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2,831,855

## METHOD FOR PREPARING FATTY ESTERS OF NON-REDUCING OLIGOSACCHARIDES IN THE PRESENCE OF PYRIDINE

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This invention relates to a process for preparing fatty esters of oligosaccharides, and more especially to the preparation of fatty esters of non-reducing oligosaccharides, such as sucrose.

Many methods of preparing fatty esters of polyhydric alcohols, sucrose and other non-reducing oligosaccharides are known and have been heretofore employed. Among these are: the direct esterification of the alcohol or oligosaccharide and fatty acids; the reaction of the alcohol or oligosaccharide with fatty acid anhydrides; the reaction of the alcohol or oligosaccharide with fatty acid halides; and the reesterification of fatty acid esters with polyhydroxy alcohols. Various disadvantages are identified with these processes such as, for example, poor yields, excessive time to carry the reaction to the desired completeness, and excessive temperatures necessary to promote the reaction with the attendant adverse effects on the organic reactants including thermal decomposition, charring, discoloration, and the like.

With the foregoing considerations in mind it is an object of the present invention to provide a method whereby fatty esters of non-reducing oligosaccharides can be prepared in good yield and under reaction conditions which will not substantially adversely affect the organic reactants.

Other objects and advantages will be apparent from the following detailed description.

I have found that these objects can be accomplished by subjecting to interesterification a mixture of a non-reducing oligosaccharide and a fatty acid ester of an aliphatic primary monohydroxy alcohol or a fatty acid ester of a polyhydroxy alcohol in the presence of pyridine.

Generally speaking, the invention contemplates reacting the non-reducing oligosaccharide with the fatty acid ester in the presence of an alkaline catalyst which shows activity in interesterification reactions, at a temperature in the range from about 50° to about 115° C. and in the presence of pyridine. Following completion of the interesterification to the desired degree, the catalyst is inactivated by the addition of water and/or acids such as acetic, phosphoric, citric, hydrochloric, and the like, and the desired reaction products are freed of solvent and purified by any suitable means.

The term oligosaccharides is used herein to differentiate the di, tri, and tetra-saccharides as a group, from the polysaccharides which are composed of a much greater number of single units. Of the oligosaccharides, we have found that only those of the non-reducing type, i. e., those having no potentially free aldehyde or ketonic group, are suitable for purposes of this invention. These include the disaccharides; sucrose, trehalose and glucosyl; the trisaccharides; raffinose, melezitose and gentianose; and the tetrasaccharide; stachyose. Thus, the oligosaccharides of concern here are non-reducing polyhydroxy compounds having from 7 to 16 hydroxyl groups per molecule.

The fatty esters which can be employed in the reaction herein concerned are the fatty acid esters of primary

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aliphatic monohydroxy alcohols having from 1 to 4 carbon atoms, for example, methanol and ethanol, a specific example being methylpalmitate. In addition, fatty acid esters of completely or incompletely esterified polyhydric alcohols having from 2 to 6 hydroxyl groups, such as glycol, glycerol, erythritol, pentaerythritol, mannitol, and sorbitol can be employed. Glycol dipalmitate, glycerol mono-, di-, and tripalmitate, mannitol partial palmitates, erythritol tetrapalmitate, pentaerythritol tetrapalmitate and sorbitol hexapalmitate are examples of operative fatty esters. In addition, fatty esters of glycosides, such as methyl glucoside tetrapalmitate, can be employed. The use of fatty acid esters of the aforementioned oligosaccharides having from 7 to 16 hydroxyl groups in the molecule is also contemplated. Thus, just as mono- and diesters of glycerol can be prepared from the triglyceride, so incompletely esterified sucrose esters can be prepared in accordance with the present invention by reaction of sucrose with completely esterified sucrose. Thus, the reaction of sucrose octapalmitate with sucrose can be carried out advantageously with the aid of the present invention.

The aforementioned polyhydric alcohols and non-reducing oligosaccharides considered as a group will for purposes herein be referred to as aliphatic and alicyclic polyhydroxy substances.

The length of the fatty acid chain of the esters above designated is not critical and is dictated primarily by the type of fatty acid material source available. For my purposes however, I have found that fatty acids containing from about 8 to 22 carbon atoms are most useful. Thus, the mixtures of fatty acids obtained from animal, vegetable, and marine oils, and fats, such as coconut oil, cottonseed oil, soybean oil, tallow, lard, herring oil, sardine oil, and the like, represent excellent and valuable sources of fatty acid radicals. In the event it is desired to produce oligosaccharide esters of single fatty acids by this invention, then the fatty acid esters of relatively volatile alcohols (e. g. methanol and ethanol), having from about 12 to about 22 carbon atoms can be reacted with the non-reducing oligosaccharide with the aid of the particular reaction medium herein covered.

