3 drops of 1% starch solution were added, and the mixture titrated with standardized 0.01 *N* iodine solution.

In the following results, periodate uptake is expressed in terms of molar equivalents. Although most of the experiments were repeated at least once, only a representative set of values is reported.

Comparison of the Periodate Oxidation Products from 3'-Amino-3'-deoxycytidine, 3'-Amino-3'-deoxyadenosine and 9-(3-Amino-3-deoxy-β-D-ribofuranosyl)-6-dimethylaminopurine (VI) with those from the Corresponding Non-amino Nucleosides.—The periodate oxidation products of the aminonucleosides and the corresponding non-amino nucleosides were compared by means of circular paper chromatography in the apparatus described[27] by Kawerau. At specific reaction times, 40–50 γ of the periodate reaction mixture were spotted on Whatman #1 circular chromatography paper (KCT-26, specially slotted for use in the Kawerau apparatus), and the paper was developed with the solvent system indicated. The butanol–water system was 1-butanol saturated with water. Spots were located by inspection under ultraviolet light. The R_f values of the limits of the spots were

Compound	Solvent	*Rf*	*Rf*(mean)
3'-Amino-3'-deoxy-adenosine	BuOH–H_2O	0.57–0.63	0.60
Adenosine	BuOH–H_2O	.55– .82	.69
VI	BuOH–H_2O	.75– .82	.79
6-Dimethylamino-9-β-D-ribofuranosyl purine	BuOH–H_2O	.77– .95	.86
3'-Amino-3'-deoxy-cytidine	Isopropyl alc.–1 *N* NH_4OH (7:2)	.52– .57	.55
Cytidine		.26– .46	.37

(27) E. Kawerau, "Chromatographic Methods," Vol. 1, H. Reeve Angel and Co., New York 7, N. Y., 1956, part 2, p. 7.

Isolation of Ammonium Iodate from Periodate Reaction with 9-(3-Amino-3-deoxy-β-D-ribofuranosyl)-6-dimethylaminopurine (VI).—To a mixture of 588 mg. of the aminonucleoside VI and 7.5 cc. of water was added 908 mg. of periodic acid (4 mmole). All the components dissolved and a white solid precipitated on standing at room temperature for 36 hours. This solid was collected and dried; 118 mg. (30%).

Anal. Calcd. for NH_4IO_3: N, 7.41; H, 2.29; I, 65.8. Found: N, 7.26; H, 2.09; I, 65.9.

To the filtrate was added 20 cc. of a saturated, aqueous picric acid solution, and the solid which precipitated was collected and washed with the minimum of cold water to afford 157 mg. (20%), m.p. 248° (some dec.). Admixture of 6-dimethylaminopurine picrate[28] did not change the m.p.

Anal. Calcd. for $C_{13}H_{12}N_8O_7$: C, 39.9; H, 3.09; N, 28.6. Found: C, 39.8; H, 3.56; N, 27.9.

6-Dimethylamino-9-β-D-ribofuranosylpurine.—A solution of 865 mg. (1.44 mmoles) of 6-chloro-9-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-purine (taken from a batch, a portion of which had been converted to adenosine in 61% yield)[21] in 25 cc. of absolute methanol containing 1.14 g. (25 mmole) of dimethylamine was heated in a stainless steel bomb at 100–110° for 5 hours. After cooling, the bomb was opened and the contents were evaporated under reduced pressure. The residual gum was redissolved in 20 cc. of methanol and 1 cc. of a 1 *N* methanolic sodium methoxide solution was added. The mixture was heated under reflux for 35 minutes and then was evaporated *in vacuo*. The residue was crystallized and recrystallized from acetone to afford 325 mg. (76%) with m.p. 183–184° undepressed by admixture of material prepared by the earlier method[12]; $[\alpha]^{27}D$ −57.8° (*c* 2.73 in water) (lit.[12] $[\alpha]^{25}D$ −62.6° in water).

