Identification of a Di-*O*-methylgalactose.—This sirup (4 mg.) constituted less than 0.7% of the hydrolyzed methylated sugars and its mobility on solvent G placed it in the di-*O*-methylhexose class. On demethylating the sirup in a sealed tube (1 ml. of 48% hydrobromic acid on boiling water-bath for 20 minutes), this compound was shown chromatographically (solvent C) to correspond to galactose.

Acknowledgment.—The authors wish to express their thanks to Drs. H. W. Kircher and N. S. Thompson for many most valuable suggestions and discussions.

SHELTON, WASH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Synthesis of Amino Sugars by Reduction of Hydrazine Derivatives[1]

BY M. L. WOLFROM, F. SHAFIZADEH AND R. K. ARMSTRONG

RECEIVED APRIL 28, 1958

Reduction of the hydrazino compounds formed by the replacement of sulfonyloxy group in the sugar series provides a convenient approach to the synthesis of amino sugars. 3-Amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and a methyl 2-amino-2-deoxy-3,4-*O*-isopropylidene-β-L-pentopyranoside have been prepared by this method. The former product was further characterized as the picrate and salicylaldehyde Schiff base. The latter product has been isolated as the salicylaldehyde Schiff base and converted to the corresponding methyl 2-amino-2-deoxy-β-L-pentopyranoside hydrochloride and 2-amino-2-deoxy-α-L-pentose hydrochloride. Some of the properties of this compound have been compared with those of other 2-amino-2-deoxyaldoses.

In a previous paper[2] a convenient method has been described for the synthesis of a variety of amino-deoxy-alditols and 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose, through the reduction of the phenylhydrazone derivative of the corresponding aldose or carbonyl compound. Application of this method for the synthesis of other amino sugars is naturally limited by the availability of the corresponding phenylhydrazone derivatives. The present work provides an extension of this work to the reduction of hydrazino compounds which may be obtained through the replacement of sulfonyloxy groups. Direct replacement of the secondary sulfonyloxy groups in general is very difficult[3] and the results obtained by the drastic treatment of methyl 3,4,6-tri-*O*-methyl-2-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside[4] and the corresponding galactopyranoside derivative[5] with alcoholic ammonia have been discouraging as a method of synthesis. The direct replacement of the secondary sulfonyloxy groups with hydrazine, however, appears to be more practical. Thus, Freudenberg and Brauns[6] obtained 3-deoxy-3-hydrazino-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (I) in 60% yield. Reduction of this compound with Raney nickel catalyst in the Parr hydrogenation apparatus readily provides 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (II), which has been converted to the salicylaldehyde Schiff base and the picrate salt. The above compound and some of its derivatives have been obtained previously by Freudenberg and associates,[7] less conveniently and in a somewhat smaller yield, through the replacement of a *p*-tolylsulfonyloxy group by ammonia (under pressure). The fact that this reaction proceeds without Walden inversion has been established by the synthesis of 3-amino-3-deoxy-D-glucose derivatives through the treatment of methyl 3,4-anhydro-β-D-allopyranoside and methyl 2,3-anhydro-4,6-benzylidene-α-D-allopyranoside with ammonia.[8]

Application of the above process to methyl 3,4-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-β-L-arabinopyranoside[9] (III) provided a methyl 2-amino-2-deoxy-3,4-*O*-isopropylidene-β-L-pentopyranoside (IV), which could have either the L-*arabino* or the L-*ribo* configuration. This product was isolated as the salicylaldehyde Schiff base. Hydrolysis of the isopropylidene group with hydrochloric acid gave the corresponding methyl 2-amino-2-deoxy-β-L-pentopyranoside hydrochloride (V) in crystalline form. As may be expected from the well established properties of 2-amino-2-deoxy-D-glucose derivatives,[10-12] the glycosidic group of the above compound was quite resistant toward acid hydrolysis. Consequently the free sugar, a 2-amino-2-deoxy-α-L-pentose hydrochloride (VI), was obtained from the acetylation of the methyl glycoside and subsequent hydrolysis of the sirupy acetate with hydrochloric acid. The free sugar displayed the rapid mutarotation shown in Fig. 1, and on acetylation with silver acetate and acetic anhydride furnished a 2-acetamido-2-deoxy-L-pentose.

