NOTES

A Water-Soluble Mannan from the Seeds of *Daubentonia Drummondii*[1]

By A. L. Curl[2] and E. K. Nelson[3]

In an investigation of the seeds of *Daubentonia drummondii*, a shrub of the pea family which grows in the coastal plain from Florida to Texas, a water-soluble fraction was obtained in 16% yield which consisted chiefly of a polysaccharide from which 43% of mannose (as the phenylhydrazone) was obtained on hydrolysis. The seeds also contained 4.4% of a semi-drying oil and an unidentified glycoside. It is believed that these seeds might be an important domestic source of mannose.

Experimental

The seeds used in this investigation were provided by S. B. Detwiler of the Soil Conservation Service, U. S. Department of Agriculture and were collected at Yellow Pine, La.

The ground seeds contained 6.5% moisture (dried six hours at 100°) and 2.8% ash. A test for cyanogenetic glycosides[4] was negative.

Eighty-five grams of the ground seeds was extracted in a Soxhlet extractor overnight successively with petroleum ether, ether, chloroform, and alcohol.

The petroleum ether extract on evaporation yielded 3.7 g. (4.4%) of a yellow oil which had an iodine no. (Wijs) of 122.6.[5]

The ether and chloroform extracts yielded, respectively, 1.0 g. (1.2%) and 1.6 g. (1.9%) of viscous green material which was not further investigated.

The alcohol extract yielded 6.5 g. (7.7%) of a light brown powder (I). A solution (I) in water gave a green color with ferric chloride, but did not have an astringent taste and did not precipitate gelatin from aqueous solution; so apparently it contained little tannin, if any. A solution of (I) in water reduced Fehling solution slowly on boiling. To another portion of (I) in water, sulfuric acid was added and the mixture was warmed (a precipitate formed), neutralized, and boiled with Fehling solution, giving a strong test. The precipitate was a resinous material, soluble in ether and in petroleum ether; it was not identified. The alcohol extract evidently contained a glycoside.

The residue from the extractions in the Soxhlet apparatus was allowed to stand overnight with 300 ml. of water, filtered, and washed with 100 ml. of water. The filtrate and washings were evaporated to 100 ml., cooled and diluted to 1 liter with absolute alcohol. The resulting white precipitate (II) after filtering and drying weighed 13.4 g. (15.8%). Ten grams of (II) on neutralization required 17 ml. of 0.5 *N* sodium hydroxide, equivalent to 0.5 g. as citric acid. Lead acetate gave a small amount of precipitate with the neutralized solution; this was filtered off, and the filtrate was de-leaded with hydrogen sulfide, concentrated and reprecipitated with alcohol. The resulting product (III) contained 0.23% nitrogen[6] and 0.8% ash; it had an optical rotation $[\alpha]^{20}_{D}$ of +50.6° in water and turned brown without melting on heating to 260°. A solution of (III) in water formed a bulky light-colored precipitate with Fehling solution and no reduction occurred on heating to boiling; a similar precipitate was formed with copper sulfate and sodium hydroxide, but none formed with copper sulfate and ammonium hydroxide nor with sodium hydroxide alone. Negative tests on (III) for proteins were given by the xanthoproteic and biuret reactions. The Schotten–Baumann test yielded a white precipitate. A solution of (III) after boiling with hydrochloric acid and neutralizing reduced Fehling solution on boiling.

One gram of (III) was heated to 130° in an autoclave with 50 ml. of 0.5% hydrochloric acid for two hours; the mixture was cooled, and sodium acetate and 1.5 ml. of phenylhydrazine added. The crystalline precipitate which formed in the cold, after filtering, washing with water and alcohol, and drying, weighed 0.65 g., equivalent to a 43% yield as mannose. The filtrate, after the addition of acetic acid, was warmed for two hours on a steam-bath but only a small amount of osazone was formed. A portion of the hydrazone, after being recrystallized from pyridine and butanol, and then from phenol and butanol, had a m. p. of 193–194° (cor.) and its mixture with mannose phenylhydrazone had a m. p. of 195° (cor.).

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(1) Agricultural Chemical Research Division Contribution No. 138. Not copyrighted.

(2) Present Address: U. S. Citrus Products Station, Winter Haven, Fla.

(3) Died November 9, 1940.

(4) "Official and Tentative Methods of Analysis," Association of Official Agricultural Chemists, Washington, D. C., fourth ed., 1935, p. 348, par. 46.

(5) Analysis by C. E. Swift, Fellow, National Cottonseed Products Assn.

(6) Analysis by B. Axelrod, Enzyme and Photochemistry Research Division.

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The Absorption Spectra of Pyrrole Blue A and B

By F. Fromm[1]

Liebermann and Häse[2] have shown that the interaction of pyrrole and isatin in presence of sulfuric acid yields a mixture of two dyestuffs, pyrrole blue A and B, while only pyrrole blue B is obtained if pyrrole and isatin react in glacial acetic acid. Pratesi[3] determined the constitution of the B compound as β-(5-pyrrolenyl)-isatin and investigated the absorption spectra of the homologous 2,3-dimethylpyrrole blue, cryptopyrrole blue and opsopyrrole blue in pyridine solution. All the three absorption curves are close together; the logarithm of their molecular extinction log ϵ rises from about 3.6 at 450 mμ to about 4.4 at 700 mμ. The logarithm of specific extinction,[4] log k for 2,3-dimethylpyrrole blue [β-(2,3-dimethyl-5-pyrrolenyl)-isatin] has been computed from Pratesi's data and has been entered as curve C in Fig. 1. Grassmann and v. Arnim[5] published a spectrum of a pyrrole blue dyestuff

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(1) Present Address: Colegio del Sagrado Corazón, Santurce, Puerto Rico.

(2) Liebermann and Häse, *Ber.*, **38**, 2851 (1905).

(3) Pratesi, *Ann.*, **504**, 263 (1933).

(4) *I. e.*, the extinction for unit concentration (g./l.) and unit thickness (cm.).

(5) Grassmann and v. Arnim, *Ann.*, **519**, 197 (1935).