nally different, for a change in the side chain structure of a monomer unit could affect the rate of liberation of its phenolic group.

While it has been implied that the amorphous ethanol lignins are analogous to the reversion products produced on ethanolysis of III,[6] our results indicate that they are nearer to being incompletely reacted fragments of the original lignin since we obtained no direct evidence of an increase in molecular weight during ethanolysis.

There is, however, an unexplained loss of oxygen (0.6 atom per C_9 unit in SI) in the re-ethanolysis. The proposed cleavage of IV produces no over-all change in oxygen content, and therefore it seems likely that the oxygen loss may be occurring in those monomer units which do not react to produce a free phenolic hydroxyl group. If this is the case, these units lose nearly one atom of oxygen per C_9 unit. Since the formation of a conjugated ethylenic bond appears to be excluded by the ultraviolet spectra and the molecular weight data seem to exclude repolymerization, we postulate an intramolecular condensation reaction to account for this oxygen loss.

SYRACUSE, NEW YORK

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

The Constitution of Corn Starch Dextrin[1]

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Commercial corn starch dextrins have been fractionated and subjected to periodate oxidation studies and one of them has been examined by methylation. Periodate oxidation shows that the amount of glucose stable to oxidation is higher (5%) in the dextrin than in the parent starch. The hydrolyzate of the methylated dextrin has been shown to contain: 2,3,4,6-tetra-*O*- (16.5%); 2,3,6-tri-*O*- (57.3%), 2,3,4-tri-*O*- (2.6%), 2,4,6-tri-*O*- (1.2%), 2,3-di-*O*- (6.3%), 2,6-di-*O*-(10.0%), 3,6-di-*O*- (3.2%), 2-*O*- (1.5%), 3-*O*- (0.8%) and 6-*O*-methyl-D-glucose (0.5%). From the periodate and methylation data it is deduced that dextrinization is accompanied by considerable transglycosidation and the development of a highly branched structure.

In spite of the industrial importance of starch dextrins, prepared from native starches by roasting usually in the presence of acidic reagents, little is known about the detailed structural changes that the starch undergoes during the dextrinization process. In the early work[2,3] it was suggested that dextrins are formed by cleavage of the starch chains with concomitant anhydro-ring formation to give smaller molecules terminated by non-reducing units of the levo-glucosan type. Dextrinization of amylose and amylopectin also has been investigated by adsorption chromatography[4] whereby it was shown that amylopectin undergoes dextrinization more readily than amylose.[4,5] Methylation studies[5] enabled the deduction to be made that the dextrinization process caused breakdown of the starch molecules to smaller fragments which were much more highly branched than the original starch. This was recognized from the increased percentage of 2,3,4,6-tetra-*O*-methyl-D-glucose obtained from the methylated dextrin as compared with the yield from the methylated derivative of the parent starch.

This paper deals with periodate oxidation studies on a number of acid converted corn starch dextrins and methylation studies on one of them.

Four commercial corn starch dextrins were fractionated from aqueous solution with ethanol and the various fractions (see Table II) were examined by a procedure[6] involving periodate oxidation, reduction and hydrolysis. This procedure not only provides the usual information on the periodate consumption and formic acid production, but it also determines the percentage of glucose residues in the dextrin that are immune to periodate cleavage. Since the native starches contain less than 1% of glucose residues that are immune to periodate oxidation, it was tentatively concluded that the relatively high percentage of glucose residues in the dextrin that survived periodate oxidation was an indication of the structural rearrangements that occur during the dextrinization process.

On the basis of these periodate oxidation studies (see Tables I and II), the dextrin fraction chosen for further investigation by the methylation technique was one which was found[6] to contain the largest percentage of glucose units that were immune to periodate oxidation.

TABLE I

PERIODATE OXIDATION OF DEXTRIN

Reacn. time, hr.	Moles anhydrohexose per mole formic acid produced	Moles of periodate consumed per mole of anhydrohexose	Reacn. time, hr.	Moles anhydrohexose per mole formic acid produced	Moles of periodate consumed per mole of anhydrohexose
0	22.6	0.19	144	4.7	0.99
17	10.7	.45	241	4.7	0.99
45	5.5	.49	480	4.5	1.00
91	4.8	.87	700	4.3	1.00

The dextrin fraction, purified through its acetate, was exhaustively methylated with methyl sulfate and alkali in the usual way after which it was hydrolyzed. The composition of the mixture of methylated sugars so formed, as revealed by column[7] partition chromatography using buta-

(1) Paper No. 3696, Scientific Journal Series, Minnesota Agricultural Experiment Station.

