution on filtering and cooling set to a gelatinous mass. It was again dissolved by warming and the hot solution was diluted with water until it became turbid. It was then boiled until a clear solution was formed. This solution on cooling deposited long shiny needles of the gluco-alkaloid. The substance was repeatedly crystallised from dilute alcohol (charcoal) till it had a constant melting point. The pure alkaloid commenced to shrink at 273° C., melted at 279° C. and decomposed at 290° C. Yield 200 g.

Analysis:

(1) 37·11 mg. Subst. : 77·79 mg. CO2 ; 27·92 mg. H2O.
15·82 mg. Subst. : 0·25 c.c., N (25° C., 685·5 mm.).
159·98 mg. Pt. double salt* yielded 13·88 mg. Pt.

(2) 20·99 mg. Subst. : 43·95 mg. CO2 ; 15·56 mg. H2O.
26·89 mg. Subst. : 0·43 c.c., N (24° C., 684 mm.).
152·22 mg. Pt. double salt yielded 13·17 mg. Pt.

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<tr>
<td>(2)</td>
<td>57·1</td>
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<td>1·6</td>
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C49H77O15N requires 57·2

Solanine-S is readily soluble in hot dilute acids, methyl and ethyl alcohols. It is moderately soluble in water and chloroform. It is insoluble in ether, petroleum ether and benzene. It dissolves in cold conc.

* This was prepared by the addition of 10% platinic chloride to the alkaloid dissolved in dilute hydrochloric acid. The precipitated salt was crystallised from water, m.p. 155° C. (decomp.).

The molecular weight of the gluco-alkaloid could not be determined by Rast's method as the gluco-alkaloid did not form a homogeneous solution in camphor.
nitric acid giving a colourless solution which soon becomes pink and then light brown; on keeping a dirty solid separates. The alkaloid dissolves in concentrated sulphuric acid forming a yellow solution which later changes its colour to orange red and finally becomes brown.

Hydrolysis of Solanine-S and Isolation of Solanidine-S

The gluco-alkaloid was heated with excess of 5% sulphuric acid on a water-bath for about 6 hours. As the hydrolysis proceeded a dirty white solid (the sulphate of the agluco-alkaloid) separated. This was filtered, washed with water and crystallised from hot alcohol.

The free base was liberated from the pure sulphate by the addition of dilute ammonia to its alcoholic solution. It was filtered, washed and crystallised repeatedly from alcohol until it had a constant melting point. It separated in the form of shining star-shaped white plates and melted at 197-5° C., $[a]_D^{20} + 113.5^\circ$ (in chloroform).

Analysis :

(1) 20·00 mg. Subst. : 54·84 mg. CO$_2$; 18·52 mg. H$_2$O.
7·34 mg. Subst. : 0·255 c.c. N (24° C., 687·5 mm.).
0·188 g. Subst., in 1·133 g. of camphor, $\Delta = 16·6^\circ$.

(2) 16·83 mg. Subst. : 46·08 mg. CO$_2$; 15·61 mg. H$_2$O.
6·32 mg. Subst. : 0·22 c.c. N (23° C., 688·5 mm.).
0·076 g. Subst., in 0·780 g. of camphor, $\Delta = 9·2^\circ$.

Found :

\[
\begin{array}{ccc}
C & H & N & \text{Mol. Wt.} \\
(1) & 74·8 & 10·4 & 3·5 & 399·9 \\
(2) & 74·7 & 10·4 & 3·6 & 423·6 \\
\end{array}
\]

C$_{26}$H$_{48}$O$_3$N requires 74·8

51 G. of this agluco-alkaloid were recovered from the acid Solution B and the mother liquors of Solanine-S.

Solanidine-S is soluble in hot ethyl and methyl alcohols, acetone, ethyl acetate and benzene. It is easily soluble in chloroform. It is insoluble in petroleum ether and soluble in hot ethyl ether. With concentrated nitric acid it behaves like the gluco-alkaloid. With concentrated sulphuric acid it gives a red solution which becomes brown on keeping. On dilution with water the solution turns blue, green and yellow as the quantity of water added is increased.

