material was eluted from the single zone with acetone and, after evaporation of the eluate, the residue was crystallized from ethanol; m.p. 174–176° cor., $[\alpha]^{22}D$ +80.4° (*c* 3.7, chloroform), X-ray powder diffraction data: 13.35[11] w[12], 12.24 vw, 11.09 vs, 9.91 w, 8.82 w, 8.34 w, 6.59 m, 6.24 vw, 6.58 s, 5.34 s, 5.01 m, 4.81 s, 4.55 w, 4.27 m, 4.12 w, 3.81 m, 3.69 m, 3.54 vw, 3.46 vw, 3.38 m.

Anal. Calcd. for $C_{18}H_{21}O_{16}(CH_3CO)_{11}$: C, 49.69; H, 5.63; CH_3CO, 11.38 ml. of 0.1 *N* sodium hydroxide per 0.1 g.; mol. wt., 966.83. Found: C, 49.87; H, 5.52; CH_3CO, 11.33; mol. wt., 957 (Rast).

Partial Hydrolysis of 6-*O*-β-Maltosyl-α-D-glucopyranose Hendecaacetate.—6-*O*-β-Maltosyl-α-D-glucopyranose hendecaacetate (3 g.) was dissolved in 40 ml. of 0.05 *N* sodium methoxide in methanol. After standing at room temperature for 5 min., a precipitate was formed which was dissolved by the addition of a small amount of water. The solution was deionized by passing successively through columns (2.5 mm. diam., × 15 mm.) of Amberlite 120[13] and Duolite A-4.[14] The effluent was evaporated under reduced pressure to a sirup which was dissolved in 75 ml. of 0.05 *N* sulfuric acid and refluxed for 7 hr. The sulfuric acid was removed by passing the solution again through the column of Duolite A-4, and the effluent was evaporated to dryness under reduced pressure; yield 1.47 g. This material was acetylated by boiling for 1 min. with 0.7 g. of anhydrous sodium acetate and 10 ml. of acetic anhydride. The reaction mixture was poured into 100 ml. of ice and water and stirred occasionally for 2 hr. The mixture was then extracted with four 25-ml. portions of chloroform. The combined chloroform extracts were washed with water, dried with anhydrous sodium sulfate and evaporated to a sirup. The sirup was dissolved in benzene and placed on a column (75 mm., diam., × 275 mm.) of Magnesol–Celite and developed with 3000 ml. of benzene–*t*-butyl alcohol (100:1 by vol.). Upon extrusion and application of the indicator, one large zone appeared in the middle of the column (the effluent will be discussed below). The carbohydrate material was eluted from the zone with acetone and the residue obtained on solvent removal was fractionally crystallized from ethanol; yield 300 mg. of 6-*O*-β-maltosyl-β-D-glucopyranose hendecaacetate, m.p. 229–231° cor., $[\alpha]^{29}D$ +39.4° (*c* 4.2, chloroform). The second fraction was impure and was rechromatographed on a column (45 mm. diam., × 220 mm.) of Magnesol–Celite (5:1 by wt.) by developing with 700 ml. of benzene–*t*-butyl alcohol (100:1 by vol.). The principal zone, near the top of the column, was sectioned and the acetone-eluted material was crystallized from ethanol; yield 200 mg., m.p. 193–195° cor., $[\alpha]^{29}D$ −3.0° (*c* 2.5, chloroform), in agreement with accepted values for β-gentiobiose octaacetate.

The above mentioned effluent from the first column was evaporated to dryness and rechromatographed on a column (50 mm. diam., × 225 mm.) of Magnesol–Celite by developing with 800 ml. of benzene–*t*-butyl alcohol (100:1 by vol.). The acetone-eluted material of the one zone which appeared was crystallized from ethanol; yield 400 mg. of β-D-glucopyranose pentaacetate, m.p. 128–130° cor., $[\alpha]^{30}D$ +4.6° (*c* 2.5, chloroform).

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(11) Interplanar spacing, Å., CuK_α radiation.

(12) Relative intensity, estimated visually; vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

(13) A product of the Resinous Products and Chemical Co., Philadelphia, Penna.

(14) A product of the Chemical Process Co., Redwood City, Calif.

