tachment of an ether linkage to a double bond is known to cause a high frequency shift toward 1250 cm.$^{-1}$ of one of the stretching vibrations associated with this linkage.[9]

The band contour of the aromatic C-3 conjugated glucosiduronate G is clearly distinguished by a relative increase in intensity and a comparative lack of resolution between 1100 and 1065 cm.$^{-1}$. The superposition of this band contour with that of the C-17 conjugated Compound H is evident from a better resolution near 1090 cm.$^{-1}$.

The strikingly similar band contour of the enol-glucosiduronates I, J and K shows also a relative intensity increase near 1075 cm.$^{-1}$. The band complex is distinguished by the resolution of an absorption peak at 1070 cm.$^{-1}$ and by narrowing of the major absorption band at 1038 cm.$^{-1}$ both of which appear to be due to a loss of band components near 1025 and 1050 cm.$^{-1}$.

BOSTON 18, MASS.

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

Constitutional Studies on the Glucomannan of Konjak Flour[1]

BY F. SMITH AND H. C. SRIVASTAVA

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Methylation of the glucomannan isolated from the bulbs of *Amorphophallus konjac* yields the corresponding methylated derivative which gives upon hydrolysis a mixture of the 2,3,4,6-tetramethyl ethers of D-glucose and D-mannose (1 mole), the 2,3,6-trimethyl ethers of D-glucose and D-mannose (11 moles) and the 2,6-dimethyl ethers of D-glucose and D-mannose (1 mole). These data are in accord with the results of periodate oxidation of the polysaccharide. The structural significance of the results is discussed.

Amorphophallus konjac C. Koch (*Syn. Conophallus konjak* Schott), a member of the family *Araceae* is the source of the so-called "konjak flour" a popular article of food in Japan. The bulbs of three year old plants are cut into thin slices which are then dried and powdered to give konjak flour.

Preliminary studies[2-6] on the konjak flour showed that the polysaccharide was composed of glucose and mannose residues but results differed with regard to the relative proportions of the two component sugars.

Degradation of the konjak polysaccharide by a sporulating bacterium isolated from konjak flour was reported[3] to produce a trisaccharide, "laevidulin" ($[\alpha]_D$ −11.5°), and a similar trisaccharide, "laevidulinose" ($[\alpha]_D$ −15°), composed of D-mannose (2 parts) and D-glucose (1 part), was obtained[6] by the action of Takadiastase on konjak flour. However, the structure of these oligosaccharides was not established. Acetolysis[7] of the konjak glucomannan followed by saponification afforded a trisaccharide ($[\alpha]_D$ −16° in water) which was shown to be composed of mannose (2 moles) and glucose (1 mole). The structure of this oligosaccharide, which appeared to be identical with laevidulin or laevidulinose, was not established. Hydrolysis of methylated konjak mannan was also reported[7] to give a mixture of 2,3,4-tri-*O*-methyl-D-glucose, 2,3,4,-tri-*O*-methyl-D-mannose and 2,3,6-tri-*O*-methyl-D-mannose and based on these results a formula for the polysaccharide was advanced. Since the proof of the structure of the components of the hydrolyzate of the methylated glucomannan did not appear to be entirely satisfactory, it seemed desirable to re-examine the constitution of konjak glucomannan using the more modern techniques that were not available to the earlier workers. This paper is concerned with the results of methylation and periodate oxidation studies on a glucomannan isolated from a commercial sample of konjak flour.

The glucomannan was isolated from konjak flour by precipitation from aqueous solution as the copper complex following the procedure adopted for the Iles glucomannan.[8] The polysaccharide was regenerated from the copper complex by adding dilute hydrochloric acid, the last traces of copper being removed by means of Versene (ethylenediaminetetraacetic acid). Konjak glucomannan was obtained as a white powder which showed $[\alpha]_D$ −38° in water and which upon hydrolysis gave rise to a mixture of D-glucose and D-mannose in a molar ratio of 2:3.

