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PROCESS FOR THE PRODUCTION OF
SUGAR ESTERS

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This invention relates to a new and improved process for preparing carboxylic esters of oligosaccharides and more especially of esters of non-reducing oligosaccharides such as sucrose, and of acetals and ketals of oligosaccharides.

It is known that esters of oligosaccharides and fatty acids have various useful applications. Some are, for instance, softening agents for plastics, ointment bases, washing agents and emulsifiers. Since the sugar esters decompose biologically, washing water containing the esters as washing agents do not form harmful waste water. Further, esters of unsaturated fatty acids represent air drying oils which can be used as additives to lacquers.

The known process for producing fatty esters of non-reducing oligosaccharides consist in interesterifying such oligosaccharides with fatty acid alkyl esters, preferably methyl and ethyl esters of fatty acids, in the presence of interesterification catalysts and inert solvents.

The use of fatty acid alkyl esters is however associated with a series of disadvantages which lead to considerable technical difficulties in the performance of the reaction. In particular the production of the technically especially important monoesters succeeds only with the use of a large excess of sugar, whereby on the one hand the working up of the resulting reaction mixture presents considerable difficulties since the large excess of sugar must be separated from the ester produced. On the other hand a substantial proportion of the solvent used remains held in the unreacted sugar present in the reaction mixture so that with a process of this kind undesirable losses of solvent are involved.

Moreover, the reaction proceeds only to a certain equilibrium. Therefore the aliphatic alcohol released in the interesterification reaction must be distilled during the course of the interesterification together with solvent and then be separated by special process steps from the solvent before its further use. Furthermore, these reactions can in general only be carried out in comparatively dilute solutions so that the attainable space-time yield is unsatisfactory.

It has now surprisingly been found that the aforesaid disadvantages can be completely avoided by the use of carboxylic acid aryl esters such as are exemplified by phenyl stearate. It is thus possible by reaction of non-reducing sugars, but also of sugar acetals and ketals, with carboxylic acid aryl esters in the presence of the usual basic or acid interesterification catalysts to produce any desired sugar ester in a smooth reaction and in high yields without the use of solvents in a heterogeneous reaction system. In particular the difficulties hitherto arising from the use of a solvent are obviated.

It is especially advantageous that the phenol released in the interesterification reaction does not need to be separated from the reaction mixture because of the rapid

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establishment and the suitable position of the esterification equilibrium during the reaction. After the reaction has been carried out, optionally however even during the interesterification, the phenol can be separated in a simple manner from the reaction mixture. By separation of the salt resulting from the interesterification catalyst the resulting crude sugar ester can, if desired, be obtained in especially pure form.

The interesterification can, if desired, also be carried out in several stages. Thus it is possible, for example, to interesterify one mol of sugar with between 1 and 7 mols of carboxylic acid aryl ester and the thus obtained mono- to hepta-ester is then again interesterified to the octa-ester optionally after addition of further quantities of carboxylic acid aryl ester. The ratio of the amounts of the reaction components to each other depends on the end product to be produced so that accordingly from one to all of the hydroxyl groups of the sugar or sugar derivative can be esterified. If, for example, the formation of an octo-ester is desired it is suitable to use stoichiometric amounts of the reactants whereby, after distilling off the calculated quantity of phenol, technically pure octo-ester is present. In the production of higher esters, however, it can also be advantageous to produce the monoester first by reaction of the sugar and the aryl ester in the approximate mol ratio of 1:1 and to produce therefrom the desired higher esters, if necessary, by stepwise further addition of aryl ester.

In the heterogeneous reactions described herein the grain size of the sugar is of some importance. Especially in the production of lower sugar esters it should be as small as possible in order to prevent higher esters from forming at the surfaces of the particles while the inner parts of the particles are not involved in the reaction. If necessary, for obtaining a uniform reaction, the stirrability of the mixture can be improved by the addition of inert dispersing agents such as, for example, toluene or xylene.

