CHEMICAL EXAMINATION OF THE FRUITS OF *SOLANUM XANTHOCARPUM.*

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Solanum xanthocarpum known as Bhoringani in Gujarati, Bhutkatya or Bhumiringani in Hindi, Kanteringani in Marathi, etc., is well known in Hindu Medicine, as its roots are one of the constituents of " Dashmul Ashava ". This plant grows abundantly in India in wild state. The stems are greenish grey with innumerable spines, and the flowers bright blue. The berries (fruits) are green when unripe and of different shades of yellow when ripe.[1]

The various parts of the plant are reputed in indigenous Hindu Medicine to have high medicinal value in various diseases like cough, asthma, fever, heart disease, etc.[2]

The plant under investigation belongs to the natural order *Solanacea.* Of the two classes of alkaloids which have been isolated from some of the plants belonging to this order one class gives alkaloids uncombined with sugars, such as atropine, hyoscyamine, hyoscine, etc., while the other class gives alkaloids combined with sugars and are known as gluco-alkaloids.

Dymock[3] states that the fruits of *Solanum xanthocarpum* were found on analysis to give alkaloidal reactions corresponding to solanine. The dried leaves gave 29·7% ash and contained a trace of an alkaloid, and an astringent acid giving a green precipitate with ferric chloride.

G. Pendse and S. Pendse[4] who have chemically examined the plant (including fruits) state that an alkaloid is present in very small quantities.

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1 Kirtikar and Basu, *Indian Medicinal Plants,* part II, page 896.

2 *Calcutta Med. Phys. Trans.,* 2, 406; Dymock's *Pharmacographia Indica,* 2, 557; Kirtikar and Basu, *Indian Medicinal Plants,* part II, p. 896.

3 Dymock, *Pharmacographia Indica,* 2, 559.

4 *Indian J. Med. Research,* 1932, 20, 663–670.

They attribute the physiological activity of the whole plant to potassium nitrate which is present in it to the extent of 1.6%.

The present authors have carried out a chemical examination of the fruits of *Solanum xanthocarpum* and isolated in the crystalline condition (1) the gluco-alkaloid $C_{44}H_{77}O_{19}N$, m.p. 288–89° C. (decomp.), which has been named "Solancarpine", (2) the alkaloid $C_{26}H_{43}O_3N$, m.p. 197–98° C. which has been named "Solancarpidine", and (3) the sterol $C_{36}H_{54}O_4$, m.p. 248° C. and named "Carpesterol". The products of hydrolysis of the gluco-alkaloid have been found to be the alkaloid (stated above), and the sugars glucose, rhamnose, and a hexose probably galactose. The hydrolysis of the gluco-alkaloid may probably be represented by the following equation :—

$$\underset{\text{gluco-alkaloid}}{C_{44}H_{77}O_{19}N} + H_2O = \underset{\substack{\text{aglucone}\\(\text{alkaloid})}}{C_{26}H_{43}O_3N} + \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{galactose ?}}{C_6H_{12}O_6} + \underset{\text{rhamnose}}{C_6H_{12}O_5}$$

There is also obtained an inorganic salt which was identified as potassium chloride.

Experimental.

The fruits of the drug under investigation after digesting with Prollius' fluid and testing the resulting extract with usual alkaloidal reagents, indicated the presence of such a material. After preliminary experiments for working out the method of extraction, 40 lbs. of the dried ground material were successively extracted with petroleum ether and alcohol.

Alcoholic extract.—The extract on cooling deposited a white crystalline inorganic material, which was identified as potassium chloride. After removing this solid, the solvent was distilled off, when a dark coloured viscid extract was obtained, which was dried at 100° C. and finally in a desiccator over sulphuric acid.

A portion (200 grams) of the dried alcoholic extract was macerated with distilled water and kept overnight. It was then well stirred and allowed to stand for a few hours. The aqueous layer was then decanted and filtered. This operation was repeated with the solid left after decantation of the aqueous solution till no more was dissolved by water as judged from the colour of the solution. This gave an aqueous solution (A). The insoluble portion was then treated with cold 2% HCl solution till no more of it was dissolved by the acid. This gave an acid solution (B). The insoluble residue left after the acid treatment was dissolved in dilute sodium hydroxide solution, which gave the alkaline solution (C).

