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MONOESTERS OF INNER ETHERS OF HEXAHYDRIC ALCOHOLS

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15 Claims. (Cl. 260—345)

This invention relates to the fatty acid mono-esters of the inner ethers of aliphatic, straight-chain, six carbon atom, hexahydric alcohols, and more particularly to the fatty acid mono-esters of the inner ethers of sorbitol, mannitol, dulcitol, etc.

The principal object of this invention is the provision of fatty acid mono-esters of the inner ethers of aliphatic, straight-chain, six carbon atom, hexahydric alcohols, such as sorbitol, mannitol, dulcitol, etc. Another object is the provision of fatty acid mono-esters of the hexitans, of fatty acid mono-esters of the hexides, and of mixtures of the fatty acid mono-esters of the hexitans and hexides, the proportions of esters of the hexitans and hexides in said mixtures being controlled by the method of preparation of the same.

In this specification by the term "fatty acid" I mean fatty acids having 6 or more carbon atoms, such as the fatty acids which are present combined with glycerine in naturally occurring animal and vegtable oils and fats and which are derived therefrom upon saponification thereof, and the equivalents of such fatty acids such as synthetically prepared aliphatic monocarboxylic fatty acids, as for instance margaric acid, or fatty acids prepared by suitably oxidizing hydrocarbons. Examples of fatty acids which may be used are the fatty acids derived from stearin, whale oil, menhaden oil, neat's-foot oil, castor oil, corn oil, cottonseed oil, coconut oil, linseed oil, palm kernel oil, rapeseed oil, China-wood oil, perilla oil, soya bean oil, sunflower oil, olive oil and the like and include fatty acids such as caproic, caprylic, capric, lauric, myristic, palmitic, oleic, linoleic, linolenic, ricinoleic, stearic, dihydroxy stearic, eleostearic, erucic, behenic acids and the like.

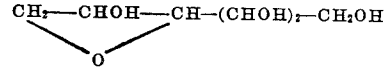
The invention contemplates the production of fatty acid mono-esters of hexitol inner ethers, said inner ethers having one to two monooxy, 4 to 7-membered carbon-oxygen rings (cyclic ether rings), either 2 or 4 hydroxyl groups, and being derivable from an aliphatic, straight-chain, six carbon atom, hexahydric alcohol.

The inner ether may be formed under the conditions of and during the esterification by using hexahydric alcohol in the original reaction mixture or the inner ether may be used as such in the original reaction mixture. The inner ethers with which the present invention is concerned, as stated above, have one to two monooxy, 4 to 7-membered carbon-oxygen rings, and at least two esterifiable hydroxyl groups available to react with the fatty acid or mixture of fatty acids. The inner ethers may be unsubstituted or may contain such non-functional substituents as are compatible with ring formation and do not prevent the esterification of the hydroxyl groups during the reaction. The inner ethers may be defined as compounds containing carbon-oxygen rings with one cyclic oxygen per ring (known as an oxido ring) and derivable from a hexahydric alcohol by intramolecular condensation. If only one molecule of water is removed by the intramolecular condensation, a monoanhydro derivative containing only one carbon-oxygen ring is obtained. If the condensation removes two molecules of water from the hexahydric alcohol, a dianhydro compound containing two carbon-oxygen rings, which may or may not be of the condensed (overlapping) type, is obtained. The number of members in the ring and the number of oxido rings in the inner ether which are obtainable depend upon the configuration of the carbon atoms in the chain of the hexahydric alcohol from which the inner ether is derived and upon the conditions of the reaction. It is possible to form the dianhydro compounds containing different membered carbon-oxygen rings, for example, a compound containing a 4 and a 6-membered ring.

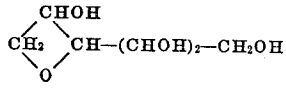
The hexahydric alcohols applicable for use in preparing the products of the invention are of such structures that the intramolecular condensation described can take place in several different ways. Whether in any particular reaction mono- or dianhydro compounds predominate depends generally upon the conditions of the reaction, the time and temperature, and particularly the type of catalyst employed. As a result of the condensation of the hexahydric alcohols, a mixture of the various inner ethers may be formed.