Methylation of the glucomannan first with methyl sulfate and alkali, and then with silver oxide and methyl iodide yielded the fully methylated polysaccharide which showed $[\alpha]_D$ −19° in chloroform. Fractional precipitation of the methylated polymer from a solution in acetone with ether and petroleum ether indicated that the substance was essentially homogeneous. Upon methanolysis followed by hydrolysis, the methylated glucomannan gave a mixture of methylated sugars which were shown by column chromatographic analysis[9] to consist of 2,3,4,6-tetra-*O*-methyl-D-glucose, 2,3,4,6-

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tetra-O-methyl-D-mannose, 2,3,6-tri-O-methyl-D-glucose, 2,3,6-tri-O-methyl-D-mannose, 2,6-di-O-methyl-D-glucose and (?) 2,6-di-O-methyl-D-mannose. The molar ratio of the tetra-, tri-, and di-O-methyl sugars was 1:11:1 indicating an average repeating unit of about 13. The major proportion of the hydrolyzate consisted of a mixture of 2,3,6-tri-O-methyl-D-glucose and 2,3,6-tri-O-methyl-D-mannose in which the molar ratio of the D-glucose to the D-mannose derivative was 2:3, a finding in good agreement with the ratio of the two sugars present in the original glucomannan.

The tetra-O-methyl derivatives of D-glucose and D-mannose could not be separated, but their presence was established by demethylation with hydrobromic acid[10] to the parent sugars, D-glucose and D-mannose, which were readily separated by paper chromatography and by paper electrophoresis.[11]

The 2,3,6-tri-O-methyl-D-mannose was obtained as a liquid, showing $[\alpha]_D$ $-2°$ in water, and characterized as its 1,4-bis-*p*-nitrobenzoate.[8] The 2,3,6-tri-O-methyl-D-glucose readily crystallized, m.p. 118–120°, $[\alpha]_D$ $+70°$(equilibrium value in water), and was further identified as the 1,4-bis-*p*-nitrobenzoate.[8]

The di-O-methyl sugars were separated by paper chromatography and the 2,6-di-O-methyl-D-glucose was characterized as its 1,3,4-tris-*p*-phenylazobenzoate.[12] The identity of the second di-O-methyl sugar was not established unequivocally, but since it proved by paper chromatography to be quite different from all the isomeric di-O-methyl-D-glucoses and identical with the product formed by epimerization[13] of 2,6-di-O-methyl-D-glucose, it is believed to be 2,6-di-O-methyl-D-mannose.

The above results reveal the general structural features of the konjak glucomannan. Thus, the isolation of the 2,3,4,6-tetramethyl ethers of D-glucose and of D-mannose shows that the glucomannan possesses terminal non-reducing residues of D-glucopyranose and D-mannopyranose. In this respect it bears a resemblance to the glucomannan isolated from the urediospores of wheat stem rust (*Puccinia graminis tritici*).[14] Contrary to a previous suggestion[7] it is now apparent that the majority of the non-terminal residues of the glucomannan of konjak flour, like those in Iles glucomannan,[8] are composed of 1→4-linked D-glucose and D-mannose residues. This follows from the isolation and characterization of 2,3,6-tri-O-methyl-D-glucose and 2,3,6-tri-O-methyl-D-mannose.

The identification of 2,6-di-O-methyl-D-glucose and the tentative characterization of 2,6-di-O-methyl-D-mannose prove that the glucomannan possesses a branched chain structure and that the D-glucose and D-mannose residues involved in the branching are joined through C_1, C_3 and C_4. This deduction is supported by the observation that certain of the D-glucose and D-mannose residues are immune to periodate oxidation.[15]

The molar ratios of the tetra-, tri- and di-O-methyl sugars indicate that the repeating unit contains on the average about 13 hexose residues whereas the periodate oxidation data indicate a value of approximately 11 residues.

Further support for the type of structure proposed above for the konjak glucomannan was afforded by the observation that the polyaldehyde resulting from the periodate oxidation of the glucomannan yielded a polyalcohol, upon reduction with sodium borohydride[15,16], which when hydrolyzed with acid was found to give rise to glyceritol, erythritol, D-glucose and D-mannose; the molar ratio of glyceritol to erythritol was found to be 1:15. This value, which also corresponds to the average repeating unit[16] of the polysaccharide, is in fair agreement with the results of methylation and periodate oxidation.

Since the konjak glucomannan and its methylated derivative display a relatively low specific optical rotation, -38 and $-19°$ respectively, it is believed that the majority of the glycosidic linkages are of the β-D-type.