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

The Constitution of the Hemicellulose of the Straw of Flax (Linum Usitatissimum Sp.). I. Identification of 2-*O*-(4-*O*-Methyl-D-glucuronosyl)-D-xylose

BY J. D. GEERDES AND F. SMITH[1]

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The acid component of the hemicellulose obtained from flax-straw (*Linum Usitatissimum* Sp.) has been isolated as an aldobiouronic acid (I) and this has been identified as 2-*O*-(4-*O*-methyl-D-glucopyruronosyl)-D-xylose.

Flax hemicellulose obtained from the delignified straw by extraction with alkali gave upon hydrolysis a mixture of an aldobiouronic acid (I), D-xylose and a small amount of L-rhamnose. The acidic component (I), which forms the subject of this communication, was separated from the hydrolysate by the use of an anion-exchange resin. The methoxyl content of I and its equivalent weight, indicated that it was composed of a methoxy uronic acid and a pentose sugar, a deduction further substantiated by the observation that, upon vigorous hydrolysis, I afforded 4-*O*-methyl-D-glucuronic acid and D-xylose as indicated by paper chromatography.

Cleavage of the aldobiouronic acid (I) with 8% methanolic hydrogen chloride at 115°, followed by treatment of the cleavage products with ammonia, yielded the crystalline amide of methyl 4-*O*-methyl-α-D-glucuronoside.[2] After removal of this uronic acid derivative, hydrolysis of the neutral sugar glycoside gave crystalline D-xylose.

When the methyl ester of the methyl glycoside of I was reduced with lithium aluminum hydride[3,4] to the corresponding disaccharide, methyl *O*-(4-*O*-methyl-D-glucopyranosyl)-D-xyloside, and the latter hydrolyzed with dilute acid, the cleavage products so formed were found by chromatographic analysis to be D-xylose and 4-*O*-methyl-D-glucose.[2,5]

The point of attachment of the 4-*O*-methyl-D-glucuronic acid unit to the D-xylose residue was derived from a study of the methylated aldobiouronic acid (II) formed when methylated flax straw hemicellulose was subjected to the action of boiling 2% methanolic hydrogen chloride.[6] Cleavage of II with 8% methanolic hydrogen chloride at 115° and treatment of the resulting glycosides with methanolic ammonia yielded the crystalline amide of methyl 2,3,4-tri-*O*-methyl-α-D-glucuronoside.[7] When the neutral component of the methylated aldobiouronic acid, namely, methyl mono-*O*-methyl-D-xyloside, was hydrolyzed and the free sugar purified by paper chromatography, there was isolated crystalline

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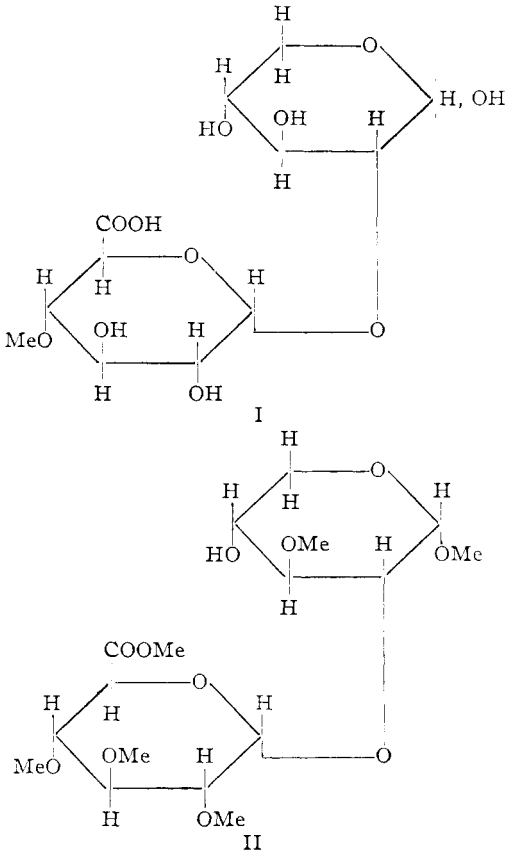

I

II

3-*O*-methyl-D-xylose.[8] The latter was further characterized in the form of its crystalline anilide.[9]