Previously the only known 2-amino-2-deoxypentose, was the D-xylose derivative, synthesized by Wolfrom and Anno[13] from the configurationally related 2-amino-2-deoxy-D-glucose. The above compound is the second member of this series. The L-arabinose configuration may be assigned to the new 2-amino-2-deoxypentose on the assumption that the direct replacement of sulfonyloxy group with

(1) Supported by Grant No. CY-3232 from the Department of Health, Education and Welfare, Public Health Service, National Institutes of Health, Bethesda 14, Md.

(2) M. L. Wolfrom, F. Shafizadeh, J. O. Wehrmüller and R. K. Armstrong, *J. Org. Chem.*, **23**, 571 (1958).

(3) R. S. Tipson, *Advances in Carbohydrate Chem.*, **8**, 107 (1953).

(4) W. O. Cutler and S. Peat, *J. Chem. Soc.*, 782 (1939); W. N. Haworth, E. L. Hirst and L. Panizzon, *ibid.*, 154 (1934).

(5) L. F. Wiggins, *ibid.*, 522 (1944).

(6) K. Freudenberg and F. Brauns, *Ber.*, **55**, 3233 (1922).

(7) K. Freudenberg, O. Burkhart and E. Braun, *ibid.*, **59**, 714 (1926).

(8) S. Peat and L. F. Wiggins, *J. Chem. Soc.*, 1810 (1938).

(9) J. Honeyman, *ibid.*, 990 (1946).

(10) J. C. Irvine and A. Hynd, *ibid.*, **101**, 1128 (1912); **105**, 698 (1914).

(11) R. C. G. Moggridge and A. Neuberger, *ibid.*, 745 (1938).

(12) A. B. Foster, D. Horton and M. Stacey, *ibid.*, 81 (1957).

(13) M. L. Wolfrom and K. Anno, THIS JOURNAL, **75**, 1038 (1953).

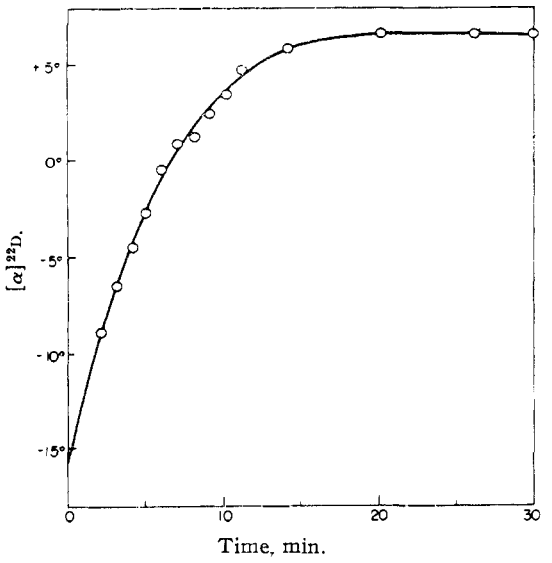
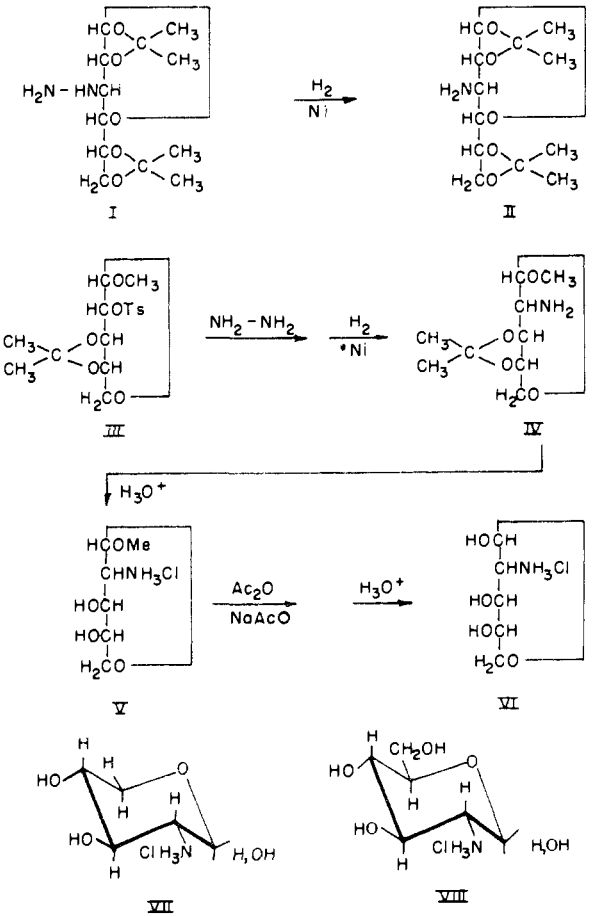


