[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Pentose Reactions. III. Xylan

BY CHARLES D. HURD AND NEILL R. CURRIE[1]

Xylan has been isolated from many plant materials such as straw, corn cobs, corn seedlings, esparto cellulose, etc., by extraction with 5–10% sodium hydroxide solution but oat hulls have never been studied in this connection. That oat hulls will give rise to xylose by an hydrolysis with dilute sulfuric acid has been demonstrated[2] recently. In the present work, it was found that xylan could be isolated from oat hulls in 22–24% yields. Prior removal of lignin from the hulls by treatment with phenol[3] had little effect on the quality or the yield of the xylan.

Since the phenol treatment does not remove the pentosan from the hulls, and since it was found to dissolve xylan quite readily, it seems evident that xylan does not exist as such in the plant material. Some kind of hydrolysis in the plant material is evidently caused by the hydroxide solution. The fact that xylan has been found to give cryoscopic molecular weight values[4] of 146, 195, and 231 in acetamide solutions of 0.45, 0.95 and 1.1% concentrations, respectively, points to a relatively simple molecule.

Diacetylxylan has been reported[5] to give molecular weight values of 400–633, depending on the method of acylation. In the present work diacetylxylan was prepared by interaction of xylan with acetic anhydride which contained very little nitric acid. The molecular weight, determined cryoscopically in nitrobenzene, indicated that it contained much of the monosaccharide derivative, $C_5H_6O_2(OCOCH_3)_2$. It regenerated xylan on saponification. This low molecular weight value for diacetylxylan aligns it with other polysaccharides (inulin acetate, mannan acetate, etc.) which give low molecular weight values in solvents. Pringsheim[6] has given a good review of the existing data.

Xylose was obtained by hydrolyzing the xylan with dilute sulfuric acid. It is interesting to note that a considerable conversion of an emulsion of the xylan in water into a reducing sugar was brought about by ethylene. A control experiment without the ethylene showed no such conversion. This is similar to the effect noted by Rea and Mullinix[7] with starch.

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(1) Holder of a Quaker Oats Fellowship, 1927–1929, administered through the Miner Laboratories, Chicago.

(2) Hurd and Isenhour, THIS JOURNAL, **54**, 323 (1932).

(3) Kolb and Schoeller, *Cellulosechemie*, **4**, 37 (1923).

(4) Reilly, Donovan and Burns, *Proc. Roy. Irish Acad.*, **B39**, 505 (1930); *Chem. Abstracts*, **25**, 1499 (1931).

(5) Hibino, *J. Chem. Soc. Japan*, **51**, 417 (1930); *Chem. Abstracts*, **25**, 4854 (1931).

(6) Pringsheim, "Chemistry of the Monosaccharides and of the Polysaccharides," McGraw-Hill Book Co., Inc., New York, 1932, pp. 291, 300–302, 312, 333–339. See also Haworth and Streight, *Helv. Chim. Acta*, **15**, 609 (1932); Haworth, Hirst and Percival, *J. Chem. Soc.*, 2384 (1932).

(7) Rea and Mullinix, THIS JOURNAL, **49**, 2117 (1927).

Experimental Part

Preparation of Xylan.—Five hundred grams of oat hulls was soaked for two days in a 2% ammonia solution, filtered off, washed and then digested for two to three hours with 6 liters of a 10% solution of sodium hydroxide. During the digestion, steam was passed through the mixture continuously. The mixture was filtered through a wire gauze and then through a cloth mat. The filtrate was added to an equal volume of 95% alcohol. After a complete mixing, another 1–2 liters of alcohol was added and the whole left overnight. The gummy alkali product was collected upon a cloth filter and washed thoroughly with alcohol. The spongy precipitate was pulverized underneath glacial acetic acid. After several hours, it was filtered off and the solid triturated with fresh acetic acid. Finally, it was collected upon a filter and rinsed free of acid with 95% alcohol; yield, 110–120 g. The xylan thus produced was a white, amorphous powder. Analysis by the colorimetric method[2] showed a purity of 96.8%. Several other methods or modifications were tried but this gave the most consistent results. The pentosan content of the original hulls, analyzed colorimetrically as before, was 28.6%.

This preparation was checked by Mr. M. E. McDougle, who also determined its rotation. The xylan taken for the rotation measurements was dissolved in sodium hydroxide solution and filtered through asbestos (Gooch funnel) to remove all solids not taken out by the cloth filter. The aqueous solution used for polarimetric measurements contained about equal weights of xylan and sodium hydroxide.

Rotation. 3.479 g. substance in 125, 180 and 250 cc. solution, reading, respectively, 3.94, 2.75 and 2.00° to the left in a 2-dm. tube at 30°: $[\alpha]^{30}_{D}$ −70.8, −71.1, −71.8°, average, −71.2°.