The evidence cited above proves that the 4-*O*-methyl-D-glucuronic acid unit is linked in the methylated aldobiouronic acids (I and II) to the xylose component through a position other than C_3. In order to determine the precise nature of the glycosidic linkage of the methylated aldobiouronic acids (I and II), II was completely methylated and then hydrolyzed. The di-*O*-methyl-D-xylose moiety was identified as the 3,4-di-*O*-methyl derivative since it afforded the known crystalline δ-lactone.[10] From these facts it is apparent that the biose link involves position 2 of the D-xylose residue and hence the fully methylated aldobiouronic acid derived from II is methyl 2-*O*-(2,3,4-tri-*O*-methyl-D-glucuronosyl)-3,4-di-*O*-methyl-D-xyloside methyl ester. This is identical with the compound obtained from aspen wood[11] and from "hemicellulose-B" of corn cobs.[12]

The aldobiouronic acid derived directly from the flax straw hemicellulose must, therefore, have the formula I and it is designated 2-*O*-(4-*O*-methyl-D-glucuronosyl)-D-xylose. The work of Bishop indicates that the biose linkage is of the α-type.[13]

Experimental

Isolation of Flax Straw Hemicellulose.—Finely ground flax straw was bleached and delignified by the sodium chlorite–acetic acid method,[14] whereby 112.5 g. of holocellulose was obtained from 150 g. of flax straw.

Flax straw holocellulose (200 g.) was stirred with a 5% potassium hydroxide solution (3 l.) for 2 hours at room temperature after which the white residue of cellulose was removed by filtration and washed with dilute acetic acid. The filtrate containing the hemicellulose was neutralized and adjusted to *p*H 4–5 with acetic acid and an equal portion of ethyl alcohol added to precipitate the hemicellulose. The latter was separated (centrifuge), redissolved in potassium hydroxide (2 l.) and centrifuged to remove a small amount of precipitate which was rejected. The alkaline solution of the hemicellulose was acidified with acetic acid and treated with an equal volume of ethanol; the resulting precipitate was washed twice with absolute ethanol, twice with anhydrous ether, and dried *in vacuo*. The yield of hemicellulose was 27 g. or 10% by weight of the original straw, $[\alpha]^{25}D$ −65° (*c* 1, in 5% sodium hydroxide); OMe, 2.95.

A portion of hemicellulose (6 g.) was dissolved in 5% potassium hydroxide (300 ml.), acidified to *p*H 4–5 with acetic acid, and fractionally precipitated by adding successive volumes of ethanol. The results of this fractionation are given in Table I.

TABLE I

Fraction no.	Ethanol:solution ratio	Fraction wt., g.	$[\alpha]^{25}D$ (in 5% NaOH)
1	1:10	0.85	−68.0°
2	1:5	0.35	−67.3°
3	1:3	1.55	−60.7°
4	1:2	2.00	−60.5°
5	2:3	0.70	−49.4°
6	3:2	0.46	−38.5°

Determination of the Acid Component in Flax Straw Hemicellulose.—A solution of hemicellulose (100 mg. of fraction 3) in *N* sulfuric acid (5 ml.) in a sealed tube was heated in boiling water for 12 hours. The solution was neutralized with barium carbonate, filtered and passed through a cation-exchange resin, Amberlite IR120, and the acidic component selectively removed by passing the solution through an anion-exchange resin, Duolite A4. The effluent containing the non-acidic free sugars was evaporated to a small volume for chromatographic determination of the component sugars using phenol saturated with water as irrigating solvent. A large spot corresponding to xylose, R_f 0.5, and two faint spots with R_f values of 0.20 and 0.31 due to xylose oligosaccharides (probably xylobiose and xylotriose) appeared when the chromatogram was sprayed with ammoniacal silver nitrate.

The acid component was displaced from the Duolite A4 resin with *N* sodium hydroxide and the free acids were again liberated by passing the effluent through a column of Amberlite IR120 cation-exchange resin. The effluent was evaporated to a small volume and examined by qualitative chromatography. Using 1-butanol–acetic acid–water (4:1:5) as irrigating solvent, spots appeared with R_f values of 0.34 and 0.66. A 4-*O*-methyl-D-glucuronic acid standard had an R_f value of 0.34 while glucuronic acid and galacturonic acid standards had R_f values of 0.36 and 0.44, respectively. The component having R_f 0.66 was not identified.