Of the fatty acid esters which may be used in the practice of my invention I prefer to use the esters of those alcohols having not more than three carbon atoms. I have found the fatty glycerides to be particularly advantageous.

The crux of my invention lies in the selection of the solvent which comprises the reaction medium. The choice of solvent is essential to the realization of efficient interesterification of the non-reducing oligosaccharide and the fatty ester under the conditions hereinbefore set forth. I have found that pyridine is eminently suitable as the solvent in my process.

The proportion of pyridine used is not critical and may be varied from 1/3 to 50 times by weight of the fatty ester employed for reaction with the oligosaccharide. It is to be understood that the solvent usage is normally adjusted depending upon the particular reactants to be interesterified, precautions being taken however to insure a homogeneous system during the interesterification reaction.

The proportion of reactants is not critical and is dictated primarily by the ultimate product which is desired. For example, in the reaction of sucrose with fatty ester, proportions can be chosen so that from one to essentially all of the hydrogen atoms of the hydroxyl groups of sucrose may be replaced by fatty acyl radicals. Or, where sucrose and a triglyceride are being reacted, proportions can be chosen so that the final product may predominate in either glycerides or sucrose esters. As a practical matter, however, I have found that molar ratios of non-

reducing oligosaccharide to fatty ester in the range from about 30:1 to about 1:20 are most satisfactory, the proportions being variable within the range depending on the completeness of replacement desired and on the number of fatty acid radicals in each mole of ester substance.

Although my process is illustrated herein principally with the use of sodium methoxide as the catalyst, effective practice of my process is not dependent upon the use of any particular catalyst. Rather, any alkaline molecular rearrangement or interesterification catalyst which will promote the interchange of radicals among the reactants of my process is suitable. Examples of usable catalysts are: sodium methoxide, anhydrous potassium hydroxide, sodium hydroxide, metallic sodium, sodium potassium alloy, and quaternary ammonium bases such as trimethyl benzyl ammonium hydroxide. A discussion of other catalysts which are active in interesterification reactions may be found in U. S. Letters Patent 2,442,532, to E. W. Eckey, column 24, line 18 et seq.

The sodium methoxide catalyst may be advantageously used in my process in amounts from about 0.3% to about 2.0% by weight of the fatty ester which is to be reacted, equimolar amounts of other catalysts being usable. The choice of catalyst and the amount which is to be used are of course dependent upon the particular constituents which are to be reacted.

In the practice of the invention, it was observed that the reaction rate for a given solvent usage and a given catalyst increased with increase in temperature. With optimum amounts of pyridine, for example, and with sodium methoxide as the catalyst, at a temperature of 100° C. I found that equilibrium was reached in about four hours reaction time. Where lower temperatures, such as 50° C., are employed, longer reaction times are required to achieve desired ester formation. Temperatures above 100° C., such as those up to the boiling point of pyridine (about 115° C.) may, of course, be employed. Temperatures in excess of the boiling point of pyridine may also be used provided that the reaction system is maintained under positive pressure. However, such temperatures may only infrequently be necessary to accomplish the desired ester formation. Generally speaking, with any of the aforementioned reactants or catalysts, and within the ranges of proportions set forth, the process of my invention is preferably carried out at a temperature in the range from about 80° to about 115° C.

Since the reaction of the present invention is an interesterification in which sucrose, for example, is reacted with a fatty ester, the resulting product of the reaction will constitute an equilibrium mixture of sucrose, esters thereof, displaced alcoholic substance from the ester originally employed, and ester of such alcoholic substance. Thus, if triglycerides are reacted with the sucrose, then the product of the reaction will contain mono- and diglycerides as well as sucrose esters. If it is desired to obtain sucrose esters which are not so contaminated with original esters and derivatives thereof, then it is preferable to react volatile alcohol esters such as methyl or ethyl esters with the sucrose. Yields of sucrose esters of high purity are obtainable in this way since unreacted volatile esters can be separated subsequently by distillation or crystallization procedures.

One way of determining whether or not ester has been formed when working with the oligosaccharides is by observing the optical activity of the recovered reaction product. As is well known, sucrose and other oligosaccharides have optical activity which may be readily determined in the usual way by polarimetric measurement. In the present case, specific rotation figures have been determined by means of a Rudolph Model 70 polarimeter, using a filtered light source of 546 millimicrons wave length. The rotation is measured at room temperature (25-27° C.) in pyridine solution at a concentration of about 2% using a sample length of 10 cm. Under such

conditions of observation, sucrose shows a specific rotation of 100°. The esters formed from sucrose also possess optical activity and since the method of recovery, as shown in the example to follow, eliminates contamination of the product with water soluble substances such as sucrose, then any optical activity of the product recovered is indicative of a content of sucrose ester. For example, the monopalmitate ester of sucrose has a combined sucrose content of 59% and a specific rotation of 59° to 60° under the above conditions.