Anal. Calcd. for $C_{12}H_{17}N_5O_4$: C, 48.80; H, 5.80; N, 23.72. Found: C, 48.80; H, 5.97; N, 23.79.

(28) B. R. Baker, J. P. Joseph and R. E. Schaub, *J. Org. Chem.*, **19**, 631 (1954).

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Addition Polymerization of Anhydrosugar Derivatives. I. A Polyanhydroglucose[1]

BY JOSÉ DA SILVA CARVALHO, WILLEM PRINS AND CONRAD SCHUERCH

RECEIVED JANUARY 29, 1959

Conditions for the polymerization of levoglucosan to high molecular weight branched polysaccharides are described. Periodate oxidations of the products can be interpreted by assuming a repeating sequence of twenty anhydroglucose units of which eleven are unsubstituted on C_2, C_3, and C_4, seven are unsubstituted on C_2 and C_3 or C_3 and C_4, and two are resistant to periodate oxidation. Molecular weights have been determined on fractionated and unfractionated samples by light scattering and are commonly from 20–50,000 and as much as 300,000 in the extreme. The monomer functionality and mechanism of polymerization are discussed and the products compared with other synthetic polysaccharides.

In 1918 Pictet[2] described the polymerization of levoglucosan, 1,6-anhydro-β-D-glucopyranose, a compound made by the simple pyrolysis *in vacuo* of cellulose or starch. Pictet heated levoglucosan to elevated temperatures in the presence of zinc chloride or platinum black and produced dimeric to octameric products which he described as dextrins. A small fraction of one of his products was also non-dialyzable.[2f] In the interim dextrans formed by bacterial action have been produced commercially as blood extenders and a condensation polymerization based on the dehydration of glucose to high molecular weight polymers in the presence of acids has been investigated in detail for its possible application for the same purpose,[3] yet this unique observation of addition polymerization in the carbohydrate series seems to have been ignored for thirty years.[4,5] In this Laboratory we have recently confirmed and improved Pictet's results and are now in the process of extending the reaction to other conditions and to related compounds.

The failure of previous workers to continue Pictet's work may have been due to the incompleteness of polymerization theory and the compara-

(1) Abstracted from a thesis submitted by J. daS. Carvalho in partial fulfillment of the requirements of the Master of Science degree.

(2) (a) A. Pictet and J. Sarasin, *Helv. Chim. Acta*, **1**, 87 (1918); (b) A. Pictet, *ibid.*, **1**, 226 (1918); (c) A. Pictet and J. Pictet, *ibid.*, **4**, 788 (1921); (d) *Compt. rend.*, **173**, 158 (1921); (e) A. Pictet and J. H. Ross, *ibid.*, **174**, 1113 (1922); (f) *Helv. Chim. Acta*, **5**, 876 (1922); (g) Hoffman-LaRoche and Co. A. G., German Patent 513,126 (Feb. 29, 1928).

(3) (a) P. T. Mora and E. Pacsu, THIS JOURNAL, **72**, 1045 (1950); (b) P. T. Mora and J. W. Wood, *ibid.*, **80**, 685 (1958); (c) P. T. Mora, J. W. Wood, P. Maury and B. G. Young, *ibid.*, **80**, 693 (1958).

(4) H. Pringsheim and K. Schmalz, *Ber.*, **55**, 3001 (1922).

(5) J. C. Irvine and J. W. H. Oldham, *J. Chem. Soc.*, 2903 (1925).

tively meager knowledge of anydrosugars at the time of his work and the relatively low molecular weights claimed by Pictet and those[4,5] who confirmed his work. Today if one considers known addition reactions of anhydrosugar derivatives of both the acetal and internal ether types and the possible variations of structure and molecular weight distributions theoretically possible in polymers produced from differently substituted monomers, one is led to conclude that this reaction may be a route to an exciting extension of polysaccharide chemistry. Since at the moment these prospects are speculative, the following discussion is restricted to the polymerization of levoglucosan.