Separation of 2-*O*-(4-*O*-Methyl-D-glucuronosyl)-D-xylose from Flax Straw Hemicellulose.—The hemicellulose (10 g.) was heated for 7.5 hours with 0.5 *N* sulfuric acid (200 ml.) on a boiling water-bath until the rotation was constant. The hydrolysate was then neutralized with barium carbonate, filtered, and the filtrate passed through a cation-exchange resin, Amberlite IR120. This gave a solution containing the free sugar acids and xylose. The effluent was then passed through an anion-exchange resin, Duolite A4, to retain the acidic component. The acidic component, recovered from the Duolite A4 column as described above and freed from solvent *in vacuo*, was obtained as a brown colored sirupy residue which contained the aldobiouronic acid (I).

The sirupy product was dissolved in water (50 ml.), the resulting solution neutralized with barium carbonate, filtered and evaporated *in vacuo* to dryness. The residual

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barium salt of aldobiouronic acid was dissolved in methanol and precipitated by adding ether. Repeated precipitation followed by washing with absolute ether and drying *in vacuo* yielded an almost white powder.

Anal. Calcd. for $(C_{12}H_{18}O_{11})_2Ba$: OMe, 7.6. Found: OMe, 6.0.

A portion of the barium salt of the aldobiouronic acid was converted to the free acid by passing it through IR120 cation-exchange resin and the neutralization equivalent determined by titration of the eluate.

Anal. Calcd. for $C_{12}H_{19}O_{11}$: equiv. wt., 339. Found: equiv. wt., 333.

The methyl aldobiouronoside methyl ester (200 mg.), prepared by treating the aldobiouronic acid with 2% methanolic hydrogen chloride for 8 hours at room temperature, failed to give a crystalline amide.

Reduction of the Methyl 2-*O*-(4-*O*-Methyl-D-glucurono-syl)-D-xylopyranoside Methyl Ester with Lithium Aluminum Hydride.[3]—To a solution of the methyl ester of the methyl-aldobiouronoside (I) (15 mg.) in dry tetrahydrofuran (10 ml.), a solution of lithium aluminum hydride (0.1 g.) in dry ether (10 ml.) was added dropwise. After 15 minutes the excess lithium aluminum hydride was cautiously destroyed with water and the hydrolyzed salts removed by filtration. The filtrate was evaporated *in vacuo* to a sirup and the latter hydrolyzed by heating with *N* sulfuric acid (3 ml.) for 12 hours in a sealed tube on a boiling water-bath. The solution was neutralized with barium carbonate, filtered and evaporated *in vacuo* to a sirup.

Qualitative chromatographic examination of the sirup yielded spots corresponding to 4-*O*-methyl-D-glucose[2] and D-xylose.

Hydrolysis of 2-*O*-(4-*O*-Methyl-D-glucuronosyl)-D-xylose (I).—Attempts to methanolize the aldobiouronic acid component (I) with a solution of 2% methanolic hydrogen chloride failed and an attempt to cleave I with 8.5% methanolic hydrogen chloride by refluxing for 15 hours also failed.

When the methylaldobiouronoside methyl ester (0.47 g.) was dissolved in methanol (15 ml.) containing 8% hydrogen chloride and heated for 12 hours at 112–115° in a sealed tube, cleavage occurred. The solution was neutralized with silver carbonate, filtered and concentrated *in vacuo* to give a pale yellow sirup.

Identification of Methyl 4-*O*-Methyl-α-D-glucuronoside.—The pale yellow sirup containing the glycoside mixture was dissolved in methanol (25 ml.) and the solution saturated with ammonia gas at 2°. After standing at room temperature for 18 hours, the mixture was evaporated *in vacuo* to a sirup which crystallized after nucleation with the amide of methyl 4-*O*-methyl-α-D-glucuronoside. After recrystallization from methanol the amide had m.p. and mixed m.p. of 234°, $[\alpha]^{24}D$ +151° (*c* 0.9, in water).[2]

