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

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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 in a minimum of time 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.

We 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 certain sulfur-containing compounds.

Generally speaking, the invention contemplates reacting the non-reducing oligosaccharides with the fatty 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 150° C., and in the presence of a sulfur-containing compound of the formula



where R and R′ are alkyl groups having from 1 to 3 carbon atoms. Following completion of 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 glucoxylose; the trisaccharides; raffinose, melezitose and gentianose; and the tetra-saccharide; 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 aliphatic monohydroxy alcohols having from 1 to about 8 carbon atoms, for example, methanol, ethanol, hexanol, and octanol, specific examples being methylpalmitate, ethylpalmitate and octapalmitate. In addition, fatty acid esters of completely or incompletely esterified polyhydric alcohols having from 2 to 6 hydroxyl groups, such as ethylene 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.

Just as mono- and diesters of glycerol can be prepared from the reaction of glycerine with a triglyceride, so incompletely esterified sucrose esters can be prepared in accordance with the present invention by 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 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 our purposes however we 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), the fatty acid portions of which have from about 12 to about 22 carbon atoms can be reacted with the non-reducing oligosaccharide with the aid of the particular sulfoxide reaction medium herein covered.

The crux of our invention lies in the selection of the solvent which comprises the reaction medium. The choice of solvent is essential to the realization of rapid and efficient interesterification of the non-reducing oligosaccharide and the fatty ester under the conditions hereinbefore set forth. We have found that in general the sulfur-containing compounds of the formula



where R and R′ are alkyl groups having from 1 to 3 carbon atoms, are suitable as solvents in our process. These compounds promote a rapid rate of reaction with minimum catalyst requirements and undergo a minimum of decomposition during the interesterification reaction.

With these sulfoxide solvents we have found in general that the rate of interesterification decreases with increase in molecular weight of the sulfoxide; that solvent volume requirements in the reaction decrease with increasing solubility of the non-reducing oligosaccharide in the solvent; and that the solubility of the non-reducing oligosaccharide in the sulfoxide decreases with increase in the number of carbon atoms in the longest chain of the alkyl groups attached to the sulfoxide nucleus.

Although it is evident from the foregoing that the amount of solvent required for any given interesterification will vary depending upon the particular solvent which is to be used, the actual amount of solvent is not critical.

The proportion of sulfoxide solvent hereinbefore defined may be varied from ⅓ to 50 times by weight of the

fatty ester employed for reaction with the oligosaccharide. In any reaction using dimethylsulfoxide as the solvent, where all variables except solvent ratio are maintained constant, for example, the amount of ester formed by the interesterification will increase with increase in the amount of sulfoxide solvent employed at the lower levels of solvent usage, i. e., from about ⅓ to 1 part of solvent per part of ester. It is to be understood, however, that the solvent usage is normally adjusted depending upon the particular reactants to be interesterified. In any event, sufficient solvent should be used so that the advantages associated with solvent usage, e. g. rapid interesterification, may be realized.

Of the sulfoxide solvents which come within the purview of the foregoing generic definition we prefer to use those which are characterized by greater solubility in water and greater volatility such as dimethylsulfoxide, diethylsulfoxide and methyl-ethyl sulfoxide. The aforementioned characteristics of these compounds are advantageously utilized in removing the solvent from the products of 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 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, we 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 radicals in each mole of ester substance. Thus, for example, if 0.1 mole of methylpalmitate is reacted with 1 mole of sucrose under the hereinbefore defined conditions, and at reduced pressure, essentially all of the sucrose ester formed will be the monoester. If the molar ratio is changed to 1:1, one obtains a high yield of monoester of sucrose, but more diester will be present. A product averaging approximately 2 palmitic acid groups per mole of sucrose may be obtained with a molar ratio of methylpalmitate to sucrose of 2:1. When molar ratios of 4:1, 8:1, or 10:1 are used the average number of palmitic acid radicals per mole of sucrose obtained may be 3.5, 6, or 7.5.

Although our process is illustrated herein principally with the use of sodium methoxide as the catalyst, effective practice of our 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 our 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 our process in amounts from about 0.2% 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 paticular 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. In a sucrose-methyl ester interesterification for example, with optimum amounts of dimethylsulfoxide solvent and with sodium methoxide as the catalyst, at temperatures of 100° C., we found that equilibrium was reached within about 5 minutes reaction time and that somewhat longer reaction times were required at lower temperatures. However, substantial ester formation was observed at reaction temperatures of about 50° C. Temperatures above 100° C., such as 150° C. may, of course, be employed, but in view of the high rate of reaction observed in use of the solvents of the present invention, such temperatures may only infrequently be necessary to accomplish the desired ester formation. Generally speaking, with any of the aforementioned reactants, catalysts, or solvents and within the ranges of proportions set forth, the process of our invention is preferably carried out at a temperature in the range from about 75° to about 125° C.