As examples of hexahydric alcohols suitable for use in carrying out the invention, any six carbon atom, aliphatic, straight chain, hexahydric alcohol may be employed, but it is preferred to use mannitol, sorbitol and dulcitol due to their availability. In order that the structures of certain of the inner ethers may be illustrated, some of them have been chosen as typical.

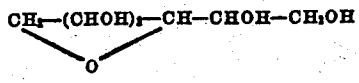
The 4-membered oxido ring, known as an oxidopropan ring:



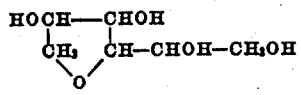
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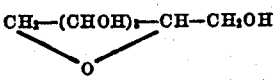
The 5-membered oxido ring, known as a furan ring:



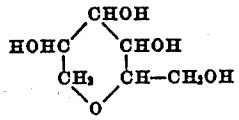
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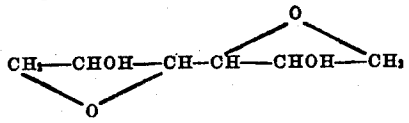
The 6-membered oxido ring, known as a pyran ring:



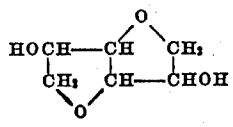
or



The dianhydro compound containing two condensed 5-membered oxido rings, known as furofuran rings:



or



It is to be understood, of course, that the structural formulae given above showing the various rings are merely by way of example, and that the ring formation may take place between any of the other non-adjacent hydroxyl-bearing carbon atoms of the hexahydric alcohol. The inner ether containing the furan ring appears to be the main product obtained in the intramolecular condensation reaction under usual conditions, although smaller amounts of other inner ethers of both the mono- and dianhydro type may be present. The inner ethers of the various hexahydric alcohols may be designated by names derived from the stem of the parent alcohol by substituting for the characteristic suffix "itol" for the alcohol, the suffix "itan" for the cyclic monoanhydro derivative or inner ether which is generically designated a "hexitan," and "ide" for the dianhydro derivative or the dicyclic inner ether which is generically designated a "hexide," thus: mann-itol, mann-itan, mann-ide; sorb-itol, sorb-itan, sorb-ide; dulc-itol, dulc-itan, dulc-ide, etc.

It is to be understood that wherever in this specification the terms "hexitan," "hexide," "sorbitan," "sorbide," "mannitan," etc. are employed, that these terms do not necessarily mean a single chemical compound but may refer to a mixture of several anhydro derivatives falling therein. Thus sorbitan is not necessarily a single monoanhydrosorbitol but may comprise several isomeric monoanhydrosorbitols.

The mono-esters of the inner ethers may be prepared directly from the hexahydric alcohols, the reaction being carried out under conditions that assure the formation of the inner ether from the hexahydric alcohol and the esterification of the inner ether with the fatty acid, or they may be prepared directly from the inner ethers themselves by esterification thereof under appropriate conditions. The type of inner ether formation from the hexitol and the esterification in situ may be controlled by the use of a catalyst, the selection of the type of catalyst depending upon the type of product I desire. I have found that the degree of anhydro formation may advantageously be controlled by the selection of the proper catalyst. I have found that the use of acid catalysts, for example, sulfuric and phosphoric acids, for the anhydro formation and esterification in situ tends to produce esters of hexides, whereas alkaline catalysts tend to produce esters of hexitans. I have also found that esters containing a preponderance of hexide esters may be prepared by the use of an alkaline catalyst, but the time and temperature of the reaction is greater than that required when an acid catalyst is employed. This longer time and higher temperature tend to impair the color of the ester so that I have found it advantageous to employ an acid catalyst whenever I desire a product containing a preponderance of hexide esters. Likewise, I may prepare a product containing a preponderance of hexitan ester by the use of a very small amount of acid catalyst but the reaction is so critical and the tendency to form the hexide ester so great that I prefer to use an alkaline catalyst wherever I desire a product having a preponderance of hexitan ester. Furthermore, I may desire to prepare a product having approximately equal amounts of both hexide and hexitan ester, and in this instance I find it advantageous to use no catalyst.

