4. The absence of a high iodine absorbing product in the reaction mixture when 3-methylglucose is treated with lime water at 35° is taken as evidence that the 2,3-monomethyl-enediol does not form.

5. When 3-methylglucose is treated with lime water at 35° to no further change, about 64% of the sugar consists of aldose and 32% is converted to 3-methylfructose. Indirect evidence is given for the formation of about 3.0% of saccharinic acid. The remainder consists of a mixture of partially demethylated hexoses.

6. At 35° in dilute alkali the methyl group in 3-methylglucose is slowly removed as methyl alcohol. At 100° under the same conditions the loss is rapid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 684]

A STUDY OF THE HYDROLYSIS OF CORN STARCH AND ITS AMYLOSES WITH REFERENCE TO THE PRODUCTION OF GENTIOBIOSE[1]

BY T. C. TAYLOR AND DAVID LIFSCHITZ

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When the starches are hydrolyzed by means of dilute acid or by enzymes the disaccharide, maltose may be isolated.[2] Its concentration in the solution passes through a maximum and then decreases.[3] With enzymes it is the only disaccharide that is produced and comes apparently directly by hydrolytic scission. For this and other reasons the maltose residue is considered to be a part of the carbohydrate structure of the starches.

Another diglucose sugar, however, has been identified recently in the solution from the hydrolysis of corn starch.[4] This sugar, gentiobiose, is a reducing β-glucoside, the link being at position 6 in contrast to maltose which is an α-glucoside and linked at position 4. As isolated both are delta lactoles.

It is known that in the presence of mineral acids glucose will undergo condensation to form amorphous uncharacterized polysaccharides. The first such synthesis was reported by Fischer.[5] It is carried out by allowing a 20% solution of glucose in *concentrated hydrochloric acid* (37%) to stand for *fifteen hours to three days* at *room temperature*, or *lower*, and at atmos-

[1] An abstract of a dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, Columbia University.

[2] (a) For bibliography see Walton, "A Comprehensive Survey of Starch Chemistry," New York, 1928; (b) Lintner and Düll, *Ber.*, **28**, 1522 (1895); (c) v. Friedrichs, *Arkiv Kemi, Min. Geol.*, **5**, No. 2 (1913–1915).

[3] Rolfe and Defren, THIS JOURNAL, **18**, 869 (1896).

[4] Berlin, *ibid.*, **48**, 2627 (1926).

[5] Fischer, *Ber.*, **23**, 3687 (1890); **28**, 3204 (1895).

pheric pressure. The unfermentable residue of this reaction after purification by alcohol–ether precipitations from water solution, is a non-crystallizing sirup, which contains some reducing disaccharide, named Fischer's isomaltose. The material has frequently been confused with Lintner's[2a,b,6] isomaltose. The two products have nothing in common except that they give phenylosazones which have identical melting points[2c] and that both sugar mixtures are split by emulsin.[2c,7] The specific rotations of the free sugars[6a,7a] and of the osazones[8] differ widely. Further, the conditions under which Lintner's isomaltose is formed are such that condensation of glucose has been found negligible.[7a]

By acetylating the material prepared according to Fischer's directions, Berlin,[9] and at about the same time Georg and Pictet,[10] isolated gentiobiose octaacetate. The yield is low; about 2 g. of acetate per 100 g. of glucose is recovered, corresponding to 1% of the free disaccharide. Berlin also found that the mother liquors (hydrol) obtained from the commercial hydrolysis of corn starch after crystallization of the glucose, contained unfermentable material resembling Fischer's isomaltose, and that gentioacetate could be isolated from this after acetylation.[4] The yield corresponds to 5.7% of the solids in the mother liquor, or about 0.57% of the original starch.