Experimental

The following solvents were used for the partition chromatography of sugars and their derivatives: (A) pyridine–ethyl acetate–water (1:2.5:3.5, v./v., upper layer)[17]; (B) butanone–water azeotrope[18] and (C) benzene–ethanol–water–ammonia (200:47:14:1, upper layer).[19] Unless stated otherwise all evaporations were carried out *in vacuo* at 30–40°. The konjak mannan flour was obtained from a local merchant as a pale yellow, granular powder.

Isolation of the Glucomannan.—To a solution of konjak flour (20 g.) in 10% sodium hydroxide (2 liters), Fehling solution B (450 ml.) and Fehling solution A (450 ml.) were added with stirring, in this order. The copper complex of the polysaccharide, which precipitated, was separated by centrifugation and washed with Fehling solution. The complex was decomposed by suspending it in cold (5°) water and adding dropwise cold (5°) 2 *N* hydrochloric acid until the solution was acid. The regenerated polysaccharide was recovered by pouring the acidic solution into 95% ethanol. The copper ions were partially removed from the polysaccharide by trituration with a mixture of acetic acid and ethanol. The residual green color was removed in the following manner. To a suspension of the polysaccharide in water, a solution of the disodium salt of ethylenediaminetetraacetic acid (Versene) was added and after stirring, the polysaccharide was centrifuged off. The polysaccharide was then triturated with methanol–concd. hydrochloric acid (100:3 v./v.), centrifuged and washed successively with absolute ethanol, ether and petroleum ether. The glucomannan was a white granular powder, yield 17.2 g., $[\alpha]^{22}_D$ $-38°$ in 20% sodium hydroxide (*c* 0.7).

Hydrolysis of the Glucomannan.—The glucomannan (50 mg.) was dissolved in *N* sulfuric acid (2 ml.) and the solution heated (sealed tube) for 24 hours in a boiling water-bath. The solution was neutralized ($BaCO_3$), filtered, and evaporated to a sirup. Paper chromatographic analysis of this sirup using solvent A and silver nitrate spray reagent[20] revealed two spots having R_f values corresponding to those of D-glucose and D-mannose. The ratio of D-glucose to D-mannose was determined by separating the mixture on a paper chromatogram and, after elution from the paper in

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the usual way,[21] the sugars were determined by the phenol-sulfuric acid method.[21] The ratio of D-glucose to D-mannose was found to be 2:3.

Methylation of the Glucomannan.—The purified glucomannan (5 g.) was dissolved in hot 30% sodium hydroxide (410 ml.) to give a clear straw-colored solution. The solution was cooled to room temperature, and after adding benzene (30 ml.) methylation was commenced by the dropwise addition of methyl sulfate (125 ml.) during 3 hr. with vigorous stirring. The temperature was then raised to 55° and the mixture stirred for 1 hr. The excess of methyl sulfate was decomposed by heating the reaction mixture at 90–100° for 1 hr. The partially methylated polysaccharide, which separated as a light straw-colored curd on the surface of the reaction mixture, was separated and the mother liquor, after removal of sodium sulfate by decantation, was stored for dialysis. The partially methylated polysaccharide was dissolved in aqueous dioxane (1:1, v./v.) and treated with 30% sodium hydroxide (435 ml.) and methyl sulfate (145 ml.) in the previous manner. Acetone (50 ml.) was added during the methylation to keep the methylated polysaccharide in solution. The reaction mixture was heated on a boiling water-bath to expel acetone and dioxane and to decompose unreacted methyl sulfate. To the resulting mixture acetone was added and the solution stirred gently. The acetone layer was decanted and the aqueous solution extracted three more times with acetone. The combined acetone extracts were evaporated. The aqueous layer was combined with the mother liquor from the first methylation and after dialysis the residual solution was evaporated. The residues from the acetone extract and the aqueous layer were combined and methylated again at 50° with 30% sodium hydroxide (300 ml.) and methyl sulfate (100 ml.) as before. Upon neutralization of the reaction mixture, the methylated polysaccharide readily separated on the surface. Acetone was added to dissolve the polysaccharide and to precipitate the sodium sulfate which was filtered and washed with acetone. The combined filtrate and washings were evaporated to give a buff-colored residue. This was dissolved in acetone and the solution centrifuged to remove insoluble material. On evaporation of the solution the partially methylated glucomannan was obtained as a light-brown, friable solid (4.4 g.; found: OCH_3, 39.5).