Preferably, the hexahydric alcohol and fatty acid are admixed and reacted in the presence of each other from the beginning. It is to be understood, however, that the hexahydric alcohol may be first treated so as to either partially or completely effect inner ether formation, and thereafter the fatty acid may be added for purposes of esterification. When the hexahydric alcohol and fatty acid are reacted in the presence of each other from the beginning, the evidence points to the fact that the intramolecular condensation forming the inner ether takes place before the hydroxyl groups are esterified, but the esterification may possibly take place first. If the latter does occur, however, it is to be understood that the product falls within the scope of the invention and within the claims.

The fatty acid esters contemplated by this invention may be either predominantly the monoesters of the monoanhydro derivatives of the hexahydric alcohols or predominantly the monoesters of the dianhydro derivatives of the hexahydric alcohols, or mixtures of the two types. I have found that products containing a preponderance of the monoesters of the hexitans are particularly suitable as emulsifying agents for certain types of emulsions, whereas for such types of emulsions the monoesters of the hexides are less satisfactory. On the other hand, the monoesters of the hexides are excellent emulsifiers for certain other types of emulsions, particularly those containing electrolytes, while the monoesters of the hexitans are less efficient as emulsifiers for this latter type of emulsion.

In order to form the monoesters contemplated herein, I react one mol of the hexahydric alcohol and one mol of fatty acid or fatty acid mixture either in the presence or absence of the catalysts mentioned above. These ingredients are commingled and heated in a kettle or other

container, preferably closed and equipped with suitable agitating means, at a temperature of 150–300° C., until the reaction reaches the desired stage. It is frequently desirable to maintain an atmosphere of inert gas, such as nitrogen or carbon dioxide, over the reacting mass, as by passing an inert gas over or through the reacting mass in order to assist removal of the water of condensation and prevent discoloration of the product. The reaction is preferably carried out either under atmospheric pressure or under a reduced pressure. A reflux condenser may be provided to condense and return any volatilized fatty acid.

It is advantageous to provide vigorous agitation for the reacting mass during the heterogeneous phase of the reaction to increase the reacting surface and also to minimize the possibility of local overheating.

For carrying out the invention, the hexahydric alcohol is generally used in the form in which it is most readily available. Thus, mannitol and dulcitol are used in the solid form. Sorbitol is available either as a solid material or as an aqueous syrup. I may use sorbitol in the form of aqueous syrup obtained by the reduction of monosaccharides such as glucose or invert sugar, and which in addition to sorbitol, contain related polyhydroxy bodies, small amounts of ash, unreduced sugar and other organic impurities. In order to obtain as light colored products as possible, it is desirable to maintain the ash, sugar content and color of the hexahydric alcohol at a minimum.

The products of the invention may be used as emulsifying agents in the formation of oil-in-water or water-in-oil emulsions. They display hydrophilic properties by reason of the unesterified hydroxyl groups and the cyclic ether groups of the hexahydric alcohol residue, and they display lipophilic properties by virtue of the fatty acid radical. As a result of this amphiphilic nature the products of the invention display surface activity.

Below I have given several specific examples of modes of carrying the invention into practice. It is to be understood that these examples are illustrative only of the preferred embodiments of the invention and are not to be taken as limiting.

Example 1

86.0 pounds of distilled coconut oil fatty acids having an acid number of 275 and containing approximately 60% of lauric acid was placed into an electrically heated closed kettle equipped with an agitator, an air reflux condenser, and a water cooled condenser connected to a receiver. 91.6 pounds of a technical sorbitol syrup containing 20.5% of water, 0.07% reducing sugar and 0.92% of ash, was added. Agitation and heating was commenced and carbon dioxide was passed over the reacting mass. The mixture was heated to 235° C. in three hours. It was then reacted for 3½ hours at 235° C. There was now added decolorizing activated carbon of the type known as Darco G–60 in an amount equal to 2% of the weight of the charge now remaining in the kettle. Application of heat was discontinued but the stirring and flow of carbon dioxide were continued until the mixture had cooled to 70° C. The mixture was then filtered to remove the activated carbon, and yielded a product having the following properties: acid number 4, viscosity at 25° C. 4433 centipoises, color 110 color units as read in a 6 mm. cell on a Hess-Ives tintphotometer. The product contained about 70% of the sorbitan monoester of coconut oil fatty acids. The remainder of the product consisted chiefly of the sorbitan diester of coconut oil fatty acids and of the sorbide monoester of coconut oil fatty acids and a small amount of unreacted sorbide with a still smaller amount of unreacted sorbitan. If it is desired to remove the small amounts of sorbide and sorbitan from the reaction product, the latter may be washed either with water or a saturated sodium sulfate solution. However, for most purposes these small amounts of unreacted sorbitan or sorbide do not impair the product.

