453. *Constituents of the Seeds of* Corchorus olitorius, *L. Part I. Corchorin and its Identity with Strophanthidin.*

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Corchorin, the crystalline bitter principle of jute seeds, is isolated from the seeds of *Corchorus olitorius,* L., and is shown to have the formula $C_{23}H_{32}O_6$ and to be identical with strophanthidin.

The occurrence of a bitter principle, corchorin, in the seeds of *Corchorus capsularis,* L. (Tiliaceæ), commonly known as jute, was first reported by Tsuno (*Monatsh. Tierheilk.*, 1896, **6**, 455), and later corchorin was described by Friebos (Dissert., Rostock; *Jahr. Pharm.*, 1907, 102) as a whitish, crystalline bitter substance. Furthermore, Kobert ("Lehrbuch der Intoxikationen," 1906, p. 1222; *Chem. Zentr.*, 1907, **1**, 1273), who was provided with an impure specimen of corchorin by Merck, recorded its pharmacological action and described its chemical and physical properties without mentioning its melting point or percentage composition.

The isolation of an isomeric, if not identical, bitter compound, capsularin, $C_{22}H_{36}O_8$, m. p. 175—176°, from jute leaves was achieved by Saha and Choudhury (*J.*, 1922, 1044), but present knowledge regarding the isolation and analysis of corchorin of jute seeds is largely due to Sen (*J. Indian Chem. Soc.*, 1930, **7**, 83). Corchorin is described by this author as whitish rhombic prisms, m. p. 174—175°, having an intense bitter taste. It develops, with concentrated sulphuric acid, a red colour with green fluorescence, and yields glucose and corchogenin, m. p. 112—114°, on hydrolysis. Sen (*ibid.*, p. 905) assigned to corchorin and corchogenin the formulæ, $C_{22}H_{36}O_8$ and $C_{16}H_{26}O_3$, respectively.

As corchorin is recorded in the literature as a cardiac glycoside (Rijn and Dieterle, " Die Glycoside," 1931, p. 317, Verlag Borntraeger, Berlin), and as the seeds of *Corchorus olitorius*, L. (Tiliaceæ), are recognised among Egyptian peasants as poisonous to cattle, whereas the plant is widely cultivated in Egypt for use as a pot herb, under the name " Melukhîya," it seemed of interest to attempt the isolation of such a glycoside from this plant. We have isolated corchorin (the properties of which suggest a genin, not a glycoside) from the alcoholic extract of the defatted seeds of *Corchorus olitorius*. Previously, the plant and its seeds were studied microscopically and chemically by Amin, Fahmy, and Fahmy (*Report Pharm. Soc., Egypt*, 1934, **6**, 12), and the occurrence of a glycosidic principle in the alcoholic extract of the defatted seeds was indicated by chemical tests. Corchorin, obtained by the method described in the experimental, crystallised from dilute methanol in rhombic prisms, m. p. 175—177° (decomp.) not depressed with an authentic specimen prepared from jute seeds.

Contrary to Saha and Choudhury (*loc. cit.*) and Sen (*locc. cit.*) we were unable to hydrolyse corchorin with 2% sulphuric acid solution, or with varying concentrations of hydrogen chloride in dilute alcohol. In certain cases the starting material was recovered unchanged, otherwise it suffered resinification without the elimination of a sugar moiety. Additional disagreement lies in the fact that we have prepared from corchorin, from either of the two species of *Corchorus*, a crystalline acetate, m. p. 242—244° (decomp.), whereas capsularin acetate and corchorin acetate were assigned by Saha and Choudhury (*loc. cit.*) and Sen (*locc. cit.*) the melting points 190° and 158°, respectively, and the formula, $C_{22}H_{31}O_8Ac_5$.

The results of analysis of our dehydrated specimens of corchorin and its acetate indicate the formulæ, $C_{23}H_{32}O_6$ and $C_{23}H_{31}O_6Ac$, and the presence of an αβ-unsaturated lactone group was shown by titration with standard alkali, by the formation of a red colour in the Légal sodium nitroprusside test, and by reduction of Tollens's reagent (Jacobs and Hoffmann, *J. Biol. Chem.*, 1925, **67**, 333; Haynes, *Quart. Reviews*, 1948, **2**, 46). In addition to the lactone group and the hydroxyl group which can be acetylated, the presence of a carbonyl group in corchorin is shown by the formation of an oxime, $C_{23}H_{33}O_6N$, m. p. 265—270° (decomp.), and a phenylhydrazone, $C_{29}H_{38}O_5N_2$, m. p. 240—243°; the remaining two oxygen atoms appear to be present in tertiary hydroxyl groups. The formulæ, melting points, and properties of corchorin and its derivatives are in agreement with those of strophanthidin. Full identity of the two lactones was established by comparison with authentic specimens (cf. Jacobs *et al.*, *J. Biol. Chem.*, 1922, **54**, 253; 1924, **59**, 713; 1927, **74**, 805; Lamb and Smith, *J.*, 1936, 444; Steldt, Anderson, and Chen, *Proc. Soc. Expl. Biol. Med.*, 1943, **53**, 198; *J. Pharm. Expl. Ther.*, 1944, **82**, 98).

It would be of a biogenetic interest should the presence of a strophanthin glycoside be proved in the bitter mother-liquor from which corchorin has been isolated, or in the extracts of the immature seeds or other parts of the plant. At present, attempts are being made along these lines and towards the elucidation of the structure of another bitter compound, corchoritin, m. p. 218—220°, which was described by Sen (*J. Indian Chem. Soc.*, 1931, **8**, 651) as a hydroxylactone, $C_{12}H_{18}O_3$. Moreover, the alcoholic extract of the defatted seeds of *Corchorus olitorius* yielded a solid from which raffinose (cf. Sen, *locc. cit.*; Annett, *Biochem. J.*, 1917, **11**, 192) and a tasteless resin were separated. On successive crystallisations of the latter, a phenolic compound, m. p. 103—105°, was obtained, and the results of its investigation will be communicated later.

