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NITRATION OF SUGARS AND THEIR
GLYCOSIDES

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My invention relates to improvements in the nitration of sugars and their glycosides, and more particularly relates to improved means for bringing about the nitration of sugars such as cane sugar, glucose, levulose, lactose, and the like, or the glycosides thereof, with the production of products having satisfactory physical characteristics and also having satisfactory chemical characteristics particularly with reference to stability. One of the objects of my invention is to provide improved means for the nitration of the various sugars and their glycosides, and another of the objects of my invention is to provide improved means for the preparation of the nitrated sugars and their glycosides in very pure condition. This application is a continuation in part of my application S. N. 728,679, filed June 2, 1934.

My present invention rests upon my discovery that the nitrated esters of certain hydroxy acids dissolve nitrated sugar readily and produce mixtures which may contain as much as 70% of nitrated sugar, while still having such physical characteristics as will permit them to be purified and stabilized by known washing and stabilizing methods. It is well known that when cane sugar, glucose, levulose, lactose, etc. are nitrated by the ordinary methods known up to this time, thick, gummy, pasty or very viscous nitrated products are obtained which are very difficult to purify and to stabilize. If such agents as glycerin, glycols, and chlorhydrins are used as partial solvents, thick solutions are obtained which, if they contain more than 25% of nitrated sugar, are too viscous to be treated by the usual washing and stabilizing methods.

As examples of the nitrated esters which I may employ in the practice of my present invention I will mention nitrated methyl glycollate, nitrated ethyl glycollate, nitrated propyl glycollate, nitrated butyl glycollate, nitrated amyl glycollate, nitrated methyl lactate, nitrated ethyl lactate, nitrated propyl lactate, nitrated butyl lactate, nitrated amyl lactate, nitrated methyl tartronate, nitrated ethyl tartronate, nitrated methyl malate, nitrated ethyl malate, nitrated dimethyl tartrate, nitrated diethyl tartrate, and the higher homologues. When the purpose of the work is to prepare the crystalline sugar nitrate I find the use of nitrated butyl lactate is particularly advantageous.

The nitrated esters may be used either directly as such, or they may be produced in the same nitration operation as is the nitrated sugar or the nitrated glycoside, by the addition of the esters to the nitration mixture.

As sugars to be used in the procedure of my invention, I may use cane sugar, glucose, lactose, levulose, etc. and as glycosides, I may use methyl glucoside, ethyl glucoside, methyl lactoside, ethyl lactoside, etc.

As examples of the application of my present invention, for the purpose of illustrating its general features, I give the following:

Example 1.—To 990 parts of mixed acid consisting of 40% H_2SO_4 and 60% HNO_3 add 60 parts of dibutyl tartrate, keeping the temperature below 30° C. Then add 60 parts of powdered cane sugar, maintaining the temperature below 30° C., and preferably below 20° C. Stir continuously throughout the nitration.

At the completion of the nitration the nitration mixture is settled and the solution of nitrated sugar in the dinitrated butyl tartrate forms the upper layer. The latter is separated, washed in dilute alkali, stabilized and settled or filtered to remove moisture and mechanical impurities.

Example 2.—To 150 parts of 98% HNO_3 cooled to below 20° C., add 20 parts of methyl glucoside with constant stirring and cooling. Then add 20 parts of butyl lactate, keeping the temperature below 20° C. Then add 200 parts of 105% oleum to complete the nitration and to cause a separation of the nitrated products as a solution floating upon the spent acid. The separated nitrated glucoside solution is then washed, neutralized, stabilized and settled or filtered to remove moisture and mechanical impurities.

Example 3.—108 parts of ethyl lactate are run into 1126 parts of a mixed acid consisting of 40% H_2SO_4 and 60% HNO_3 maintained at a temperature below 30° C. Then add 80 parts of cane sugar, a little at a time, keeping the temperature below 25° C. and preferably lower than 10° C. The nitration mixture is then allowed to stand, when separation into two layers will occur. The upper layer is the nitrated product and can be readily separated, and should then be washed, filtered and neutralized according to the methods well known in the art.