Neither O-methyl groups (Vieböck) nor N-methyl groups (Pregl) were found to be present in the agluco-alkaloid.
Identification of Sugars formed by the Hydrolysis of Solanine-S

The sugar solution obtained by the hydrolysis of the gluco-alkaloid (20 g.) was treated with excess of barium carbonate and filtered. The filtrate was concentrated under reduced pressure to the consistency of a syrup (10 c.c.).

A portion of the above syrup was heated with three times its weight of phenyl hydrazine hydrochloride and five times its weight of crystalline sodium acetate. The separated mixture of osazones was filtered, washed and dried. It was then refluxed with acetone for some time. The solution was cooled, filtered and the solid was washed with acetone.

The acetone insoluble osazone was crystallised from alcohol until it had a constant melting point (205° C. decomp.), and was found to be identical with glucosazone.

The acetone extract of the mixed osazones was slowly evaporated until it began to deposit crystals. It was then cooled and the solid that separated was filtered off. The residue from the acetone solution was repeatedly crystallised from benzene. It melted at 183° C. and was identical with the osazone prepared from rhamnose.

3 c.c. of another portion of the syrup was evaporated with 20 c.c. of dilute nitric acid (d. 1·15) on a water-bath to a small bulk. The evaporated bulk was stirred next morning with about 5 c.c. of water when a crystalline solid separated. After 24 hours, it was filtered, washed with excess of water and crystallised from water, when it melted at 214–15° C. (decomp.). Its identity with mucic acid obtained by the oxidation of galactose was established.

Galactose in a synthetic mixture of equal quantities of glucose, galactose and rhamnose, has been identified by conversion to mucic acid in the manner described above.

Preparation of Tribenzoyl Solanidine-S

The agluco-alkaloid (1 g.) was dissolved in pyridine (5 c.c.) and on the addition of small quantities of benzoyl chloride and shaking, a white solid separated (pyridine hydrochloride). The mixture was well shaken and left aside for about an hour when the solution turned red. Water was then added when the solid dissolved and a heavy red oil separated and settled at the bottom. It was then treated with sodium carbonate. The oil was separated from the supernatant liquid and repeatedly washed with water until it was free from the smell of pyridine. It was finally suspended in water and set aside for a few days when it solidified. The solid
was washed with water. After some time it again became pasty. The pasty mass was dissolved in hot alcohol and when the solution was cooled white granules separated. These were filtered, washed with alcohol and crystallised several times from alcohol. The pure derivative was obtained in fine needles and melted at 227° C.

Analysis:

(1) 20·24 mg. Subst.: 57·30 mg. CO₂; 14·40 mg. H₂O.
(2) 15·91 mg. Subst.: 0·345 c.c. N (31° C., 685 mm.).

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<td>77·2</td>
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\( \text{C}_{26}\text{H}_{40}\text{O}_3\text{N} \left(\text{CO.C}_6\text{H}_5\right)_3 \)

requires 77·4 7·6 1·9

It may be remarked that no definite product could be obtained by the Schotten-Bauman reaction or by attempts to acetylate the alkaloid.

Preparation of the Methiodide of O-Trimethyl-N-methyl Solanidine-S

The alkaloid was refluxed with acetone and methyl iodide for about 3 hours in presence of finely powdered anhydrous potassium carbonate. The excess of acetone and methyl iodide were distilled off and the residual solid was crystallised several times from alcohol. The substance separated in plates and melted at 233–34° C.

Analysis:

22·03 mg. Subst.: 48·63 mg. CO₂; 17·45 mg. H₂O.
10·42 mg. Subst.: 0·27 c.c., N (30° C., 687·5 mm.).
13·36 mg. Subst.: 5·19 mg. AgI.

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\( \text{C}_{26}\text{H}_{39}(\text{OCH}_3)_3\text{N(CH}_3)_2\text{I} \)

requires 60·5 8·8 2·3 20·7

REFERENCES

3 Proc. Ind. Sci. Congress, 1934, 244.
6 Oddo and Caronna, Ber., 1936, 69 B, 283.