Fig. 1.—Mutarotation of the 2-amino-2-deoxy-α-L-pentose hydrochloride in aqueous solution; *c* 2.02.

hydrazine is not accompanied by a Walden inversion. This assumption can be justified by analogy with similar replacements of sulfonyloxy group with ammonia[4,7] and identity of the 3-amino-3-deoxyaldose derivative prepared from the hydrazino compound with that obtained directly by Freudenberg and associates[7] as described above. If so, this pentosamine should bear the same configurational relationship to the naturally occurring 2-amino-2-deoxy-D-galactose as D-xylosamine does to D-glucosamine. This is being verified by another series of experiments.

The new compound displays the properties which may be regarded as being characteristic of 2-amino-2-deoxyaldoses in general. It is strongly reducing and gives positive Elson–Morgan[13,14] and ninhydrin[15] tests. An interesting reaction of 2-amino-2-deoxyaldoses is the nitrous acid deamination of these compounds.[16–19] This reaction is stereospecific and has been shown to result in the formation of 2,5-anhydro-D-mannose and 2,5-anhydro-D-talose from 2-amino-2-deoxy-D-glucose and 2-amino-2-deoxy-D-galactose, respectively, whereas 2-amino-2-deoxy-D-mannose apparently behaves in a different manner.[19,20] The reaction of the resulting furan derivatives (2,5-anhydro compounds) with indole is the basis of a color test developed by Dische and Borenfreund,[21] and applied to 2-amino-2-deoxy-D-glucose and 2-amino-2-deoxy-D-galactose as the representatives of the hexosamine series. The results obtained from the application of this test to the known pentosamines as well as the above hexosamines are shown in Fig. 2, which indicates that 2-amino-2-deoxy-D-xylose and 2-amino-2-deoxy-D-glucose provide stronger reactions. A possible interpretation of this phenomenon is that, in analogy with 2-amino-cyclohexanols,[22,23] the contraction of the six-membered ring to a five-membered ring, on deamination with nitrous acid, takes place through the chair conformation in which the amino group is equatorial (VII and VIII). Thus, the extent of the reaction may be related to the stability of this conformation which in the D-pentose and D-hexose series is more favored by the D-*xylo* (VII) and D-*gluco* (VIII) configurations, respectively. It is to be noted that D-glucose and D-galactose are further stabilized in the above conformation because of an equatorial residue at C5.



