The action of hydroxylamine upon furmaric nitrile has been studied and we have prepared the diamidoxime of fumaric acid. Its properties are described.

ST. LOUIS, MO.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

THE OXIDATION OF MALTOSE IN ALKALINE SOLUTION BY HYDROGEN PEROXIDE AND BY AIR.

THE PREPARATION AND STUDY OF MALTOBIONIC ACID.

BY J. W. E. GLATTFELD AND MILTON T. HANKE.[1]

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The work reported in this paper was begun under the direction of the late Dr. Nef and was part of the program laid out by him for solving the problem of the mechanism of the oxidation of sugars in alkaline solution. His theory of this mechanism has already been published[2] and consists, in part, of the assumptions that 1,2-, 2,3- and 3,4-di-enols, *i. e.*, $CH_2OH - CHOH - CHOH - COH = COH - CH_2OH$ (2,3-di-enol), are formed from the ordinary hexoses under these conditions, and that these di-enols later break at the double bonds giving rise to methylene-enols which undergo oxidation to produce acids. To ascertain whether the same theory, which has proved adequate for the ordinary hexoses, also applies to oxidation of the disaccharides, the oxidation of maltose here reported, was undertaken. The results are in complete harmony with the theory as far as it was possible for us to determine. That is, the presence of the oxidation products here reported can be explained by assuming that the "free" glucose unit of maltose is first enolized and the enols, after breaking, either become oxidized at once or undergo certain rearrangements with or without subsequent oxidation. An unexpected development was the discovery that a C_4-saccharinic acid was present in the oxidation mixture in the case of the oxidation with air. Up to the time of the work here reported only aldonic acids, *i. e.*, acids obtained by oxidizing the aldehyde group of aldo-monosaccharides directly to the carboxyl group, had been found in the reaction mixtures obtained in the oxidation experiments with the sugars in alkaline solutions. Although unexpected, the presence of a saccharinic acid is not unexplainable. It is well known that saccharinic acids are formed by the action of alkalies on sugars in the absence of an oxidizing agent.[3] It is therefore, quite conceivable that such acids should be formed during the oxida-

[1] The dissertation, of which this paper is a condensation, was presented by Milton T. Hanke as part fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[2] *Am. Chem. J.*, **50**, 137 (1913).

[3] *Ann.*, **376**, 1–120 (1910).

tion of a sugar in alkaline solution with such a mild oxidizing agent as air, when this oxidation requires 2 days for completion.

In 1914 a paper was published by Lewis and Buckborough[1] on the subject of the oxidation of maltose in alkaline solution with hydrogen peroxide. Our results are in only partial harmony with those of these authors. Their results show that the main oxidation product is glucosido-glycollic acid, while in the experiments here reported it was not possible to prove the presence of glucosido-glycollic acid. Glycollic acid was found as an oxidation product in both experiments, however, in the simple-acid fraction. From the results of the following experiments, it does not seem justifiable, therefore, to draw a final conclusion as to the structure of maltose. Much more work is necessary to show, first of all, exactly what the complete list of oxidation products of the maltose under these conditions is.

In order to get a clue as to the reason for the discrepancy between our results and those of Lewis and Buckborough, several experiments were carried out which showed that such factors as duration of oxidation and method of removing the excess hydrogen peroxide, greatly affect the results. Thus there was a decided decrease in the rotation when the glucosido acids, separated, by methods described in this paper, from the simple acids, were allowed to stand for one month with alkali and hydrogen peroxide. Furthermore, in every oxidation experiment with maltose and hydrogen peroxide, the reducing sugar had almost entirely disappeared at the end of 24 hours as shown by tests with Fehling's solution. The small amount of the remaining sugar then disappeared very slowly, so that a total of from 12 to 13 days was required to give a solution that would no longer reduce Fehling's solution.

In one set of experiments the oxidation mixtures were allowed to stand for 16 days before distillation was begun; about 16 g. of simple acids were obtained in this case. In another set of experiments the oxidation mixture stood for 13 days; approximately 13 g. of simple acids were obtained. In still another set of experiments, the oxidation mixtures stood for 21 days; approximately 20 g. of simple acids were obtained. It would seem, then, that if the oxidation were stopped at the end of 24 hours, practically no simple acids will have been formed, and the oxidation products should consist almost entirely of glucosido acids. Work, which, it is hoped, will prove or disprove this conclusion will be carried out by one of us in the future.

I. MALTOSE AND HYDROGEN PEROXIDE.

1. Experimental Procedure.

When maltose, which consists essentially of 2 *d*-glucose units, is oxidized under the conditions which pertained in these experiments, 2 classes

[1] THIS JOURNAL, 36, 2385 (1914).

of acid oxidation products may be formed. One class consists of acids which still contain *d*-glucose units and which are called glucosido acids; the other class consists of acids which do not contain *d*-glucose units and which we shall call "simple" acids. Both glucosido- and simple acids were produced in these experiments. The first step, therefore, in the separation of the products formed, was to effect a separationin to glucosido and simple acid fractions. The next step was to effect the hydrolysis of the glucosido acids and to study the products of this hydrolysis. The final step was to separate the simple acids originally present in the oxidation mixture from each other as completely as possible.

The experimental procedure was as follows: Maltose hydrate 51.52 g., melting interval 114–130°, $[\alpha]_D^{20} = +133.4°$, was dissolved in 1280 cc. of 3% hydrogen peroxide. To this cold solution, which was vigorously shaken during the addition, was added 9 equivalents—80.7 g. of 89.2%—potassium hydroxide, dissolved in 1500 cc. of water. Enough additional water was then added to bring the total volume of the solution up to 3200 cc. The solution was allowed to stand at room temperature. The larger part of the sugar disappeared within 48 hours; but the solution was allowed to stand until it no longer had the power of reducing Fehling's solution. At the end of 13 days, the mixture was still strongly alkaline and gave an unmistakable test for hydrogen peroxide but no test for sugar. This procedure was followed in each of 3 simultaneous experiments.

The solution was then subjected to distillation under reduced pressure. Distillation was allowed to proceed at 50° until the volume of the solution was about 800 cc. This procedure removed the hydrogen peroxide completely. Hydrochloric acid —250 cc. of 5.606 *N* strength was added. The solution was again subjected to distillation and the distillate preserved. When potassium chloride began to crystallize out, distillation was interrupted and the work of determining the nature of the acids present begun.

2. The Products of Oxidation.

Formic Acid Determination.—Formic acid has usually been determined in experiments of this nature in this laboratory by a method in which the acidified oxidation liquid is subjected to complete distillation in vacuum, the distillate condensed, collected, measured and titrated with 0.1 *N* potassium hydroxide. This method is not absolutely accurate owing to loss of formic acid during the vacuum distillation. It was therefore modified as follows:

The solution was acidified and subjected to distillation in vacuum. To the end of the condenser was fitted an adapter which dipped below the surface of a measured quantity of an approximately normal solution of potassium hydroxide. After the distillation had proceeded as nearly to completion as possible, water was added to the contents of the distilling

flask and distillation carried on to completion. The second distillate was collected in the same potassium hydroxide as the first. This process was repeated until the contents of the distilling flask no longer had a sharp acid odor. The volume of the solution in the receiver was then measured, and aliquot portions titrated with acid, and for chloride. In this way it was determined that the total amount of formic acid from 100 g. of maltose hydrate was 43.30 g.

