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 $[\alpha]^{20}\mathrm{D}$ 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).

which is entirely different from Pratesi's diagram; it shows log k about 0.2 at 625 mμ and falls off to log k about −0.5 at 470 mμ and log k about −0.25 at 800 mμ without reaching a minimum. The solvent used is not indicated.

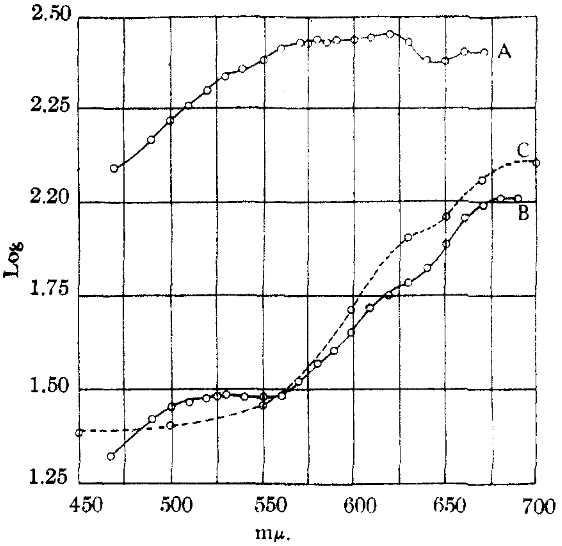

Fig. 1.—A, Pyrrole blue A, 50.94 mg. per liter of glacial acid; B, pyrrole blue B, 15.5 mg. per liter of glacial acetic acid; C, 2,3-dimethyl pyrrole blue in pyridine calculated from Pratesi's data.

The absorption curves of pyrrole blue A and B are not known since Pratesi measured only homologous substances of these dyestuffs and Grassmann and v. Arnim's curve differs so much from Pratesi's that it is improbable that it belongs to the B compound. A determination of the spectra of pyrrole blue A and B seemed therefore indicated.

Pyrrole blue B was prepared according to Liebermann and Häse[2] and dissolved in glacial acetic acid. The extinction was measured in a Hilger–Nutting spectrophotometer[6] with glacial acetic acid as a compensating liquid. The results are given in Fig. 1 curve B. Measurements in alcoholic hydrochloric acid gave a very similar picture. The curve resembles Pratesi's diagram for the homologous pyrrole blues (see curve C).

Both the acetic acid and the alcoholic solution are very unstable. They begin to change their spectrum after a few hours; the change continues through several days. The maximum at 520 mμ increases to log k about 1.9 while the maximum at 680 mμ disappears completely; no minimum could be observed in the visible range. The material represented in spectrum B seems therefore to contain some of the decomposition product.

Pyrrole blue A was prepared according to Pratesi and Zanetta[7]; these authors have pointed out that pyrrole blue A is not an oxidation product or derivative of pyrrole blue B but the result of a completely different reaction between pyrrole and isatin. Its absorption spectrum measured in glacial acetic acid in the Hilger–Nutting spectrophotometer is given in curve A Fig. 1. It confirms the assumption that the structure of pyrrole blue A is different from that of the B compound. Also the solutions of dyestuffs A are extremely unstable.

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[6] The author is greatly indebted to the Chemistry Department of the University of Michigan for the permission of using this instrument and to Dr. F. F. Blicke for the supply of pyrrole.

[7] Pratesi and Zanetta, *Atti Accad. nazion. Lincei, Ren.*, [6] **22**, 159 (1935).

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The Basic Nitrite of Lanthanum

By G. R. Sherwood

In 1914 Holden and James[1] reported that they got unusually rapid separation of yttrium from the other yttrium earths by the method of fractional precipitation with sodium nitrite. The method has been used and improved by other workers, but there seems to be no record of a quantitative study of the precipitate nor of the most favorable conditions under which it should be produced.

The lanthanum material used for these experiments showed only very faint spectral lines of praseodymium and neodymium. In addition it contained traces of cerium and manganese. It was therefore of satisfactory purity.

Some of the lanthanum solutions used were chlorides, others were nitrates. Either salt seemed to work about equally well. The lanthanum basic nitrite was prepared from these approximately 0.05 molar lanthanum solutions using the method as modified by Sherwood and Hopkins.[2]

The precipitated basic nitrite liberated iodine from hydroiodic acid, reduced acidified permanganate, and behaved in general as one would expect a nitrite to behave. All but the merest trace of sodium salts could be removed from it by simply washing it with water. The basic nitrite was surprisingly stable toward heat, at least up to approximately the boiling point of concentrated sulfuric acid.

It was found that the speed of precipitation increased with increased nitrite ion concentration, being too slow in half molar nitrite solution but satisfactory if the nitrite ion concentration was two molar.

Attempts were made to dry the first precipitates to constant weight in an oven at 110°. This was difficult to accomplish and the results did not seem significant. So subsequent precipitates were analyzed for La_2O_3 and N_2O_3 and the ratio of La_2O_3 to N_2O_3 determined for each sample.

A study was made to see whether the composi-

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[1] Holden and James, This Journal, **36**, 1418 (1914).

[2] Sherwood and Hopkins, *ibid.*, **55**, 3117 (1933).