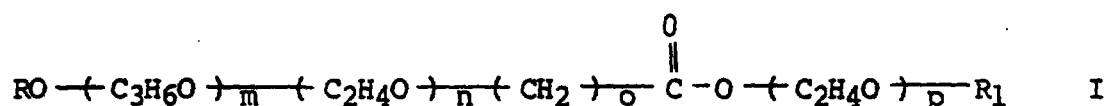


ALKYL POLYOXYALKYLENE CARBOXYLATE ESTERS

This invention relates to surface active agents useful as emollients in skin care compositions.

The invention provides compounds of formula I, and mixtures thereof,



- 5 in which R is C₈-C₂₂ alkyl;
 R₁ is C₁-C₂₂ alkyl;
 m is 0 or an integer 1 to 4;
 n is an integer 3 to 20;
 o is an integer 1 to 4; and
 10 p is 0 or an integer 1 to 20, with the provisos that:
 1) when R₁ is C₁-C₃ alkyl, then p is 0; and
 2) when m is 0, n is an integer 6 to 20.

R is preferably C₁₀-C₁₈ alkyl, more preferably C₁₀-C₁₆alkyl.

15 R₁, when p is other than 0, is preferably C₆-C₁₈ alkyl, more preferably C₁₀-C₁₆ alkyl.

R₁, when p is 0, is preferably C₃-C₁₈ alkyl, particularly isopropyl or cetyl.

The variable m is preferably 0 or 2.

20 The variable n, when m is 0, is preferably 6 to 18, more preferably 6 to 14.

The variable n, when m is other than 0, is preferably 3 to 12, more preferably 3 to 10.

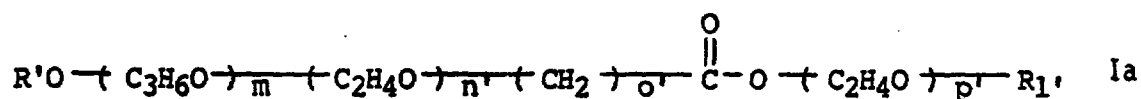
The variable o is preferably 1 to 3, more preferably 1 or 2, particularly 1.

- 5 The variable p is preferably 0 or an integer 1 to 16, more preferably 0 or an integer 1 to 12, most preferably 0.

The variables m, n, o and p are average values. As is clearly evident, the variables m, n, o and p must be whole numbers in the individual compounds of this invention.

- 10 All alkyl groups may be straight or branched chain unless otherwise stated.

Preferred compounds and mixtures are those of formula Ia:



in which R' is C₁₀-C₁₈ alkyl;

- 15 R₁, when p' is 0, is C₃-C₁₈ alkyl or, when p' is other than 0, is C₆-C₁₈ alkyl;

m is as defined above;

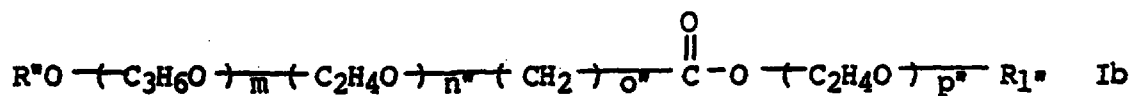
n', when m is 0, is an integer 6 to 18 or, when m is other than 0, is an integer 3 to 12;

o' is an integer 1 to 3;

- 20 and p' is 0 or an integer 1 to 16.

The more preferred compounds and mixtures are those of formula

Ib:



in which R" is C₁₀-C₁₆ alkyl;

R₁" when p" is 0, is C₃-C₁₈ alkyl and, when p" is other than 0, is C₁₀-C₁₆ alkyl;

m is as defined above;

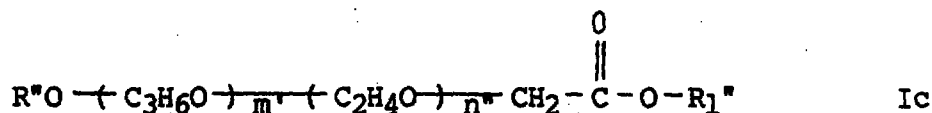
5 n", when m is 0, is an integer 6 to 14 or, when m is other than 0, is an integer 3 to 10;

o" is an integer 1 or 2;

and p" is 0 or an integer 1 to 12.

The most preferred compounds and mixtures are those of formula

10 Ic



in which R", n" and R₁" are as defined above

and m' is 0 or 2,

particularly those in which R₁" is isopropyl or cetyl.

Suitable alcohol precursors of the alkyl polyoxyalkylene
 15 carboxylate esters of this invention are straight or branched chain primary alcohols having from 8 to 22 carbon atoms. A mixture of alcohols may be used and this will generally be the case when using commercial alcohols which are often available as a blend of several alcohols. Specific examples are a mixture of C₁₂-C₁₅ straight chain
 20 alcohols available commercially from Union Carbide; a mixture of C₁₂-C₁₅ predominantly straight chain alcohols containing approximately 20% branching available commercially from Shell Chemical Co.; and a mixture of alcohols, at least 70 mol % of which is branched 1-decanols available commercially from Exxon Chemical Co.
 25 When employing a mixture of alcohols, the number of carbon atoms in the alcohol is referred to as an average number which can be determined by vapor phase chromatography and the hydroxyl number.

The compounds and mixtures of formula I are produced by conventional methods. Thus, the alkyl polyoxyalkylene carboxylate

esters of this invention may be prepared by carboxyalkylating the adduct resulting from the propoxylation and/or ethoxylation of a straight or branched chain primary alcohol having from 8 to 22 carbon atoms and then esterifying the resulting carboxyalkylated acid with a
5 straight or branched chain primary or secondary alcohol optionally containing one or more ethylene oxide groups.