The partially methylated glucomannan (4.4 g.) was dissolved in methyl iodide (50 ml.) and the solution refluxed while silver oxide (5 g.) was added in six portions during 12 hr. The mixture was refluxed for a further 8 hr., the excess of methyl iodide was distilled and the residue extracted with acetone. The extract was centrifuged and evaporated to give a light brown glass (4.4 g.) which was subjected to two more Purdie methylations, using 50 ml. of methyl iodide and 5 g. of silver oxide each time, in the previous manner. Isolation by extraction with acetone afforded the fully methylated polysaccharide (4.3 g.).

Fractional Precipitation of the Methylated Glucomannan.—The methylated glucomannan (4.3 g.) was dissolved in the minimum amount of dry acetone and to this solution dry ether was added until a flocculent precipitate was formed. This precipitate was centrifuged and the supernatant liquid poured with stirring into dry petroleum ether when there was formed fraction I, 0.91 g., $[\alpha]^{28}D$ −19.8° in chloroform (c 1) (found: OCH_3, 44.3). The residue from the first precipitation was dissolved in acetone, ether added, the precipitated polysaccharide centrifuged off and the supernatant liquid poured into petroleum ether to give fraction II, 2.05 g., $[\alpha]^{28}D$ −19.5° in chloroform (found: OCH_3, 44.1). Repetition of this process yielded fraction III, 0.78 g., $[\alpha]^{28}D$ −19.1° (in chloroform) (found: OCH_3, 43.4) and fraction IV (0.07 g.).

Methanolysis of the Methylated Glucomannan.—A solution of the methylated glucomannan (1 g., fraction II) in 3% methanolic hydrogen chloride (80 ml.) was refluxed when the rotation changed from $[\alpha]^{31}D$ −34° (after 10 min.) to +77° (16 hr., constant value). The reaction mixture was neutralized (Ag_2CO_3), filtered, and the filtrate evaporated to give a sirup (1.06 g.) which was distilled giving a colorless liquid (0.935 g.), b.p. (bath temp.), 120–130° (0.005 mm.), $n^{30}D$ 1.4570, $[\alpha]^{28}D$ +65° in methanol (c 3.5) (found: OCH_3, 52.7).

Hydrolysis of the Methylated Glycosides and Separation of the Methylated Sugars.—The mixture of methylated glycosides (0.7614 g.) was dissolved in N sulfuric acid (20 ml.) and the solution refluxed; the rotation changed from $[\alpha]^{26}D$ +51° (after 1 hr.) to +22° (20 hr., constant value). The hydrolyzate was neutralized ($BaCO_3$), filtered, and the filtrate evaporated to a sirup (700 mg.). Upon chromatographic analysis of the mixture using solvent B and p-anisidine trichloroacetate spray,[10] components with R_f values corresponding to those of 2,6-di-O-methyl-D-glucose, 2,3,6-tri-O-methyl-D-mannose, 2,3,6-tri-O-methyl-D-glucose, 2,3,4,6-tetra-O-methyl-D-mannose and 2,3,4,6-tetra-O-methyl-D-glucose were detected.

The mixture of methylated sugars (645 mg.) was separated on a hydrocellulose–cellulose column using solvent B as previously described.[9] The results are given in Table I.

TABLE I

SEPARATION OF THE MIXTURE OF METHYLATED SUGARS ON A HYDROCELLULOSE–CELLULOSE[9] COLUMN

Tube no.	Components	Yield, mg.	Mole ratio
5–10	2,3,4,6-Tetra-O-methyl-D-glucose	43	2.0
	and 2,3,4,6-tetra-O-methyl-D-mannose	22	1.0
20–25	2,3,6-Tri-O-methyl-D-glucose	109	
26–39	2,3,6-Tri-O-methyl-D-glucose	98	10.2
	and 2,3,6-tri-O-methyl-D-mannose	120	
40–55	2,3,6-Tri-O-methyl-D-mannose	196	15.6
130–140	2,6-Di-O-methyl-D-glucose and (?) 2,6-di-O-methyl-D-mannose	55	2.8

Identification of 2,3,4,6-Tetra-O-methyl-D-mannose and 2,3,4,6-Tetra-O-methyl-D-glucose.—The sirupy product (65 mg.), $[\alpha]^{26}D$ +67° in methanol (c 1) from tubes 5–10 (Table I), had an R_f value very close to that of 2,3,4,6-tetra-O-methyl-D-glucose and of 2,3,4,6-tetra-O-methyl-D-mannose. The amount of each component was estimated from the specific rotation of the mixture and that of the pure components. A crystalline aniline derivative could not be obtained from the mixture of tetra-O-methyl-D-mannose and tetra-O-methyl-D-glucose, a phenomenon encountered on a previous occasion.[14] The mixture of the two tetra-O-methyl sugars (10 mg.) was demethylated with 48% hydrobromic acid[10] to give a sirup which was found to contain glucose and mannose by paper chromatography using solvent A and by paper electrophoresis in a borate buffer pH 9.2.[11] No other sugar was present in the mixture.