Example 4.—1126 parts of a mixed acid consisting of 60% HNO_3 and 40% H_2SO_4 are placed in a suitable nitrating vessel and cooled to about 10° C. Then, with continued cooling, add 108 parts of ethyl lactate. This nitration step is very readily controlled and takes place smoothly and evenly. When all of the ethyl lactate has been added, 88 parts of powdered, dried sucrose are added in small portions, maintaining the temperature below 10° C. The stirring is continued for about one hour after the feeding of the sugar

in order to complete the nitration. The total time of nitration is often about four hours.

The nitrated charge is then run to a settler where the mixture separates into two layers. The lower layer is the spent acid and contains only a small amount of nitrated products. The upper layer consists of the nitrated ethyl lactate and nitrated sugar. At times this upper layer has a small amount of crystalline nitrated sugar suspended in it.

The upper layer is then drowned in tap water, washed, neutralized by stirring in 2% sodium bicarbonate, washed with water and allowed to settle. The lower layer is a mixture of nitrated ethyl lactate and sucrose nitrate with some occluded water. By settling overnight only a small amount of water remains in suspension.

This lower layer is then treated with 95% ethyl alcohol, while the mixture is being stirred until a crystalline precipitate of sucrose octonitrate separates. Only enough alcohol is added to cause this precipitation. The mixture is filtered, the precipitate is washed with alcohol and dried at about 40° C. The yield of crystals is about 145 parts.

Example 5.—1126 parts of a mixed acid consisting of 45% nitric acid and 50% sulfuric acid and 5% water are placed in a suitable nitrating vessel and cooled to about 0° C. Then, with continued stirring and cooling, add 108 parts of nitrated butyl lactate. When all the nitrated butyl lactate has been added, add 130 parts of powdered dried sucrose, maintaining the temperature around 0° C. The stirring and cooling is continued for about one hour after the feeding of the sugar in order to complete the nitration.

The nitrated charge is handled in the manner as described in Example 4.

Instead of drowning the nitrated sugar mixture in water, and thereafter extracting the nitrated mixture with a solvent, it is of course possible to drown the nitrated sugar mixture directly in a mixture of ethyl alcohol and a hydrocarbon to obtain directly, the precipitated crystalline nitrated sugar.

While the above examples represent preferred methods of nitration, it should be noted that I do not confine myself to these narrow limits. The characteristic part of my invention is the presence of a nitrated ester of a hydroxy acid in the nitration mixture at the time of the separation of the nitrated sugar or glycoside from the spent acid, and it will readily be understood that I may vary the strengths and proportions of acids, the temperatures of the components and the temperature of nitration, the ratio of nitrated ester to sugar or to acids, the order of addition of materials to be nitrated, etc. without departing from the essence of this invention.

I have discovered that when a sugar is nitrated in the presence of a nitrated hydroxy acid the resulting nitrated mixture is capable of being separated to give the pure nitrated sugars in higher purity and in better yield than can be obtained by methods previously known, and this can be accomplished without the use of repeated extractions or fractionations. I have discovered, for example, that the nitration products made in accordance with my present invention may be extracted with such solvents as ethyl alcohol or propyl alcohol, or with such solvents as propane, butane, heptane, pentane, hexane, benzene, or ordinary commercial gasoline, or with mixed solvents such as pentane, hexane, etc. with chloroform or carbon tetrachloride, or with mixed

solvents such as an alcohol and a chlorinated hydrocarbon, all of these solvents and solvent mixtures possessing greater solvent action for the nitrated hydroxy acid esters than they do for the nitrated sugars. I have discovered, for example, that by the method herein described I can obtain sucrose octonitrate in the form of crystals from the nitration mixture of nitrated butyl lactate and cane sugar, without any recrystallization whatever, using in this case either ethyl alcohol or pentane as the differential solvent for dissolving the nitrated hydroxy acid ester and thus separating it from the insoluble nitrated sugar, and that these crystals, by a simple stabilizing treatment such as stirring them in a two percent solution of bicarbonate of soda, or by first stirring them in a two percent solution of bicarbonate of soda, and thereafter washing them in a one percent solution of ammonia, may be obtained as the pure sucrose octonitrate having substantially the theoretical nitrogen content, and possessing substantially the same stability as the sucrose octonitrate previously obtained as the result of extensive recrystallization and stabilization treatments.