Although our process is normally carried out at atmospheric pressure, it can if desired be carried out under reduced pressure, an operation which at times is decidedly advantageous. For example, when a fatty acid ester of methanol is reacted with sucrose, operation under reduced pressure, such as about 80 mm. of mercury, enables the methanol formed as a result of the interesterification to be removed from the reaction zone substantially as rapidly as it is liberated, thus promoting a substantially complete conversion of the methyl ester to sucrose fatty ester.

When the fatty esters of aliphatic monohydroxy primary alcohols are reacted with a non-reducing oligosaccharide, at a temperature of 100° C., and in the presence of sodium methoxide catalyst and any of the aforementioned sulfoxide solvents, we have found that the interesterification is substantially complete in about three minutes. When, on the other hand the fatty esters of polyhydroxy compounds are reacted with a non-reducing oligosaccharide under these conditions, a slightly longer time is normally required and we have found in this latter instance that the reaction is substantially complete in from about 5 to 15 minutes.

No adverse effects have been noted if the interesterification is allowed to continue for as long as one to two hours but from a practical standpoint little advantage is gained from such practice. Because of the rapidity at which the reaction progresses under the conditions of our process, times of less than two minutes, and even as little as about 30 seconds at temperatures of 100°–125° C. may be found to be adequate to achieve the degree of reaction, so that the process lends itself well to continuous as well as to batch methods.

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 and, as suggested above, to conduct the reaction under vacuum so that displaced alcohol is distilled off. High yields of sucrose esters are obtainable in this way and, of course, unreacted volatile esters can be separated subsequently by distillation or other means, such as solvent partition, to yield sucrose esters of high purity.

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 concen-

tration 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 examples 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 examples will illustrate the manner in which the invention may be practiced. It will be understood, however, that the examples are not to be construed as limiting the scope of conditions claimed hereinafter.

Examples 1, 2, 3, and 4.—A number of sulfoxide compounds coming within the scope of the definition hereinbefore given were employed in the formation of sucrose esters. In each case 3.13 grams of sucrose (0.009 mole) and 5.5 grams (0.006 mole) of a mixture of 80% soybean oil and 20% cottonseed oil hydrogenated to an iodine value of about 76 and 31 ml. of the sulfoxide reaction medium were introduced into a reaction vessel provided with mechanical stirring means. The whole was heated to 100° C., and then 1 milliliter of a 10% suspension of sodium methoxide in xylene was added.

5 milliliter aliquots were removed from the reaction mix after 2, 5 and 20 minutes respectively and in each instance the catalyst was inactivated by the addition of 5 ml. of a 50% aqueous solution of acetic acid.

After one hour the catalyst in the remaining portion of the reaction mix was inactivated by the addition of 10 ml. of the 50% aqueous acetic acid solution.

In all cases the reaction mixture containing the inactivated catalyst was taken up in a 4:1 ethyl acetate and n-butanol mixture and washed three times with hot water. The ethyl acetate-n-butanol solvent was removed from the washed mixture by evaporation on a steam bath under a nitrogen atmosphere. The mixture substantially free of the solvent was then steam deodorized at a pressure of 3 mm. of mercury for ½ hour at 130–140° C. The thus recovered reaction product was measured for optical activity in accordance with the aforedescribed method with the results indicated in the table below. Substantial production of sucrose ester is indicated in all cases.

Solvent	Specific Rotation After Minutes of Reaction Time			
	2 Min.	5 Min.	20 Min.	60 Min.
dimethylsulfoxide	[1] 23.2	29.4	[2] 31.2	------
methyl-ethyl sulfoxide	31.8	31.2	31.9	30.7
diethylsulfoxide	32.8	31.6	31.1	31.2
dipropylsulfoxide	22.4	27.9	21.6	------

[1] 3 minutes reaction time.
[2] 15 minutes reaction time.

Example 5.—3.42 grams (0.01 mole) of sucrose, 7.38 g. (0.02 mole) of octylpalmitate and 34 ml. of dimethyl sulfoxide were introduced into a reaction vessel provided with mechanical stirring means. The whole was heated to 100° C. and then 2 ml. of a 10% suspension of sodium methoxide in xylene was added. After stirring and heating for one hour at 100° C. the catalyst was inactivated by the addition of 10 ml. of 50% aqueous acetic acid solution. The reaction mixture was taken up in an equal volume of a 4:1 ethyl acetate and n-butanol mixture and washed three times with hot water. The ethyl acetate-n-butanol solvent was removed from the washed mixture by evaporation on a steam bath under a nitrogen atmosphere. The mixture substantially free of this solvent was then steam deodorized at a pressure of 3 mm. of mercury for ½ hour at 130–140° C. The product was found to have a specific rotation of 9.85.