Since the hydrolysis of corn starch to produce glucose, commercially, is carried out at 142–145° (3 atmospheres' pressure) in 0.16% hydrochloric acid, the conditions to which the newly liberated glucose is subjected are substantially different from those that obtain in the Fischer treatment of glucose. It is rather surprising, therefore, to find gentiobiose in both places. The nearest approach to an actual polysaccharide synthesis from glucose under acid concentrations which are at all similar to those in the starch hydrolysis was carried out by Scheibler and Mittelmeier.[11] They heated a 10% solution of glucose in 2.5% sulfuric acid for twelve hours on a water-bath and were able to isolate from the reaction mixture an osazone of approximately the same melting point as Fischer's isomaltosazone. Harrison[12] also prepared some material which he considered as isomaltose, by heating a solution of 500 g. glucose and 0.7 mole of hydrochloric acid in each liter of solution for forty-eight hours at 75°. These experiments were

[6] (a) Lintner and Düll, *Ber.*, **26**, 2533 (1893); (b) Pictet and Vogel, *Helv. Chim. Acta*, **12**, 700 (1929).

[7] (a) V. Friedrichs, *Arkiv. Kemi., Min. Geol.*, **5**, No. 4 (1913–1915); (b) Armstrong, *Proc. Roy. Soc.* (London), **B76**, 597 (1905).

[8] Article by Ling, "Enzymic Hydrolysis of Starches in Relation to Constitution," in Walton, Ref. 2a.

[9] Berlin, THIS JOURNAL, **48**, 1107 (1926).

[10] Georg and Pictet, *Helv. Chim. Acta*, **9**, 444, 612 (1926).

[11] Scheibler and Mittelmeier, *Ber.*, **24**, 301 (1891).

[12] Harrison, THIS JOURNAL, **36**, 586 (1914).

performed long before Berlin's work, so that there is no indication that gentiobiose was a constituent of the mixtures. While many so-called Fischer's isomaltoses have been made, the only similarity among them has been their non-fermentability and ability to form osazones. The physical properties of the sirups and the osazones obtained therefrom vary widely.

The disaccharide gentiobiose in the corn starch hydrolytic liquors may come from the condensation of glucose in acid media catalyzed perhaps by impurities[13] or from a direct hydrolytic scission of one of the amyloses that makes up the corn starch. It must be remembered in this connection that the two corn amyloses[14] are widely different in physical properties, the alpha (15%) being non-dispersable and carrying combined with it certain fatty acids[15] while the beta (85%) is pure carbohydrate. Even when the corn α-amylose has had the fatty acid hydrolyzed away from it, the remaining carbohydrate is still non-dispersable and totally different from the corn β-amylose.

The present investigation involved a systematic study of the action of dilute hydrochloric acid, namely, 0.06 molar (equivalent to commercial concentration 0.16%) on glucose, whole corn starch, corn α-amylose, corn β-amylose and on gentiobiose under conditions of concentration, time, temperature and environment that obtain during the commercial hydrolysis of corn starch.[16]

Wherever possible the gentiobiose was isolated as the octaacetate and weighed, but in the runs on small batches specific rotations, reducing values or osazone formation had to suffice. Details are given later.

I. **Materials.**—The glucose used was the usual anhydrous alpha glucose. Gentiobiose was made from gentian root and isolated as the beta octaacetate. Some of this latter substance was also supplied by the Bureau of Standards.

Air-dried, alkali washed, whole corn starch containing 11% moisture and the corn amyloses with about the same moisture content were prepared in sufficient amounts for the entire set of experiments.

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[13] Ebert, Newkirk and Moskowitz, U. S. Patent 1,668,308, May 1, 1928.

[14] Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

[15] (a) Taylor and Nelson, THIS JOURNAL, **42**, 1726 (1920); (b) L. Lehrman, "The Fatty Acids in Corn Starch and Synthesis of Corn Beta Amylose Palmitate," Columbia Dissertation, 1925.