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TABLE II

PERIODATE OXIDATION OF STARCH DEXTRIN FRACTIONS

Dextrin fraction Commercial No.	Water: ethanol ratio used to ppt. dextrin	Oxidn. time, hr.	No. anhydro-hexose units per mole of formic acid produced	Moles periodate consumed per anhydro-hexose unit	Glucose not oxidized (by chromatographic analysis), %
724[a]	1:1	284	4.96	1.05	1.56
724[a]	1:2	278	4.35	1.06	1.87
800[a]	1:1	277	10.77	1.00	
		650	10.37	1.02	1.40
800[a]	1:2	276	8.73	1.05	
		650	7.94	1.03	2.33
9533-R[b]	1:1	276	5.35	1.07	
		650	5.03	1.09	4.11
9533-R[b]	1:2	275	4.84	1.08	
		650	4.47	1.14	4.92
B-2[c]	1:1	275	10.85	0.98	
		650	10.68	1.00	2.38

[a] Supplied by Clinton Foods, Inc., Clinton, Iowa. [b] Supplied by Stein Hall Co., New York, N. Y. [c] Supplied by American Maize Products Co., Roby, Indiana.

none:water azeotrope as the solvent,[8] is given in Table III (see later). The identity of these components was established by preparing suitable crystalline derivatives.

Since the commercial dextrin was produced from native starch, which contains amylopectin and amylose, a detailed structural discussion is not warranted. However, it is possible to make certain deductions concerning the structural changes that occur during the dextrinization process by an inspection of the nature and amounts of the components of the hydrolyzate of the methylated dextrin (see Table III).

Of the ten components in Table III only 1, 2 and 5 are obtained in quantity from methylated amylopectin and only components 1 and 2 from methylated amylose. The characterization of the other seven components, 3, 4 and 6–10, derived from the methylated dextrin coupled with the isolation of a relatively high percentage of component 1 (2,3,4,6-tetra-*O*-methyl-D-glucose), indicates that the dextrin has a much more complicated structure than either the amylose or the amylopectin of the parent corn starch.

The highly branched character of the dextrin molecule is shown by the complexity of the mixture of the di-*O*- and mono-*O*-methyl derivatives of glucose (Table III) and also by the fact that one out of every 6 glucose units occupies a terminal non-reducing position as revealed by the yield of 2,3,4,-6-tetra-*O*-methyl-D-glucose. This last finding is in agreement with that derived from a previous methylation study of a dextrin.[5] Support for this highly branched structure for the dextrin as revealed by the methylation studies is also provided by the results of the periodate oxidation studies which showed that 1.14 moles of periodate were consumed per anhydroglucose unit with the concomitant formation of 1 mole of formic acid for every 4.5 moles of anhydroglucose.

The identification of the 2,4,6-tri-*O*-, 2,6- and 3,6-di-*O*- and the 2-, 3- and 6-*O*-methyl-D-glucose also agrees with the observation that the dextrin contains a considerable number of glucose units that are stable to periodate oxidation.

While it is conceivable that certain of the partially methylated glucose derivatives obtained in small yield may have arisen as a result of incomplete methylation or demethylation during hydrolysis, it is not believed that this is the explanation for the isolation of the relatively large amount (10%) of 2,6-di-*O*-methyl-D-glucose. On the contrary, it is believed that the identification of the latter proves that the dextrinization process not only involves a shortening of the chains as shown by periodate oxidation and methylation studies and a decrease in molecular weight as revealed by viscosity studies, but also by a considerable amount of transglycosidation. This phenomenon which is probably one of the chief characteristics of the dextrinization process is most likely responsible for the formation of new glycosidic linkages and development of the highly branched structure as revealed by the identification of components 6–10 as well as components 3 and 4. This deduction is supported by the observation that starch dextrins are stable to β-amylase.[5] Although the possibility of anhydro-ring formation has been suggested,[2,3] a careful search of all the components of the hydrolyzate of the methylated dextrin failed to produce any supporting evidence for this hypothesis; no methyl derivatives of 3,6-anhydro-D-glucose were isolated and moreover there was no evidence for sugars other than D-glucose that might arise from ethylene oxide type sugar units.

