

## EXAMINATION OF THE CONSTITUENTS OF JUTE SEEDS

### Part I.—Isolation of Jute Seed Oil, Strophanthidin and Raffinose

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From the seeds of *Corchorus capsularis* and *Corchorus olitorius*, jute seed oil to the extent of 15%, strophanthidin to 0.5%, and raffinose to 4.5% have been obtained along with some glucosides. Small quantities of sucrose and arabinose have also been obtained but could not be separated.

The seeds of *Corchorus capsularis* L. and *Corchorus olitorius* L. have been examined by many persons in the past and conflicting claims have been recorded by them. A systematic examination of these seeds, in comparatively larger quantities, has been undertaken in these Laboratories with a view to making adequate use of the entire quantity of seed that is produced in East Pakistan, and in the course of work some important and interesting observations have been made which are recorded in this paper.

Kobert<sup>1</sup> described a product isolated from *Corchorus fascicularis*, *olitorius*, *capsularis*, *bengalensis*, *acutangulus*, *argutus* and *triangularis* spp. which had marked physiological activity. Annett<sup>2</sup> described raffinose obtained from *Corchorus capsularis* Linn., in only 2.25% yield, while Saha and Choudhury<sup>3</sup> mentioned about the isolation of a glucoside, capsularin. Sen describes the isolation of an oil<sup>4</sup> from jute seeds and also a bitter principle, corchorin,<sup>5</sup> which he has classified as a glucoside and corchoritin<sup>6</sup> as a crystalline bitter. Soliman and Saleh<sup>7</sup> have pointed out that corchorin was actually identical with strophanthidin. Karrer and Banerjee<sup>8</sup> mentioned about the cardiac aglycone, corchortoxin, from *Corchorus capsularis* and again corchorgenin has been mentioned as a cardiac active aglycone by Chakravarti and Sen.<sup>9</sup> Mention has also been made of corchsularin as a new bitter by Khalique and Ahmed.<sup>10</sup> The confusion about these bitters and cardiac aglycones appears to have been clarified to some extent in a joint paper by Sen, Chakravarti, Kries, Tamm and Reichstein,<sup>11</sup> but the question does not seem to have been completely settled and some further work appears to be necessary particularly because of its economic importance.

The present work corroborates some of the earlier findings, and presents a few new facts regarding the constituents of the jute seed.

Jute seeds of both the species of plants, *Corchorus capsularis* and *Corchorus olitorius*, have

yielded almost similar results, so far as the isolation of their main constituents is concerned. The seeds on being powdered and extracted with petroleum ether gave an oil with only small quantities of a little carotenoid, some  $\beta$ -sitosterol and phosphatides.

The defatted seed powder was first extracted with rectified spirit and then with 80% alcohol. The first extract gave several glucosides along with the entire quantity of the main bitter principle, strophanthidin, along with some raffinose, while the extract with 80% alcohol gave some more raffinose with a sugar mixture which could not be separated, but appears to contain some raffinose along with sucrose and arabinose.

Raffinose has been characterized by its tendency to hydrolyse into a mixture of glucose, galactose and fructose and also by the formation of its hendecacetate. From the way raffinose has been separated, it is concluded that some of it is present in the seed in free state and its quantity goes up to about 6% of the weight of the seed powder. Further work with the residual powder is still in progress which suggests that raffinose exists in combination with some other products also. A detailed account of the residual powder is expected to form the subject matter of a future communication.

The quantity of strophanthidin isolated from the seeds amounts to about 0.5% of its weight. This promises to give a fairly large quantity of the commodity from the seeds. Experiments have, therefore, been undertaken to convert strophanthidin into some other more useful products, and the results of these experiments will be communicated in the near future.

### Experimental

The process of separation described here has already been patented under Pakistan Patent 110,064, dated March 8, 1960.

*Isolation of Jute Seed Oil.*—Finely powdered sun-dried seeds of *Corchorus capsularis* Linn. and *Corchorus olitorius* Linn., commonly known as jute seeds, in batches of 10 kg. were separately but repeatedly extracted in the cold for 88 hrs., using light petroleum ether (b.p. 60°-80°, 50 l.). The solvent was then distilled off on a steam bath and the last traces of the solvent were removed under reduced pressure when a golden yellow oil (1.5 kg., 15%) was obtained.

*Characteristics of the Oil.*—Its specific gravity at 28°C. was 0.925; refractive index at 30°C., 1.4705; solidifying point, -20°C.; iodine value, 106-113; saponification value, 185; acid value, 1.3; R.M. value, 0.17; unsaponifiable matter, 5.7% (containing carotenoid, 0.003%, phosphatide, 1.12% and the rest sterol); saturated acids, 20%; and unsaturated acids, 80%.

The constituents of the oil were further examined to find out its nature. From the urea complexes prepared, it was concluded that the total acid, in the acid form, can be divided as shown in column 1 of Table 1, column 3 representing the quantities of the same in percentages of their glycerides.

TABLE 1.

Acids in oil	Percentage in total acid	Percentage in oil
Stearic acid	13	11.05
Palmitic acid	5.16	4.39
Oleic acid	36.2	31.05
Linoleic acid	39.8	33.8
Linolenic acid	5.8	4.93

A comparison of these properties with cottonseed oil shows some similarities in iodine value, refractive index and density, but differs considerably in many other respects. The constituents of unsaturated and saturated acids vary to some extent. Although jute seed oil contains 80% of unsaturated and 20% of saturated acids, cottonseed oil contains some 75% of unsaturated and 25% of saturated acids. From these data it will be possible to determine the various uses, which jute seed oil can be put to.