Separation of Non-volatile Acids from Potassium Chloride.—The residue in the distilling flask was dissolved in the smallest possible quantity of water. Alcohol was then added in portions until, instead of granular potassium chloride, a slight sticky precipitate of glucosido acids appeared. The potassium chloride was collected on a suction filter and washed with 50% alcohol.

Three simultaneous experiments were carried out in this way in order to provide enough material.

Resolution of Non-volatile Acids.—The alcoholic filtrates and washings from the potassium chloride from the 3 experiments, were united and subjected to complete distillation *in vacuo*. A stiff gum was left in the flask. When this gum was dissolved in its own weight of water, and 10 times its weight of absolute alcohol was added, a copious precipitate was obtained. The aqueous alcohol was removed from the precipitate by decantation, and the precipitate was washed with absolute alcohol by decantation. This very insoluble gum, which was unquestionably glucosido acid in character, was set aside and will be referred to as the C gum.

The alcoholic mother liquor and washings from the C gum were united and subjected to distillation *in vacuo*. When the gum left in the flask was again treated according to the above procedure with water and alcohol, more soluble C gum was obtained and added to the first lot. After the combined mother liquors and washings had been subjected to distillation *in vacuo*, the gum left behind was extracted with boiling absolute alcohol and thus a third residue of C gum was obtained. In all, 47 g. of C gum, which contained some potassium chloride, was obtained.

The hot absolute alcohol extract deposited, on cooling, an apparently crystalline substance which was separated by filtration and which weighed 10.08 g. Attempts to prepare a crystalline brucine salt[1] and a crystalline

[1] To prepare brucine salts, the following procedure was invariably followed: The acid, whose brucine salt was to be prepared, was dissolved in water and treated with slightly more than the theoretical quantity of brucine, usually calculated on the basis of a titration. The mixture was heated on the boiling water bath until the brucine had dissolved and then for one hour longer. At the end of the hour, the solution was cooled and extracted 5 times with benzene to remove the excess brucine. The aqueous solution was then subjected to complete distillation *in vacuo* at 50 to 60°, and the residue, referred to in this paper as the "crude brucine salt" was recrystallized from the proper solvent.

phenylhydrazid[1] of portions of this solid by the usual methods failed. Gums were obtained. A small portion of the solid was lost in these studies.

The mother liquor and washings from this 10.08 g. of solid, left, after distillation *in vacuo*, a gum which weighed 39.25 g. This gum was subjected to repeated alternate treatments with absolute alcohol and ethyl acetate. The ethyl acetate-soluble fractions were united. The ethyl acetate-insoluble fractions were added to the 10.08 g. of solid.

The non-volatile acid gum from the oxidation of 154.56 g. of maltose hydrate was thus divided into 3 fractions. A very insoluble glucosido acid gum called the C gum—47 g.—which was undoubtedly free from simple acids; a more soluble gum partly glucosido acid and partly simple acid—total 31.75 g.—which we shall call the B gum and which consisted of what remained of the solid, together with the ethyl acetate-insoluble gum; and a simple acid fraction soluble in ethyl acetate—11.3 g.—which we shall call the A gum.

Some experiments had been carried out in this laboratory which showed that certain acids produced insoluble basic lead salts when their water solutions are treated with a basic lead acetate solution, while other acids produce, under these conditions, soluble basic lead salts. These experiments suggested the use of basic lead acetate in effecting separations of acids such as were attempted in the work reported in this paper.

A concentrated aqueous solution of the C gum made by dissolving the 47 g. of gum in a small amount of cold water, was poured into a solution of basic lead acetate prepared by making a suspension in water of 90 g. of crystalline lead acetate and 72 g. of lead oxide, and heating the mixture until a clear solution was produced. A very heavy precipitate of basic lead salts was produced. The solution was promptly filtered and the insoluble salt washed with a large volume of water. The filtrates gave no further precipitate when treated with a fresh portion of basic lead acetate solution. The precipitated basic lead salts were suspended in water and treated with hydrogen sulfide to precipitate the lead. After having been filtered, the solution was subjected to distillation at reduced

[1] The method of preparing phenylhydrazids used by us was as follows: The acid gum, dissolved in one to two parts of absolute alcohol, was treated with a quantity of phenylhydrazine equal in volume to the amount of alcohol used. The mixture was shaken or stirred until it was homogeneous and then allowed to stand for from 1 to 24 hours according to the rapidity of the hydrazid formation. Alcohol was then added in quantities just large enough to render the mass fluid enough to be transferred to a filter, upon which the crystals were washed with small amounts of absolute alcohol and then with ether until they were white. The mother liquor and washings were subjected to complete distillation *in vacuo* at 40°. The residue was dissolved in water and this solution extracted with ether until the ether was no longer colored. The aqueous solution was then subjected to complete distillation *in vacuo* at 40° and the residue dissolved in from one to two parts of hot absolute alcohol from which a second crop of phenylhydrazid was usually deposited on cooling.

pressure to remove the hydrogen sulfide. When this had been accomplished, distillation was interrupted and the solution treated with a suspension of freshly precipitated silver carbonate to remove the hydrogen chloride. The precipitated silver chloride was separated by filtration and the filtrate was again treated with hydrogen sulfide to remove the slight excess of silver. The filtrate and washings from the silver sulfide were subjected to complete distillation. The gum so obtained was united with a similar gum obtained from the insoluble lead salts of the B gum (see below).

The filtrate and washings from the insoluble basic lead salts from the C gum were similarly treated with hydrogen sulfide, etc., to remove the lead and hydrogen chloride. The gum finally obtained, was united with a similar gum obtained from the soluble basic lead salts from the B gum (see below).

The B gum weighed 31.75 g. It was dissolved in water and subjected to exactly the same basic lead acetate treatment as the C gum. The gums from the insoluble and soluble basic lead salts in this case seemed to be identical with the corresponding gums from the C fraction and were therefore united with those. This gave a total of 30.3 g. of gum from the insoluble basic lead salts with $[\alpha]_D^{20} + 92.52°$ and from the soluble basic lead salts, a gum which, when freed from potassium chloride, weighed 33.3 g. with $[\alpha]_D^{20} + 69.78°$.

These gums still contained some simple acids and these were removed by treating the gums with a small amount of hot absolute alcohol, precipitating most of the glucosido acids from the cold alcoholic solution with ethyl acetate, recovering the gum soluble in the alcohol-ethyl acetate mixture and extracting it repeatedly with hot ethyl acetate. There was thus removed 8.28 g. of ethyl acetate-soluble gum. This was added to the A gum which then totalled 19.5 g. with $[\alpha]_D^{20} -18.2°$. For the treatment of this gum see "The Simple Acids." The glucosido acid gum from the insoluble basic lead salt now weighed 27.2 g. with $[\alpha]_D^{20} +95.4°$ and that from the soluble basic lead salt weighed 28.3 g. with $[\alpha]_D^{20} +77.75°$. The rotations were made in 5% solutions.