Since transglycosidation is the characteristic reaction of "high conversion" dextrins, it would appear that the progress and control of dextrinization could be ascertained by determining the increase in the number of glucose residues in the dextrin that are resistant to periodate oxidation. It is also apparent that, inasmuch as dextrinization is accompanied by transglycosidation, it should be possible to bring about the synthesis of new carbohydrate polymers by a process of co-dextrinization (co-polymerization) with other substances such as sugars, oligosaccharides, polyhydric alcohols and also with other polysaccharides.

Experimental

Isolation of Dextrin Fractions.—The various "acid converted dextrins" (hereinafter called dextrins) were each extracted with 4 parts of water at room temperature and the solution centrifuged. To the supernatant liquid an equal volume of ethanol was added slowly with stirring to give one fraction, and after this had been removed (centrifuge) another volume of ethanol equal to the first was added to give a second fraction. Each fraction was redissolved in water and precipitated by pouring with stirring into about 4 volumes of ethanol. The white amorphous precipitates so obtained were washed successively with ethanol, ether, light petroleum ether and dried *in vacuo*. The two dextrin fractions so obtained were slightly reducing to Fehling solution while the product remaining dissolved in the aqueous ethanolic mother liquor from the initial precipitation was strongly reducing, doubtless due to the presence of glucose and oligosaccharides.

Acetylation and Fractionation of Dextrin.—The fraction (35 g.) of Dextrin #724, precipitated with two volumes of ethanol, was dissolved in formamide (250 ml.) with stirring at room temperature and acetylated by adding pyridine (250 ml.) followed by acetic anhydride (200 ml.), the latter

(8) L. Boggs, L. S. Cuendet, I. Ehrenthal, R. Koch and F. Smith, *Nature*, **166**, 520 (1950).

being added over a 1-hr. period.[9] After standing at room temperature for 3 hr., the solution was poured into water (3 l.) with stirring. The precipitated acetate was filtered and washed with water. Further purification of the acetate was effected by dissolving it in chloroform, drying this solution with anhydrous magnesium sulfate, and reprecipitating the product by pouring the chloroform solution into light petroleum ether. The dry purified dextrin acetate was dissolved in chloroform (175 ml.) and fractionally precipitated in the usual way by adding increasing amounts of diethyl ether. Each fraction was separated, washed with petroleum ether and dried *in vacuo*. Examination of the 8 fractions so obtained showed that fractions 1–5 amounting to 7.1, 14.0, 11.3, 6.0 and 3.6 g., respectively, showed $[\alpha]^{25}D$ +140° (approx.) in chloroform (*c* 1), while fractions 6–8, amounting to 3.1, 1.3 and 1.9 g., respectively, showed $[\alpha]^{25}D$ +132° (approx.) in chloroform (*c* 1). Reacetylation of the second fraction caused no change in rotation (Found: OAc, 43.5).

Periodate Oxidation of Dextrin.—A portion (12.0 g.) of the dextrin acetate (composite of fractions 1–5) was deacetylated by treatment with a mixture of acetone (100 ml.) and *N* sodium hydroxide (150 ml.) for 1 hr. at 50°. The acetone was then removed under reduced pressure leaving an aqueous alkaline solution of the dextrin. The solution was neutralized with acetic acid and the dextrin precipitated by pouring the solution slowly with stirring into ethanol (4 volumes). The polysaccharide was dried as described above to give a fine white amorphous powder.

The dextrin (0.5000 g.) was dissolved in 0.1 *N* sodium periodate (500 ml.) and the oxidation allowed to proceed at 5° in the dark; at suitable intervals an aliquot (5 ml.) of the reaction mixture was withdrawn and added to 0.1 *N* As_2O_3 (5 ml.), sodium bicarbonate (2 g. approx.) and a crystal of potassium iodide. After standing for 0.5 hr. the excess arsenite was titrated with standard iodine solution in the usual way.[10] The periodate consumption was determined after correcting for a blank carried out under identical conditions.

An additional aliquot (20 ml.) was withdrawn and added to a solution containing 50% ethylene glycol (2 ml.) to destroy the excess of the periodate present and the formic acid was titrated with 0.01 *N* sodium hydroxide using methyl red as the indicator. A blank was carried out at the same time. The results are recorded in Table I.

Similar oxidations were carried out on other dextrin fractions with results given in Table II, the procedure being the same except that a 3-g. sample was oxidized in 2 liters of 0.05 *N* sodium periodate.