*Isolation of Raffinose.*—The defatted seed powder was next repeatedly percolated with cold rectified spirit (95%, 30 l.) for 53 hrs. until the Raymond test<sup>12</sup> for strophanthidin was negative. The total alcoholic extract was thereafter concentrated

(ca. 15 l.) on a steam bath, and refrigerated (-5°C.). During the next morning, a voluminous white flocculent precipitate was formed. This was found to be a glucoside, and will be dealt with in a subsequent communication.

The mother liquor from this glucoside was then further concentrated (1.8 l.). This concentrated solution, when treated with ethanol, produced turbidity. On being allowed to stand, it gave a fairly large quantity of a precipitate, which was filtered (100 g.). It melted at 74-80°C. and on crystallisation from rectified spirit melted at 80°C. It is optically active and had  $[\alpha]^{32}_D + 103.2^\circ$  (c 4.3% in water). It does not reduce the Fehling solution readily but on prolonged boiling it does so to some extent, showing the characteristics of a polysaccharide. It could be hydrolysed by dilute acids to a mixture of three monosaccharides. Paper chromatography clearly pointed out this to be a mixture of glucose, galactose and fructose. It was therefore concluded to be raffinose which also melts at this temperature. Found: C, 42.70; H, 6.81.  $C_{18}H_{32}O_{16}$  requires: C, 42.81; H, 6.39. It was converted into an acetate which melted at 98-99°C., which is the melting point of hendecacetate of raffinose. The melting point of the sugar was not depressed when mixed with an authentic sample of raffinose (Merck). Paper chromatography of the sugar also supported the same view.

*Separation of Strophanthidin.*—From the mother liquor of raffinose, alcohol was distilled off and the residue was diluted with water to 3 l. A saturated solution of lead acetate was added till there was no further precipitation, the precipitate having been allowed to settle, filtered, and the excess of lead in the filtrate removed by hydrogen sulphide. This was concentrated to ca. 1.1 l., and to the warm solution concentrated hydrochloric acid (1 ml.) was added, and shaken when immediately some crystalline solid (50 g.) was thrown down (yield 0.5%). This gave a positive Legal colour reaction<sup>13</sup> and a strong Raymond test,<sup>12</sup> and melted at 164-176°C. It crystallised from ethanol and had m.p. 175-176°,  $[\alpha]^{23}_D + 36.9^\circ$  (c 0.8 in EtOH),  $\lambda_{max.}$  (in EtOH) 303 m $\mu$  and 217 m $\mu$ ,  $\gamma_{max.}$  (in KCl) 3401 (OH), shoulder at 1786 (lactone), 1724 (C=O), 1631 (C=C), 1451 (C-CH<sub>3</sub>) cm.<sup>-1</sup>. Found: C, 68.15; H, 7.8.  $C_{23}H_{32}O_6$  requires: C, 38.61; H, 7.9. It had the same  $R_f$  value with an authentic sample of strophanthidin obtained from Prof. Reichstein and, on admixture with the latter, the m.p. remained undepressed.

The acetate of strophanthidin was prepared by the usual method. It melted at 240-242°C. and had  $[\alpha]^{22}_D + 30.1^\circ$  (c 0.87% in ethanol).

A sample of strophanthidin (2.1 g., m.p. 175-176°) dissolved in *n*-butanol (15 ml.) was allowed to react with a mixture of semicarbazone hydrochloride (0.7 g.) and sodium acetate (0.7 g.) (dissolved in a minimum quantity of water), on a steam bath for an hour and kept standing overnight, when the semicarbazone (1.9 g.) m.p. 240-242°C. separated out. This was recrystallised from *n*-butanol when strophanthidin semicarbazone melted at 241-242°C. Found N, 8.60.  $C_{24}H_{34}O_7N_3$  required: N, 8.83.

*Extraction of a Sugar Mixture with 80% Alcohol.*—The residue after extraction with rectified spirit was repeatedly percolated with 80% alcohol-water mixture (4:1) in the cold for 45 hrs. until the Molisch test for sugar was negative. The total extract (28 l.) was concentrated to 700 ml. on a steam bath. To the concentrated mass ethanol was added to make it turbid and the turbidity was just removed by a few drops of water. Seeded with raffinose it was left overnight in the refrigerator when a considerable mass of white crystals was obtained. This (350 g.) was filtered. It melted at 74-80°C., crystallised from ethanol in needles m.p. 80°C. and had  $[\alpha]^{32}_D + 102.2^\circ$  (*c* 5.2 in water). This was identical with the raffinose previously described.

From the mother liquor of these crystals a syrupy mass was ultimately obtained. All attempts to separate the constituents of this mixture, have upto now proved to be unsuccessful. A paper chromatographic identification of the sugar constituents of this thick syrup showed that besides raffinose, it contained some sucrose with arabinose.

*Estimation of Sugars in Jute Seeds.*—An estimation of the sugars in the sun-dried seeds was carried out by an application of the method of Spengler.<sup>14</sup> For this, finely powdered seeds of *Corchorus capsularis* (500 g.) were first defatted with light petroleum and then exhaustively extracted with 80% spirit in the cold, till Molisch's test for carbohydrate was negative. The solvent was removed on the steam bath under reduced pressure when a brown

viscous mass (40.15 g.) was obtained, which on paper chromatography gave three spots identical with raffinose, sucrose and arabinose. The sugars were then estimated volumetrically and found to contain raffinose, 7.47%; sucrose, 0.99%; and arabinose, 1.03% on the weight of the seeds taken.

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