Aqueous solution (A).—This solution was clarified with neutral lead acetate. Excess of lead was removed by passing hydrogen sulphide gas in the solution.

The solution was then heated on a water-bath to remove hydrogen sulphide gas and precipitated with dilute ammonia. The precipitate was filtered, washed with a small bulk of water and dried. The dried solid was then dissolved in alcohol and the solution boiled with animal charcoal, filtered and kept for crystallisation. The separated white solid was recrystallised from the same solvent till the melting point was not further raised. The final product crystallised in the form of white, flat needles, which melted with decomposition at 288–89° C. Yield 19·4 grms., *i.e.*, 1·3% on the weight of the dried fruit.

Found : C, 56·93 ; H, 8·49 and N, 1·529. $C_{44}H_{77}O_{19}N$—requires C, 57·2 ; H, 8·34 and N, 1·51%.

The gluco-alkaloid is soluble in water and dilute acids. It is readily soluble in ethyl and methyl alcohols, moderately soluble in chloroform and acetone, and only sparingly soluble in benzene. With concentrated sulphuric acid it produces red colouration, which on keeping gradually turns blue, green and finally disappears. Concentrated nitric acid dissolves the substance on boiling producing a pink colour.

Acid hydrolysis of the gluco-alkaloid.—The substance (20 grms.) was heated with excess of 5% sulphuric acid under reflux on a boiling water-bath for about two to three hours. The separated solid was filtered, washed and dried. It was then powdered, decomposed with 20% ammonia, and extracted with ether. The ether extract was washed with water and dried over calcium chloride. Most of the solvent was then distilled off and the concentrated solution allowed to evaporate slowly, when a shining, white solid separated, which was crystallised from alcohol. It separated in the form of shining, white plate crystals, m.p. 197–98° C. Yield of the aglucone (alkaloid) 4·6 grms., *i.e.*, 0·3% on the weight of the dried fruits.

Found : C, 74·59 ; H, 10·39 and N, 3·37. $C_{26}H_{43}O_3N$ requires C, 74·82 H, 10·31 and N, 3·35%.

The alkaloid is soluble in hot ethyl and methyl alcohols, acetone, ethyl acetate, benzene and toluene. It is easily soluble in hot chloroform. With concentrated sulphuric acid it gives a reddish yellow colouration, which then changes to violet, and on addition of increasing proportion of water, to green, then yellow and finally disappears. With concentrated nitric acid it produces colouration similar to that of the gluco-alkaloid. The acid alcoholic solution of the substance gave tests for an alkaloid with the usual alkaloidal reagents.

The filtrate obtained from the acid hydrolysis of the gluco-alkaloid, after removing the solid, contained sugars which were identified by the

formation of their mixed osazones by (1) Perkin's method[5] and (2) their varying solubility in acetone. These experiments showed the presence of glucose, rhamnose, and another hexose, probably galactose.

The following salts of the alkaloid with different acids were prepared :—

(1) *Hydrochloride.*—A dilute solution of HCl was added to the solution of the alkaloid in acetone. The separated white solid was filtered, washed and crystallised from alcohol. White flat needle crystals, m.p. 313–14° C. (decomp.).

Found: Cl, (i) 7·58 and (ii) 7·65. $C_{26}H_{43}O_3N$–HCl requires 7·82 %.

(2) *Hydrobromide.*—This was prepared as (1) White flat needle crystals, m.p. 307–308° C. (decomp.).

Found: Br, (i) 15·71 and (ii) 15·94. $C_{26}H_{43}O_3N$–HBr requires 16·07 %.

(3) *Hydriodide.*—The alcoholic solution of the alkaloid was refluxed with a dilute solution of hydriodic acid for about 15 minutes. The resulting solution yielded white plate needles on slow evaporation of the solvent, m.p. 283–84° C. (decomp.).

Found: I, (i) 22·95 and (ii) 23·05. $C_{26}H_{43}O_3N$–HI requires 23·3 %.

(4) *Sulphate.*—The alcoholic solution of the alkaloid was refluxed with a 5 % alcoholic solution of sulphuric acid for about 5 minutes. The sulphate crystallised in shining white plate crystals, m.p. 293–94° C. (decomp.).