The technically especially important sugar mono- or di-esters may readily be produced by mixing 1 mol of sugar with about 1 or 2 mols of carboxylic acid aryl ester at an elevated temperature is the presence of an interesterification catalyst. The use of a great excess of sugar is thus not necessary. The reaction is advantageously carried out in a kneading machine since the reaction mixture tends at first to agglomerate. After some time, however, a homogeneous, readily stirrable mass is formed. The melt thus obtained consists, after distilling off the phenol, for the most of pure sugar mono- or di-ester and can be purified by separation of the catalyst and from the salt resulting from the latter.

The sugar or sugar derivative can be reacted with carboxylic acid aryl esters, if desired, also in a homogeneous system, i.e., using solvents which enable the sugar to be dissolved. Since the use of an excess of sugar such as was necessary hitherto in the interesterification with fatty acid alkyl esters for the production especially of lower sugar esters, is avoided, the disadvantages brought about in the previous processes by the presence of large quantities of unreacted sugar in the resulting reaction mixture do not arise. Furthermore it is no longer necessary to distil the phenol set free by the interesterification continuously from the reaction mixture since in the use of carboxylic acid aryl esters the equilibrium lies, as mentioned above, substantially on the side of the sugar ester. After the reaction has ended the solvent can readily be distilled from the reaction mixture.

The further working up of the mixture thus obtained that contains the sugar ester and catalyst residues is effected in a manner analogous to that described hereinbefore in the case of the heterogeneous reaction systems. Since in this manner of operation of the process furthermore only very small additions of interesterification catalysts are required, the crude reaction product obtained after the separation of the phenol can be used for many technical purposes directly without removal of the salt resulting from the catalyst. The colouring of the crude product is so slight that a bleaching, for instance, with hydrogen peroxide, is not necessary.

The solvent distilled off can be reused directly without further purification since small quantities of phenol which may have been entrained during the distillation from the reaction mixture together with the solvent distilled off may be allowed to remain in the solvent inasmuch as their presence during the interesterification has no adverse influence on the course of the reaction.

Non-reducing oligosaccharides which are suitable for treatment in accordance with the process of the invention are those having no potentially free carbonyl radical. These include the disaccharides: sucrose, trehalose (yields two molecules of glucose or hydrolysis) and glucoxylose (yields one molecule of glucose and one molecule of xylose on hydrolysis), the trisaccharides: raffinose (yields one molecule of each of galactose, glucose and fructose on hydrolysis), melezitose (yields 2 molecules of glucose and 1 molecule of fructose on hydrolysis) and gentianose (yields two molecules of glucose and 1 molecule of fructose on hydrolysis), and the tetrasaccharide: stachyose (yields 2 molecules of galactose and 1 molecule of each of glucose and fructose on hydrolysis). Thus the oligosaccharides of concern here are non-reducing polyhydroxy compounds having from 7 to 60 hydroxyl groups per molecule.

As mentioned above, there may be used besides non-reducing oligosaccharides also acetals and ketals of sugars. The following may be named for example: methyl, ethyl, propyl, butyl and benzyl glucosides, cyclic bisacetals and ketals of e.g. glucose, fructose and sorbose such as bis-propylidene, bis-isobutylidene and bis-benzylidene glucose etc., bis-cyclohexylidene glucose etc. and diacetone, dimethyl ethyl ketone, and diethylketone glucose etc.

As to the carboxylic acid aryl esters which may be used for the process according to the invention, in principle, all esters are suitable which are derived from aromatic monohydroxy compounds distillable under the interesterification conditions. Especially there may be named the phenyl, the cresyl, the naphthyl and the simple substituted phenyl esters, for instance, chlorophenyl and anisyl esters.