[16] The commercial hydrolysis[13] consists in treating about 2300 gallons of a 12.5° Bé. starch suspension with 90 pounds of commercial hydrochloric acid in a copper autoclave, and blowing in steam at 40–45 pounds per sq. inch pressure. The conversion is usually run for thirty minutes after the steam pressure has become constant. It is claimed that the walls of the autoclave, and the soluble copper salts formed by the action of the hydrolyzing acid on them, act as catalysts for the condensation of glucose.[13] To diminish the amount of synthetic material formed, it is recommended that the hydrolysis be carried out in vessels lined with glass-enamel or a similar material.[13] Translated to laboratory conditions the above would be equivalent to 344 g. of starch in 1 liter of 0.06 molar hydrochloric acid at a temperature of 141 to 142°. Since the pressure in the autoclave becomes constant at about 110° [45 lb. per sq. inch], all time intervals were started from the moment of attainment of the temperature.

The amyloses were obtained according to the directions of Taylor and Beckmann;[17] 300 g. of corn starch was ground in a porcelain ball mill with 3900 g. of quartz balls for one hundred and sixty-eight hours. The starch was dispersed in water and the components separated by electrophoresis. The β-amylose was obtained by concentrating the clear supernatant solutions under reduced pressure and then precipitating the carbohydrate with alcohol. The α-amylose was considered free of β-amylose when two successive dispersions in fresh water yielded supernatant liquids which no longer gave a blue color with iodine. It was dried by heating in a vacuum oven at 60° until it contained about 11% moisture (see V) [about equilibrium moisture for starch in air during winter].

II. Rate of Hydrolysis of Whole Corn Starch and Corn β-Amylose.—Since any synthesis of gentiobiose from glucose would depend obviously on the amount of glucose present, it was thought advisable to make a preliminary study of the rate of hydrolysis of whole starch and β-amylose, both of which produce glucose. The change was followed by a fall in specific rotation during treatment at 141° with the hydrochloric acid.

3.440 grams of carbohydrate and 10 cc. of 0.06 molar hydrochloric acid were sealed in heavy-walled Pyrex test-tubes and placed in a glycerin bath. The latter was then heated so that it took thirteen minutes to reach 110°, fifteen minutes more to reach 141°, where it was kept constant. At the stated intervals after the attainment of 110°, samples were removed and chilled in cold water to stop the reaction. The solutions were filtered and diluted to about 50 cc. Rotations were obtained in a 2-dm. tube with the green mercury line $\lambda = 5461$ Å. They were converted to the sodium D line by multiplying by the factor[18] 0.849. The weight of the dissolved material was determined by evaporating 10-cc. portions to dryness on ignited sand and drying for three hours at 110°.

The results of these experiments are given in Table I.

TABLE I

THE RATE OF HYDROLYSIS OF WHOLE STARCH AND β-AMYLOSE

Time in minutes after reaching 110°	Whole starch $[\alpha]_D^{25}$	β-Amylose $[\alpha]_D^{25}$
10	151	147
	149	149
15	120	104
20	69.0	63.1
	76.0	70.1

The nearer the specific rotation of these solutions approaches an $[\alpha]_D^{25}$ of 52.5°, the greater is the glucose content.[3,19] Apparently the concentration of glucose during most of the reaction is greater for β-amylose than for whole starch.

Later experiments on a larger scale show that at the end of a thirty-minute period the glucose content of a hydrolyzed β-amylose and whole starch solution are practically identical, the $[\alpha]_D^{25}$ being approximately

[17] Taylor and Beckmann, THIS JOURNAL, **51**, 294 (1929).

[18] Taylor and Walton, *ibid.*, **51**, 3431 (1929).

[19] Nanji and Beazeley, *J. Soc. Chem. Ind.*, **45**, 215T (1926).

62°. By extending the treatment to forty-five minutes other factors enter such as destruction of the glucose, etc.