Identification of D-Xylose.—The mother liquor, from which the amide of methyl 4-*O*-methyl-α-D-glucuronoside had been separated, was dissolved in water and 0.3 *N* barium hydroxide (10 ml.) was added. The solution was heated on a water-bath at 80° to hydrolyze any remaining amide and a stream of carbon dioxide-free air was bubbled through the solution during the hydrolysis to sweep out the ammonia generated. When ammonia was no longer evolved (tested with red litmus) the excess barium hydroxide was neutralized with carbon dioxide, the precipitated barium carbonate filtered, and the solution evaporated to a pale yellow sirup under reduced pressure. The residual sirupy glycoside was dissolved in *N* sulfuric acid and hydrolyzed by heating on a boiling water-bath for 11 hours after which the rotation was constant. The solution was neutralized with barium carbonate, filtered, and the filtrate evaporated to a sirup *in vacuo*. The barium salt of the acid present was removed by dissolving the sirup in water and passing the solution through a column of cation-exchange resin Amberlite IR120 and then through a column of anion-exchange resin Duolite A4. The eluate when evaporated to a sirup yielded crystalline D-xylose, m.p. and mixed m.p. 145° (after recrystallization from ethanol), $[\alpha]^{23}D$ +58° (10 minutes) +18.3° (2 hours, constant) (*c* 0.8, in water). The dibenzylidenedimethyl acetal derivative[15] had m.p. and mixed m.p. 210°.

Examination of the Aldobiouronic Acid from Methylated Flax Straw Hemicellulose.—The methylated aldobiouronic acid component was obtained from the glycosides formed by the selective methanolysis of the methylated hemicellulose.[6] The acid component was absorbed on Duolite A4 anion-exchange resin and eluted as the sodium aldobiouronate with 0.01 *N* NaOH. The free acid was obtained by passing the alkaline eluate through a column of cation-exchange resin Amberlite IR120 and concentrating the resulting solution to a glassy solid. This compound proved to be a methylated aldobiouronic acid (II), methyl 2-*O*-(2,3,4-tri-*O*-methyl-D-glucuronosyl)-3-*O*-methyl-D-xyloside.[11,12]

Anal. Calcd. for $C_{16}H_{28}O_{11}$: OMe, 39.2; equiv. wt., 396. Found: OMe, 37.8; equiv. wt., 382.

A portion of the methylated aldobiouronoside (II) was converted to the barium salt by adding barium hydroxide, heating, neutralizing the excess alkali with carbon dioxide, filtering and washing and removing the solvent by evaporation. The neutralization equivalent was determined by passing a solution of the barium salt through a column of Amberlite IR120 cation-exchange resin and titrating the eluate with standard alkali.

Anal. Calcd. for $(C_{16}H_{27}O_{11})_2Ba$: OMe, 33.4; equiv. wt., 464. Found: OMe, 32.2; equiv. wt., 456.

Hydrolysis of Methyl 2-*O*-(2,3,4-Tri-*O*-methyl-D-glucuronosyl)-3-*O*-methyl-D-xyloside and Identification of the Products.—A solution of the acid component (200 mg.) in methanol (22 ml.) containing 8% hydrogen chloride was heated in a sealed tube for 8 hours at 112–114°. The solution was neutralized with silver carbonate, filtered and evaporated to a sirup. The sirup was dissolved in water (50 ml.) and the solution extracted twice with chloroform (50 ml.).

The chloroform extract containing the methyl ester of the methylated methyl glucuronoside was dried and evaporated to a sirup. The latter was dissolved in methanol, and the solution saturated with ammonia gas at 5°. After standing at room temperature for 18 hours, the solution was evaporated to a sirup. Crystallization occurred after nucleating the sirup with the amide of methyl-2,3,4-tri-*O*-methyl-α-D-glucuronoside.[7] Recrystallization from ethyl alcohol–petroleum ether yielded colorless needles having m.p. and mixed m.p. 185°, $[\alpha]^{27}D$ +139° in water (*c* 0.8).

