Constitution of Corchorin—the Active Principle of Jute Seeds (Corchorus Capsularis). Part I.

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Corehorin, the active principle of jute seeds has been first isolated by the author in a very pure form by extracting Corchorus, capsularis with alcohol. In a previous paper (J. Indian Chem. Soc., 1930. 7. 83) an account was given of its chemical and physical properties and a short description of its pharmacologicali ation. Although the amount of corchorin available did not permit of much information regarding its constitution. a number of interesting results have been obtained which are embodied in the present paper.

Corchorin is a bitter glucoside having the composition, $C_{22}H_{36}O_8$ which on hydrolysis yields one molecule of glucose and one molecule of corchogenin. Corchorin gives a crystalline pentacetyl derivative but the benzoyl derivative is an oil and could not be obtained in a crystalline condition.

Corchogenin, the sugar-free compound, has the composition $C_{16}H_{36}O_3$. The presence of a free carboxyl or alkyloxy-group in it could not be established in the usual manner but the presence of a lactonic grouping is shown by the results of the slow titration of its alcoholic solution with aqueous alkali hydroxide in presence of phenolphthalein, and hence its formula may be written as

 $(C_{15}H_{26}O) < \bigcup_{O}^{CO}$. It exhibits great stability towards the ordinary reagents.

An attempt to prepare an oxime as also a semicarbazone were unsuccessful. But it reacted on prolonged heating with phenylhydrazine forming an amorphous compound and with phosphorus pentachloride forming a chloro-derivative which also could not be obtained in a pure condition.

When corchogenin is brominated in chloroform solution a crystalline dibromide is produced showing the presence of a double bond in the molecule. By oxidation with potassium permanganate in the

Read before the Indian Science Congress, Allahabad, January, 1930.

cold corchogenin yields corchoric acid having the composition $C_{15}H_{24}O_5$, while corchorin gives glucocorchoric acid which, on hydrolysis, gives corchoric acid and glucose.

Attempts were made to detect whether corchogenin contains any benzene or fused benzene nuclei by the application of the method of Ruzicka (*Helv. Chim. Acta*, 1921, 4, 505); although hydrogen sulphide was evolved in quantity no trace of naphthalene hydrocarbon or simpler hydrocarbons could be isolated from the reaction products.

Corchogenin probably belongs to the homologous series having the general formula $C_n H_{2n-8}O_3$ (Abderhalden, "Biochemisches Hand Lexikon," Band 7, pp. 181, 187. Further work to elucidate the constitution of corchorin is in progress.

It may be further mentioned here that indication was obtained which led the author to suspect the presence of a second compound very similar in composition and property with corchorin in the motherliquor from which the latter had been separated. A sufficient quantity of the mother-liquor is now being collected for further investigation which will form the subject matter of a subsequent communication.

EXPERIMENTAL.

Acetylcorchorin. — This compound was prepared by heating corchorin (1·1 g.) with acetic anhydride (12 c.c.) and pyridine (4 drops) under reflux for about two hours on a sand-bath, the solution being then poured in a thin stream into a large volume of water. A sticky matter separated which solidified on standing; it was collected, washed with water and dried. The acetyl compound crystallised from dilute alcohol (animal charcoal) slowly in colourless needles, m. p. 158° with decomposition. (Found: C, 60°35; H, 6°95; CH₃.CO by Perkin's method, 32'4. $C_{22}H_{31}O_8(CH_3CO)_5$ requires C, 60°18; H, 7°21; CH₃CO, 83°69 per cent.).

It was very soluble in acetone, acetic acid and strong alcohol but insoluble in water. It gave a magenta colour with strong nitric acid.

Bromination of Corchorin: Monobromocorchorin Dibromide. Corchorin (2 g.) dissolved in 40 c.c. of glacial acetic acid was treated with an excess of bromine dissolved in the same solvent. The mixture was allowed to stand at the ordinary temperature for about 4 hours and then warmed on the water-bath for half an hour. The excess of bromine and acetic acid were distilled off and the residual liquid washed several times with a mixture of aqueous potassium iodide and sodium thiosulphate and finally with water. The product was then dissolved in a small quantity of glacial acetic acid and slowly poured into a large volume of water with constant stirring when a yellow solid was obtained. It was crystallised from dilute acetic acid in orange-red crystalline powder melting at 100° (decomp.). It had no bitter taste. (Found: Br, 35.68. $C_{22}H_{35}O_8Br_3$ requires Br, 35.9 per cent.).

On the addition of water to the mother-liquor a light yellow substance separated, which on fractional crystallisation from dilute acetic acid yielded another bromide melting at 146°. The quantity, was too small for further investigation.