Determination of Anhydroglucose Units Not Oxidized by Periodate.—Following the periodate oxidation of the dextrin fractions, the number of anhydroglucose units not oxidized was determined by quantitative paper chromatography as previously described.[11] The results are recorded in Table II.

Methylation of Starch Dextrin.—The fraction of the "acid converted dextrin" No. 9533, precipitated from aqueous solution with 2 volumes of ethanol, was chosen for the methylation study since the periodate oxidation procedure showed that this was most highly branched and contained more periodate-stable glucose residues than the other dextrins examined (see Table II).

The dextrin (20 g.) was acetylated[9] as described above and freed from impurity by dissolution in acetone and precipitation with water (yield 26 g.). The acetate (20 g.) was dissolved in acetone and methylated with methyl sulfate (100 ml.) and 30% (w./w.) aqueous sodium hydroxide during 2 hr. in the usual way. The temperature was kept below 25° until the reaction mixture no longer reduced Fehling solution after which it was raised to 55°. The methylated product readily separated upon completion of the reaction. Seven further methylations were applied in the same manner at 55°, acetone being used as the solvent medium. The product from the final methylation was dissolved in chloroform and washed with water to remove inorganic impurities. After drying ($CaCl_2$) the chloroform solution was freed from solvent and the residual methylated dextrin further purified by extraction with diethyl ether followed by precipitation from ethereal solution with petroleum ether (b.p. 30–60°). Filtration and drying yielded the methylated dextrin as a white powder (yield 12 g. (approx.)). The material, which left no ash upon ignition, showed $[\alpha]^{25}D$ +173° (*c* 1.3) in chloroform, OMe, 43.0%; a sample examined after seven methylations had the same properties.

Fractional Precipitation of the Methylated Dextrin.—The methylated dextrin obtained above was dissolved in ether and subjected to fractional precipitation with light petroleum ether in the usual way. Examination of the 6 fractions so produced showed that the methylated dextrin was essentially homogeneous, the rotation ranging from $[\alpha]^{25}D$ +173 to +166° in chloroform (*c* 1) and the OMe from 43.2 to 42.8%.

Hydrolysis of the Methylated Starch Dextrin.—A composite sample (5.0 g., $[\alpha]^{25}D$ +173° in chloroform (*c* 1), OMe, 43.0) of the first 5 fractions of the methylated dextrin was dissolved in methanol (150 ml.) containing 2% hydrogen chloride and the solution refluxed until the rotation was constant, $[\alpha]^{26}D$ +169° (initial), +72° (7 hr.), +72° (12.5 hr.) (constant value). The solution was neutralized with ethereal diazomethane and evaporated *in vacuo* to a sirupy mixture of methyl glycosides (5.8 g.).

A solution of the mixture of glycosides in *N* sulfuric acid (110 ml.) was heated on a boiling water-bath until the rotation was constant, $[\alpha]D$ +74° (initial), +88° (constant value after 9 hr.). The solution was neutralized ($BaCO_3$), filtered and evaporated to a sirup. The sirup was dissolved in water and the solution, after treatment with a little charcoal, filtered and passed successively through a cation (Amberlite IR 120) and an anion (Duolite A4) exchange resin. Concentration of the effluent *in vacuo* gave a clear colorless sirup (yield 5.26 g.).

Separation of Component Sugars by Column Chromatography.—A portion (1.77 g.) of the sugar mixture from the hydrolysis above was separated into its component sugars by column chromatography using cellulose–hydrocellulose[7] and butanone:water azeotrope as the solvent.[8,12] The eluate from the column was collected in tubes automatically changed every 10 minutes for the faster moving components (1 to 4) and every 30 minutes for the rest. The location of sugars in the various tubes was determined by spotting a small amount of eluate from each tube on filter paper and spraying with *p*-anisidine–trichloroacetic acid reagent.[13] The eluates from any tubes which appeared to be free of sugars by this color test were first evaporated to dryness before discarding to check for possible non-reducing sugars. Fractions that showed overlapping were resolved by paper chromatography. The yields of the various methylated sugars obtained by this separation are recorded in Table III.