Although the polymerization of levoglucosan is reminiscent of ethylene oxide polymerization, it is more profitably compared to the acid-catalyzed addition of a chemical agent such as ROH to a glucosan (Fig. 1). The product resulting from such a reaction consists exclusively of that expected by addition of RO to the C_1-position and hydrogen to the oxide oxygen. Therefore, inversion can only occur on the aldehydic carbon and the sugar derivative is that of the parent sugar. Pictet reports the hydrolysis of his dextrins to glucose as might be expected.[2b]

Since there are three hydroxyl groups and one acetal function per monomer unit, levoglucosan addition polymerization should produce branched polymers, for the reaction is analogous to the condensation polymerization of a monomer RAB_3, as described by Flory.[6] It differs from Flory's case, however, in that the reactivities of the B functions are not identical and do not remain the same during reaction and, more unusual, the number of B functions per mer is independent of the extent of polymerization. The latter follows from the fact that whenever an acetal ring is cleaved by an hydroxyl function as during combination of two monomers, a primary hydroxyl is liberated.

Some differences are apparent between this reaction and the interesting condensation polymerization of glucose by Mora and Pacsu.[3a] Experimentally the addition reaction is substantially simpler since the evolution of water is not required for the reaction to proceed and the monomer need only be sealed in an evacuated tube with catalyst and heated to cause polymerization. Curiously Pictet determined number average molecular weights corresponding only to octamers or less, while Mora[3b,3c] obtained from the less favorable case molecular weights up to 32,800. Either Pictet's molecular weights were in error, as was commonly the case in the period in which he worked, or else his conditions of polymerization could be vastly improved.

The experimental attack on this problem consists of first an attempt to find mild conditions under which polymerization occurs without decomposition, second a partial evaluation of structure of the products by periodate oxidation and optical rotation, and finally a demonstration that dextrans of truly high molecular weights can be synthesized by this method. Since weight average molecular weights have been determined by light scattering,

(6) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 365.

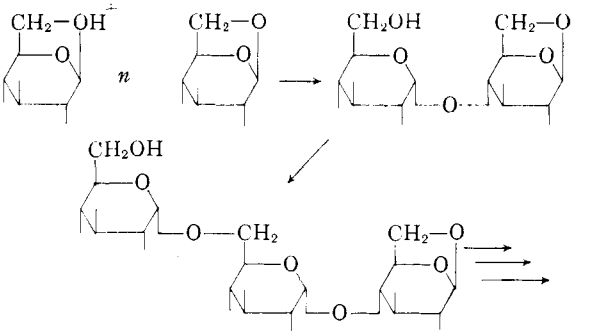

Fig. 1.—Polymerization of levoglucosan.

the values cannot be compared directly with the results of Pictet or Mora.

Experimental

Polymerization of Levoglucosan.—Levoglucosan was prepared by pyrolysis of starch and purified by recrystallization from methanol and decolorization with carbon until a constant m.p. of 178–179° was obtained. This product was placed with catalyst (usually chloroacetic acid) and occasionally solvent in a common Pyrex test-tube fused to a narrower tube. A constriction was made, the tube evacuated and sealed off. When solvent was used the substance was frozen and thawed under vacuum a few times to eliminate air, before sealing off the tube. The tubes were heated in an oil-bath for polymerization, sometimes with occasional swirling at the beginning of the reaction to make the mixture homogeneous, or with rotation. The details are described in Table I.