Carboxylic acids from which the carboxylic acid aryl esters may be prepared by reaction with a phenol or metal phenoxide in conventional manner include all organic saturated and unsaturated mono- and polycarboxylic acids such as fatty acids, for instance, capronic acid, oenanthic acid, caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, palmitic acid, margaric acid, stearic acid, nonadecylic acid, arachidic acid, behenic acid, gallic acid, phenyl acetic acid, chlorophenyl acetic acid, phenyl methyl acetic acid, etc., acrylic, protonic acid, sorbic acid, the acids of rosin and of saturated and unsaturated fats and fatty oils, for instance, abietic acid, the acids of tallow, coconut oil, spermwhale oil, lard, cocoa butter, palm oil, castor oil, corn oil, olive oil, soya bean oil, herring oil, menhaden oil, etc., further linoleic acid, ricinoleic acid (12-hydroxy-9-octadecenoic acid) and ricinenic acid (9,11-octadecadienoic acid), other aliphatic monocarboxylic acids, such as synthetic fatty acids, pyruvic acid, leoulinic acid, aromatic acids, for instance, benzoic acid, methyl benzoic acid, chlorobenzoic acid, cinnamic acid, salicylic acid etc., alicyclic carboxylic acids, for instance, cyclopropane monocarboxylic acid, cyclobutane monocarboxylic acid, cyclopentane

monocarboxylic acid, cyclohexane monocarboxylic acid, quinic acid, etc., and heterocyclic carboxylic acids, for instance, furan- α -carboxylic acid, nicotine carboxylic acids, etc.

As suitable aryl esters of polycarboxylic acids there may be mentioned, for instance, the di- and polyphenyl etc. esters of carbonic, oxalic, malonic, succinic, glutaric, adipic, pimelic, sebacic etc. acid, mesoxalic acid, acetone dicarboxylic acid, oxal acetic acid, α -keto-glutaric acid, maleic, fumaric, itaconic, citraconic, acetylene dicarboxylic acid etc., phthalic, iso- and terephthalic, chlorophthalic and hexachloroendomethylenetetrahydrophthalic acid (which is commonly referred to as chlorendic acid), naphthalene dicarboxylic acid, cyclopentadienedicarboxylic acid, and cyclohexadiene dicarboxylic acid, tricarboxylic acid, and hexachloroendomethylenetetrahydrophthalic acid (1,2,3-propenetricarboxylic acid), trimellitic acid (benzene-1,2,4-tricarboxylic acid) and trimesic acid (benzene-1,3,5-tricarboxylic acid), pyromellitic acid, mellitic acid (benzenhexacarboxylic acid), etc.

With aryl esters of such polycarboxylic acids one obtains polymeric sugar esters which may be used, for instance, as softening agents for plastics, lacquer materials, coatings, adhesives, impregnating agents, textile auxiliaries, etc. The sugar esters of unsaturated acids are often air drying and may be polymerized and copolymerized with other polymerizable compounds such as styrene, allyl esters and ethers, acrylic and methacrylic esters and so on.

The interesterification is in general expediently carried out in the presence of the usual basic or acid interesterification catalysts. For this purpose there may be mentioned, for example, alkali metals, such as lithium, sodium and potassium, alkali metal oxides, hydroxides and methoxides, for instance, sodium and potassium methoxide, alkaline earth metals, such as calcium, strontium and barium, alkaline earth metal oxides, hydroxides and methoxides such as calcium methoxide, quaternary ammonium bases such as trimethyl benzyl ammonium hydroxide, methoxides such as tetramethyl ammonium methoxide and lauryl benzyl dimethyl ammonium methoxides. In addition to the methoxides there may be used the corresponding ethoxides, propoxides, butoxides and alkoxides made from alcoholic compounds in general such as lauryl alcohol, ethylene glycol, oleic acid monoglyceride and others, alkali metal salts such as carbonates, phosphates and acetates, further alcoholates, e.g. sodium dimethylpentylate and sodium sucrose, and phenolates, and alkali metal organic compounds containing the alkali metal atom directly bound to a carbon atom as in triphenyl methyl sodium, or to a nitrogen atom as in potassium pyrrole, moreover *p*-toluene sulphonic acid and acid clays.

The catalysts can be applied according to the reaction conditions in quantities of about 0.05 to about 30 percent by weight calculated on the quantity of the carboxylic acid aryl ester used, to the reaction mixture.

Suitable interesterification temperatures lie in general between about 40 and about 170° C. and especially between about 60 and 120° C. In reactions involving a heterogeneous phase the formation of lower sugar esters by the use of higher temperatures e.g. between about 100 and 190° C. and especially between about 130 and 170° C. is favoured, since the reaction mixture under these conditions soon forms a readily stirrable melt. On the other hand a production of sugar mono- or di-esters in the presence of inert solvents, and especially in the production of the technically especially important sugar mono-fatty acid esters, lower temperatures e.g. between about 60 and about 160° C., especially between about 90° and 130° C., are required.