The aqueous layer obtained above, from which the methylated glucuronic acid had been extracted, was evaporated *in vacuo* to a sirup, dissolved in *N* sulfuric acid and heated on a boiling water-bath until the rotation became constant. The hydrolysate was neutralized with barium carbonate, filtered and concentrated to a sirup. Purification of the sirup by means of sheet paper chromatography using methyl ethyl ketone–water azeotrope as the solvent[16] yielded a sirup which crystallized completely, after nucleating with 3-*O*-methyl-D-xylose prepared by the method of Levene and Raymond.[8] After recrystallization from acetone it had m.p. 103° alone or admixed with a pure specimen of 3-*O*-methyl-D-xylose, $[\alpha]^{22}D$ +15.3° in water (*c* 0.9).

The anilide of 3-*O*-methyl-D-xylose was prepared by refluxing 3-*O*-methyl-D-xylose in absolute ethanol containing aniline (1.5 moles, freshly distilled) for 2 hours on a water-bath. Evaporation of the solution yielded the crystalline anilide which when recrystallized from acetone had m.p. 138° and mixed m.p. 137–138°.[9,17]

Methylation of Methyl 2-*O*-(2,3,4-Tri-*O*-methyl-D-glucuronosyl)-3-*O*-methyl-D-xyloside.—The aldobiouronic acid (0.4 g.) was dissolved in 30% sodium hydroxide (10 ml.) and methylated by the simultaneous addition of methyl sulfate (30 ml.) and 30% sodium hydroxide (120 ml.) over a period of 4 hours with vigorous stirring. For the first two hours the reaction was carried out at room temperature after which the temperature was maintained at 50° for an additional two hours. The excess methyl sulfate was then decomposed by heating at 95–98° for one hour. The solution was made slightly acid to congo red by adding dilute sulfuric acid and extracted six times with chloroform. The sirupy acidic product obtained by evaporation was remethylated in the same manner except that the entire reaction was carried out at 50°. The chloroform extract from the second methylation was dried and evaporated to a pale yellow sirup. Purification by extraction with ether gave methyl 2-*O*-(2,3,4-tri-*O*-methyl-D-glucuronosyl)-3,4-di-*O*-methyl-D-xyloside as a sirup, $[\alpha]^{23}D$ +105° (*c* 2.4 in water).

(15) L. J. Breddy and J. K. N. Jones, *J. Chem. Soc.*, 738 (1945).

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(17) E. V. White, THIS JOURNAL, **75**, 257 (1953).

Anal. Calcd. for $C_{17}H_{30}O_{11}$: OMe 45.3; equiv. wt., 410. Found: OMe 45.0; equiv. wt., 425.

Methanolysis of Methyl 2-*O*-(2,3,4-Tri-*O*-methyl-D-glucuronosyl)-3,4-di-*O*-methyl-D-xyloside.—A solution of the fully methylated aldobiouronic acid in methanol containing hydrogen chloride (8%) was heated (sealed tube) for 8 hours at 110–115°. The reaction mixture was neutralized with silver carbonate, filtered, and the filtrate evaporated to a sirup. The material was extracted with ether, the ether extract concentrated and hydrolyzed by heating with *N* sulfuric acid on a boiling water-bath until the rotation became constant. The hydrolysate was neutralized with barium carbonate, filtered, concentrated *in vacuo* to a volume of 10–15 ml. and passed successively through a column of ion-exchange resin Amberlite IR120 and of Duolite A4 to remove the acid component. The eluate was evaporated to give the neutral sugar component. Paper chromatographic examination of this neutral sugar fraction using methyl ethyl ketone–water azeotrope as the irrigating solvent revealed a heavy spot having an R_f value of 0.57. Comparison standards of 2,3-di-*O*-methyl-D-xylose and 3,5-di-*O*-methyl-D-xylose gave spots having R_f values of 0.56 and 0.63, respectively. The wide variation in R_f values between 3,5-di-*O*-methyl-D-xylose and the sugar in question discounted the possibility that the former was the derivative obtained from the fully methylated aldobiouronic acid. When sprayed with *p*-anisidine–trichloroacetic acid[18] the 2,3-di-*O*-methyl-D-xylose gave a dark reddish-brown spot while the spot produced by the neutral sugar from the aldobiouronic acid was light tan in color. Heavy spotting on paper chromatograms indicated possible contamination with mono-*O*-methyl-D-xylose so the material was purified by sheet paper chromatography. The 3,4-di-*O*-methyl-D-xylose so produced was a sirup, $[\alpha]^{25}D$ +22.1° (*c* 0.7, in methanol).