Hydrolysis of Corchorin: Corchogenin.—Corchorin (6 g.) was hydrolysed by heating with dilute sulphuric acid (400 c.c. of 10%) under reflux on a water-bath for 2 hours. The substance gradually went into solution giving a yellow opalescent solution. The resulting mixture when cold was extracted with ether and the ethereal solution washed several times until free from mineral acid, the ethereal solution being dried over anhydrous sodium sulphate and the ether evaporated off when a light yellow brittle substance wa obtained, which when crystallised from very dilute alcohol separated in glistening thin plates of irregular shape melting with decomposition at 112-114° (shrinks at 84°).

The aqueous acid-liquid was warmed to remove the ether and neutralised with excess of barium carbonate, filtered and evaporated to dryness; the residue was digested with absolute alcohol and the mixture filtered. On evaporating the alcoholic filtrate a small amount of a brown syrupy residue was obtained which reduced Fehling's solution, decolourised alkaline methylene blue sclution at once in the cold and when heated gave the smell of burnt sugar. The syrup yielded an osazone melting and decomposing at 202^o. It was thus evident that the sugar consisted of dextrose and the absence of ketose was proved by Pinoff's test (*Chem. Ztg.*, 1914, 38, 629).

The hydrolysis of the glucoside took place in accordance with the equation,

 $C_{22}H_{36}O_8 + H_2O = C_{16}H_{26}O_3 + C_6H_{12}O_6.$

The amount of glucose was estimated volumetrically with Benedict's solution (J. Biol. Chem., 1911, 9, 57). (Found: 41.61. Calc. 42.05 per cent.).

Corchogenin, the sugar-free compound, was found to be insoluble in water, sodium bicarbonate, sodium carbonate and in cold caustic sods but readily soluble in hot alkali and in almost all organic solvents and was sparingly soluble in acid solution. From its alkaline solution mineral acid precipitated a yellow amorphous mass which on warming with water was immediately changed into corchogenin. Its alcoholic solution was neutral to litmus. With concentrated sulphuric acid it dissolved with a reddish-brown colour and on addition of water a yellow substance (probably corchogenin) separated out. It did not reduce Fehling's solution but reduced hot ammoniacal silver nitrate and on prolonged heating reacted with phenylhydrazine giving an amorphous compound. With ferric chloride it gave an intense yellow colour in alcoholic solution and with acetic anhydride, chloroform and concentrated sulphuric acid it gave a blue colouration which rapidly changed to green. It decolourised bromine in chloroform and potassium permanganate in acetone solution. It burnt completely with a slightly sooty flame on a platinum foil leaving no residue. (Found: C, 71.85; H, 9.5; M. W. (cryoscopic in acetic acid), 250. C₁₆H₂₀O₃ requires C, 72⁻¹⁸; H. 9.77 per cent. M. W. 266).

Repeated attempts to acetylate and benzoylate corchogenin under different conditions were unsuccessful.

Action of Hydriodic Acid on Corchogenin.—When corchogenin (0.8152 g.) was heated with strong hydriodic acid (d 1.7) in a current of dry carbon dioxide according to the classical method of Zeisel as described by Benidict and Bamberger (Montash., 1890, 11, 260) and modified by Greger (Montash., 1898, 19, 116) there was no evidence of the presence of methoxy groups.

It was, however, noticed that a solid remained suspended in the acid after the treatment. This proved to be the unchanged material, the amount recovered being 0.095 g.

Bromination of Corchogenin: Corchogenin Dibromide.—The substance (2.1 g.) dissolved in chloroform (40 c.c.) was treated with an excess of bromine dissolved in the same solvent. The mixture was then heated under reflux for 3 hours. It was then treated in a manner similar to the preparation of bromocorchorin. When crystallised from dilute acetic acid it was obtained as a bright yellow crystalline powder, m.p. 180-82° (decomp.) (sintering at 110°). (Found: Br, 37.56. $C_{16}H_{26}O_{3}Br_{2}$ requires Br, 37.55 per cent.).

Action of Phenylhydrasine.—Corchogenin (0°3 g.) dissolved in glacial acetic acid was heated with a solution of phenylhydrazine acetate on the water-bath for about two hours. On cooling a yellow amorphous solid separated. m.p. 165-170° (decomp.). It contained nitrogen, but could not be obtained sufficiently pure for analysis.

Action of Phosphorus Pentachloride.—A mixture of corchogenin (1¹18 g.) and excess of phosphorus pentachloride was heated for four hours on a water-bath. On cooling, the product—a dark red liquid—was poured into water and the precipitate collected and washed several times until free from acid. A dirty yellow product. was obtained which could not be crystallised and melted at 120-125° with decomposition and charring. It was soluble in alcohol but slightly in benzene and petroleum ether. (Found : Cl, 33'9 per cent.).