Example 2

182 grams, dry basis, of technical sorbitol syrup were placed in a flask and adjusted to a pH of 2.0 by the addition of 2.0 cc. of 85% phosphoric acid. To the resulting material was added 216 grams of distilled coconut oil fatty acid, similar to that used in Example 1. This quantity of coconut oil fatty acid was 1.054 times the equivalent weight of fatty acid, the 5.4% excess of acid being used to compensate for acids distilled during the reaction. The reactants were heated together with agitation and in an inert atmosphere of carbon dioxide for a total of 2½ hours at 225° C. The reaction mixture had become uniformly clear in appearance after 2 hours at 225° C. and was then given a Darco G–60 decolorization (2% Darco on the total weight of charge) for the final ½ hour at 225° C. It was subsequently filtered free of carbon. The product had a viscosity of 439 centipoises at 25° C. The ester portion was composed largely of the sorbide monoesters of coconut oil fatty acids together with a small amount of sorbitan monoesters and diesters. The hydroxyl value of the ester was 205, and its saponification value was 170. The product was a reddish yellow oil having a color of 60 units when read on a Hess Ives tintphotometer using a 6 mm. cell. It proved especially useful in the preparation of emulsions made in the presence of electrolytes such as water in oil emulsions where aluminum chloride or aluminum sulfate was present in the emulsion mixture.

Example 3

4,968 g. (23 equivalent weights plus 5.4% excess of fatty acid used to compensate for acids distilled during the reaction) of distilled coconut oil fatty acid were reacted with 4,186 g. (23 mols) of mannitol in the presence of 1.54 g. NaOH as catalyst for a total of 3 hours at 260° C. The reaction was carried out in an inert atmosphere of carbon dioxide. During the last ½ hour at 260° C. the reaction mixture, which had by that time become uniformly clear in appearance, was decolorized by the addition thereto of Darco G–60 in amount equal to 2% of the weight of the charge. The charge was cooled to 180° C. and filtered free of carbon. The product was a yellow oil having a viscosity of 6200 cp. at 25° C. and an acid number of 4. The product had a hydroxyl value of 340 and a saponification value of 172. It was composed largely of the mannitan monoesters of the fatty acids present in distilled coconut oil fatty acid.

The above product may be used directly as an emulsifier for high ratio shortenings. However, to improve its taste and odor the ester may be washed with a 20% sodium sulfate solution, dried, and then deodorized by means of superheated steam.

Example 4

5,523 grams of white oleine (which contains a preponderance of oleic acid) having an acid value of 192, were reacted with 3,276 grams (dry basis 18.0 mols) technical sorbitol syrup in a 4 gallon aluminum reaction kettle equipped with an agitator, carbon dioxide inlet tube to permit the use of an inert gas for the reaction, thermocouple and inverted U condenser leading into a receiving kettle. The amount of white oleine used was 18 equivalent weights plus approximately 5% excess of acid used to compensate for acids distilled during the reaction. The reactants were heated for a total of 4½ hours at 260° C. During the last ½ hour at 260° C. Darco G–60 activated carbon, in an amount equal to 2% by weight of the reaction charge, was added to the kettle for the purpose of decolorizing the ester. The mixture was filtered to remove the Darco. The product was a brown oil having a color of 73 as measured directly in a 6 mm. Hess-Ives photometer cell. The viscosity of the product was 1810 cp. at 25° C. The product was composed of about 60% of sorbitan mono-esters of the fatty acids present in white oleine, the remainder of the product consisting chiefly of the sorbide monoesters of the fatty acids present in white oleine, with a small amount of unreacted sorban and sorbide.

Example 5

284 grams of triple pressed stearic acid was reacted with 182 grams of technical sorbitol syrup, weighed on its dry basis, in an inert atmosphere of carbon dioxide for 3 hours at 250° C. At the end of this time the reaction mixture was uniformly clear in appearance. The product was given a Darco treatment, employing 2% of Darco G–60 on the charge weight, for an additional ½ hour at 250° C. and was subsequently filtered free of the activated carbon. The product had an acid value of 2. Its color was 100 Hess Ives units calculated on a direct basis for a 6 mm. Hess Ives photometer cell. The product had a hydroxyl value of 310. It was composed largely of sorbitan monostearate and sorbide monostearate.