The Glucosido Acids.—The gum from the insoluble basic lead salts was hydrolyzed by treatment with 130 cc. of 0.4 *N* sulfuric acid and heating for 25 hours on the boiling water bath. The sulfuric acid was quantitatively removed from the solution with barium hydroxide and the aqueous filtrate from the barium sulfate was heated at 60° for 21 hours with 6 g. of calcium carbonate. The aqueous filtrate and washings from the undissolved calcium carbonate were subjected to complete distillation *in vacuo*. The residue was dissolved in one-half its weight of water. The calcium salts were precipitated with 5 parts of absolute alcohol and washed with aqueous alcohol by decantation. To free the precipitated

calcium salts completely from sugar, they were again dissolved in water and again precipitated and washed with alcohol. They were now transferred to a porcelain mortar by means of small amounts of hot water and enough alcohol was added to the cooled solution to precipitate them completely. The mixture of gummy salts and mother liquor was triturated until the gummy salts were transformed into a crystalline powder, which was separated by filtration, washed first with alcohol and then with ether, and finally dried *in vacuo*. The dry salts weighed 9.9 g. All the mother liquors and washings from these calcium salts were now united and subjected to complete distillation. A residue which weighed 17.5 g. and which contained the sugar produced by the hydrolysis of the glucosido acids, was thus obtained.

The gum from the soluble basic lead salts was hydrolyzed by treatment with 140 cc. 0.4 *N* sulfuric acid and heating for 25 hours on the boiling water bath. The solution was subjected to the treatment described in the preceding paragraph. There was thus obtained 11.28 g. of vacuum-dried calcium salt and 19.9 g. of crude sugar gum. The latter was added to the 17.5 g. of crude sugar gum mentioned in the preceding paragraph. This gave a total of 37.4 g. of crude sugar gum from the glucosido acids. The 2 lots of calcium salts were treated separately.

The Sugar Fraction.—The gum was dissolved in water and the solution decolorized with animal charcoal in the cold. The clear filtrate was subjected to complete distillation and yielded a nearly colorless gum. In order to free this gum from calcium salts, it was dissolved in an equal quantity of water and treated with 10 times this quantity of absolute alcohol. This treatment precipitated a gum which weighed 5 g. This gum was again taken up in water and precipitated with alcohol as before. In this way there was obtained 4.1 g. of insoluble material which, after the removal of 0.22 g. of crude *d*-arabonic phenylhydrazid, m. p. 205°, was proved by titration with Fehling's solution, to contain 1.47 g. of *d*-glucose.

The alcohol-soluble gum was recovered and subjected to a series of crystallizations in which one part by weight of water and 10 parts by weight of absolute alcohol were used. In this way, 15.60 g. of pure crystalline *d*-glucose was obtained, m. p. 149°, $[\alpha]_D^{20}$ +50.25°.

The remaining gum was oxidized in water solution by means of bromine and the acids thus formed converted into calcium salts. The crude calcium salts obtained as a residue by the distillation of the water, were recrystallized from a mixture of an equal part of water and 6 parts of 95% alcohol. This yielded 14.5 g. of salt which is proved by the following experimental data to have been calcium *d*-gluconate:

Calc. for $(C_6H_{11}O_7)_2Ca$: CaO, 13.03. Found: 13.14.

Reported for calcium gluconate: $[\alpha]_D^{20}$ +10.50°.[1] Found: +9.75°.

[1] *Ann.*, **357**, 270 (1907).

The 14.15 g. of calcium salt is equivalent to 11.76 g. of *d*-glucose.

Of the 37.40 g. of crude sugar gum, therefore, a total of 28.83 g. were proved to have been *d*-glucose.

The Calcium Salt from the Insoluble Lead Salt Fraction.—This salt weighed 9.9 g. It was treated with the theoretical amount of oxalic acid based on an analysis for calcium oxide. The gum thus obtained weighed 7.36 g. It was treated with 800 cc. of acetone, in which 7.04 g. of gum, with $[\alpha]_D^{20}$ +7.1°, dissolved. This gum was dissolved in 14 cc. of absolute alcohol and treated with 7 cc. of phenylhydrazine. The phenylhydrazid thus formed was separated from the mother liquor by filtration and washed with absolute alcohol until pale yellow. It weighed, after having been dried in vacuum, 3.80 g. and had a melting interval of 190–194°. This phenylhydrazid was obtained from several gums discussed later and their further treatment will be found under "High Melting Phenylhydrazids" (see below).

The mother liquor and washings from the 3.80 g. of crystalline phenylhydrazid just mentioned, were subjected to complete distillation. The gum obtained was dissolved in water and the water solution was extracted with ether to remove the excess of phenylhydrazine. The gum obtained from the water solution weighed 7.46 g. It was resolved by crystallization from alcohol-ethyl acetate and alcohol-acetone mixtures into 0.15 g. of phenylhydrazid, m. p. 185–200°, which was added to the "High Melting Phenylhydrazids" (see below) and a mother liquor which is discussed under the title "The Soluble Phenylhydrazids" (see below).

The Calcium Salt from the Soluble Lead Salt Fraction.—This salt weighed 11.28 g. It was treated as the calcium salt from the insoluble lead salt had been treated. The gum obtained had $[\alpha]_D^{20}$ —16.30°. It yielded a phenylhydrazid with a melting interval of 160–185°, which weighed 3.34 g. and which was added to the "High Melting Phenylhydrazids" (see below). The mother liquor from this hydrazid was added to the "Soluble Phenylhydrazid" (see below).

The High Melting Phenylhydrazids; *d*-Arabonic Phenylhydrazid.—These weighed 7.29 g. They were recrystallized from 450 cc. of 95% alcohol. The crop of crystals weighed 4.46 g. and had a melting point of 214° $[\alpha]_D^{20}$ —14.00°, *i. e.*, 0.4000 g. dissolved in water and the solution made up to 20 cc. gave α in a 1 dcm. tube —0.28°. The recorded[1] constants for *d*-arabonic phenylhydrazid are m. p. 214°; $[\alpha]_D^{20}$ —13.90°. This phenylhydrazid was mixed with some pure *d*-arabonic phenylhydrazid. The melting point of the mixture was 214°. There can be no doubt, therefore, that the 4.46 g. of substance under consideration was *d*-arabonic phenylhydrazid.

Further attempts to obtain equally pure *d*-arabonic phenylhydrazid

[1] *Am. Chem. J.*, **50**, 144 (1913).

from the mother liquor were failures. Crystals of much lower melting point were obtained. The entire mother liquor from the 4.46 g. of substance was therefore added to "The Soluble Phenylhydrazids" fraction.