Suitable inert solvents to be used, if desired, in the interesterification, which are able to dissolve the sugar, are, for example, alkylated acid amides, e.g. dimethyl and diethyl formamide and acetamide, dialkyl sulphoxides,

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e.g. dimethyl and diethyl sulphoxide, pyrrolidone, N-methyl-2-pyrrolidone, tertiary amines, e.g. trimethyl and triethyl amine, N-methyl morpholine, pyridine, quinoline, pyrazine, methylpyrazine, dimethylpyrazine, further formyl morpholine, acetyl morpholine, propionyl morpholine and acetyl piperidine.

The interestification can be carried out at normal pressure or in vacuum. The time required to complete the reaction depends on the reaction temperature, the quantity of catalyst and possibly also the concentration of the reactants in the solution. It amounts in general to between about 2 minutes and several hours.

The phenol set free can be removed during the reaction by distillation in vacuum. It can, however, remain in the reaction mixture since the equilibrium of the interesterification lies almost completely on the side of the sugar ester.

On the other hand the esterification when using esters of aliphatic alcohols proceeds only substantially completely when the alcohol set free is continuously removed from the reaction mixture. In the use, for example, of natural triglycerides, because of the slight volatility of the glycerol, one obtains mixtures which are difficult to separate since they contain for example, cane sugar esters and mono-, di- and tri-esters of the glycerol whereas according to the process of the invention cane sugar esters of higher purity are obtained directly.

Example 1

A mixture of 34.2 grams (0.1 mol) of powdered cane sugar, 283 grams (0.8 mol) of linoleic phenyl ester and 3-4 grams of powdered anhydrous potassium carbonate are heated with stirring to 110-120° C. At a pressure of 0.1-0.3 mm. mercury gauge the phenol is at first distilled off very rapidly the quantity corresponding after 3-4 hours to the approximately theoretically expected amount. The sugar suspension present at the beginning of the reaction goes over into a slightly coloured oil. The saccharose octolinoleic ester obtained in almost quantitative crude yield is taken up in ligroin or methylene chloride for separation of the potassium carbonate, the solution treated if necessary with animal charcoal and freed from the solvent whereby the analytically pure product precipitates. The octolinoleic ester of saccharose is an outstandingly dry oil. Saponification value calculated: 185; found: 186. Acid No. calculated: 0; found: less than 2.

Analysis.—Calculated: C, 77.3%; H, 10.15%; O, 12.55%. Found: C, 77.4%; H, 10.69%; O, 12.6%.

Example 2

A mixture of 34.2 (0.1 mol) of finely powdered cane sugar, the equivalent amount of lauric acid phenyl ester (221 grams=0.8 mol) and 3 grams powdered anhydrous potassium carbonate are heated with stirring to 115° C. The phenol which separates is distilled off during the reaction at a pressure of 0.3-0.1 mm. mercury gauge whereby within 4 hours over 96 percent of the expected phenol has been obtained, the quantity rising after a further 3 hours heating to 98 percent of the theoretical. The resulting oil obtained in a yield of above 94 percent of the saccharose octalauric acid ester is separated either by taking up in a solvent and filtering or by decanting from the catalyst. Saponification value calculated: 249; found: 242.

Example 3

A mixture of 68 grams (0.2 mol) of bicyclohexylidene glucose, 72 grams of stearic acid phenyl ester (0.2 mol) and 2.3 grams of powdered anhydrous potassium carbonate are heated with stirring 110-115° C. At a pressure of 0.1 to 0.3 mm. mercury gauge practically all phenol is distilled off within about 2 hours. The viscous reaction product is taken up in ligroin or methylene chloride, the solution treated, if necessary, with animal charcoal and filtered whereby after evaporation the 3-stearic

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acid ester of 1,2,5,6-bicyclohexylidene glucose is obtained as a colourless semi-solid product in a yield of 90-100 percent of the theoretical. Saponification value calculated: 92.5; found: 97.