If desired, the above procedure may be modified by the addition of say 3.3 grams of sodium hydroxide as a catalyst to the initial mixture. The alkaline catalyst enables the use of lower temperatures and results in a greater proportion of sorbitan monostearate in the product. Such a product is particularly suitable for the cosmetic trade.

Example 6

5,680 grams (about 20 mols) of triple pressed stearic acid and 3,640 g. (20.0 mols) of mannitol were reacted in the presence of 1.34 g. NaOH in a four-gallon aluminum reaction kettle equipped with a CO_2 inlet tube to permit the use of inert gas during the reaction, agitator, thermocouple and inverted U air condenser. The reaction mixture was brought to 265° C. in the course of 2 hours. It was then reacted for 5 hours at 265° C., at the end of which time the reaction mixture was uniformly clear in appearance. The reaction mixture was given a further heating for ½ hour at 265° C. in the presence of Darco G–60, the amount of Darco being 2% of the weight of the charge. The charge was filtered free of carbon. The product had an acid number of 6 and a color of 35 as measured in a 6 mm. Hess-Ives photometer cell.

4,087 grams of the above ester were washed by admixture with 2,050 grams of aqueous sodium sulfate solution containing 410 grams of sodium sulfate and 2 grams of sulfuric acid. The ester was washed for 5 minutes at 90–100° C., agitation being effected by passing carbon dioxide rapidly through the emulsified mixture. The mixture was passed through a Sharpless Super Centrifuge. The ester separated from the mixture was found to contain 6% of water and 0.5% ash.

The washed ester was deodorized without further drying or filtration by means of superheated steam. The deodorization was carried out for 6 hours at 180° C. under a reduced pressure of 10 mm. The ester was then given a second Darco treatment, using 2% of Darco based upon ester weight, for an additional ½ hour at 180° C. and was subsequently filtered free from the activated carbon. The ester had a final ash content of 0.0%, an acid number of 1.8 and a Hess-Ives color of 30, measured in a 6 mm. Hess-Ives photometer cell. The product consisted chiefly of mannitan monostearate, mannide monostearate together with some mannitan distearate.

Example 7

3,185 grams (17.5 mols) technical sorbitol syrup measured on its dry basis were adjusted to a pH of 2.0 by the addition of 24 cc. 85% phosphoric acid. This sorbitol was then reacted with 4,970 grams (about 17.5 mols) of triple pressed stearic acid in an inert atmosphere of carbon dioxide for 3 hours, 25 minutes at 245° C. The ester was treated with 2% of its weight of activated carbon, Darco G–60, for ½ hour at 200° C. and subsequently filtered free of carbon. The ester was then deodorized for 2 hours at 140° C. by means of superheated steam and subjected to a second 2% Darco treatment. The final product had a color of 89 as measured in a 6 mm. Hess-Ives photometer cell. Its acid number was 4.5 and its melting point 42–43° C. The hydroxyl number of the product was 218. The ester portion was composed essentially of 70% of sorbide mono-esters of triple pressed stearic acid and 30% of sorbitan monoesters of triple pressed stearic acid.

Example 8

50 g. of refined ricinoleic acid, about ⅛ mol, were reacted with 30.3 g., dry basis, ⅛ mol., technical sorbitol syrup for 3 hours at 240° C. The product was a yellowish red oil having a color of 105 Hess-Ives units as measured in a 6 mm. Hess-Ives photometer cell. The oil had a viscosity of 5200 cp. at 25° C. The product consisted chiefly of sorbitan and sorbide monoricinoleate together with some unreacted sorbitan and sorbide self-esterified ricinoleic acid.

One hundred grams of petroleum jelly and one hundred grams of water formed a very stable water in oil emulsion when beaten in a hand mixer with ten grams of the above ester.