TABLE I

CONDITIONS OF PREPARATION AND RESULTS FOR SELECTED POLYMERS

Polymer	Catalyst CH_2Cl-CO_2H, mmole/mole levoglucosan	Time Hr.	Time Min.	Temp., °C.	Yield by precipitation in EtOH (85%), %	$\bar{M}w$
27	10.2		55	123.5	46[a]	4,235
29	10.2	3		123.8	28	8,000
28	21.4	3		123.8	44	9,950
36[a]	21.4	6		124	57.5	43,300
37	21.4	1		115	52	24,300
		2		125–121		
		3		121		
			40	121–125		
40[a]	21.4		40	110	67	49,200
			30	110–115–120		
		5	10	123.8		
20A	21.4	20		116.5	66	309,000
32[a]	10.7	12		123.8	71	29,400
34	21.4	3		121–127	..	.....

[a] Polymer 27 did not give any appreciable precipitate with alcohol. Its yield in table was obtained by precipitation in acetone (85% acetone, 15% water). Polymer 36 and 40 were, respectively, stirred and rotated in the early stages of polymerization. Polymer 32 was prepared in 30% solution in tetramethylenesulfone; all others were prepared without solvent.

Isolation and Fractionation of Polyanhydroglucose.—The entire product (1 or 2 g.) of each polymerization was dissolved in a small amount of water with sodium carbonate in slight excess over the amount of catalyst in the sample. After complete solution and filtration through a sintered glass filter, the product in 15 ml. of solution was transferred to a centrifuge cup and 85 ml. of alcohol added. A white or light colored precipitate formed after a few ml. of alcohol was added and separated as an oily layer after addition of the remaining alcohol and centrifugation for two hours at

1500 r.p.m. The precipitate was separated, redissolved in at most 40 ml. of distilled water, freeze-dried and finally dried to constant weight *in vacuo*. These products, insoluble in 85% alcohol, were used in the subsequent investigations.

All of the 85% alcohol-insoluble portion of the 2-g. polymerization numbered 40 (Table I), except for a small sample, was dissolved in 10.6 ml. of water. Fifteen ml. of absolute ethanol was added dropwise to incipient turbidity; the solution then was agitated and 5 ml. more of ethanol was added. The fraction I was separated by centrifugation and isolated by freeze-drying from 20 ml. of water. Successive fractions II, III and IV were obtained in the same way by adding additional amounts: 10, 22 and 45 ml. of alcohol to the mother liquors. By adding to one-half of the resulting 108 ml. of solution, an equal volume of acetone, a fifth fraction (V) was collected as before. The yields of these fractions and their molecular weights are listed in Table II.

TABLE II

FRACTIONATION OF POLYMER 40

Polymer fraction	Alcohol concn. by volume	Yield, % of starting material	$\bar{M}w$
Total	85	67.0	49,200
I	65	14.2	86,500
II	74	23.0	38,300
III	83	12.9	25,000
IV	90	7.0	22,750
V	45 (alcohol) 50 (acetone)	7.2	38,650

Periodate Oxidations.—A quantity (50–125 mg.) of carbohydrate equivalent to about 0.0020 mole of periodate was dissolved in about 15 ml. of water and added together with washings from the weighing bottle to a 100-ml. low actinic glass volumetric flask. Twenty-five ml. of 0.1 *M* sodium periodate was added with shaking and the volume made up to 100 ml. The oxidations were carried out in the dark at room temperature. A blank was prepared similarly with the same concentration of periodate and no carbohydrate and titrated several times during the course of each oxidation. Parallel experiments on levoglucosan gave values for periodate consumption and formic acid liberation essentially the theoretical in 18 hours or less. Oxidations of Polymer 40 were carried out for 100 hours and were essentially constant after 50 hours.

For measurement of periodate consumption, 2-ml. aliquots were pipetted into excess acidic potassium iodide (50 ml. of water, 3 ml. of 20% potassium iodide and 3 ml. of 0.5 *N* H_2SO_4) and titrated to a "thyodene" (Fisher Scientific Co.) end-point with thiosulfate. Total acidity was determined using 5- or 10-ml. samples of periodate solution treated with excess ethylene glycol for 10 minutes and to which 3 ml. of 20% KI then was added. Results are reported in Table III.