The Soluble Phenylhydrazids; *d*-Erythronic Lactone.—The weight of the crude hydrazid obtained by subjecting the combined solutions under this head, to complete distillation *in vacuo*, was 15.1 g. The crude gum obtained from it by hydrolysis with barium hydroxide[1] weighed 8.28 g., of which 7.2 g. was soluble in ethyl acetate. This gum was somewhat mobile and in 4% aqueous solution $[\alpha]_D^{20}$ —30.00°. To remove the *d*-erythronic acid, which, according to previous indications, was undoubtedly present in this gum, the brucine salts were crystallized from absolute alcohol. In this way 21 g. of salt was obtained, which had a melting interval of 195–205°. This salt was recrystallized from a mixture of one-half its weight of water and 5 times its weight of absolute alcohol. A total of 18.15 g. of a very insoluble salt was obtained in 2 crops, melting interval 205–210°. The material in the filtrates was not identified.

The crude gum obtained by the hydrolysis[2] of the 18.15 g. of brucine salts weighed 3.95 g., of which 3.70 g. was soluble in absolute alcohol. This gum crystallized to a solid mass in the course of a few hours. In

[1] The 15.1 g. of crude phenylhydrazid was dissolved in 15 cc. of water. Fifteen g. of crystalline barium hydroxide was then added to the solution and the whole covered with a layer of toluene. The flask containing the mixture was now provided with a reflux condenser and placed on the boiling water bath. The toluene layer removed the phenylhydrazine as fast as it was formed by hydrolysis. By the use of toluene the "smearing" and loss of material, that usually accompanied such hydrolyses, was entirely avoided. Scarcely any color was developed. This mixture was kept on the boiling water bath for seven hours, then cooled. The toluene was separated, and the water solution, much diluted, extracted 5 times with ether to remove the last traces of the phenylhydrazine. The solution was now heated to boiling again, and that amount of sulfuric acid added which was necessary to precipitate all but a trace of the barium present. The barium sulfate was separated by filtration and the clear filtrate and washings subjected to complete distillation *in vacuo*. There remained, after complete distillation, 8.28 g. of crude gum. This procedure was always followed in this work in hydrolyzing phenylhydrazids.

[2] The procedure followed in hydrolyzing brucine salts was as follows: The salts were dissolved in water (example, 50 g. salts in 1500 cc. of water) and the solution heated on the boiling water bath. About 1½ to 2 times the amount of crystalline barium hydroxide necessary to hydrolyze the brucine salts was then dissolved in water. The latter solution was also heated to boiling and added, in very small portions, to the hot brucine salt solution to which a few crystals of brucine had been added as seeds, and which was shaken vigorously during the addition. (If the barium hydroxide solution is added quite slowly, the brucine will be precipitated as a crystalline mass; if it is added too rapidly, the brucine will be precipitated as a gum, which later solidifies into balls.) When all the barium hydroxide had been added, the mixture was heated for half an hour on the boiling water bath, then cooled and allowed to stand for an hour. The brucine was then removed by filtration. The filtrate was extracted 5 times with benzol and the barium was removed with sulfuric acid.

4% aqueous solution $[\alpha]_D^{20}$ —54.10°. It was dissolved in a small amount of hot ethyl acetate. The solution was allowed to cool, whereupon it deposited 2.1 g. of *d*-erythronic lactone, m. p. 101–103°, and $[\alpha]_D^{20}$ —70.90°; *i. e.*, 0.4598 g. of these crystals dissolved in water and the solution made up to 20 cc. gave α in a 1 dcm. tube —1.63. This solution of 0.4598 g. of crystals was titrated with 0.1 *N* potassium hydroxide. Only 0.07 cc. of the alkali was needed to bring about the first change of color in the indicator, and a total of 39.4 cc. 0.1 *N* alkali was found to have been neutralized after the solution of the lactone had been allowed to stand for one hour with an excess of alkali. The amount of 0.1 *N* alkali theoretically necessary for 0.4598 g. of a C_4-aldonic acid lactone is 39.00 cc. The recorded constants[1] for *d*-erythronic lactone are m. p. 103°, and $[\alpha]_D^{20}$ —73°. There is, therefore, no doubt that the above 2.1 g. of crystals were *d*-erythronic lactone. The material in the mother liquors from the 2.1 g. of *d*-erythronic lactone was not identified.

The Simple Acids.—The simple acids obtained from the original oxidation gum weighed 19.5 g., $[\alpha]_D^{20}$ —18.2°. This gum was entirely consumed in obtaining methods for the separation of its constituents. The simple acids whose separation is discussed here, were obtained by identical methods as above described, from another experiment.

This simple acid fraction weighed 20.22 g. and $[\alpha]_D^{20}$ —22.97°. It was treated with 40 cc. of absolute alcohol and 20 cc. of phenylhydrazine. The first crop of crystals weighed 4.5 g. and melted, with some previous softening, at 180°. From the filtrate, a second lot of crystals was obtained which weighed 0.50 g., m. p. 200°. These two lots of crystals were united and are discussed under the heading "The Crystalline Phenylhydrazids" (see below). The combined mother liquor and washings yielded a residue which weighed 29 g. This residue is discussed under the heading, "The Non-crystalline Phenylhydrazids."

The Crystalline Phenylhydrazids; Oxalic and *d*-Arabonic Acid.—These were recrystallized from 95% alcohol and gave 3.12 g. of crystals which had a melting interval of 180–193°. The mother liquor was discarded.

The 3.12 g. of crystalline phenylhydrazids were dissolved in 10 cc. of water and hydrolyzed as usual with barium hydroxide. The barium was removed by means of sulfuric acid. In order to remove oxalic acid, the presence of which had been indicated, an excess of calcium carbonate was added to the solution and the mixture heated on the boiling water bath for 5 hours. The insoluble material was then separated from the solution by filtration and examined for calcium oxalate. It was alternately dissolved in dil. hydrochloric acid and precipitated with ammonia several times. There was thus obtained an insoluble salt, which weighed, after having been dried for one hour at 100°, 0.2143 g. This salt was

[1] Ruff, *Ber.*, 32, 3679–80 (1899).

ignited to constant weight and left a residue of 0.0820 g. of calcium oxide.

Calc. for $CaC_2O_4.H_2O$: CaO, 38.39. Found: 38.25.

Oxalic acid was therefore present in the oxidation mixture.

The filtrate from the mixture of calcium carbonate and calcium oxalate was subjected to complete distillation *in vacuo*. There was obtained a residue which weighed 2.00 g. It was dissolved in 4 cc. of hot water. The solution was allowed to cool and deposited 1.75 g. of crystals, the analysis of which agreed with that of calcium *d*-arabonate, *i. e.*, 0.2321 g. of the salt gave on complete ignition 0.0283 g. of CaO.

Calc. for $Ca(C_5H_9O_6)_2.5H_2O$: CaO, 12.18. Found: 12.20.