Example 9

114 grams (about 0.5 mol) of commercial myristic acid were reacted with 91 grams, dry basis, sorbitol syrup, which had been adjusted to a pH of 1.8 by the addition of phosphoric acid, for a period of 1 hour at 210° C. The reaction mixture by this time had become perfectly clear in appearance. The product was given an additional ½ hour heating treatment at 210° C. in the presence of 2% G–60, decolorizing carbon, and was subsequently filtered free of carbon. The product had a color of 60 Hess-Ives units as read

directly in a 6 mm. Hess-Ives tintphotometer cell. The acid number of the product was 15. The product comprising sorbide monomyristate was an excellent emulsifier. A 1% solution of the myristate in corn oil reduced the interfacial tension between this corn oil and water from 22.2 dynes/cm. to 2.6 dynes/cm.

Example 10

335 grams of distilled coconut oil fatty acids were reacted with 235 grams mannitol in the presence of 1.71 cc. 85% phosphoric acid for a total of 2¼ hours at 235° C. During the last ½ hour at 235° C. the reaction mixture was given a Darco G–60 decolorizing treatment, employing 2% Darco based upon reaction weight. The reaction mixture was cooled to 130° C. and filtered free of carbon. The product was a reddish oil having a color of 70 Hess-Ives units as measured directly in a 6 mm. Hess-Ives photometer cell. The product was composed chiefly of the mannide monoesters of the acids present in distilled coconut oil fatty acid.

Example 11

378 g. (about 1⅓ mol) triple pressed stearic acid were reacted with 242 g. (about 1⅓ mol) mannitol in the presence of 0.55 cc. 85% phosphoric acid for a total of 4 hours at 245° C. During the last ½ hour at 245° C. the reaction mixture was given a 2% Darco G–60 decolorizing carbon, treatment. The product was cooled to 180° C. and filtered free of carbon. The product was a yellow solid having a melting point of 41–42° C. It was composed chiefly of mannide monostearates.

It is to be understood that in the production of the products of the present invention the processes described herein may be varied over a wide range. Thus the fatty oils may be employed in the reaction mixture instead of the fatty acids and the process suitably controlled so as to produce the products of the present invention by alcoholysis.

While for purposes of illustration I have given a description of the physical properties and characteristics of several of the products employed in the present invention, it is to be understood that the invention is not to be considered as limited thereby, as the physical properties and characteristics of the products may be varied over a wide range.

Having fully described my invention, what I claim is:

1. A fatty acid monoester of an inner ether of a hexitol, said fatty acid having at least 6 carbon atoms.

2. A hexitan mono-fatty acid estér, said fatty acid having at least 6 carbon atoms.

3. A surface active ester product consisting essentially of a mixture of a hexitan fatty acid monoester, and a hexide fatty acid monoester, said fatty acid having at least 6 carbon atoms.

4. A surface active ester product consisting essentially of a hexitan monoester of the mixed fatty acids derived from coconut oil.

5. A surface active ester product consisting essentially of a mixture of a fatty acid monoester of a hexitan selected from the class consisting of mannitan and sorbitan, and a fatty acid monoester of a hexide selected from the class consisting of mannide and sorbide, said fatty acid having at least 6 carbon atoms.

6. A surface active ester product as in claim 5 wherein the said fatty acid has from 12 to 18 carbon atoms.

7. A mono-fatty acid ester of a hexitan selected from the class consisting of mannitan and sorbitan, said fatty acid having at least 6 carbon atoms.

8. An ester as in claim 7 wherein the said fatty acid has from 12 to 18 carbon atoms.

9. A fatty acid monoester of an inner ether of a hexitol selected from the class consisting of mannitol and sorbitol, said fatty acid having at least 6 carbon atoms.

10. An ester as in claim 9 wherein the said fatty acid has from 12 to 18 carbon atoms.

11. A surface active ester product consisting essentially of a fatty acid monoester of an inner ether of a hexitol, said fatty acid having at least 6 carbon atoms.

12. A surface active ester product consisting essentially of a fatty acid monoester of an inner ether of a hexitol, said fatty acid having from 12 to 18 carbon atoms.

13. A surface active composition consisting essentially of a hexitan fatty acid monoester, said fatty acid having at least 6 carbon atoms.

14. A surface active composition consisting essentially of a fatty acid monoester of an inner ether of a compound of the class consisting of mannitol and sorbitol, said fatty acid having at least 6 carbon atoms.

15. A surface active composition consisting essentially of a fatty acid monoester of a compound of the class consisting of mannitan and sorbitan, said fatty acid having at least 6 carbon atoms.

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