TABLE III

PERIODATE OXIDATION OF POLYMER 40

	Mole IO_4 reduced per mer	Mole HCOOH formed per mer
Polymer 40 unfractionated	1.41–1.44	0.47–0.54
Fraction I	1.36–1.43	.47– .54
Fraction II	1.36–1.38	.48– .53
Fraction III	1.36–1.41	.50– .56

Optical Rotations.—The dextrans numbered 20A, 34, 36 and 37 were dissolved in water at concentrations of 2.5 to 5.0 g./100 ml. Optical rotations were measured in one-fourth decimeter tubes at 22°. The solution of 20A was too dark for use, the other three were colorless or light straw colored. Specific rotations were 91 ± 5°.

Light Scattering.—The molecular weights of the various products were determined by means of the light scattering technique[7] with a Brice–Phoenix instrument (model 1000-series, Phoenix Precision Instrument Co., Philadelphia, Pa.). The calibration, as given by the factory, was checked by measuring an 0.128 g./ml. aqueous sucrose solution, whose excess scattering over that of the water has been found by Maron and Lou[8] to be $R_{90} = 1.27 \times 10^{-5}$ cm.$^{-1}$.

To eliminate dust, which causes a great deal of trouble in light scattering measurements, the solutions repeatedly were filtered through an ultrafine Pyrex filter. Extreme care in cleaning the glassware and handling of the solutions is imperative. The pipets, flasks and cells, were cleaned in apparatus fashioned after Thurmond.[9]

Even so, we never obtained completely dust-free solutions. Since, however, all the samples but one showed molecular weights too small to cause real, intrinsic dissymmetry, all the observed dissymmetry could be attributed to dust. In order to be able to subtract this "dusty solvent" scattering from the solution scattering a "dust correction" procedure was followed. Water of various dust contents was measured at 45°, 90° and 135°. By plotting $i_{45}-i_{135}/i_0$ *versus* i_{90}/i_0 an approximate straight line relationship was found. Thus it was possible to subtract the most probable solvent scattering of measurements on the solutions. One simply measured $i_{45}-i_{135}/i_0$ of the solution, and looked up the corresponding 90° scattering of the dusty water on the graph. The method is not, however, entirely satisfactory. Some solutions which exhibited large dissymmetries ($z \cong 2$) were not used in the extrapolation for the molecular weight.

The refractive index increments, $\Delta n/\Delta c$, were measured in a differential refractometer (Phoenix Precision Instrument Co., model 1 100-T, after a design by P. P. Debye). The instrument had been factory calibrated with KCl solutions. For all products $\Delta n/\Delta c$ was found to be 0.1445 ml./g. which corresponds closely with the value 0.145 for sucrose as found by Maron and Lou.[8]

The molecular weights range from 4235 to 309,000, the latter being the only one where intrinsic dissymmetry existed. From the average experimental z-value of 1.24 the correction term $1/P_{90}$, needed for the calculation of $\bar{M}_w$ (see ref. 9), was found to be 1.16, selecting a solid sphere as the molecular model.[10] Any other model would give a larger interference factor and therefore a larger $\bar{M}_w$. Thus the value 309,000 is a conservative estimate. It should be mentioned also that this polymer was the only one which exhibited a strong absorption at the wave length 436 mμ used for the light scattering measurements. However, by diluting the solution the transmittance in a 10-mm. Beckman cell became sufficiently high (42%) to neglect the absorption correction which one should in principle apply when measuring the light scattered by colored solutes.[11]