As many modifications may be made within the limits of the disclosure of my invention as herein set forth, it is to be understood that the examples herein given are for purposes of illustration and the figures therein given are not to be considered as limitations, and no limitations should be placed upon the scope of my invention except such as are indicated in the appended claims.

I claim:

1. The process of nitrating a member of the group consisting of a sugar and a sugar glycoside in the presence of a nitrated alkyl ester of a saturated hydroxy aliphatic carboxylic acid, said carboxylic acid containing not more than two carboxyl groups.
2. The process of nitrating cane sugar in the presence of a nitrated alkyl ester of a saturated hydroxy aliphatic carboxylic acid, said carboxylic acid containing not more than two carboxyl groups.
3. The process of nitrating methyl glucoside in the presence of a nitrated alkyl ester of a saturated hydroxy aliphatic carboxylic acid, said carboxylic acid containing not more than two carboxyl groups.
4. The process of nitrating a sugar in the presence of a member of the group consisting of nitrated methyl glycolate, nitrated ethyl glycolate, nitrated propyl glycolate, nitrated butyl glycolate, nitrated amyl glycolate, nitrated methyl lactate, nitrated ethyl lactate, nitrated propyl lactate, nitrated butyl lactate, nitrated amyl lactate, nitrated methyl tartronate, nitrated ethyl tartronate, nitrated ethyl malate, nitrated dimethyl tartrate and nitrated diethyl tartrate.
5. The process of nitrating glucose in the presence of a member of the group consisting of nitrated methyl glycolate, nitrated ethyl glycolate, nitrated propyl glycolate, nitrated butyl glycolate, nitrated amyl glycolate, nitrated methyl lactate, nitrated ethyl lactate, nitrated propyl lactate, nitrated butyl lactate, nitrated amyl lactate, nitrated methyl tartronate, nitrated ethyl tartronate, nitrated ethyl malate, nitrated dimethyl tartrate and nitrated diethyl tartrate.
6. The process of nitrating methyl glucoside in the presence of a member of the group consisting of nitrated methyl glycolate, nitrated ethyl glycolate, nitrated propyl glycolate, nitrated butyl glycolate, nitrated amyl glycolate, nitrated methyl lactate, nitrated ethyl lactate, nitrated

propyl lactate, nitrated butyl lactate, nitrated amyl lactate, nitrated methyl tartronate, nitrated ethyl tartronate, nitrated ethyl malate, nitrated dimethyl tartrate and nitrated diethyl tartrate.

7. The process of nitrating a sugar which comprises the addition of the sugar and of the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid and the separation of the products of nitration from the spent acid.

8. The process of nitrating cane sugar which comprises the addition of an alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a mixed acid consisting of approximately 60% HNO_3 and 40% H_2SO_4 followed by the addition of the cane sugar, maintaining the temperature of the mixture below 30°C . and separating nitrated products from the spent acid.

9. The process of nitrating cane sugar which comprises the addition of ethyl lactate to a mixed acid consisting of approximately 60% HNO_3 and 40% H_2SO_4 followed by the addition of the cane sugar, maintaining the temperature of the mixture below 30°C . and separating nitrated products from the spent acid.

10. The process of nitrating a sugar which comprises the addition of the sugar and the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowning of the nitrated sugar-nitrated hydroxy acid ester mixture in water, the separation of the nitrated sugar-nitrated hydroxy acid ester mixture from the excess of water, and the solution of the nitrated hydroxy acid ester in a solvent in which nitrated sugar is substantially insoluble.