Analysis.—Calculated: C, 71.2%; H, 10.23%; O, 18.48%. Found: C, 71.65%; H, 10.40%; O, 18.70%.

Example 4

A mixture of 68.4 grams (0.2 mol) of finely ground cane sugar, 72 grams (0.2 mol) of stearic acid phenyl ester and 6 grams of powdered anhydrous potassium carbonate are heated with stirring under nitrogen atmosphere to 155-160° C. The reaction mixture agglomerates. After some time it forms a homogeneous, readily stirrable mass. After distilling off the phenol split off in vacuum (18.6 grams) there is obtained in theoretical yield a product which is soluble in hot water as well as in toluene and thus contains no unreacted sugar, the analysis data shows the presence of a cane sugar mono-stearate.

Example 5

A mixture of 68.4 grams (0.2 mol) of cane sugar and 72 grams (0.2 mol) of stearic acid phenyl ester are heated as in Example 4 with addition of 6 grams of potassium carbonate to 160° C. After about 30 minutes a further 72 grams (0.2 mol) of stearic acid phenyl ester are added. After a period of heating of altogether about 45 minutes the phenol is distilled off in vacuum. Cane sugar distearate is obtained in practically quantitative yield which contains only traces of unreacted sugar and the small quantity of catalyst as impurities.

Example 6

68.4 grams (0.2 mol) of cane sugar, 144 grams (0.4 mol) of stearic acid phenyl ester and 6 grams of powdered potassium carbonate are heated together to 155-160° C. The reaction proceeds as in Example 4. After distilling off the phenol split off cane sugar distearate is obtained in high yield.

Example 7

The procedure of Example 5 is followed with the difference that about 10 minutes after the addition of the second equivalent of stearic acid phenyl ester a third equivalent of stearic acid phenyl ester (72 grams=0.2 mol) are added. After removal of the phenol a cane sugar triester is obtained in quantitative crude yield (230 grams).

Example 8

The procedure of Examples 5 and 7 is followed except that altogether seven equivalents of stearic acid phenyl ester are added portionwise and reacted with the cane sugar. Total reaction time amounts to about 2 hours. The product is principally heptastearate of cane sugar.

Example 9

A mixture of 34.2 grams (0.1 mol) of cane sugar, 252 grams (0.7 mol) of stearic acid phenyl ester and 3 grams of potassium carbonate are heated to 150° C. After 3 hours reaction time the phenol is distilled off in vacuum, whereby a heptastearate of cane sugar is obtained in quantitative crude yield (223 grams) as a pale, brown, waxlike product.

Example 10

68.4 grams (0.2 mol) of cane sugar and 70.8 grams (0.2 mol) of linoleic acid phenyl ester are heated to 160° C. with stirring and under nitrogen. After addition of 6 grams of potassium carbonate the mass agglomerates, dissolves however already after only a few minutes. After about 1 hour the phenol is distilled off in vacuum. The remaining crude product (121 grams), the mono-linoleic acid ester of cane sugar, is completely soluble in toluene and hot water.

Example 11

A mixture of 68.4 grams (0.2 mol) of cane sugar and 55.2 grams (0.2 mol) of lauric acid phenylester are heated with stirring and under nitrogen to 160° C. and treated with 6 grams of potassium carbonate. After about 30 minutes a further equivalent of lauric acid phenyl ester (55.2 grams=0.2 mol) are added and after a further 30 minutes the phenol split off (37 grams) is distilled off in vacuum. The crude product obtained in quantitative yield is cane sugar dilaurate.

Example 12

A mixture of 102.7 grams (0.3 mol) of cane sugar and 108 grams (0.3 mol) of stearic acid phenyl ester are heated to 160° C. at normal pressure with stirring and under nitrogen atmosphere. As soon as this temperature is reached 7.5 grams of potassium hydroxide are added to the suspension. After a few moments a clear melt is formed. The temperature is maintained for a further 15 minutes at 155-160° C. After cooling to 110° C. substantial bleaching is achieved by the addition of hydrogen peroxide. The product obtained after distilling off the phenol in vacuum is water soluble and can be used in this form as a washing raw material.