Results and Discussion

Polymerizations were carried out by sealing levoglucosan and an acidic catalyst in an evacuated glass tube, and heating at temperatures ranging from 100 to 130°. The molar ratios were from 0.001 to 0.05 mole of catalyst per mole of monomer. Preliminary experiments were carried out with formic, acetic, hydrochloric, oxalic, phosphorous and chloroacetic acids and zinc chloride in the presence and absence of dimethyl sulfoxide and tetramethylene sulfone as solvents. Most satisfactory polymerizations occurred at 115–120° in the absence of solvent and with chloroacetic acid as catalyst as described. Under these conditions amber-colored brittle resins were formed which were completely water-soluble and free of gel. The products were isolated by solution in water, precipitation by 85% alcohol or acetone and freeze-drying from water. In one case the polymer was fractionated by solvent precipitation. Higher molecular weight dextran fractions were slightly darker in color than the more soluble material even from the same preparation. Typical preparations are de-

(7) See, for example, K. A. Stacey, "Light Scattering in Physical Chemistry," Butterworth, London, p. 19.

(8) S. G. Maron and R. L. Lou, *J. Phys. Chem.*, **59**, 231 (1955).

(9) C. D. Thurmond, *J. Polymer Sci.*, **8**, 607 (1952).

(10) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).

(11) B. A. Brice, G. C. Nutting and M. Halwer, THIS JOURNAL, **75**, 824 (1953).

scribed in Table I. Since clear straw-colored solutions were obtained on dissolving nearly all these products without prior decolorization, these conditions apparently are superior to those used previously.[3-5]

It is clear from the results reported in Tables I and II that the products are macromolecules and that lower molecular weight materials remain in solution when the product is precipitated in 85% ethanol. The fractionation of polymer 40 was successful in separating a series of products of decreasing molecular weight so long as a single precipitant was used. However, the addition of acetone succeeded in removing from solution a fraction of higher molecular weight than those precipitated by alcohol alone. Structural differences other than molecular size, therefore, as usual affect precipitability in this series. It is also of interest that the weighted average of the molecular weights of the fractions closely approximates the molecular weight of the total sample.

From the structure of the monomer, one would expect multiple branching, relatively spherical molecules and a broad molecular weight distribution. The viscosity of solutions of these polymers is very low as would be expected of highly branched spherical polymer molecules, but if one assumes that the fractions of polymer 40 listed in Table II are relatively narrow, the ratio of weight average to number average molecular weight is lower than expected (1.2). However, the assumption is not valid and, furthermore, the low molecular weight third of the product has been eliminated previously and is not accounted for in the calculation.

Some insight into the branched character of the polymer, and the relative reactivities of the hydroxyl groups is obtained from sodium metaperiodate oxidations of the alcohol-insoluble portion of polymer sample 40 and three main fractions obtained from it. The periodate consumption was about 1.44 moles and the formic acid liberated about 0.55 mole per anhydroglucose unit. Only minor differences were apparent between fractions (Table III). A close approximation to these values can be made by assuming a repeating sequence of twenty mers which include eleven glucose residues containing all three secondary hydroxyls (on C_2, C_3 and C_4) unsubstituted and seven glucose residues with an unsubstituted glycol (C_2, C_3 or C_3, C_4). The remaining two units must be disubstituted on secondary positions or substituted on the three position. Apparently the C_3-hydroxyl must be less reactive than the average of secondary hydroxyls. Furthermore on manipulation of the various structural combinations, it appears that the results of periodate oxidation are not consistent with any structure, however branched, unless there are between nine and twelve unsubstituted primary hydroxyls per twenty glucose units. Tosylation data on these polymers would therefore probably not be too enlightening. Since structures varying between one completely linear and others with eleven end units per twenty are consistent with the results of periodate oxidation, methylation studies like those reported on similar products should be more revealing[3a,5] of the degree and kind of branching.

Dextrans prepared by Irvine and Oldham[5] from levoglucosan, for example, gave on methylation and methanolysis methyl-2,3,4,6-tetramethylglucoside, methyl 2,3,4-trimethylglucoside, and di- and monomethylated glucosides. Methylated dextrans prepared similarly by Pringsheim[4] gave on hydrolysis 2,3,4,6-tetramethylglucose and a sirupy dimethylglucose mixture which did not give an osazone. Apparently reaction with the C_6- and probably C_4-hydroxyl groups is favored.[12] (*cf.* ref. 3a).