Extraction with Phenol.—Oat hulls, which had stood for twenty-four hours in a 2% ammonia solution, were washed thoroughly and dried. Then a 24-g. portion was heated at 100° for six hours with 300 g. of phenol which contained 10 drops of concd. hydrochloric acid.[3] After filtering off the undissolved hulls they were washed well with water, dilute acetic acid and finally with water until the washings were free from acid. This residue, after drying at 95°, weighed 13.1 g. From it, with the procedure outlined above, there was obtained 4.9 g. of xylan. This yield is 20.4% of the weight of the original hulls, which is about the same as without the phenol treatment.

All except 0.04 g. of a 0.5-g. sample of xylan dissolved in 10 g. of phenol which contained one drop of hydrochloric acid. After removal of the phenol from the filtrate by steam distillation, and solution of the non-volatile residue in sodium hydroxide solution, the sodium derivative of xylan was precipitated by addition of alcohol in the usual manner. The xylan which was thereby obtained weighed 0.39 g.

Xylose from the Xylan.—Thirty grams of xylan was refluxed for an hour with 1.2 liters of 5% sulfuric acid. Then it was filtered, the filtrate neutralized with barium carbonate, filtered, acidified slightly with phosphoric acid, filtered again and the filtrate concentrated to a thick sirup. Absolute alcohol was added and the solution seeded with crystals of xylose. Ultimately, 4.5 g. of crystalline xylose, m. p. 146°, separated. The sirup also contained much xylose, for it readily gave the characteristic double salt[8] of cadmium bromide and cadmium xylonate by reaction with cadmium carbonate, water and bromine.

Ethylene and Xylan.—Two 10-g. samples of xylan were boiled with 100 cc. of water and cooled to 22°. One of these emulsions was stoppered and left as a control. The other was saturated with ethylene, the flask stoppered and allowed to stand for three weeks. The solid material was then filtered off and washed with 20 cc. of water. An aliquot portion of the filtrate was dropped slowly into hot Fehling's solution and the mixture boiled for two minutes. By weighing the red cuprous oxide which was produced,

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(8) Bertrand, *Ber.*, **35**, 1460 (1902).

it was found that there had been a 10% conversion into a reducing sugar. The control specimen showed practically no conversion.

Diacetylxylan.—Previous workers[5,9] have synthesized this compound by heating xylan with acetic anhydride alone or with pyridine or zinc chloride. In the present work, good results were obtained by heating xylan (10 g.) for six hours at 70° with acetic anhydride (200 cc.) which contained a little nitric acid (2 cc., concd.). Prior to the heating the xylan was soaked in water for a day, filtered off and washed on the filter with glacial acetic acid. At the end of the heating, the light brown colored solution was filtered and the diacetylxylan precipitated by addition of methanol. The weight of the white, amorphous product was 8.5 g.

Anal.[10] Subs. 0.5018; acetic acid $\approx$ 10.47 cc. of 0.4332 *N* KOH. Calcd. CH_3-COOH from $C_5H_6O_2(OCOCH_3)_2$, 55.5; found, 55.1.

Diacetylxylan was soluble in nitrobenzene, aniline and quinoline; very slightly soluble in benzene and glacial acetic acid; and insoluble in carbon tetrachloride and camphor. Nitrobenzene was a suitable cryoscopic solvent.

Mol. Wt.[11] Subs. 0.0605; grams of nitrobenzene, 36.12; f. p. lowering, 0.0393°. Calcd. for $C_9H_{12}O_6$, mol. wt. 216; found, 298.

Saponification of the Diacetylxylan.—Three grams of the ester and 150 cc. of 10% potassium hydroxide solution were refluxed for two hours. The diacetate slowly dissolved. Then it was cooled and treated with alcohol till no further precipitation occurred. The brown gum was filtered off, washed with alcohol and allowed to stand overnight in glacial acetic acid. One gram of xylan was thus produced which was light brown in color.

The preparation of diacetylxylan and its saponification were also checked by Mr. M. E. McDougle. The rotation of the xylan produced by saponification of the diacetate was determined as before.

Rotation. Subs. 0.775 g. in 44 and 74 cc. of sodium hydroxide solution, reading, respectively, 2.49 and 1.50° to the left in a 2-dm. tube at 30°, $[\alpha]^{30}_{D}$ −70.6, −71.6°, average, −71.1°.

Summary

Xylan was isolated from oat hulls in 22–24% yields by extraction with sodium hydroxide solution. Evidence is offered to show that the xylan which is isolated in this way is simpler in structure than the pentosans in the original plant material. An emulsion of xylan in water was changed into a reducing sugar in about ten per cent. yields by the action of ethylene. In nitrobenzene as solvent diacetylxylan was found to have a molecular weight of about 300.

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[9] Heuser and Schlosser, *Ber.*, **56**, 392 (1923).

[10] By method of Perkin, *J. Chem. Soc.*, **87**, 107 (1905).

[11] Mr. R. W. McNamee also confirmed the low molecular weight of the diacetylxylan on some material independently prepared.