Example 13

A mixture of 274 grams (0.8 mol) of cane sugar, 342.4 grams (1.6 mol) of salicylic acid phenyl ester and 24 grams of potassium carbonate are heated to 140° C. A few minutes after reaching the latter temperature the suspension becomes homogeneous. After a reaction time of 45 minutes the calculated quantity of phenol is distilled off in vacuum. The disalicylic acid ester of saccharose is obtained in high yield.

Example 14

A solution of 102.7 grams (0.3 mol) of cane sugar and 108 grams (0.3 mol) of technical stearic acid phenyl ester in 400 milliliters of dimethylformamide are treated at 105° C. with 1.5 grams potassium hydroxide. After about 2 minutes the potassium hydroxide has dissolved the temperature simultaneously rising to 110° C. A test taken after a few minutes and free from solvent is already soluble in water. After 2 hours heating to 110° C. the solvent and the phenol resulting from the reaction are distilled off in vacuum. Without any working up one obtains a product soluble in water and toluene the analysis data for which indicate the presence of a saccharose mono-stearate.

Corresponding results are obtained if dialkyl sulphoxides, pyridine, alkylated pyridines or their technical mixtures, diethyl formamide or dimethyl acetamide are used as solvents.

Example 15

A solution of 102.7 grams of cane sugar (0.3 mol) and 248.4 grams (0.9 mol) of lauric acid phenyl ester in 400 milliliters of dimethylformamide are treated as in Example 14 with 1.5 grams potassium hydroxide. After 2 hours reaction time, after distilling off the solvent and the phenol a saccharose trilaurate is obtained in quantitative yield.

Example 16

102.7 grams (0.3 mol) of cane sugar and 540 grams (1.5 mol) of stearic acid phenyl ester are dissolved in 400 milliliters of dimethylformamide and treated at 110° C. with 0.5 gram of potassium hydroxide. The temperature rises to 120° C. it is further treated as in Example 14. A saccharose pentastearate is obtained.

Example 17

111.3 grams (0.3 mol) of dehydrated castor oil acid phenyl ester are added at 110° C. to a solution of 112.9 grams (0.33 mol) of cane sugar in 400 milliliters dimethylformamide. After the addition of 1.5 grams of potassium hydroxide and heating for a further 2 hours the

solvent and phenol are distilled off. A mono-dehydrated castor oil ester of saccharose results.

Example 18

102.7 grams (0.3 mol) of cane sugar and 216 grams (0.6 mol) of stearic acid phenyl ester are dissolved in 400 milliliters of dimethylformamide. After the addition of 1.5 grams potassium hydroxide at 110° C. the solution is heated for a further 15 minutes to 110° C. After distilling off the solvent and the phenol a saccharose distearate is obtained in high yield.

Example 19

102.7 grams (0.3 mol) of cane sugar and 216 grams (0.6 mol) of stearic acid phenyl ester are dissolved in 200 milliliters of dimethylformamide. After the addition of 1.5 grams of potassium hydroxide at 110° C. the solution is heated for a further 2 hours at 110° C. After distilling off the solvent and the phenol a saccharose distearate is obtained in high yield.

Example 20

A solution of 102.7 grams (0.3 mol) of cane sugar and 108 grams (0.3 mol) of stearic acid phenyl ester in 1200 milliliters of pyridine are treated at 110° C. with 1.5 grams KOH. After 2 hours heating to 110° C. the solvent and the phenol are distilled off in vacuum. A colourless product is obtained which corresponds to that of Example 14.

Example 21

A mixture of 102.7 grams (0.3 mol) of cane sugar and 112.6 grams (0.3 mol) of stearic acid cresyl ester are dissolved in 400 milliliters of dimethylformamide and further reacted as in Example 14. After distilling off the solvent and the cresol in vacuum a product is obtained which corresponds to that resulting in Example 14.

Example 22

A mixture of 112.9 grams (0.33 mol) of cane sugar, 108 grams (0.3 mol) of stearic acid phenyl ester and 12 grams potassium phenylate are heated for 30 minutes to 155° C. After distilling off the phenol in vacuum a product is obtained which compares in its properties with the saccharose esters obtained with potassium carbonate.