The remaining 1.52 g. of calcium salt was treated with oxalic acid on the basis of the above analysis. There was obtained 0.95 g. of stiff gum which yielded by crystallization from ethyl acetate 0.62 g. of crystals. That these crystals were the lactone of *d*-arabonic was shown by a rotation and a titration. $[\alpha]_D^{20}$ +71°; *i. e.*, 0.4998 g. of crystals dissolved in water and the solution made up to 25 cc. gave α in a 1 dcm. tube +1.42. The solution which contained the 0.4998 g. of crystals was then titrated with 0.1 *N* alkali; less than 1 cc. of the alkali was necessary to produce the first change of color in the indicator, and 33.47 cc. of alkali was necessary for complete neutralization, whereas 33.75 cc. alkali is necessary theoretically for this amount of *d*-arabonic lactone.

The Non-crystalline Phenylhydrazids; Glycollic Acid.—These weighed 29 g. They were hydrolyzed with barium hydroxide in the usual way, and yielded 16.12 g. of gum which had $[\alpha]_D^{20}$ —28.55° This gum was converted into brucine salts. The crude salts were crystallized from 2 parts of absolute alcohol and 41.17 g. of salts were obtained in 3 crops which varied in melting point from 189 to 199°. These brucine salts were carefully studied but could not be identified. They yielded a gum whose $[\alpha]$ was —53°. A crystalline quinine salt and a hydrazid were made from the gum. It was finally concluded that the gum was a mixture of saccharinic acids. A study of the saccharinic acids is being made in this laboratory in the hope of throwing some light on this identification.

The mother liquor and washings from the crystalline brucine salts were subjected to complete distillation and yielded 32.8 g. of non-crystalline brucine salts. The gum obtained from these weighed 3.41 g. and had $[\alpha]_D^{20}$ —3.22°. This gum was so obviously composed largely of glycollic acid that it was at once converted into the calcium salt by heating the water solution containing the gum with an excess of calcium carbonate. The crude salt weighed 4.03 g. and yielded, as a result of recrystallization from 2 parts of water, 2.19 g. of crystalline salt. Another crop of 0.31 g. was obtained from the residue by using 50% alcohol. The mother liquors were discarded. These 3 crops were well mixed and

then analyzed; 0.5311 g. of salt lost 0.1478 g. of water and left a residue of 0.1126 g. of calcium oxide on ignition to constant weight.

Calc. for $Ca(C_2H_3O_3)_2.4H_2O$: H_2O, 27.48; CaO, 29.47. Found: H_2O, 27.80; CaO, 29.35.

This salt was, therefore, calcium glycollate.

II. MALTOSE AND AIR.

1. Experimental Procedure.

The maltose was oxidized in 2 lots, 150 g. in all, and the oxidation products of the two lots united after the formic acid had been removed. The plan for separating the oxidation products was the same as that followed in the previous experiment. The glucosido acid gums were separated as completely as possible from the simple acid gum, and each gum then studied separately.

Seventy-five g. of maltose hydrate, m. p. 115°, $[\alpha]_D^{20}$ +131.1°, was dissolved in 1000 cc. of water. This solution was slowly added to a solution of 104.9 g. of 89.2 % potassium hydroxide (8 equivalents) in 3000 cc. of water. More water was then added to bring the final volume up to 5000 cc. A rapid stream of carbon dioxide-free air was drawn through the solution by means of the device described in a recent paper from this laboratory.[1] The water bath which surrounded the flask containing the sugar solution, was kept at a temperature of from 30 to 40° throughout the experiment. At the end of 48 hours the still strongly alkaline solution was entirely free from sugar, which indicated that oxidation was complete.

2. The Products of Oxidation.

Formic Acid Determination.—This determination was carried out before the better method of collecting the acid distillates under potassium hydroxide was introduced. A determination of the amount of formic acid produced, made precisely as indicated in the discussion of the preceding experiment except that the distillates were condensed and collected in the usual way (*i. e.*, not under potassium hydroxide), showed that 8.94 g. of formic acid per 100 g. of maltose hydrate was formed. Although this method of determination is now known to give slightly low results, it is sufficiently accurate to show that very much less formic acid was formed in the oxidation with air, than in the corresponding oxidation with hydrogen peroxide.

The Non-volatile Acids.—The residues left in the distilling flasks after the formic acid had been removed, were freed from practically all the potassium chloride in precisely the same way as in the previous experiment.

The alcoholic filtrates and washings in the 2 experiments were united, and left, after complete distillation *in vacuo*, 137 g. of gum, $[\alpha]_D^{20}$ +15°. A titration of a small portion of this gum showed that most of it was sim-

[1] THIS JOURNAL, 39, 1639 (1917).

ple acid in character. Therefore it was subjected to extraction with a total of 2500 cc. of ethyl acetate. This caused a separation into 86.5 g. of ethyl acetate-soluble gum and 50.5 g. of insoluble gum which, when extracted with 250 cc. of hot 95% alcohol, gave 33.1 g. of alcohol-soluble gum B and 16.7 g. of insoluble gum C. The 86.5 g. of gum was then extracted with 3000 cc. of hot ether which caused a separation into 58.6 g. of ether-soluble gum $[\alpha]_D^{20}$ —17.92°, which will be referred to as "Simple Acid Gum Soluble in Ether" (see below), and 22.3 g. of ether-insoluble gum $[\alpha[_D^{20}$ +11.86°.

The B and C gums were then subjected to the basic lead acetate treatment. There was thus obtained, by a process in every detail identical with that discussed in the previous experiment, 12.45 g. of glucosido-acid gum insoluble in ethyl acetate from the combined soluble lead salts with $[\alpha]_D^{20}$ +72.50°; 10.90 g. of glucosido acid gum insoluble in ethyl acetate from the combined insoluble lead salts with $[\alpha]_D^{20}$ +94.25°; and 13.7 g. of simple acid gum soluble in ethyl acetate with $[\alpha]_D^{20}$ +19.50° to which the 22.3 g. of gum $[\alpha]_D^{20}$ +11.86° was added. This combined gum (13.78 and 22.3 g.) will be referred to as "Simple Acid Gum Insoluble in Ether but Soluble in Ethyl Acetate" (see below).