TABLE III

COLUMN CHROMATOGRAPHY OF THE HYDROLYZATE OF METHYLATED DEXTRIN

Component	Methyl derivative of D-glucose	Yield		
		Wt., g.	%	Mole ratio
1	2,3,4,6-Tetra-*O*-	0.299	16.5	35
2	2,3,6-Tri-*O*-	.979	57.3	123
3	2,3,4-Tri-*O*-	.045	2.6	6
4	2,4,6-Tri-*O*-	.020	1.2	3
5	2,3-Di-*O*-	.101	6.3	14
6	2,6-Di-*O*-	.160	10.0	21
7	3,6-Di-*O*-	.052	3.2	7
8	2-*O*-	.022	1.5	3
9	3-*O*-	.012	0.8	1.7
10	6-*O*-	.007	0.5	1
	Wt. recovd.	1.697 g. (or 96%)		

Identification of the Components of the Hydrolyzate of the Methylated Dextrin. (a) 2,3,4,6-Tetra-*O*-methyl-D-glucose.—Component 1 (Table III), crystallized completely and after recrystallization from petroleum ether gave 2,3,4,6-tetra-*O*-methyl-α-D-glucose, m.p. and mixed m.p. 97°, $[\alpha]^{24}D$ +113° → +84.4° in water (*c* 0.8); lit.[14,15] m.p. 96°

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and $[\alpha]_D$ +92° → +84° in water. *Anal.* Calcd. for $C_{10}H_{20}O_6$: OMe, 52.5. Found: OMe, 52.7.

(b) **2,3,6-Tri-*O*-methyl-D-glucose.**—The sirupy component 2 (Table III, 0.979 g.) crystallized when nucleated with 2,3,6-tri-*O*-methyl-D-glucose and had m.p. 117–118° undepressed when mixed with an authentic specimen after recrystallization from ethyl ether, $[\alpha]^{24}D$ +92° → +68.7° in water (*c* 1.1); lit.[16-18] m.p. 122–123° and $[\alpha]_D$ +90.2° → +70.5° in water.

(c) **2,3,4-Tri-*O*-methyl-D-glucose.**—The sirupy component 3 (Table III, 0.045 g.) had $[\alpha]^{24}D$ +61° in methanol (*c* 0.7) and was chromatographically identical with 2,3,4-tri-*O*-methyl-D-glucose when developed either with butanone:water azeotrope or with benzene:ethanol:water:ammonium hydroxide (200:47:14:1). Treatment of component 3 with aniline in ethanol yielded the crystalline anilide of 2,3,4-tri-*O*-methyl-D-glucose, $[\alpha]^{23}D$ −103° in ethanol (*c* 0.4), and m.p. 150°, undepressed by admixture with an authentic specimen; lit.[19] m.p. 145–146°.

(d) **2,4,6-Tri-*O*-methyl-D-glucose.**—The sirupy product (0.065 g.) recovered from the mother liquors of the 2,3,6-tri-*O*-methyl-D-glucose was allowed to react with 0.5% methanolic hydrogen chloride (10 ml.) at room temperature for 20 hr. until the rotation became constant (final value, $[\alpha]^{23}D$ +20°). Neutralization (Ag_2CO_3), filtration and concentration gave a sirupy product which was resolved by paper chromatography using butanone:water azeotrope into two components. The faster moving component consisted of methyl 2,3,6-tri-*O*-methyl-D-glucofuranoside while the slower component (0.020 g.) proved to be 2,4,6-tri-*O*-methyl-D-glucose, $[\alpha]^{24}D$ +64° in methanol (*c* 0.3). Treatment of this slower moving tri-*O*-methyl-D-glucose with ethanolic aniline in the usual way afforded N-phenyl-D-glucopyranosylamine 2,4,6-tri-*O*-methyl ether, m.p. and mixed m.p. 156–158°, lit.[20] m.p. 162–166°.

(e) **2,3-Di-*O*-methyl-D-glucose.**—Component 5 (Table III, 0.101 g.) yielded crystalline 2,3-di-*O*-methyl-D-glucose when nucleated with an authentic specimen. After recrystallization from ethyl acetate it had m.p. and mixed m.p. 117–119°, $[\alpha]^{26}D$ +51.3° in acetone (*c* 0.8); lit.[21] m.p. 110°, $[\alpha]_D$ +50.9° in acetone. Treatment of the 2,3-di-*O*-methyl-D-glucose with aniline in ethanol yielded the crystalline anilide of 2,3-di-*O*-methyl-D-glucose, m.p. 133–135°; lit.[22] m.p. 134°.