Experimental

Preparation of 3-Amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose.—A solution of 20 g. of 1,2:5,6-di-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (0.0482 mole) in 50 g. of anhydrous hydrazine was heated at 145° for 20 hr. The reaction mixture was then extracted with three 50-ml. portions of ether. The extract was washed with 10 ml. of 50% potassium hydroxide, dried with anhydrous potassium carbonate and evaporated to dryness. The residue was dissolved in 50 ml. of 95% alcohol and the solution was hydrogenated in the Parr apparatus at 3-atm. pressure for 18 hr., using Raney nickel catalyst.[24] The hydro-

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(16) P. A. Levene, "Hexosamines and Mucoproteins," Longmans, Green and Co., London, 1925.

(17) S. Peat, *Advances in Carbohydrate Chem.*, **2**, 37 (1946).

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(20) P. A. Levene, *J. Biol. Chem.*, **39**, 69 (1919).

(21) Z. Dische and Ellen Borenfreund, *ibid.*, **184**, 517 (1950).

(22) G. E. McCasland, THIS JOURNAL, **73**, 2293 (1951).

(23) W. Klyne, in "Progress in Stereochemistry," W. Klyne, ed., Butterworths Scientific Publications, London, 1954, Vol. 1, p. 72.

(24) No. 28 Raney active nickel catalyst in water, obtained from the Raney Catalyst Co., Chattanooga, Tenn.

genated mixture was then filtered and the filtrate was evaporated under reduced pressure, to a sirup which crystallized. The resulting product of 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose was recrystallized from a mixture of ether and petroleum ether; yield 3.1 g., m.p. 88–89°, $[\alpha]^{22}D$ +41.0° (*c* 2.67, tetrachloroethene) (Freudenberg and associates[7] report m.p. 92–93°, $[\alpha]^{18}D$ +40.5°).

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3-salicylideneamino-α-D-glucofuranose.—A solution of 1.25 g. of 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and 0.6 g. of salicylaldehyde in 50 ml. of ether was heated briefly and concentrated to 5 ml. Addition of petroleum ether to incipient turbidity resulted in the crystallization of 3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-salicylideneamino-α-D-glucofuranose; yield 1.1 g. This was purified by three recrystallizations from a mixture of ether and petroleum ether; m.p. 94–95°, $[\alpha]^{23}D$ + 179° (*c* 2.04, N,N-dimethylformamide).

Anal. Calcd. for $C_{19}H_{25}NO_6$: C, 62.79; H, 6.93; N, 3.85. Found: C, 62.73; H, 7.07; N, 3.90.

3-Amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose Picrate.—3-Amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1.25 g.) was dissolved in 50 ml. of absolute ethanol containing 0.69 g. of picric acid. The solution was concentrated to a sirup which crystallized on trituration with a mixture of ether and petroleum ether. Recrystallization from the same solvents gave 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose picrate; yield 1.2 g., m.p. 170–171°, $[\alpha]^{21}D$ + 26.5° (*c* 2.56, N,N-dimethylformamide).

Anal. Calcd. for $C_{18}H_{24}N_4O_{12}$: C, 44.24; H, 4.45; N, 11.48. Found: C, 44.85; H, 4.75; N, 11.07.

Methyl 2-Deoxy-3,4-*O*-isopropylidene-2-salicylideneamino-β-L-pentopyranoside.—Methyl 3,4-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-β-L-arabinopyranoside[9] (20 g.) was treated with 100 g. of anhydrous hydrazine at 145° for 24 hr. as described above. After cooling, the partially crystalline reaction mixture was extracted with four 100-ml. portions of ether. The extract was evaporated to a sirup and treated with 100 ml. of water. This resulted in the crystallization of 7 g. of the starting material which was removed by filtration. The filtrate was concentrated to 50 ml. The concentrated solution, still containing some hydrazine, was treated with Raney nickel[24] catalyst for 2 hr. This resulted in the destruction of the excess hydrazine with evolution of ammonia and nitrogen.[25] The reaction mixture was then hydrogenated in the Parr apparatus as described before. The reduction product then was concentrated to 20 ml. and treated with 3 ml. of salicylaldehyde and sufficient amount of absolute ethanol to provide a clear solution. This solution was heated at 60° for 1 hr. and then evaporated to a sirup which crystallized. The product of methyl 2-deoxy-3,4-*O*-isopropylidene-2-salicylideneamino-β-L-pentopyranoside was recrystallized from aqueous ethanol; yield 3.78 g., m.p. 118–120°, $[\alpha]^{22}D$ + 112° (*c* 2.4, chloroform); X-ray powder diffraction data[26]: 9.43m, 7.51m, 7.03m, 5.79s(2,2), 5.37s-(2,2), 5.10m, 4.81vs(1), 4.42m, 4.22vw, 3.76s, 3.57vw, 3.30m, 3.02w, 2.91w.