Action of Soda Lime.—Corchogenin (0.6 g.) was mixed with soda lime and heated in a dry tube fitted with a delivery tube. Combustible fumes were given off and a sticky strongly-odoured solid condensed at the neck of the tube which in presence of chloroform absorbed bromine.

Action of Sulphur.—The dehydrogenation of corchogenin by heating it with excess of sulphur at 200-250° was carried out by Vesterberg's method (Ber., 1903, 36, 4200). There was a copious evolution of sulphuretted hydrogen and the melt was distilled at 12 mm. pressure. The dark coloured distillate was extracted with alcohol and on evaporation of alcohol a yellow, sweet-smelling oil was obtained which gradually darkened on exposure to air. The product was insufficient for purification, analysis and further studies.

Action of Alkaline Hydrogen Peroxide.—An alcoholic solution of corchogenin made alkaline with caustic potash was treated with hydrogen peroxide (Merck's perhydrol) with the addition of a little bromine as a starter. The action was vigorous and the solution gradually became colourless. After standing for some time it was acidified when nothing separated. It was then poured into water when a faintly yellow gelatinous mass separated out which was filtered. It contained bromine and when heated in a capillary tube it began to sinter at 82° and decompose with evolution of gas at about 128°. It was insoluble in caustic alkalis, sodium bicarbonate and on warming with caustic soda it resinified and turned yellow. Inspite of repeated attempts the substance could not be obtained sufficiently pure for analysis.

Oxidation of Corchorin : Glucocorchorio Acid.-Powdered potassium permanganate (6.8 g.) was added gradually to corchorin (5 g.) in ice-cold mechanically stirred acetone (250 c. c.), the colour of the permanganate disappeared slowly and the oxidation seemed to be complete after 24 hours. On reducing the manganese precipitate suspended in water with sulphurous acid a yellow turbid solution was obtained. This was repeatedly extracted with chloroform and the extract was washed with water and dried over anhydrous sodium sulphate. On evaporating the chloroform there remained a pale yellow solid which separated from alcohol in lustrous nacreous mass. m. p. 146-148°. It was soluble in hot water and in cold caustic soda and from the latter it could be re-precipitated by mineral acids; it slowly dissolved in sodium carbonate with the liberation of carbon dioxide. It dissolved in cold concentrated sulphuric acid with a faint yellow colour and did not reduce Fehling's solution. On heating with dilute hydrochloric acid it yielded an insoluble white product and the filtrate after neutralisation with soda readily reduced Fehling's solution. (0.2740g. neutralised 6.0 c. c. N/10-caustic potash. Neutralisation value, 122 86. Mean molecular weight, 456 6. (Found: C, 56'3; H, 7'5. C₂₁H₃₄O₁₀ required C, 56'5; H, 7'6 per cent. M. W., 446). On evaporating the acetone a further quantity of glucocorchoric acid was obtained. The yield of the acid was about 10 per cent.

Hydrolysis of Glucocorchoric Acid .- The substance was heated with dilute hydrochloric acid for one hour and the mixture on cooling was extracted with ether; the ethereal solution was washed until free from mineral acid, dried and the ether removed when a semi-solid substance having a characteristic smell separated out. On standing over concentrated sulphuric acid in vacuum it solidified and was crystallised from dilute alcohol in glistening plates, m. p. 67-70° and decomposing with evolution of gas at 94°. It was slightly soluble in water and the solution was acidic to litmus. It did not give any colouration with ferric chloride and dissolved readily in ammonia. From alcoholic solution an amorphous lead salt was precipitated by lead acetate. When heated on a platinum foil it first melted, charred and then burnt with a smoky flame leaving no residue, It slightly reduced Fehling's solution on prolonged heating but not ammoniacal silver nitrate solution. For this acid the name corchoric acid is proposed. (Found: C, 63.2; H, 8.6. C15Hg4O5 requires C, 68.88; H, 8.45 per cent.).

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There was not sufficient substance left to determine its molecular weight.

The aqueous acid-liquid was warmed on a water-bath and on neutralisation with sodium carbonate readily reduced Fehling's solution. It was then concentrated on a water-bath and warmed with sodium acetate and phenylhydrazine hydrochloride. Glucosazone, which separated very slowly, after being washed and dried. melted at 206°, alone or mixed with an authentic specimen.

It was afterwards found that the acid obtained by oxidising corchogenin with neutral potassium permanganate in the cold in a similar manner as in the case of glucocorchoric acid was identical with corchoric acid.

The author desires to thank the Indian Chemical Society for grants-in-aid of this work and to express his most sincere thanks to Professor S. N. Bose for his constant interest and inspiration. He also wishes to acknowledge his indebtedness to Prof. J. C. Ghosh and Dr. S. Dutt for their kind criticism.

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Received June 28, 1980.