The Glucosido Acid Gums.—These gums were similar in properties to the corresponding gums from the hydrogen peroxide experiment in which it was found that there was very little difference between the acid gums obtained finally by the hydrolysis of the glucosido acids from the soluble and insoluble basic lead salts. The acid gums and sugar fractions obtained from the glucosido acid gums at present under discussion (12.45 g. and 10.98 g.) by a treatment exactly corresponding to the one discussed under the hydrogen peroxide experiment were therefore united. There were finally obtained a total of 12.98 g. of calcium salt and 14.98 g. of crystallized *d*-glucose, melting interval 149–155°; $[\alpha]_D^{20}$ +52.00°. The 12.98 g. of calcium salt was treated with oxalic acid, etc., as in the hydrogen peroxide experiment and yielded finally a very stiff gum which weighed 8.69 g., which was partially crystalline and which had $[\alpha]_D^{20}$ +18.90°. This gum was subjected to the phenylhydrazine treatment, and there was finally obtained 2.75 g. of crystalline phenylhydrazid, m. p. 198–202°, which is discussed under "The High Melting Phenylhydrazids" (see below), and 10.72 g. of non-crystalline hydrazids, which when hydrolyzed, gave 6.76 g. of gum. This gum was divided into 2 portions by extraction with acetone; a soluble gum which weighed 5.5 g. $[\alpha]_D^{20}$ +6.36°, and a tarry residue, which was discarded. The brucine salt of this gum was then made. The crude salt was separated by fractional crystallization from water and alcohol into 2 fractions; 8.31 g. of crystalline salt, m. p. 204°, and 10.30 g. of non-crystalline salt.

The Crystalline Brucine Salt; *d*-Erythronic Lactone.—The 8.31 g. of

brucine salt was hydrolyzed and gave 1.90 g. of a very stiff, pale yellow gum, with $[\alpha]_D^{20}$ —29.40°. By careful crystallization and recrystallization from ethyl acetate, a total of 0.50 g. of *d*-erythronic lactone, m. p. 101–103°, was separated from the mixture. $[\alpha]_D^{20}$ was —71.60°; *i. e.*, 0.3126 g. dissolved in water and the solution made up to 20 cc. gave α in a 1 dcm. tube —1.12°. A titration of the same 0.3126 gram showed that only 0.04 cc. 0.1 *N* potassium hydroxide was required to cause the first color in the indicator and that a total of 26.68 cc. was required for complete neutralization. The theoretical amount required for 0.3126 g. of *d*-erythronic lactone is 26.50 cc.

The 0.50 gram of crystals was, therefore, *d*-erythronic lactone.

The Non-crystalline Brucine Salt.—This salt weighed 10.30 g. It was hydrolyzed and gave 2.13 g. of gum $[\alpha]_D^{20}$ +25.2°. The phenylhydrazid of this gum was made. There was obtained 0.45 gram of phenylhydrazid, m. p. 200°, which is discussed under "The High Melting Phenyl Hydrazids" (see below). The non-crystalline phenylhydrazid was discarded.

The High Melting Phenylhydrazids; *d*-Arabonic Phenylhydrazid.—The combined high melting phenylhydrazids weighed 3.25 g. They were recrystallized from a mixture of 150 cc. of 95% alcohol and 10 cc. of water. The first crop of crystals weighed 2.43 g., m. p. 215°; the second crop of crystals weighed 0.48 g., m. p., 214°. $[\alpha]_D^{20}$ of the two crops, well mixed, was —14.86°; *i. e.*, 0.5892 g. dissolved in water and the solution made up to 25 cc. gave α in a 1 dcm. tube —0.35°. This phenylhydrazid was mixed with some pure *d*-arabonic phenylhydrazid. The mixture melted at 214°. There can be no doubt, therefore, that the phenylhydrazid under consideration was *d*-arabonic phenylhydrazid.

The Simple Acid Fraction Soluble in Ether.—This fraction weighed 58.60 g. and had $[\alpha]_D^{20}$ —17.92°. The gum was divided into 2 parts; one part was preserved.

The part used for the study here reported weighed 28 g. It was converted into the brucine salts. The crude salt obtained was crystallized from 2 parts of absolute alcohol and yielded a total of 65.35 g. of crystalline brucine salt which ranged in melting point from 174 to 189°, and 60.33 g. of non-crystalline brucine salts.

The Crystalline Brucine Salts.—The 65.35 g. of crystalline brucine salt was hydrolyzed with barium hydroxide and yielded 11.50 g. of very soluble mobile gum, which had $[\alpha]_D^{20}$ —25°. This gum was extracted repeatedly with ether and yielded a very soluble fraction, 8.24 g., which had $[\alpha]_D^{20}$ —35°, a moderately soluble fraction, 2.30 g., which had $[\alpha]_D^{20}$ —26.5°, and a residue of 0.95 g.

The moderately soluble gum and the residue were subjected to the phenylhydrazine treatment and yielded, respectively, 0.07 g. of phenylhydrazid,

melting interval 200–204°, and 0.12 g. of phenylhydrazid, melting interval 198–200°. The treatment of these 2 lots of phenylhydrazid is discussed under "The High Melting Phenylhydrazids" (see below). The non-crystalline hydrazids were discarded.

The 8.24 g. of gum $[\alpha]_D^{20} = -35°$, extremely soluble in ether, was examined for *d*-erythronic acid. This could not be proved present. A search for lactic acid showed none to be present. Glyceric acid was next sought for by conversion of the gum—now 7.46 g.—into the quinine salt.[1] The crude salt was crystallized from a small amount of water. There was thus obtained 3.00 g. of quinine salt insoluble in water, melting interval 175–178°, and 26.45 g. of quinine salt soluble in water.

Quinine Salt Insoluble in Water; Quinine *l*-Glycerate.—The salt was recrystallized from 30 cc. of absolute alcohol to free it from excess quinine. There was obtained 2.10 g. of crystals which were recrystallized from water and gave 1.17 g. of salt with the melting interval 178–180° and $[\alpha]_D^{20}$ —116.50°; *i. e.*, 1.0000 g. of crystals in 20 cc. aqueous solution gave α in a 1 dcm. tube —5.82°. Quinine *l*-glycerate prepared from Kahlbaum's calcium *dl*-glycerate was found to have a melting interval of 176–180° and $[\alpha]_D^{20}$ —116.90°. There is, therefore, no doubt that *l*-glyceric acid was present in the gum under discussion.

Quinine Salts Soluble in Water; a C_4-Saccharinic Acid.—The soluble quinine salts weighed 26.45 g. They were recrystallized from 3 parts of absolute alcohol and yielded a total of 8.49 g. of crystalline salt with melting interval 168–172°, $[\alpha]_D^{20}$ —120.30°. The mother liquor was discarded.

The 8.49 g. of crystalline quinine salt was hydrolyzed.[2] The ether-soluble gum finally obtained weighed 1.79; $[\alpha]_D^{20}$ —52.5°. A titration showed that 0.167 g. of this gum required 3.5 cc. of 0.1 *N* alkali to produce the first color in the indicator and that a total of 15.55 cc. was necessary for complete neutralization. This is almost exactly the theoretical amount for a C_4-saccharinic acid—$C_4H_8O_4$—calculated as 77.5% lactone.

The remaining gum (1.50 g.) was converted into the phenylhydrazid. Three crops of crystals were obtained: 0.65 gram, m. p., 102°; 0.55 g., melting interval 100–102°; and 0.30 g., melting interval 95–100°. These 3 crops of crystals were combined and recrystallized from 4 parts of absolute alcohol. There was thus obtained a crop of crystals, triangular plates with rounded corners, which weighed 1.15 g. They melted at

[1] The quinine salts of acid gums were made in precisely the same manner as the brucine salts except that the extractions to remove the excess quinine were made with ether instead of benzol.