Since substitution on the hydroxyl groups of methyl glycosides does not greatly change the molecular rotation from that of the parent compound, one would expect that the optical rotation of these polymers would be affected primarily by three structural features: the proportion of unopened levoglucosan in the polymer, the basic skeleton of the monomer, and the proportion of α- and β-glycosidic links between mers. Since any unopened levoglucosan present must correspond to the reducing end group of other polysaccharides and can only be present to the extent of one mer per chain, its effect will be trivial on the rotation of the high molecular weight fractions investigated. The basic skeleton of the monomer is probably entirely glucopyranose. Therefore it is to be expected that the optical rotations of these polymers should be primarily a reflection of the proportion of α- and β-glycosidic linkages between mers.

One might expect in the initial reaction a back side approach to the C_1-carbon atom and a α-glycosidic linkage appearing in the product. In the case of a condensation polymer of glucose in contrast an equilibrium mixture of α- and β-glycosidic linkages would be expected.[3b,c] Actually a variety of rotations have been reported for products of both reactions. At elevated temperatures glucose produces condensation polymers with specific rotations of 60–85° while levoglucosan polymers have rotations up to 111.9,[2e] and are usually (see ref. 4 and our Experimental part) near or above 90°. Thus some minor preference for an α-configuration is exhibited in levoglucosan polymerization. It is, however, not significantly greater than that in condensation polymerization at low temperatures,[3a] and is substantially less than that reported for polyglucoses produced by the action of nearly anhydrous hydrogen fluoride[13] at *ca.* 30° ($[\alpha]^{18}D$ 143.5°).

There seem to be three possible explanations for the lack of a great predominance of a single configuration in the levoglucosan polymers: The attack at C_1 with inversion is not greatly preferred over attack without inversion, transacetalization occurs following polymerization, or the C_2-hydroxyl is involved in the attack on the C_1 during cleavage of the 1,6-oxide bridge. The first explanation is improbable and the second seems less probable sterically than the third. Many reactions are known in which interconversions of 1,6-anhydro and 1,2-an-

(12) The preferential formation and acid hydrolysis of acetals and ketals and the methylation studies of Pringsheim[4] and Pacsu and Mora[3a] on synthetic glucosans suggests that attack by positively charged agents is more probable at alcoholic positions distant from the electron-withdrawing carbonyl function.

(13) B. Helferich and S. Bottger, *Ann.*, **476**, 150 (1929).

hydro structures occur[14-17] and we suggest that the polymerization of 1,6-anhydroglucose probably proceeds in part *via* some intermediate related structurally to 1,2-anhydroglucopyranose. One cannot but be impressed by the variety of compounds produced by these similar reactions under various experimental conditions, but the system is so complex that there seems little value in speculating on the effect of experimental factors on the course of the reaction.

It is perhaps surprising that levoglucosan polymerizes at all since it contains a fused five- and six-membered ring. A bicyclic lactone of a similar 3:2:1 system does not polymerize and the driving force for the polymerization of the corresponding lactam is apparently supplied by the conversion of a non-planar amide linkage in the monomer into a planar one in the polymer in which more nitrogen–carbonyl interaction was possible.[18] Levoglucosan, however, is not in the preferred conformation for glycosidic structures.[19] By opening the 1,6-oxide ring, the more favorable ring conformation is permitted and this transformation to a lower energy state probably assists the polymerization.

Acknowledgment.—The authors wish to acknowledge with gratitude the active interest and assistance of the Director of Portuguese Forest Service, Eng. J. Mendes Frazão to J. daS. C. and the valuable financial support of the Calouste Gulbenkian Foundation. Some exploratory experiments related to this research were carried out by Mr. Edwin J. Quinn and supported by the United States Army, Office of Ordnance Research.