Although optical activity can not be accepted as an absolute measure of the percent oligosaccharide content of the ester unless the exact nature of the ester is known, there is a close correlation between the percent combined sucrose content and the observed specific rotation. Thus, for example, the specific rotation of the octa ester of sucrose will be substantially less than the monoester of sucrose because of its lower content of combined sucrose. Moreover, the specific rotation of the product will depend on the nature and concentration of the oligosaccharide ester, whatever it is, in the product being measured. Thus, figures for specific rotation, sometimes designated as "[α]" are indicative of ester formation in the interesterification reaction, the degree of esterification being indicated by other characteristics such as hydroxyl value, saponification value, and total fatty acid content as determined by procedures well known in the art.

The following example will illustrate the manner in which the invention may be practiced. It will be understood, however, that the example is not to be construed as limiting the scope of conditions claimed hereinafter.

#### Example I

10 gms. of sucrose, 18 gms. of a mixture of 80% soybean oil and 20% cottonseed oil hydrogenated to an iodine value of about 76, and 100 milliliters of pyridine were mixed and heated to 100°±3° C. After the above temperature was reached 0.18 gm. of sodium methoxide catalyst was added to the heated mixture and the interesterification reaction was allowed to proceed. At various time intervals, 20 milliliter aliquots were removed from the reacting mixture and the catalyst in these aliquots was inactivated by addition thereto of one milliliter of a 50% aqueous solution of acetic acid. Following inactivation of the catalyst the aliquot was subjected to distillation to remove substantially all of the pyridine. The distillation residue was taken up in 100 mls. of a 4 to 1 mixture of ethyl acetate and n-butanol and water washed. The water washed fatty products were recovered by evaporating the ethyl acetate-n-butanol solvent in a steam bath under a stream of nitrogen. The recovered reaction product was measured for optical activity in accordance with the procedure described above. The results obtained are shown in the following table.

Solvent	Specific Rotation After Minutes of Reaction Time		
	20 Min.	60 Min.	240 Min.
Pyridine.....	1.9	7.4	21.8

It is to be understood that in the foregoing example the sucrose may be replaced with any of the non-reducing oligosaccharides hereinbefore mentioned with comparable results. Similarly other fatty esters of the character hereinbefore indicated may be substituted for the glyceride oils of the example, which is intended to be illustrative only.

I claim:

1. A process for preparing fatty esters of non-reducing oligosaccharides which comprises reacting a non-reducing oligosaccharide with a fatty acid ester selected from the group consisting of fatty acid esters of aliphatic primary monohydroxy alcohols having from 1 to 4 carbon atoms

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and fatty acid esters of aliphatic and alicyclic polyhydroxy substances, in the presence of an interesterification catalyst, at a temperature in the range from about 50° to about 115° C. and in the presence of pyridine, the said non-reducing oligosaccharide being in a molar ratio to the said fatty acid ester of from about 30:1 to about 1:20 and the pyridine being present in an amount from 1/2 to 50 times by weight of the said fatty acid ester.

2. The process of claim 1 wherein the non-reducing oligosaccharide is sucrose.

3. A process for preparing fatty esters of sucrose which comprises reacting sucrose with a fatty acid ester selected from the group consisting of fatty acid esters of aliphatic primary monohydroxy alcohols and fatty acid esters of polyhydroxy alcohols, all of said alcohols having not more than 3 carbon atoms, in the presence of an interesterification catalyst, at a temperature in the range of from about 80° to about 115° C. and in the presence of pyridine.

4. A process for preparing fatty esters of sucrose which comprises reacting sucrose with a fatty acid ester of glycerol, in the presence of from about 0.3% to about 2% of an interesterification catalyst by weight of the glycerol ester, at a temperature in the range from about 80° to about 115° C. in a reaction medium comprising essentially pyridine.

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5. The process of claim 4 wherein the fatty acid ester is a triglyceride.

6. The process of preparing fatty esters of sucrose which comprises reacting sucrose and a fatty triglyceride in the presence of an interesterification catalyst at a temperature of about 100° C. in a reaction medium comprising essentially pyridine, inactivating the catalyst by acidulation, distilling substantially all the pyridine from the reaction mixture, taking up the residue in a solvent and water-washing the resultant solution, whereby undistilled pyridine and unreacted sucrose are removed therefrom.

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