Found: N, 2·82. $C_{26}H_{43}O_3N$–HSO_4 requires N, 2·72 %.

(5) *Nitrate.*—Prepared like (4). White needles, m.p. 271-72° C. (decomp.).

Found: N, 5·67. $C_{26}H_{43}O_3N$–HNO_3 requires 5·83 %.

(6) *Acid oxalate.*—Prepared like (4). White needles, m.p. 238–39° C. (decomp.).

Found: N, 2·82. $C_{26}H_{43}O_3N$–HC_2O_4 requires 2·76 %.

(7) *Acid tartarate.*—Prepared like (4). White needles, m.p. 224–25° C. (decomp.).

Found: N, 2·48. $C_{26}H_{43}O_3N$–$H_5C_4O_6$ requires 2·47 %.

(8) *Picrate.*—The alcoholic solution of the alkaloid was refluxed with a concentrated alcoholic solution of picric acid for about 15 minutes. The picrate crystallised in long bright yellow needles, m.p. 148–49° C.

Found: N, 8·28. $C_{26}H_{43}O_3N$–$C_6H_3N_3O_7$ requires 8·66 %.

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[5] *J.*, 1920, 97, 1777.

The above described salts are moderately soluble in hot ethyl and methyl alcohols; soluble in traces in benzene, acetone and ethyl acetate. They are sparingly soluble in boiling water, and very sparingly soluble in boiling chloroform. They can be recovered from their solutions unchanged. The picrate was more soluble in benzene and chloroform than the other salts.

Decomposition of the salts by alkali.—All the salts described above, on decomposition with dilute alkalies, yielded the original alkaloid, m.p. 197–98° C. Its mixed melting point showed no depression.

Acid solution (B).—This solution gave the same alkaloid that was obtained from the aqueous solution on hydrolysis of the gluco-alkaloid.

Alkaline solution (C).—This solution on acidification gave a granular solid too small for further investigation.

Petroleum ether extract.—After the removal of the greater portion of the solvent the concentrated extract was kept aside for a day, when a crystalline white solid separated which was removed, and the extract further freed from the solvent by distilling under reduced pressure. This yielded an oil (about 4½ lbs.). The solid was recrystallised from alcohol. Shining white plate crystals, m.p. 248° C.

Found: C, 78·86 and H, 9·4. $C_{36}H_{54}O_4$ requires C, 78·54 and H, 9·81%.

This substance is soluble in boiling ethyl and methyl alcohols. Sparingly soluble in hot benzene, chloroform and acetone, but very sparingly soluble in petroleum ether. It gives characteristic colour tests of a sterol.

Acetylation.—0.5 grms. of the substance was heated with an excess of acetic anhydride for about one and half hour. It was then poured on crushed ice. A white solid separated after 3–4 hours, which was filtered, washed and recrystallised from alcohol. White silky needles, m.p. 193–94° C.

Found: C, 77·09 and H, 10·13. $C_{38}H_{56}O_5$ requires C, 77·03 and H, 9·5%.

This result shows the presence of at least one —OH group in the original compound.

Analysis of the ash.—A quantity (4·6 grms.) of the dried powder of the fruits was strongly heated in a platinum crucible. It left ash (0·28 grms. equal to 5·9%, and gave tests for K, Na, Mg, traces of Fe, Cl and CO_2).

Summary.

The material used in this investigation consisted of fresh fruits collected from Thana (near Bombay), and dried in air. The material was ground

and successively extracted with petroleum ether and alcohol. From the petroleum ether extract were obtained : (1) an oil, and (2) a sterol $C_{36}H_{54}O_4$, m.p. 248° C., designated "carpesterol". From the alcoholic extract were obtained : (1) a gluco-alkaloid $C_{44}H_{77}O_{19}N$, m.p. 288–89° C. (decomp.) named "solancarpine," (2) an alkaloid $C_{26}H_{43}O_3N$, m.p. 197–98° C. named "solancarpidine," (3) sugars : (i) glucose, (ii) rhamnose, and (iii) a hexose, probably galactose, and (4) an inorganic salt "potassium chloride".

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