A solution of the 3,4-di-*O*-methyl-D-xylose (15 mg.) in water (1 ml.) from the fully methylated aldobiouronic acid was oxidized with bromine (0.1 ml.). The reaction mixture was allowed to stand in the dark for 50 hours after which time the di-*O*-methyl-D-xylose had disappeared from the solution as determined by descending paper chromatography. The excess bromine was then removed by aeration, the hydrogen bromide neutralized with silver carbonate and the resulting solution filtered. Residual silver ions were removed by passing hydrogen sulfide through the solution which was then filtered and evaporated *in vacuo* to a sirup. The latter was heated at 95–100° for 3 hours at 15 mm. pressure in order to bring about lactonization. Upon nucleation of the resulting sirup with 3,4-di-*O*-methyl-D-xylono-δ-lactone complete crystallization took place at once. Recrystallization from ether yielded long colorless needles having m.p. and mixed m.p. 67°, $[\alpha]^{23}D$ −51° (25 minutes); −23° (69 hours, constant).[10]

Acknowledgment.—The authors wish to thank Dr. E. V. White for a sample of 3,4-di-*O*-methyl-D-xylono-δ-lactone, and the Graduate School of the University of Minnesota for financial support.

ST. PAUL, MINN.

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[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

The Constitution of the Hemicellulose of the Straw of Flax (Linum Usitatissimum Sp.). II. Hydrolysis of the Methylated Hemicellulose

BY J. D. GEERDES AND F. SMITH[1,2]

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The hemicellulose isolated from delignified flax straw by extraction with alkali has been shown to be a branched chain 4-*O*-methyl-D-glucurono-L-rhamnoxylan. The side chains are composed of single units of 4-*O*-methyl-D-glucuronic acid which are attached to position 2 of a D-xylopyranose unit of the xylan molecular framework of which L-rhamnopyranose units are also an integral part. The methylated flax straw hemicellulose gives upon hydrolysis: 2,3,4-tri-*O*-methyl-D-xylose (1 mole), 2,3-di-*O*-methyl-D-xylose (105 moles), 2-*O*-methyl-D-xylose (2 moles), 3-*O*-methyl-D-xylose (15 moles), 2,4-di-*O*-methyl-L-rhamnose (2 moles) and 2,3,4-tri-*O*-methyl-D-glucuronic acid (15 moles). The general structural features of the polysaccharide are discussed.

An aldobiouronic acid, 2-*O*-(4-*O*-methyl-D-glucuronosyl)-D-xylose, has been shown[3] to be a component of the hemicellulose of flax straw. This paper is concerned with the main structural features of the hemicellulose itself.

Paper chromatographic examination of the sugars produced from the acid hydrolyzed hemicellulose showed D-xylose to be the principal component with a small amount of a second neutral sugar component having an R_f value which corresponded to that of L-rhamnose. In addition there was an acidic component consisting of 2-*O*-(4-*O*-methyl-D-glucuronosyl)-D-xylose.[3]

When the hemicellulose was hydrolyzed with acid there was a marked increase in optical rotation. This is generally attributed to the cleavage of β-glycosidic bonds which would be in agreement with the proposed linkage in other xylans.[4,5] The high proportion of xylose in the hemicellulose was shown by the fact that crystalline D-xylose could be obtained readily from the neutral fraction of the hydrolysate of the flax hemicellulose.

In order to ascertain the mode of union of the building units of the flax hemicellulose the latter was acetylated[6] and then methylated with methyl sulfate and alkali. Fractional precipitation with the usual solvents gave products which appeared to be homogeneous as determined by specific rotation, methoxyl values, and neutralization equivalents. Following methanolysis with 2% methanolic hydrogen chloride under conditions which retain the sugar acid in the form of a disaccharide, the glycosides were separated into neutral and acidic components using ion-exchange resins. The acidic component was shown[3] to be methyl 2-(2,3,4-tri-*O*-methyl-D-glucuronosyl)-3-*O*-methyl-D-xyloside.

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(2) Extracted from a thesis submitted by J. D. Geerdes to the graduate faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Ph.D., 1953. This paper was presented at the 125th A.C.S. meeting in Kansas City, 1954.

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