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.52; H, 6.89; N, 4.56. Found: C, 62.40; H, 6.81; N, 4.63.

Methyl 2-Amino-2-deoxy-β-L-pentopyranoside Hydrochloride (V).—A suspension of 2 g. of the methyl 2-deoxy-3,4-*O*-isopropylidene-2-salicylideneamino-β-L-pentopyranoside in 50 ml. of 2 *N* hydrochloric acid was heated at 100° for 1 hr. The resulting solution was decolorized with activated carbon and concentrated to a sirup, which crystallized after 2 days. Recrystallization from a mixture of methanol and ether gave methyl 2-amino-2-deoxy-β-L-pentopyranoside hydrochloride; yield 1.0 g., m.p. 171–180° dec., $[\alpha]^{22}D$ + 92.7° (*c* 2.77, water); X-ray powder diffraction data[26]: 11.29vs, 7.61m, 6.74vw, 6.33w, 5.92m, 5.61s, 5.16m, 4.81w, 4.43w, 4.19vs-(1), 4.02vw, 3.77s(3), 3.49s, 3.18m, 3.01vs(2), 2.90vw, 2.77s, 2.62vw, 2.56vw, 2.50vw, 2.44w, 2.28m.

Anal. Calcd. for $C_6H_{14}ClNO_4$: C, 36.10; H, 7.07; Cl, 17.76; N, 7.02. Found: C, 35.81; H, 6.92; Cl, 17.93; N, 7.22.

(25) J. K. Dixon, THIS JOURNAL, **54**, 4262 (1932).

(26) Interplanar spacing, Å., CuK_α radiation. Relative intensity, estimated visually: s, strong; m, medium; w, weak; v, very. First three strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities.

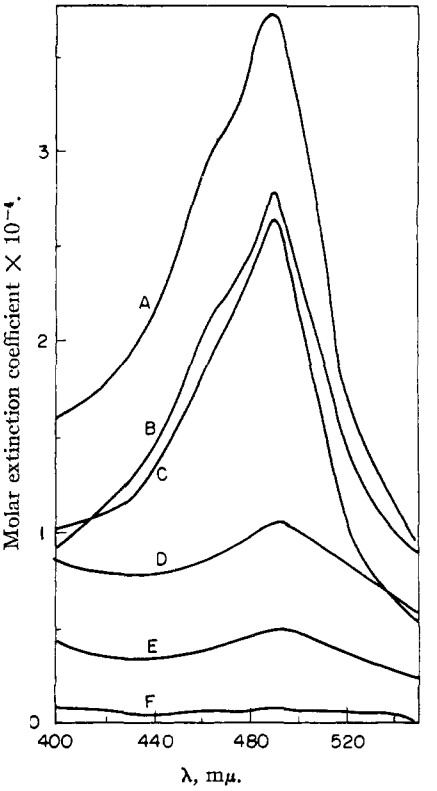

Fig. 2.—Intensity of the color developed in the Dische test by D-xylosamine hydrochloride, A; D-glucosamine hydrochloride, B; D-galactosamine hydrochloride, C; the L-pentosamine hydrochloride, D; 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucose, E; and D-glucose, F. See Experimental section for details.