Example 23

A mixture of 102.7 grams (0.3 mol) of cane sugar and 118 grams (0.3 mol) of stearic acid-(o-chlorophenyl)-ester are dissolved in 400 milliliters of dimethylformamide and reacted further as in Example 14. After distilling off the solvent and the o-chlorophenol in vacuum a product is obtained which corresponds to that produced in Example 14.

Example 24

A mixture of 102.7 grams (0.3 mol) of cane sugar and 98 grams (0.3 mol) of lauric acid-(α -naphthyl)-ester are dissolved in 400 milliliters of dimethylformamide and reacted further as in Example 14. After distilling off the solvent and the α -naphthol in vacuum a mono-lauric acid ester of sucrose is obtained.

Example 25

50 grams (0.1 mol) of anhydrous raffinose are heated to 120° C. together with 72 grams stearic acid phenyl ester (0.2 mol) and 1 gram potassium hydroxide as catalyst for half an hour. After distilling off the dimethylformamide and the phenol in vacuum the distearic acid ester of raffinose is obtained in practically quantitative yield.

Example 26

25 grams (0.05 mol) of anhydrous finely ground raffinose, 138 grams (0.5 mol) of lauric acid phenyl ester and 3 grams of powdered sodium hydroxide are heated in

a kneading machine for 1 hour at 130° C. The clear melt obtained is freed from phenol in vacuum at 120° C. A deca-lauric acid ester of raffinose is obtained in practically quantitative yield.

Example 27

A mixture of 102.7 grams (0.3 mol) sucrose, 42.8 grams (0.2 mol) diphenyl carbonate and 106.2 grams (0.3 mol) linoleic acid phenyl ester is heated under nitrogen and under stirring at 150° C. while adding 9 grams sodium carbonate. The reaction proceeds according to Example 4. After distilling off of the phenol one obtains an air-drying product soluble in water and in toluene.

Example 28

A mixture of 51.3 grams (0.15 mol) sucrose, 30 grams (0.1 mol) adipic acid diphenyl ester and 70.8 grams (0.2 mol) linoleic acid phenyl ester is heated at 130° C. After adding 9 grams sodium carbonate the mixture is heated for 1½ hours at 130° C. under nitrogen with stirring. Then an additional 106.2 grams (0.3 mol) linoleic acid phenyl ester are added. The heating is continued for another hour. After distilling off of the calculated amount of phenol under vacuum one obtains a very well air-drying product.

Example 29

136.8 grams (0.4 mol) sucrose and 90 grams (0.3 mol) adipic acid diphenyl ester are dissolved in 533 milliliters of dimethylformamide. After the addition of 1 gram sodium hydroxide at 110° C. the solution is heated for 3 hours at 115° C. After distilling off of the solvent and of the phenol one obtains a slightly yellow, water-soluble resin.

Example 30

To a solution of 171.2 grams (0.5 mol) sucrose, 75 grams (0.25 mol) adipic acid diphenylester and 53.5 grams (0.25 mol) diphenyl carbonate in 600 milliliters of dimethylformamide there are added 1.25 grams sodium hydroxide at 110° C. After a reaction time of 2 hours the dimethylformamide and the phenol are distilled off. One obtains a slightly coloured, water-soluble resin.

Example 31

To a solution of 171.2 grams (0.5 mol) sucrose and 88.6 grams (0.25 mol) sebacic acid diphenyl ester in 600 milliliters of dimethylformamide there are added 1.25 grams sodium hydroxide at 110° C. One proceeds as in Example 30 and obtains a glass-clear, water-soluble product.

Example 32

To a solution of 171.2 grams (0.5 mol) sucrose, 150 grams (0.5 mol) adipic acid diphenyl ester and 160.5 grams (0.75 mol) diphenyl carbonate in dimethylformamide there are added 1.25 grams sodium hydroxide. The solution is heated at 115° C. for 2 hours. After working up the solution one obtains a cross-linked, non-soluble, slightly coloured resin.

If the addition of the sodium hydroxide to the solution is carried out at 110° C. the reaction is highly violent.