Identification of 2,3,6-Tri-O-methyl-D-glucose.—The 2,3,6-tri-O-methyl-D-glucose component (98 mg. from tubes 20–25), which had $[\alpha]^{25}D$ +64° in methanol (c 0.5), crystallized spontaneously. After recrystallization from ether the 2,3,6-tri-O-methyl-D-glucose had m.p. and mixed m.p. 118–120°, $[\alpha]^{24}D$ +100° → +70° (equil. value) in water (c 0.6) (lit.[22] m.p. 123°, $[\alpha]D$ +70° (equil. value) in water). The 2,3,6-tri-O-methyl-D-glucose (53 mg.) was treated in pyridine (2 ml.) with p-nitrobenzoyl chloride (500 mg.) as previously described.[8] The characteristic 2,3,6-tri-O-methyl-D-glucose 1,4-bis-p-nitrobenzoate was obtained, m.p. and mixed m.p. 190–192°, $[\alpha]^{25}D$ −34° in chloroform (c 0.7) (after recrystallization from methanol) (lit.[8] m.p. 190°, $[\alpha]D$ −33° in chloroform).

Identification of 2,3,6-Tri-O-methyl-D-mannose.—The 2,3,6-tri-O-methyl-D-mannose component (120 mg. from tubes 40–55), which was chromatographically pure, had $[\alpha]^{25}D$ −2° in water (c 2) (lit.[23] −10°). When treated with p-nitrobenzoyl chloride as described above it gave 2,3,6-tri-O-methyl-D-mannose 1,4-bis-p-nitrobenzoate, m.p. and mixed m.p. 189–190°, $[\alpha]^{26}D$ +36° in chloroform (c 1) (lit.[8] m.p. 188°, $[\alpha]D$ +33° in chloroform). *Anal.* Calcd. for $C_{23}H_{24}O_{12}N_2$: N, 5.4. Found: N, 5.5.

Identification of 2,6-Di-O-methyl-D-glucose.—The sirupy product (55 mg.) from tubes 125–140 was found by paper chromatographic analysis, using solvents B and C, to be a mixture of two components. One of these had the same R_f value as 2,6-di-O-methyl-D-glucose. The mixture was resolved by sheet paper chromatography using solvent C to give 2,6-di-O-methyl-D-glucose (6 mg.) which was dis-

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solved in pyridine (3 ml.) and after addition of *p*-phenylazobenzoyl chloride (150 mg.) the mixture was kept at 37° for 2 days. The reaction mixture was poured into water, kept for 3 hr., and evaporated. The residue was extracted with chloroform and the extract chromatographed on a column of zinc carbonate.[12] On evaporation of the eluate, a sirup was obtained which crystallized on trituration with ethyl acetate. The crystals were filtered, washed with ethanol and dried, m.p. and mixed m.p. with an authentic specimen of 2,6-di-*O*-methyl-D-glucose 1,3,4-tris-*p*-phenylazobenzoate, 205–207°.[12]

Identification of 2,6-Di-*O*-methyl-D-mannose.—The second component of the mixture of di-*O*-methyl sugars had an R_f value which did not correspond to 2,3-, 2,4-, 3,4-, 3,6- or 4,6-di-*O*-methyl-D-glucose. That it is probably 2,6-di-*O*-methyl-D-mannose is indicated by the fact that when 2,6-di-*O*-methyl-D-glucose was epimerized with alkali[13,24] it gives 2,6-di-*O*-methyl-D-mannose which had the same R_f value as the unknown di-*O*-methyl sugar, and gave the same color on a chromatogram developed with *p*-anisidine. The unknown di-*O*-methyl sugar was readily distinguished by paper chromatography from 2,3- and 3,4-di-*O*-methyl-D-mannose.