A solution of this compound (0.2%) in *N* hydrochloric acid (200 ml.) was heated at 100° under reflux. Analysis[27] of the reducing sugar in several aliquots withdrawn at different intervals indicated that the hydrolysis proceeds very slowly; after 27 hr. only 60% of the compound had been hydrolyzed. Under identical conditions the hydrolysis of methyl β-L-arabinopyranoside was 95% complete within 30 min.

2-Amino-2-deoxy-α-L-pentose Hydrochloride (VI).—A mixture of 0.9 g. of the methyl 2-amino-2-deoxy-β-L-pentopyranoside hydrochloride, 1.75 g. of anhydrous sodium acetate and 20.5 ml. of acetic anhydride was heated with continued stirring until it boiled briefly and then it was kept at 80° for 1 hr. The reaction mixture was poured into 400 ml. of ice and water and extracted with chloroform. The extract was washed with an aqueous solution of sodium bicarbonate and then with water, and concentrated to a sirup which failed to crystallize. This was hydrolyzed with 50 ml. of 4 *N* hydrochloric acid at 100 °for 1 hr. The hydrolyzate, after decoloration with activated carbon, was evaporated to a sirup which crystallized immediately. Recrystallization from a mixture of methanol and acetone gave the 2-amino-2-deoxy-α-L-pentose hydrochloride; yield 0.33 g., m.p. 142–148° dec., $[\alpha]^{22}D$ −15.6° (initial, extrapolated, Fig. 1) → +6.7° (*c* 2.02, water final); X-ray powder diffraction data[26]: 7.60m, 6.36m, 7.63s, 4.83vw, 4.21vs(1), 3.94w, 3.78vs(2), 3.58vw, 3.47vw, 3.22vw, 3.02s(3), 2.92w, 2.76m, 2.62w, 2.57w, 2.43vw, 2.25vw, 2.16vw, 1.97vw.

Anal. Calcd. for $C_5H_{12}ClNO_4$: C, 32.36; H, 6.52; Cl, 19.10; N, 7.55. Found: C, 32.56; H, 6.75; Cl, 18.96; N, 7.27.

This compound was strongly reducing toward Benedict solution and furnished positive Elson-Morgan[13-14] and ninhydrin tests.

The Dische amino sugar color test was conducted with the following solutions according to the exact conditions de-

(27) M. Somogyi, *J. Biol. Chem.*, **160**, 61 (1945).

scribed by Dische[21]; 2.5×10^{-4} *M* 2-amino-2-deoxy-D-xylose hydrochloride (A, Fig. 2), 7.5×10^{-4} *M* 2-amino-2-deoxy-D-glucose hydrochloride (B), 7.5×10^{-4} *M* 2-amino-2-deoxy-D-galactose hydrochloride (C), 8.6×10^{-4} *M* 2-amino-2-deoxy-L-pentose hydrochloride (VI) (D), 6.5×10^{-4} *M* 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (E) and 8.9×10^{-4} *M* D-glucose (F). The light absorption properties of the resulting cherry-red solutions were measured in a Cary, model 10, recording spectrophotometer,[28] within the wave length range of 400–550 mμ. The data obtained are presented in Fig. 2.

2-Acetamido-2-deoxy-L-pentose.—A solution of 0.3 g. of the 2-amino-2-deoxy-L-pentose hydrochloride in 3 ml. of methanol was treated with 0.25 g. of silver acetate and 0.3 ml. of acetic anhydride and the mixture was left at 0° for 18 hr. and at 25° for 5 hr. It was then filtered and the filtrate was treated with 3 ml. of 0.1 *N* hydrochloric acid for 2 hr. and refiltered. The solution was concentrated to a sirup which was dissolved in abs. ethanol and deionized with Amberlite MB-1. The deionized solution and the washings were concentrated to 10 ml. and then ether was added to incipient turbidity. The resulting product of 2-acetamido-2-deoxy-L-pentose was recrystallized from a mixture of ethanol and ether; yield 15 mg., m.p. 115–123°.