[2] Quinine salts were hydrolyzed in precisely the same manner as brucine salts except that the aqueous filtrate from the precipitated quinine was extracted with ether instead of benzol.

102.5° and had $[\alpha]_D^{20}$ —12.98°; *i. e.*, 0.7519 g. of substance in 25 cc. aqueous solution gave α in a 1 dcm. tube —0.39°.

That the gum now under discussion was a C_4-saccharinic acid and not a C_4-aldonic acid is, we think, established by analyses of the above mentioned 1.15 g. of phenylhydrazid.

	Calc. for C_4-sacc. phenylhydrazid, $C_{10}H_{14}N_2O_3$:	Calc. for C_4-aldonic phenylhydrazid, $C_{10}H_{14}N_2O_4$:	Found.		
			I.	II.	III.
C.....	57.14	53.1	56.80	57.00	...
H.....	6.72	6.20	6.85	6.88	...
N.....	13.34	12.39	...	...	13.64

There seems to us to be little doubt that this substance is the phenylhydrazid of a dioxybutyric acid. Unfortunately, it is at present impossible to identify it further; that is, to determine of which particular one of the 10 possible optically-active stereoisomeric dioxybutyric acids it is the phenylhydrazid. Work has been begun in this laboratory on the preparation of all the possible dioxybutyric acids with a view to identifying this phenylhydrazid as well as to the furnishing of information as to the properties and physical constants of these acids and their derivatives to be used in future work on the sugars.

The "preserved" part of the original oxidation gum soluble in ether also yielded this C_4-saccharinic phenylhydrazid. The following additional information was supplied by this material. The acid itself is extremely soluble in ether and has $[\alpha]_D^{20}$ —72.4°. The brucine salt has a melting point of 178° and $[\alpha]_D^{20}$ —23.60°.

The Non-crystalline Brucine Salt; Calcium Glycollate.—This salt weighed 60.33 g. It was hydrolyzed and yielded 10.90 g. of gum. This gum was converted into calcium salts. The crude calcium salts were crystallized from water and yielded 5.03 g. of crystals. That these were crystals of calcium glycollate was proved by the following analysis: A portion of the air-dried salt, 0.5504 g., was heated at 110° to constant weight and left a residue of 0.3954 g. of anhydrous salt. This anhydrous salt was ignited to constant weight and left a residue of 0.1160 g. of calcium oxide.

Calc. for $Ca(C_2H_3O_3)_2.4H_2O$: H_2O, 27.48; CaO, 29.47. Found: H_2O, 27.98; CaO, 29.33.

Attempts to identify the constituents of the non-crystalline calcium salts proved unsuccessful.

The Simple Acid Fraction Insoluble in Ether but Soluble in Ethyl Acetate.—This gum weighed 36 g. and had $[\alpha]_D^{20}$ about +15°. It was divided into 2 parts. The part used for the separation here described weighed 18 g. The gum was quite mobile. It was extracted with ether in which 9.75 g., $[\alpha]_D^{20}$ = +1.85°, dissolved. The insoluble part was then extracted with absolute alcohol. The residue from this extraction was

discarded and the alcohol-soluble gum treated with phenylhydrazine. There was obtained a total of 3.22 g. crystalline phenylhydrazid melting interval 209–210°, which is discussed under "High Melting Hydrazids," and a quantity of non-crystalline phenylhydrazid which was hydrolyzed and gave 32 g. of gum with $[\alpha]_D^{20}$ +6.25°. This gum was reunited with the 9.75 g. of gum, $[\alpha]_D^{20}$ +1.85°, which made a total of 12.75 g. This gum was then converted into brucine salts. Recrystallization of the crude salts from 2 parts of absolute alcohol effected a separation into 26.40 g. crystalline brucine salts, melting interval 180–196°, and 25 g. of non-crystalline salts which have been preserved for future study.

The Crystalline Brucine Salts; Quinine *l*-Glycerate.—The 26.40 g. of brucine salts were hydrolyzed and gave 6.15 g. of very mobile gum. This gum was extracted with cold ether in which 4.65 g. gum, $[\alpha]_D^{20}$ —14°, dissolved. From the ether-insoluble part there was obtained 0.60 g. of phenylhydrazid, melting interval 205–206°, which is treated under "High Melting Phenylhydrazids."

The 4.65 g. of gum, $[\alpha]_D^{20}$ —14°, was converted into the quinine salt. There was obtained 11.50 g. of crude quinine salt which by recrystallization from 2 parts of absolute alcohol gave 2.1 g. of crystals. These crystals when recrystallized from water yielded a crop of 1.34 g. of salt with melting interval 179–180° and with $[\alpha]_D^{20}$ —116.20°; *i. e.*, 0.9346 g. of salt in 20 cc. of aqueous solution gave α in 1 dcm. tube —5.43°. This salt was undoubtedly quinine *l*-glycerate.

The High Melting Phenylhydrazids; *d*-Arabonic Phenylhydrazid.—The high melting phenylhydrazids had a total weight of 3.82 g. They had $[\alpha]_D^{20}$ —13.12°. They were recrystallized from 300 cc. of 95% alcohol. The crystals obtained weighed 2.84 g. and had a melting point of 214°, which is the recorded melting point for *d*-arabonic phenylhydrazid. Analysis gave the following results:

Calc. for $C_{11}H_6N_2O_5$: C, 51.56; H, 6.30; N, 10.94. Found: C, 51.50; H, 6.58; N, 10.97.

The substance was undoubtedly *d*-arabonic phenylhydrazid.

III. THE PREPARATION AND PROPERTIES OF MALTOBIONIC ACID.

This study of maltobionic acid and some of its derivatives was undertaken to provide information about the properties of glucosido acids, to be useful in the experiments just discussed. The method of oxidation described here, although practically a duplicate of that of Emil Fischer,[1] differs considerably from Fischer's procedure in detail.

Oxidation of Maltose to Maltobionic Acid.—Fifty g. of maltose hydrate was dissolved in 500 cc. of water. To this solution was added 8.5 cc. of bromine and 41.28 g. of lead carbonate. The flask was provided with

[1] *Ber.*, **22**, 1941 (1889).

a reflux condenser and was vigorously shaken until the bromine had dissolved. The mixture was allowed to stand for 7 days at room temperature. The resulting pale yellow solution was separated from the precipitated lead bromide by filtration. A vigorous current of air was drawn through the filtrate to remove the excess bromine. This left a clear, colorless solution. To remove the bromide ion completely, a suspension of silver carbonate in water was added to the solution until it gave a faint test for silver. In order to remove the silver and lead completely from the filtered solution, the latter was saturated with hydrogen sulfide. After the sulfides of silver and lead had been separated by filtration, the filtrate was subjected to distillation *in vacuo* for a time to remove the hydrogen sulfide, whereupon the solution in the distilling flask was made up to 1000 cc. and aliquot portions used for tests. These tests showed that α of the solution was $+105°$; that 83% of the sugar had been oxidized, and that the acid was present as free acid to the extent of 78%.