Example 6.—10 grams (0.03 mole) of sucrose, 16 grams (0.06 mole) of methyl palmitate and 100 ml. of dimethyl sulfoxide were introduced into a reaction vessel provided with mechanical stirring means. The whole was heated to 100° C. and then 2.5 ml. of a 10% suspension of sodium methoxide in xylene was added. 10 milliliter aliquots were removal from the reaction mixture after varying lengths of time and in each instance the catalyst was inactivated by the addition of 5 ml. of a 50% aqueous solution of acetic acid. The mixture containing the inactivated catalyst was taken up in 4:1 ethyl acetate and n-butanol and washed three times with hot water. The ethyl acetate-n-butanol solvent was removed from the washed mixture by evaporation on a steam bath under a nitrogen atmosphere. The resultant substantially solvent-free mixture was then steam deodorized at a pressure of 3 mm. of mercury for ½ hour at 130–140° C. The thus recovered reaction product was measured for optical activity with the results indicated in the table below.

Time, Min.	Specific Rotation of Product
1	21.6
3	28.3
4	29.7

The reaction product obtained from an aliquot taken after 30 minutes had a specific rotation of 25.0 suggesting the possibility of an optimum reaction time between 4 and 30 minutes.

Example 7.—This run was carried out according to the procedure of Example 6 but employing 8.55 g. (0.025 mole) of sucrose and 14.2 g. (0.05 mole) of ethylpalmitate in 86 ml. of dimethylsulfoxide. The reaction products recovered from aliquots taken at various times were measured for optical activity with the results indicated below.

Time, Min.	Specific Rotation of Product
2	24.0
5	25.7
20	24.7
60	27.3

Example 8.—A solution of 12.5 g. (0.021 mole) of raffinose pentahydrate in a mixture of 50 ml. of dimethyl sulfoxide and 100 ml. of benzene was heated at reflux with mechanical stirring while removing and collecting the evolved water in a Dean and Stark trap. When the solution was dry, as evidenced by no further evolution of water, the benzene was distilled off and an additional 75 ml. of dimethylsulfoxide was added to the residue. After 12.5 g. (0.014) of a mixture of 80% soybean oil and 20% cottonseed oil hydrogenated to an iodine value of about 76 was added to this mixture, the mixture was heated to 100° C. whereupon 2 ml. of a 10% suspension of sodium methoxide in xylene was added. Ten milliliter

aliquots were removed from the reaction mixture and treated as in Example 6. The specific rotation of the product recovered from the various aliquots is given in the following table.

Time, Hours	Specific Rotation
0.5	41.2
1	46.1
2	51.0

It is to be understood that the reaction product may be recovered in ways other than that described in the foregoing examples. Thus, if desired, the crude reaction mixture may simply be water washed to remove substantially all of the sulfoxide solvent and unreacted sucrose and then steam deodorized. Alternatively the sulfoxide solvent may first be removed substantially completely by distillation and the residue may then be water washed and deodorized.

Having thus described our invention, we 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 the fatty acid esters of aliphatic primary monohydroxy alcohols having from 1 to about 8 carbon atoms and fatty acid esters of polyhydroxy substances, in the presence of an interesterification catalyst, at a temperature in the range from about 50° to about 150° C. and in the presence of sulfur-containing compound of the general formula



wherein R and R′ are alkyl groups having from 1 to 3 carbon atoms.

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

3. The process of claim 1 wherein the sulfur-containing compound is dimethyl sulfoxide.

4. The process of claim 1 wherein the sulfur-containing compound is methyl ethyl sulfoxide.

5. The process of claim 1 wherein the sulfur-containing compound is diethyl sulfoxide.

6. The process of claim 1 wherein the sulfur-containing compound is dipropyl sulfoxide.

7. The process of claim 1 wherein the sulfur-containing compound is dimethyl sulfoxide and wherein the amount of sulfur-containing compound is from one third to fifty times by weight of the fatty ester.

8. A process for preparing fatty esters of sucrose which comprises reacting sucrose with a fatty acid ester selected from the group consisting of the fatty acid esters of aliphatic primary monohydroxy alcohols and the 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 from about 75° to about 125° C., and in the presence of a sulfur-containing compound of the general formula



wherein R and R′ are alkyl groups having from 1 to 3 carbon atoms.

9. 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 0.2 to 2.0% of an interesterification catalyst by weight of the glycerol esters, at a temperature in the range from about 75° to about 125° C. in a reaction medium comprising essentially dimethyl sulfoxide.

10. The process of claim 9 wherein the fatty acid ester is a triglyceride.

11. A process for preparing fatty esters of sucrose which comprises reacting sucrose with a fatty acid ester of methanol in a reaction medium comprising essentially dimethyl sulfoxide, in the presence of from about 0.2 to about 2.0% of an interesterification catalyst by weight of the methyl ester, at a temperature in the range from about 75° to about 125° C. and at such a sufficiently low pressure that the methanol liberated during the reaction is continuously distilled from the reaction mix whereby the reaction proceeds to substantial completeness.

12. The process for 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 dimethyl sulfoxide, inactivating the catalyst by acidulation, and thereafter freeing the reaction mixture of dimethyl sulfoxide and unreacted sucrose.

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