(14) C. M. McCloskey and G. H. Coleman, *J. Org. Chem.*, **10**, 184 (1945).
(15) M. P. Bardolph and G. H. Coleman, *ibid.*, **15**, 169 (1950).
(16) A. Dyberman and B. Lindberg, *Acta Chem. Scand.*, **4**, 878 (1958).
(17) R. U. Lemieux and C. Brice, *Can. J. Chem.*, **30**, 295 (1952).
(18) H. K. Hall, Jr., THIS JOURNAL, **80**, 6412 (1958).
(19) R. E. Reeves, *ibid.*, **71**, 2116 (1949).

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Alkaline Degradation of Periodate-oxidized Xylan and Dextran[1]

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RECEIVED JANUARY 12, 1959

Xylan from corn cobs is oxidized with sodium metaperiodate and then treated with dilute sodium hydroxide solution at room temperature. The major products are acidic, with glycolic and lactic acids predominating. Similarly, oxidized dextran from *Leuconostoc mesenteroides*, when treated with alkali in the same way, also yielded glycolic and lactic acids predominantly. It is concluded that both oxidized polysaccharides undergo alkaline degradation mainly by β-alkoxycarbonyl elimination, but that alternative modes of degradation also occur, which yield glycolic but not lactic acid.

Recent work on the alkaline degradation of model compounds[2] and on periodate oxidized cellulose[3] and starch[4] has shown that both of the oxidized 1→4-linked glucans degrade in alkali predominantly by β-alkoxycarbonyl elimination at the C5 position of the original D-glucose unit. Since other periodate-oxidized polysaccharides also contain the β-alkoxycarbonyl grouping, this type of degradation should be general.

Xylan from corn cobs,[5] which is essentially linear and 1→4-linked, is partially oxidized with sodium metaperiodate and the product treated with oxygen-free dilute sodium hydroxide at room temperature. Acidic and neutral products are separated by ion exchange resins and the former are further resolved by paper chromatography. Glycolic and lactic acids are identified as the acidic products, together with formic acid and a resinous acidic product similar to that obtained from periodate oxystarch.[4] The results of semi-quantitative analyses are expressed in Table I.

It is concluded that the predominant course of alkaline degradation of periodate oxyxylan is analogous to that proposed for the corresponding oxystarch[4] and may be expressed as shown (I → IV + V). In accordance with arguments already expressed[2,4] it is assumed that the intermediate III will react readily as shown, while the intermediate II will rearrange to lactic acid so long as the group R represents another oxidized unit. The excess of glycolic over lactic acid and the low yields of both suggest that competing reactions also occur and probably result from alternative modes of degradation of the original oxyxylan, analogous to those discussed earlier.[4]

TABLE I

PRODUCTS ISOLATED FROM DEGRADATION WITH 1 *N* SODIUM HYDROXIDE SOLUTION

Except for the first line, yields are expressed in equivalents per mole of oxidized D-glucose unit.

	Oxyxylan	Oxydextran
Neutral products	18%	18%
Total acids	1.15	0.91
Volatile acids	0.13	.08
Formic acid	.08	.06
Glycolic acid	.62	.51
Lactic acid	.32	.25

A dextran, which is mainly a linear, 1→6-linked glucan, is also oxidized with periodate and the product treated with dilute sodium hydroxide at room temperature. The acidic products again consist mainly of glycolic and lactic acids together

(1) Journal Paper No. 1362 of the Purdue University Agricultural Experiment Station, Lafayette, Ind.
(2) D. O'Meara and G. N. Richards, *J. Chem. Soc.*, 1204 (1958); *Chemistry & Industry*, 41 (1958).
(3) D. O'Meara and G. N. Richards, in press.
(4) R. L. Whistler, P. K. Chang and G. N. Richards, THIS JOURNAL, **81**, 3133(1959).
(5) R. L. Whistler, J. Bachrach and D. R. Bowman, *Arch. Biochem.*, **19**, 25 (1948).