Example 33

136.8 grams (0.4 mol) sucrose and 80.6 grams (0.3 mol) fumaric acid diphenyl ester are dissolved in 533 milliliters of dimethylformamide. The solution is heated at 115° C. and 1 gram sodium hydroxide is added. The reaction proceeds as in Example 29. After distilling off of the solvent and of the phenol a slightly coloured, polymerizable resin is obtained.

Example 34

136.8 grams (0.4 mol) sucrose and 127.3 grams (0.4 mol) isophthalic acid diphenyl ester are dissolved in 600

milliliters of dimethylformamide. After the addition of 1.5 grams sodium hydroxide the solution is treated as in Example 29. After distilling off of the solvent and of the phenol a corresponding polyester is obtained.

Example 35

To a solution of 102.7 grams (0.3 mol) sucrose and 131.4 grams (0.3 mol) of trimesic acid triphenyl ester (triphenyl trimesate) in 500 milliliters of dimethylformamide there are added 1.5 grams sodium hydroxide. The solution is heated at 115° C. for 3 hours. After working up a highly cross-linked product is obtained.

Example 36

68.4 grams (0.2 mol) sucrose, 36 grams (0.1 mol) stearic acid phenyl ester and 30 grams (0.1 mol) adipic acid diphenyl ester are dissolved in 300 milliliters of dimethylformamide. The solution is heated to 115° C. 1 gram potassium hydroxide is added. After a reaction time of 3 hours at 115° C. the solvent and the phenol split off are distilled off in vacuum. One obtains a product which is well soluble in water and surface active.

We claim:

1. A process for preparing an ester of a carboxylic acid and a saccharide comprising heating one mol of a component selected from the group consisting of non-reducing oligosaccharide and the ketal of a monosaccharide with 1-7 mols of a carboxylic acid aryl ester obtained from (1) carboxylic acid and (2) a member selected from the group consisting of a phenol, methyl phenol, chloro phenol, methoxy phenol, and naphthol, in the presence of a catalytic amount of an esterification catalyst at a temperature of about 40-190° C.; and recovering the resulting product.

2. A process of claim 1 in which 0.05-30% by weight of catalyst is employed, based on the ester component.

3. The process of claim 1 wherein the ratio of carboxylic acid to saccharide is 2:1 and the aryl ester is obtained from a fatty acid and an aromatic monohydroxy compound selected from the group consisting of a phenol, methyl phenol, naphthol, chloro phenol, and methoxy phenol.

4. A process for preparing a distearic acid ester of sucrose which comprises heating a mixture of equimolecular proportions of sucrose and stearic acid phenyl ester in the presence of a catalytic amount of potassium carbonate at a temperature of about 160° C., adding a further reactive amount of stearic acid phenyl ester to the reaction mixture, heating, and thereafter recovering the resulting product.

5. A process for preparing a monostearic acid ester of sucrose which comprises heating an equimolecular mixture of sucrose and stearic acid phenyl ester at a temperature of about 160° C., with a catalytic amount of potassium hydroxide, separating the resulting by-product under vacuum.

6. A process for preparing the monostearic acid ester of sucrose which comprises heating a solution containing an equimolecular amount of sucrose and stearic acid phenyl ester in dimethylformamide with a catalytic amount of potassium hydroxide at a temperature of 105-110° C., distilling off the solvent and the phenol by-product split off in vacuum.

7. A process for preparing the distearic acid ester of sucrose which comprises heating a sucrose solution and stearic acid phenyl ester in a molecular ratio of 1:2 at a temperature of 110° C. in the presence of a catalytic amount of potassium hydroxide, distilling off the solvent and the phenol-product split off in vacuum.

8. A process for preparing a mixed ester of sucrose and stearic and adipic acids which comprises heating a solution of sucrose, stearic acid phenyl ester and adipic acid diphenyl ester in a molecular ratio of 2:1:1 in the presence of dimethyl formamide at a temperature of 115° C., with a catalytic amount of sodium hydroxide, distilling

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off the solvent and the phenol by-product split off in vacuum.

9. A process of claim 1 wherein the reaction is effected in the presence of an inert dispersing agent selected from the group consisting of toluene and xylene.

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