III. **Treatment of Corn α-Amylose, β-Amylose and Glucose with 0.06 Molar Hydrochloric Acid.**—It is obvious from the results given under II that whole corn starch hydrolyzes less readily than the corn β-amylose. As previously mentioned,[14,15] whole starch has in it 85% of β-amylose and 15% insoluble fatty acid containing α-amylose. The experiments in this part were designed to find out the condition of affairs in the solution after corn α-amylose by itself is treated as under II for thirty minutes. In order to cover all conditions, corn β-amylose admixed with the fatty acids in kind and amount found in the given weight of α-amylose were treated also. Finally, glucose was similarly treated. This was done because these impurities are reputed to cause side reactions, possibly condensations. In the latter two instances the concentrations of β-amylose and glucose were taken equivalent both to the amount of α-amylose and of β-amylose as it occurs in the whole starch used in experiments under part II.

The time was again measured from the moment the bath reached 110°. Data from these experiments are found in Table II.

TABLE II

SPECIFIC ROTATION OF SOLUTION OF AMYLOSE AND GLUCOSE AFTER THIRTY MINUTE TREATMENT WITH 0.06 MOLAR HYDROCHLORIC ACID

Expt.	Material	Ref.	Concn. equiv. to	$[\alpha]_D^{25}$
1	α-Amylose	*a*	15% starch	49.4
2	α-Amylose		15% starch	50.6
3	α-Amylose	*b*	15% starch	47.4
4	β-Amylose	*c*	15% starch	60.6
5	β-Amylose		15% starch	59.5
6	Glucose	*d*	15% starch	61.2
7	Glucose		15% starch	56.7
8	β-Amylose	*e*	85% starch	61.4
9	β-Amylose		85% starch	61.1
10	Glucose	*f*	85% starch	59.6
11	Glucose		85% starch	58.6

References: (*a*) 0.52 g. in 10 cc., (*b*) 12.9 g. + 250 cc. in autoclave, (*c*) 0.26 g. in 5 cc. + 8 mg. of mixed fatty acids, (*d*) 0.26 g. glucose + 5 cc. acid + 8 mg. fatty acid, (*e*) 1.46 g. + 5 cc. acid + 8 mg. fatty acid, (*f*) 1.46 g. glucose + 5 cc. acid + 8 mg. fatty acid. The fatty acids were added to the material in a chloroform solution and the solvent evaporated.

The intermediate scission products occurring in the hydrolysis of β-amylose have specific rotations greater than equilibrium glucose. This has been noted also for whole starch (see II). However, corn α-amylose when hydrolyzed by itself free from the large amount of β-amylose that accompanies it in whole corn starch gives a solution of distinctly lower

specific rotation than glucose when the hydrolysis has reached the thirty-minute mark.

Gentiobiose has an $[\alpha]_D^{25}$ of 9.8° at equilibrium and this disaccharide is found in hydrolyzed whole corn starch solutions;[4] therefore, the low specific rotation of the hydrolyzed α-amylose solution above is due probably to the presence of this sugar. Further, although the amounts are small, the solutions from all the hydrolyses of the corn α-amylose were combined and heated with phenylhydrazine and acetic acid for one and one-half hours on a water-bath. The glucosazone formed was filtered off and the filtrate cooled. A small amount of yellow crystals, needles, separated and after recrystallization twice from hot water they had a m. p. of 170–172°, softening at 168°; reported for gentiobiosazone, 168–170° (Georg and Pictet),[10] 179–181° (Berlin).[9]

There is, therefore, strong presumptive evidence that the gentiobiose found here has its origin in the corn α-amylose and is a direct scission product of part of that material.

IV. **Condensation of Glucose to Gentiobiose.**—In order to obtain larger amounts of material so that attempts could be made actually to isolate gentiobiose as its octaacetate if it were present, an autoclave capable of taking a 500-cc. porcelain beaker was employed. Here again the concentration was fixed so that the commercial runs could be simulated. In the hydrolysis of a given weight of starch to glucose there is an 11% increase in weight of solids due to the addition of water. Since the moisture content of the starch and its amyloses is about 10%, it is sufficiently precise for this work to consider equal weights of glucose, starch and the components as equivalent weights. Accordingly 172 g. of glucose in 500 cc. of 0.06 molar hydrochloric acid was heated for stated periods, the temperature being followed by a thermometer in a glass-covered well projecting into the solution and by the steam gage on the cover of the autoclave.