Anal. Calcd. for $C_7H_{13}NO_4$: C, 43.98; H, 6.85; N, 7.32. Found: C, 44.12; H, 7.03; N, 7.78.

(28) Made by Applied Physics Corp., Pasadena, Calif.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

Uronic Acid Fragments from Slash Pine (*Pinus elliottii*) and their Behavior in Alkaline Solution[1,2]

BY ROY L. WHISTLER AND G. N. RICHARDS

RECEIVED APRIL 24, 1958

4-*O*-Methyl-D-glucuronic acid is identified as the major acidic component of the hemicellulose fraction of slash pine. Other uronic acids are not present in more than trace amounts. The predominant mode of linkage of the uronic acid is indicated by the isolation of the aldobiouronic acid, 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-α-D-xylose in high yield, but the presence of a complex mixture of other acidic oligosaccharides suggests that other types of linkage may also be present to a small extent. The resistance of glycosides derived from uronic acids toward acidic hydrolysis is discussed. The action of lime-water on 4-*O*-methyl-D-glucuronic acid follows a similar course to that previously observed with 4-*O*-methyl-D-glucose and yields a dibasic acid analogous to the monobasic D-gluco*iso*saccharinic acid. The aldobiouronic acid in lime-water yields no further acids.

As a preliminary step to the examination of the polysaccharide components of slash pine, examination was made of the acidic fragments produced by acidic hydrolysis of the whole hemicellulose-B fraction. This hemicellulose fraction is prepared by alkaline extraction[3] of holocellulose and is subject to partial hydrolysis with sulfuric acid. During acid treatment the separation of a water-insoluble polysaccharide results from rapid hydrolysis of solubilizing side-chains as observed previously[4] with birch wood hemicellulose. Isolation of the acidic fragments from the hydrolysis mixture is effected by a strongly basic polystyrene resin in the carbonate form.[5] There is thus reasonable certainty of complete uptake of all acids, including stable lactones which may form, and of their complete recovery on elution. This separation procedure also tends to avoid alkaline degradation or rearrangement of neutral sugars.

Analysis of the acidic products on a cellulose column yields fractions shown in Table I. Each fraction gives only a single spot on paper chromatography, but results of further hydrolysis and subsequent examination of the minor fractions (3, 4 and 5) indicate that they are probably mixtures. On further hydrolysis each fraction yields chromatographic evidence that 4-*O*-methyl-D-glucuronic acid is the major acidic component and there is tentative evidence of traces of galacturonic acid. The major fractions (1 and 2) are 4-*O*-methyl-D-glucuronic acid (I) and 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose (II), respectively. 4-*O*-Methyl-D-glucuronic acid is obtained as its brucine salt and this appears to be the first simple crystalline derivative of the acid to be reported.

4-*O*-Methyl-D-glucuronic acid also is found as the predominant acidic component of other soft woods[6] such as poplars[7,8] and Scots pine.[9] Some of these woods also yield the same 1→2-linked aldobiouronic acid as observed in slash pine.

TABLE I

ACIDS FROM HYDROLYSIS OF HEMICELLULOSE-B

Fraction	Yield from hemicellulose, %	$[\alpha]^{25}D$ in water	R_x (solvent A)
1	0.9	+47°	1.48
2	3.9	+94	0.75
3	0.2	+61	.47
4	.5	+55	.31
5	.2	+45	.24

The aldotriouronic acid previously isolated[10] from slash pine must almost certainly have contained the same aldobiouronic acid unit (II), although in the present work the aldotriouronic acid was not produced in more than trace amount.

The ease of isolation of aldobiouronic acids and their resistance to further hydrolysis have often

(1) Presented before the Division of Cellulose Chemistry at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

(2) Journal Paper No. 1272 of the Purdue University Agricultural Experiment Station, Lafayette, Ind.

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(10) E. Anderson, J. Kesselman and E. C. Bennett, *J. Biol. Chem.*, **140**, 563 (1941).