(f) **2,6-Di-*O*-methyl-D-glucose.**—The sirupy component 6 (Table III, 0.160 g.) which had $[\alpha]^{23}D$ +65.5° in water (*c* 1.2)[23] was chromatographically identical with 2,6-di-*O*-methyl-D-glucose; lit.[22] $[\alpha]_D$ +63.3° in water. Treatment of the sirup with *p*-phenylazobenzoyl chloride in pyridine gave 2,6-di-*O*-methyl-D-glucose 1,3,4-tri-azobenzoate, m.p. 206–208°, $[\alpha]^{25}D$ −341° (*c* 0.4 in chloroform), after recrystallization from ethyl acetate–light petroleum ether. The mixed melting point with an authentic specimen (m.p. 200°, $[\alpha]^{25}D$ −329° in chloroform) was 205°; lit.[24] m.p. 205–207°.

(g) **3,6-Di-*O*-methyl-D-glucose.**—Component 7 (Table III, 0.052 g.) was chromatographically identical with 3,6-di-*O*-methyl-D-glucose. When a portion (0.017 g.) of it was treated with methanolic hydrogen chloride (0.5%) at 20°, the rotation changed from $[\alpha]_D$ +75° to +22° in 2 hr. indicating furanoside formation and hence the presence of a free hydroxyl group at C_4 in the di-*O*-methyl-D-glucose. Component 7 crystallized completely when nucleated with an authentic specimen[25] of 3,6-di-*O*-methyl-D-glucose. After recrystallization from ethyl acetate, 3,6-di-*O*-methyl-α-D-glucose was obtained, m.p. 118–119°, $[\alpha]^{24}D$ +60° in water (*c* 0.6). Admixture with an authentic specimen (m.p. 111–112°)[25] gave m.p. 111–112°; lit.[26] m.p. 114–115°, $[\alpha]^{18}D$ +61.5° in water.

(h) **2-*O*-Methyl-D-glucose.**—Component 8 (Table III, 0.022 g.) which crystallized spontaneously was chromatographically identical with 2-*O*-methyl-D-glucose. After recrystallization from ethanol the 2-*O*-methyl-β-D-glucose had m.p. and mixed m.p. 156–158°, $[\alpha]^{23}D$ +63° (equilibrium value) in water (*c* 0.8); lit.[27] m.p. 157–159° and $[\alpha]_D$ +66° (equilibrium value) in water.

(i) **3-*O*-Methyl-D-glucose.**—Component 9 (Table III, 0.012 g.) which was chromatographically identical with 3-*O*-methyl-D-glucose, crystallized spontaneously as the β-anomer, m.p. and mixed m.p. 135°, $[\alpha]^{24}D$ +58° (equilibrium value) in water (*c* 0.4); lit.[28,29] m.p. 133.5–135° and $[\alpha]_D$ +55° (equilibrium value) in water.

(j) **6-*O*-Methyl-D-glucose.**—Component 10 (Table III, 0.007 g.), which showed the same R_f and color on paper chromatograms when sprayed with *p*-anisidine–trichloroacetic acid as 6-*O*-methyl-D-glucose, crystallized when nucleated with the authentic specimen. The crystalline 6-*O*-methyl-α-D-glucose had m.p. and mixed m.p. 143–144° and $[\alpha]^{26}D$ +54° (equilibrium value) in ethanol (*c* 1.2); lit.[30,31] m.p. 143–145° and $[\alpha]_D$ +60° (equilibrium value) in water. The osazone prepared in the usual way had m.p. and mixed m.p. 175–180°.

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

Degradation of Glycogen to Isomaltotriose[1] and Nigerose

BY M. L. WOLFROM AND A. THOMPSON[2]

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Isomaltotriose and nigerose were found among the oligosaccharides in the acid hydrolyzate of beef liver glycogen, indicating that some of the α-D-(1 → 6) linkages in this molecule lie in adjacent positions and that a small amount of α-D-(1 → 3) linkages are present. Crystalline panose is shown to be dimorphous.

There are five predictable trisaccharides bound by α-D-glucopyranosyl-(1 → 4) or (1 → 6) linkages or combinations thereof. Three of these entities, *O*-α-D-glucopyranosyl-(1 → 6)-*O*-α-D-glucopyranosyl-(1 → 4)-D-glucopyranose (panose),[3-5] *O*-α-

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