To obtain the steam for heating the charge, water (150 cc.) was placed in the bottom of the autoclave, which was heated with a Méker burner. The rate of heating was such that thirteen minutes were required to obtain a gage reading of 45 pounds. The temperature of the reaction mixture was then about 110°. This is the point as mentioned previously from which all reaction periods were timed. The burner was then regulated so that the pressure remained constant. The temperature continued to rise and reached its constant value of 141° in fifteen minutes. To stop the reaction the pressure was released through the safety valve, the beaker and its contents removed and the solution made neutral to methyl orange with sodium carbonate, cooled and diluted with water to a liter. In order to get rid of the glucose, 50 g. of starch-free bakers' yeast was added with 25 cc. of yeast juice as nutriment and the whole allowed to ferment at 37° for three days. At this time no glucosazone was found in test portions of the solution, showing that glucose was for practical purposes absent. Following further an adaptation of Berlin[4] and Brauns[20] the procedure was as follows. The

[20] Brauns, THIS JOURNAL, 49, 3170 (1927).

solution was boiled, cooled to room temperature, neutralized with saturated barium hydroxide solution, filtered and simultaneously decolorized, by means of hot norite on a Büchner funnel. The residue was washed several times with hot water and the washings combined with the filtrate. This filtrate was evaporated *in vacuo* to a thick sirup and extracted under reflux for three hours with 600 cc. of absolute methyl alcohol. After standing overnight the alcoholic solution was filtered from the small amount of precipitate, the latter washed with absolute methyl alcohol and the combined washings and filtrate evaporated *in vacuo* to a sirup. The latter was acetylated by heating on a water-bath with six times its weight of acetic anhydride and one-half its weight of fused sodium acetate. When solution was complete, the reaction mixture was heated for an hour, then let stand overnight at room temperature, and subsequently poured into three liters of ice water. The insoluble residue, after washing in the beaker with fresh water to remove as much of the acetic acid as possible, was stirred with cold absolute methyl alcohol. The gentiobiose octaacetate remained undissolved. After standing in the cold for several days it was filtered and recrystallized from absolute methyl alcohol. One recrystallization was usually sufficient to yield a product of the correct melting point and mixed melting point with a sample from gentian root. β-Gentiobiose octaacetate of highest purity melts at 195–196°.[9,21] The samples isolated melted over one degree ranges in the interval 190–194.5°, most of them 192.5–193.5°. Mixed melting points never differed by more than one degree. The alcoholic solutions from which the crystals were separated were subsequently worked up according to Berlin's method for isolating the acetate from the crude acetylated non-fermentable residues. These solutions were evaporated to dryness and the residue taken up in ether. The resulting solution was washed with water until neutral, then with 3% sodium bicarbonate solution and finally with water until neutral again. The ether was evaporated, the residue dissolved in absolute methyl alcohol and seeded. No more than traces of the acetate, however, were ever isolated by this further treatment.

The results of these experiments are given in Table III.

TABLE III

CONDENSATION OF GLUCOSE TO GENTIOBIOSE WITH 0.06 MOLAR HYDROCHLORIC ACID

Time of treatment in mins.	Yield of gentiobiose octaacetate in grams	Yield of gentiobiose in grams
30	2.24	1.12
30	1.77	0.89
45	1.70	.85
45	1.33	.67

It is evident that glucose in the presence of dilute acid and at high temperatures (141°) condenses to give some gentiobiose. It must be borne in mind, however, that this gentiobiose is only a small part, 10–15%, of the entire non-fermentable residue. When, for example, an acetylated sirup after the removal of the gentiobiose octaacetate is saponified with aqueous barium hydroxide and the barium ion removed quantitatively as barium sulfate, the resulting solution has an $[\alpha]_D^{25}$ of 76.6°. This value is close to that frequently reported for Fischer's isomaltose, (v. Friedrich +72.8,[7] Ost +70,[22] Harrison +84.1°[12]) though Georg and Pictet[10] report a higher value +98.5°. The latter assume that the lower rotations are due

[21] Zemplén, *Z. physiol. Chem.*, **85**, 399 (1913).