The remaining solution, 950 cc., was heated at 60° for 10 hours with an excess of calcium carbonate. The crude calcium salt obtained was twice dissolved in one part of water and precipitated with 5 parts of absolute alcohol. There was thus obtained 40.90 g. of gummy calcium salt. To this was added a similar lot of calcium salt from a previous experiment. The combined salt, 81.1 g., was once more dissolved in one part of water, and precipitated with 5 parts of 95% alcohol. The precipitated salt was transferred to a mortar with small amounts of water, covered with absolute alcohol, and ground to a powder. A total of 67.70 g. of vacuum-dried calcium salt in the form of a powder, which was practically free from sugar, was finally obtained.

Analysis and Rotation of Calcium Maltobionate.—That this salt was pure calcium maltobionate was proved by an analysis. A portion of it, 0.5575 g., was ignited to constant weight in a platinum crucible and left a residue of 0.0413 g. of calcium oxide.

Calc. for $Ca_{12}(H_{21}O_{12})_2$: CaO, 7.42. Found: 7.41.

The salt in water solution was found to have $[\alpha]_D^{20} +97.5°$, *i. e.*, 0.3386 g. of salt dissolved in 8.6672 g. of water gave α in a 1 dcm. tube 3.71°.

Maltobionic Acid.—The remaining 66.77 g. of calcium salt was dissolved in water and treated at 60° with 11.16 g. of oxalic acid. The filtrate from the calcium oxalate was made up to 1000 cc. This solution had $[\alpha]_D^{20} +98.3°$ calculated on the basis of its having contained 63.4 g. of maltobionic acid, *i. e.*, α in 1 dcm. tube $+6.23°$.

Further studies of portions of this solution gave the following information about maltobionic acid: It exists in water solution practically entirely as free acid; 15 cc. of the solution which contained 0.951 g. of acid required 24.6 cc. of 0.1 *N* alkali for the first appearance of color in phenol-

phthalein and 26.6 cc. for complete neutralization. It exhibits slight tendency to form a lactone; after a portion of the solution had been subjected to complete distillation *in vacuo*, the residue heated *in vacuo* at 100° for 5 hours, dissolved in water and titrated quickly with 0.1 *N* alkali, the titration showed the acid to be present practically entirely as free acid. It does not reduce Fehling's solution. It is miscible with water in all proportions, is practically insoluble in absolute alcohol and in ethyl acetate and quite insoluble in boiling ether. It is not hydrolyzed by approximately 0.2 *N* sodium hydroxide; 10 cc. of the solution to which 7.09 cc. of 0.5 *N* sodium hydroxide had been added was heated for 10 hours on the boiling water bath under a reflux condenser, after which the resulting solution had a brown color, did not reduce Fehling's solution and had suffered almost no change in rotation. It is completely hydrolyzed by approximately 0.2 *N* sulfuric acid; to 9.51 g. of the acid gum was added 19.88 cc. of 0.5 *N* sulfuric acid and 30 cc. of water, the mixture was heated for 20 hours under a reflux condenser, the sulfuric acid was removed with barium hydroxide, and the filtrate from the barium sulfate treated with calcium carbonate. By this treatment there was obtained, finally, 4.30 g. of pure calcium gluconate and 3.60 g. of glucose, m. p. 149°.

The Brucine Salt of Maltobionic Acid.—The crude salt made in the usual way from 50 cc. of the solution and 3.48 g. of brucine could not be induced to crystallize. It was finally ground to a powder in a mortar in the presence of absolute alcohol and ether. The powder so obtained was dried *in vacuo* over sulfuric acid. A portion of it, 2.25 g., was dissolved in 1 cc. of water and 5 cc. of absolute alcohol. Crystals, 1.45 g., separated from the solution after long standing. The entire powder was transformed into crystals in the same manner. To obtain the pure salt, 4 g. of these crystals was dissolved in 4 cc. of water and 35 cc. of absolute alcohol. Crystals began to form in this solution at the end of 10 hours, but the salt had crystallized out completely only after having stood a week. In this way 2.85 g. of crystals was obtained. Dried to constant weight *in vacuo* over sulfuric acid, these melted at 153°. They had $[\alpha]_D^{20}$ +38.05°, *i. e.*, 0.4872 g. of salt dissolved in 9.869 g. of water gave α in a 1 dcm. tube +1.79°. This positive rotation of a brucine salt is unusual, if not, indeed, unique.

Other Derivatives of Maltobionic Acid.—The phenylhydrazid and strychnine, quinine and cinchonine salts of maltobionic acid were prepared. The crude products were in all cases gums. They could be ground to powders in a mortar in the presence of absolute alcohol; but these powders could not be recrystallized and became gummy in the presence of even traces of moisture.

Summary.

TABLE I.—SUBSTANCES ACTUALLY ISOLATED FROM THE OXIDATION PRODUCTS OF MALTOSE, PER 100 G. OF MALTOSE HYDRATE.

	Maltose and H_2O_2. Grams.	Maltose and air. Grams.
Formic acid	43.30	8.94
Glucosido acids	37.0	15.56
d-Glucose	19.22	9.98
d-Erythronic lactone	1.40	0.32
d-Arabonic phenylhydrazid	2.96	1.94
Simple acids	13.0	63.06
Calcium glycollate	1.66	6.68
Calcium oxalate	0.14	...
Quinine *l*-glycerate	...	3.34
C_4-Saccharinic phenylhydrazid	...	1.54
Calcium *d*-arabonate	1.16	...
d-Arabonic phenylhydrazid	...	3.78

A study of the preparation and properties of maltobionic acid, its calcium, brucine, strychnine, quinine and cinchonine salts and its phenylhydrazid is also reported.

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE ISOMERIC TETRACETATES OF *l*-ARABINOSE AND BETA-TRIACETYL-METHYL-*l*-ARABINOSIDE.

BY C. S. HUDSON AND J. K. DALE.

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The possibility of the existence of 2 isomeric tetracetates of arabinose has been foreshadowed by the preparation of an isomeric pair of completely acetylated derivatives of most of the other naturally occurring mono- and disaccharides. Stone[1] acetylated arabinose by heating it with acetic anhydride and sodium acetate for one hour at 105°, but he obtained only a sirup. By shaking a solution of bromoacetyl-arabinose in acetic acid with silver carbonate, Chavanne[2] obtained crystals melting at 80° which he supposed were tetracetyl-arabinose but the quantity was too small for analysis.

Although the form of arabinose tetracetate that can be obtained directly by the acetylation of arabinose crystallizes readily when nearly pure, its preparation caused us great difficulty because there was formed at the same time a large proportion of sirupy material which interfered with its crystallization. With the aid of crystals that were produced by the method of Chavanne, the sirups that resulted from the acetylation of ara-

[1] *Am. Chem. J.*, **15**, 653 (1893).

[2] *Compt. rend.*, **134**, 661 (1902).