11. The process of nitrating cane sugar which comprises the addition of the sugar and the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowning of the nitrated sugar-nitrated hydroxy acid ester mixture in water, the separation of the nitrated sugar-nitrated hydroxy acid ester mixture from the excess of water, and the solution of the nitrated hydroxy acid ester in a solvent in which nitrated sugar is substantially insoluble.

12. The process of nitrating glucose which comprises the addition of the sugar and the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowning of the nitrated sugar-nitrated hydroxy acid ester mixture in water, the separation of the nitrated sugar-nitrated hydroxy acid ester mixture from the excess of water, and the solution of the nitrated hydroxy acid ester in a solvent in which nitrated sugar is substantially insoluble.

13. The process of nitrating methyl glucoside which comprises the addition of the sugar and the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowning of the nitrated sugar-nitrated hydroxy acid ester mixture in water, the separation of the nitrated sugar-nitrated hydroxy acid ester mixture from the excess of water, and the solution of the nitrated hydroxy acid ester in a

solvent in which nitrated sugar is substantially insoluble.

14. The process of nitrating a sugar which comprises the addition of the sugar and the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowning of the nitrated sugar-nitrated hydroxy acid ester mixture in water, and the solution of the nitrated hydroxy acid ester in a solvent selected from the group of ethyl alcohol, propyl alcohol, propane, butane, pentane, benzene, gasoline, hexane, heptane, carbon tetrachloride and chloroform.

15. The process of nitrating cane sugar which comprises the addition of the sugar and the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowning of the nitrated sugar-nitrated hydroxy acid ester mixture in water, and the solution of the nitrated hydroxy acid ester in a solvent selected from the group of ethyl alcohol, propyl alcohol, propane, butane, pentane, benzene, gasoline, hexane, heptane, carbon tetrachloride and chloroform.

16. The process of nitrating glucose which comprises the addition of the sugar and the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowning of the nitrated sugar-nitrated hydroxy acid ester mixture in water, and the solution of the nitrated hydroxy acid ester in a solvent selected from the group of ethyl alcohol, propyl alcohol, propane, butane, pentane, benzene, gasoline, hexane, heptane, carbon tetrachloride and chloroform.

17. The process of nitrating methyl glucoside which comprises the addition of the glucoside and the alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowning of the nitrated sugar-nitrated hydroxy acid ester mixture in water, and the solution of the nitrated hydroxy acid ester in a solvent selected from the group of ethyl alcohol, propyl alcohol, propane, butane, pentane, benzene, gasoline, hexane, heptane, carbon tetrachloride and chloroform.

18. The process of nitrating a sugar in the presence of a nitrated alkyl ester of a saturated hydroxy aliphatic carboxylic acid, said carboxylic acid containing not more than two carboxyl groups.

19. The process of nitrating a sugar which comprises the addition of an alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a mixed acid consisting of roughly 60% nitric acid and 40% sulfuric acid followed by the addition of the sugar, maintaining the temperature of the mixture below 30°C . and separating nitrated products from the spent acid.

20. The process of nitrating a sugar which comprises the addition of ethyl lactate to a mixed acid, roughly 60% nitric acid and 40% sulfuric acid, followed by the addition of the sugar, maintaining the temperature of the mixture below 30°C ., and separating nitrated products from the spent acid.

21. The process of nitrating a sugar which comprises the addition of the sugar and an alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups, to a nitrating acid, the separation of the products of nitration from the spent acid, the drowing of the nitrated sugar-nitrated hydroxy acid ester mixture in water, and the solution of the nitrated hydroxy acid ester in a solvent selected from the group of ethyl alcohol, propyl

alcohol, propane, butane, pentane, benzene, gasoline, hexane, heptane, carbon tetrachloride and chloroform.

22. The process of nitrating a member of the group consisting of cane sugar, glucose, levulose, lactose, and their glycosides in the presence of an alkyl ester of a saturated hydroxy aliphatic carboxylic acid containing not more than two carboxyl groups.

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