[22] Ost, *Chem.-Ztg.*, **20**, 762 (1896).

to contamination with gentiobiose $[\alpha]_D^{25}$ +9.8°. The condensation of glucose to gentiobiose takes place apparently when there is a large amount of glucose present.

V. Treatment of Gentiobiose with 0.06 Molar Hydrochloric Acid.—That gentiobiose itself in the absence of glucose is hydrolyzed to glucose is shown in the following experiments. Weighed amounts of gentiobiose were added to the requisite amount of 0.06 molar hydrochloric acid and the mixture placed in Pyrex tubes which were sealed and heated for specified periods as under (II). Since the low rotations of these solutions made polarimetric observations of slight value, the course of the reaction was followed by titrating the carbohydrates by the Willstätter–Schudel method.[23] Five cc. of the neutral solutions were treated with excess $N/20$ iodine and double this volume of $N/20$ sodium hydroxide was then slowly added. The solutions were kept in the dark for twenty minutes, acidified with N hydrochloric acid and the liberated iodine titrated with $N/40$ sodium thiosulfate. The iodine is a measure of the glucose and gentiobiose present, according to the reaction $RCHO + I_2 + 3NaOH = RCOONa + 2NaI + 2H_2O$. One mole of gentiobiose yields two moles of glucose. Hence the percentage hydrolysis can be calculated by the equation, $\% (R_1 - R_0)/R_0 \times 100$ where R_0 = cc. of iodine required by the unheated solution and R_1 = cc. required after heating for a specified time. The results are given in Table IV.

TABLE IV

HYDROLYSIS OF GENTIOBIOSE IN 0.06 MOLAR HYDROCHLORIC ACID

Time in minutes after reaching 110°	Concentration of gentiobiose per 100 cc. 0.230 g.	0.306 g.	0.942 g.
0	1.66%	1.88%	...
15	53.3%	65.6%	80.90%
30	100 + (decomp.)	100 + (decomp.)	100 + (decomp.)

The minimum concentration of gentiobiose used corresponds to about the maximum isolated from the hydrolytic liquors. The values in excess of 100% hydrolysis show that decomposition, with the formation of more reducing substances, had occurred. In fact, these solutions were discolored. All values may also be slightly high due to over-oxidation[24] by the alkaline iodine.

We have seen that corn β-amylose upon hydrolysis (see II) under the conditions set forth gives according to the specific rotatory value of the solution the highest concentration of glucose early in the treatment. This condition ought to be conducive, in the light of experiments under III, to the maximum yield of gentiobiose via the synthetic route.

[23] (a) Willstätter and Schudel, *Ber.*, **51**, 780 (1918); (b) Goebel, *J. Biol. Chem.*, **72**, 801 (1927).

[24] Kline and Acree, *U. S. Bur. Standards J. Research*, **5**, 1063 (1930).

Whole corn starch which gives less glucose (see II) early in the treatment, again according to the specific rotation, would be expected to be a less fertile source of gentiobiose by synthesis.

VI. **Hydrolytic Liquors of Whole Corn Starch and its Amyloses.**—In these experiments the autoclave was used as in (IV) and large samples (172 g.) were used in order to isolate if possible the gentiobiose itself. Since it took over a year to collect sufficient β-free α-amylose the experiment could not be duplicated and unfortunately only one period of treatment could be tried.

The results of these runs show that whole corn starch after thirty minutes' treatment in the 0.06 molar hydrochloric acid will give a solution with an $[\alpha]_D^{25}$ of 62° from which 0.52 g. of gentiobiose may be isolated through the fermentation and acetylation procedure (see IV). A duplicate run gave 0.53 g. of gentiobiose. New samples treated for forty-five minutes gave solutions with an $[\alpha]_D^{25}$ of 58.2° and yielded 0.70 and 0.62 g. of gentiobiose, respectively.