EXPERIMENTAL.

(M. p.s are not corrected; micro-analyses were by Drs. Weiler and Strauss, Oxford, and unless otherwise stated the analytical specimens were dried (and dehydrated) at 110° in a high vacuum over phosphoric oxide.)

Extraction.—The powdered seeds of *Corchorus olitorius* (obtained from the Minia district in Upper Egypt) were extracted three times with light petroleum (b. p. 60—80°). The combined extracts yielded on evaporation a dark greenish oil (14—15%) which deposited a waxy solid when kept in the ice-chest. The defatted meal (5 kg.) was refluxed with alcohol for about 8 hours and the liquid filtered hot; this process was repeated twice and, after cooling, the yellow-brown deposit was separated from the combined filtrates. By successive concentration and cooling, more of the yellow-brown deposit (" A ") (300 g.) was collected. Finally, the extract was freed from most of its alcoholic content by distillation under reduced pressure on the water-bath, and a dark brown, bitter syrup (" B ") was left.

Isolation of Corchorin.—The syrup " B " (2 l.) was diluted with hot water (1·5 l.), clarified by filtration, and mixed with basic lead acetate (150 g.) in hot water (500 ml.), then the mixture was kept overnight at room temperature. After the mixture had been filtered excess of lead was removed from the filtrate by hydrogen sulphide, and the clear solution concentrated under reduced pressure on the water-bath to about 2 l. At this stage, corchorin began to separate as small crystals (12 g.), m. p. 162—165°, which lost most of their bitter taste on crystallisation (charcoal) from dilute methanol or ethanol. Pure corchorin is readily soluble in methanol, ethanol, or pyridine, is sparingly soluble in water, chloroform, or benzene, and crystallises from dilute methanol in whitish rhombic prisms, m. p. 175—177° (decomp.), solidifies and remelts at 235°, and does not depress the melting points of corchorin from jute seeds or strophanthidin [Found, in specimens dried over phosphoric oxide: C, 66·8, 66·8; H, 8·1, 8·2%; *M* (by titration), 410·5, 418·8. Calc. for $C_{23}H_{32}O_6,\frac{1}{2}H_2O$: C, 66·8; H, 8·1%; *M*, 413·3], $[\alpha]_D^{18}$ +40·8° (*c*, 7·350 in methanol) [Found in dehydrated specimens: C, 68·3, 68·3; H, 8·0, 7·9%; *M* (Rast), 396; *M* (by titration), 404·2, 408·1. Calc. for $C_{23}H_{32}O_6$: C, 68·3; H, 8·0%; *M*, 404·3], $[\alpha]_D^{18}$ +42·7° (*c*, 3·845 in methanol). It dissolves in concentrated sulphuric acid to a red solution with a green fluorescence, and its solution in alcohol or pyridine becomes red on the addition of sodium nitroprusside and sodium hydroxide solutions; it readily reduces Tollens's reagent. The acetate was prepared by heating corchorin (0·5 g.) in pyridine–acetic anhydride (10 ml.; 1 : 1) for two hours on the water-bath, the solution was concentrated by distillation under reduced pressure at a low temperature, and the residue was crystallised from dilute methanol, and recrystallised from benzene–methanol; it formed prisms, m. p. 242—244° (decomp.) (Found: C, 67·3, 67·4; H, 7·6, 7·7. Calc. for $C_{25}H_{34}O_7$: C, 67·2; H, 7·7%), $[\alpha]_D^{18}$ +39·30° (*c*, 3·051 in methanol). The oxime crystallised from alcohol in rhombic prisms, m. p. 265—270° (decomp.), identical with strophanthidin oxime (Found: C, 66·0, 65·7; H, 8·1, 8·0; N, 3·3, 3·4. Calc. for $C_{23}H_{33}O_6N$: C, 65·8; H, 7·9; N, 3·3%). The phenylhydrazone crystallised from ethyl acetate in colourless prisms, m. p. 240—243° (cf. Thoms and Unger, *Z. angew. Chem.*, 1924, **37**, 721) (Found: C, 70·1; H, 7·7; N, 5·6. Calc. for $C_{29}H_{38}O_5N_2$: C, 70·4; H, 7·8; N, 5·7%).

For comparison, corchorin was prepared by extraction of the seeds (2 kg.) of *Corchorus capsularis*; the product (0·2%) crystallised from dilute methanol in rhombic prisms, m. p. 175—177° (decomp.) (Found in specimens dried over phosphoric oxide: C, 66·8, 67·0; H, 8·1, 8·3%. Found in dehydrated specimens: C, 68·3, 68·2; H, 8·1, 8·2%), $[\alpha]_D^{18}$ +42·5° (*c*, 6·642 in methanol). It gave an acetate, m. p. 242—244° (decomp.) (Found: C, 67·2; H, 7·7%). Sen's results are C, 61·6; H, 8·5%; $[\alpha]_D$ +33·4° in ethanol for corchorin, and C, 60·4; H, 7·0% for its acetate.

When the solid deposit " A " was refluxed with ethyl acetate, the fluorescent solution deposited a yellowish-brown resinous product on cooling, and the insoluble gummy residue gave on crystallisation from 90% alcohol white rhombic crystals, m. p. 75°, identical with raffinose. After several crystallisations of the resinous product from ethyl acetate and then from benzene, a substance, m. p. 103—105°, was obtained and characterised by the formation of a green colour with ferric chloride and a colourless acetate, m. p. 74°.

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