The ratio of the methylated sugars was determined in a separate experiment by separation of the components of the hydrolyzate on paper using solvent B, extraction of the appropriate areas of paper, purification of the products by extraction with water, and weighing the residues left after evaporation. The result was tetra-*O*-methyl sugars (1.0 mole), tri-*O*-methyl sugars (11 moles) and di-*O*-methyl sugars (0.93 mole). The corresponding results calculated from the column chromatography are 1:9:1 approx.

Periodate Oxidation of the Glucomannan.—The glucomannan (0.5 g.) was treated with 0.1 *N* sodium metaperiodate (250 ml.) at 5°[25] and the consumption of periodate and the generation of formic acid were determined according to the standard procedures.[26] The molar consumption of periodate per hexose residue was: 0.61 (5 hr.), 0.72 (27 hr.), 0.86 (45 hr.), 0.88 (72 hr.), 0.95 (95 hr.), 1.0 (140 hr.), 1.03 (209 hr., constant value). The number of hexose residues producing 1 mole of formic acid was: 14 (18 hr.), 13.3 (27 hr.), 12.5 (46 hr.), 12.1 (72 hr.), 11.1 (94 hr.), 10.9 (116 hr.), 10.4 (140 hr.).

Reduction of the Periodate-oxidized Glucomannan.—The periodate-oxidized, reaction mixture was neutralized with barium hydroxide and the barium iodate and barium periodate were removed by centrifugation. To the supernatant liquid sodium borohydride (500 mg.) was added and the solution allowed to stand at room temperature for 3 hr. The solution was acidified with acetic acid and evaporated to dryness. The residue was hydrolyzed by heating on the steam-bath for 3 hr. with *N* sulfuric acid. The hydrolyzate was neutralized ($BaCO_3$), filtered, and the solution deionized by passing first through a cation (Amberlite IR 120)[27] and then an anion exchange resin (Duolite A_4).[28] The resulting solution was evaporated to a sirup which, upon chromatographic analysis using butan-1-ol–ethanol–water (4:1:5)[20] and ammoniacal silver nitrate spray, was found to contain D-glucose, D-mannose, glyceritol and erythritol. The monosaccharides were determined by the phenol-sulfuric acid method[21] and the polyhydric alcohols[29] by oxidation with periodate[16] followed by the determination of formaldehyde with chromotropic acid.[30] The ratios of the components in the hydrolyzate were: D-glucose (1.8 moles), D-mannose (0.7 mole), glyceritol (1.0 mole) and erythritol (14.8 moles).

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[Contribution from the Department of Agricultural Biochemistry, University of Minnesota]

Oxidation of Glycogen with Periodic Acid[1]

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The periodate oxidation product of glycogen, glycogen polyaldehyde, is isolated in 97% yield by a simple freezing method. The course of the periodate oxidation of glycogen was investigated and the structure of the polyaldehyde discussed.

In extending our investigations into the reduction products of periodate oxidized glycosides[2,3] to polysaccharides[4] it was necessary to obtain the intermediate glycogen polyaldehyde in a pure form for structural studies. Unlike starch, which reacts with periodic acid to give a polyaldehyde that is insoluble in cold water,[5] the glycogen polyaldehyde like the original polysaccharide remains dissolved in the reaction mixture. It is shown herein, however, that if the reaction mixture is frozen overnight at −5 to −10° and allowed to thaw at room temperature the glycogen polyaldehyde remains as a cold-water insoluble, flocculent precipitate, which may be washed with water to remove inorganic impurities. Other methods such as dialysis and ion exchange resins were used but they were inferior to this freezing technique.

The polyaldehyde from different samples of glycogen showed very similar properties; the material is a white, amorphous powder which is insoluble in water and the usual solvents, but soluble in warm, aqueous potassium or sodium acetate giving solutions having $[\alpha]_D$ +20°. The polyaldehyde reduced Fehling solution strongly, gave a deep blue color with the Molisch reagent and showed a positive Schiff test; unlike the parent polysaccharide, however, it gave no color with iodine.

The polyaldehyde was sensitive to both acid and alkali. Upon hydrolysis with mineral acid, the polyaldehyde underwent decomposition and a brown precipitate was produced; glucose was detected by paper chromatography in the hydrolyzate. Heating the polyaldehyde with a solution of sodium hydroxide also caused decomposition.

In a discussion of the structure of the starch polyaldehyde,[6] it was pointed out that the eryth-

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