β-Amylose after twenty minutes gave a solution with $[\alpha]_D^{25}$ of 67.7° and no gentiobiose, while three runs for a thirty-minute period gave solutions whose $[\alpha]_D^{25}$ ranged between 61.4 and 68° but yielded no gentiobiose. Duplicate runs for forty-five minutes gave solutions with an $[\alpha]_D^{25}$ of 56.4 and 57.8°, respectively, and no gentiobiose.

The only difference between whole corn starch and β-amylose is the 15% α-amylose.

A thirty-minute treatment of corn α-amylose showed that its hydrolysis when not dispersed in the β-amylose as when present in whole corn starch is slow, for the $[\alpha]_D^{25}$ of the solution is still 89.4° at the end of thirty minutes. Apparently scission of the amylose had taken place to give relatively large units of the dextrin type, for no gentiobiose could be isolated. The treatment of corn α-amylose for a longer time is to be tried in the near future.

Although it is true that glucose will condense under these experimental conditions to give gentiobiose, yet the β-amylose which gives glucose in high concentration early in the treatment gives no gentiobiose. On the other hand, the slow hydrolyzing material such as the α-amylose in whole starch or the α-amylose itself gives the most gentiobiose. It seems then that when whole corn starch is hydrolyzed under three atmospheres' pressure with dilute hydrochloric acid, the major portion if not all of the gentiobiose formed comes directly by scission of the α-amylose rather than through condensation of the glucose. The implications are interesting in connection with the make-up of corn α-amylose for they point to the presence of a polysaccharide composed of gentiobiose units instead of maltose units in this fraction of corn starch.

Acknowledgment.—The authors wish to thank the Fleischmann

Yeast Company for generously supplying starch-free yeast and the Bureau of Standards for a sample of gentiobiose octaacetate.

Summary

1. Glucose in 0.06 molar hydrochloric acid under three atmospheres' pressure condenses to give in thirty minutes about 1.5% gentiobiose.

2. Whole corn starch under the same conditions give some gentiobiose.

3. Corn β-amylose which constitutes 85% of the starch gives no gentiobiose.

4. Corn α-amylose gives under the same hydrolytic conditions a solution of low specific rotation from which gentiobiose osazone has been isolated.

5. The gentiobiose found in solution from the hydrolysis of corn starch under the stated conditions seems to come from the direct scission of a polysaccharide in the insoluble α-amylose fraction of corn starch rather than from condensation of glucose.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

THE SYNTHESIS OF THYMOL, CHLOROTHYMOL AND HOMOLOGS OF THYMOL BY THE INTRAMOLECULAR REARRANGEMENT OF META-CRESYL ETHERS

BY JOSEPH B. NIEDERL AND SAMUEL NATELSON

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Theoretical Part

The syntheses of thymol may be divided into two general classes; those which begin with benzene hydrocarbons as the starting point and those which start with *m*-cresol, condensing this phenol with acetone, isopropyl alcohol or propylene. The first class may be still further divided into those which start from *p*-cymene and those which begin with benzene itself.

Béhal and Tiffeneau[1] were the first to synthesize thymol starting with *p*-cymene. Since then a number of syntheses have appeared with this substance as the starting material. These methods depend upon the occupying of the position ortho to the methyl group with an amino group and then sulfonating. Finally the amino group is replaced by hydrogen and the sulfonic acid group by hydroxyl.[2] Austerweil and Lemray[3] have synthesized thymol starting from benzene using the standard methods.

[1] Béhal and Tiffeneau, *Bull. soc. chim.*, [4] **3**, 729 (1908).

[2] Andrews, U. S. Patent 1,306,512 (1919); Philips, *ibid.*, 1,332,680 (1920); Austerweil, British Patent 221,226 (1923); Bert and Dover, *Compt. rend.*, **182**, 634 (1926).

[3] Austerweil and Lemray, *Bull. soc. chim.*, **41**, 454 (1927).