The alkoxylation step may be carried out in the presence of an alkaline catalyst, e.g. sodium or potassium hydroxide, in an amount e.g. from 0.2% to 1% by weight of the total reaction mixture.

10 Optionally, a small amount of a reducing agent may be added to the alcohol, or mixture thereof, to be alkoxyated to minimize discoloration of the resulting polyalkoxyated alcohol. Suitable reducing agents which may be employed include sodium borohydride, lithium aluminum hydride and diborane, preferably sodium borohydride.

15 In preparing a polyoxyalkylated alcohol in which the polyoxyalkylene chain contains a propylene oxide first block and an ethylene oxide second block, an amount of propylene oxide calculated to provide the desired degree of propoxylation is introduced and the resulting mixture is allowed to react until the propylene oxide is
20 consumed, as indicated by a drop in reaction pressure. A similar introduction and reaction of a calculated amount of ethylene oxide serves to provide the second block which completes the alkoxylation. Customarily, the alkoxyated product is finally treated with weak acid, e.g., glacial acetic acid, to neutralize any basic catalyst
25 residues.

It should be understood that each separate alkoxylation procedure serves to introduce a desired average number of alkylene oxide units per alcohol molecule. Thus, for example, the initial treatment of an alcohol mixture with m moles of propylene oxide per
30 mole of alcohol serves to effect the propoxylation of each alcohol moiety with propylene oxide to an average of m propylene oxide moieties per alcohol moiety, although some alcohol moieties will have become combined with more than m propylene oxide moieties and some

will have become combined with less than m . In general, the maximum number of propyleneoxy units in a single molecule will not exceed 8 and the number of ethyleneoxy units in a single molecule will not exceed 30. The variation in the number of alkylene oxide moieties is not critical as long as the average for the number of units in each block is within the limits set out for the m and n terms in formula I above, which terms, as average values, are other than whole numbers in some instances.

Alkoxylation is carried out under conventional conditions of temperature e.g. 140-160°C; at a pressure below atmospheric; and in the absence of water.

The resulting alkyl polyalkoxide intermediates are then carboxyalkylated by the Williamson synthesis, involving reaction with the appropriate chloro- or bromocarboxylic acid or a salt thereof in the presence of sodium hydroxide or metallic sodium. Such reaction is ordinarily not complete; hence the reaction product often contains minor amounts of uncarboxylated alkyl polyalkoxide. While methods are available for separating the uncarboxyalkylated material as well as for assuring essentially complete carboxyalkylation, they are usually tedious and expensive. Fortunately, it has been found that minor proportions of such uncarboxylated material are not particularly harmful, and may even be advantageous. Preferably, the carboxyalkyl group is a carboxymethyl group, i.e. the variable o is preferably 1.

The alkyl polyalkoxide carboxylic acid is then esterified by reaction with a straight or branched chain C_1 - C_{22} primary or secondary alcohol optionally containing one or more ethylene oxide groups at a mole ratio of alcohol to carboxylic acid of from greater than 5:1 to 1:1, and in the presence of a catalyst. Typical catalysts include sulphuric acid, hydrogen chloride, *p*-toluenesulphonic acid and boron trifluoride. To drive the reaction to completion, water may be removed as it is formed for example by azeotropic distillation. Alternatively, a large excess of one of the reactants (usually the alcohol) may be used. For example, an alkyl polyalkoxide carboxylic acid dried under vacuum can be dissolved in a molar excess of an

anhydrous alcohol which forms a low boiling azeotrope with water. An acidic catalyst is then added to the mixture, and the reaction is allowed to proceed at reflux until the reaction is essentially complete (usually between 2 and 48 hours). The excess alcohol and
5 water are then removed by distillation at atmospheric pressure and the ester is obtained by decantation. Alternatively, an anhydrous alkyl polyalkoxide carboxylic acid is mixed with an equimolar portion of a high boiling alcohol. An acidic catalyst is then added and the resultant mixture is heated under vacuum, the water of reaction being
10 removed at a temperature between 120° and 200°C. After the theoretical amount of water is collected, the mixture is cooled, the vacuum is broken with nitrogen and the ester is obtained by decantation.

The compounds of formula I are useful as surface active agents,
15 and are suitable as emulsifiers, dispersing agents, lubricants, wetting agents, levelling agents, softening agents and the like in the textile, leather, paper, lacquer, personal care, e.g., toiletries, cosmetics, etc., and rubber industries. For instance, they can be used as wetting, softening or lubricating agents in the
20 treating and refining of textiles; and for converting liquid or solid substances which are insoluble in water (such as hydrocarbons, higher alcohols, oils, fats, waxes and resins) into creamy emulsions, clear solutions or fine, stable dispersions.

In addition, the compounds of formula I are useful as
25 emulsifiers for insecticide compositions and agricultural sprays such as DDT, 2,4-D and the like; are useful as additives to petroleum products, hydraulic fluids, lubricating oils, cutting oils and greases; may be employed as coating aids for use in coating compositions comprising a hydrophilic, film-forming colloid; may be
30 employed as tackifiers in the adhesive layer of adhesive tapes in, e.g., the photographic industry; and as foaming agents, emulsifying agents and softening agents in a wide variety of food products.

The alkyl polyoxyalkylene carboxylate esters of the instant invention are especially useful as the essential emollient component

in skin care compositions, e.g., skin creams, lotions, etc. Their incorporation serves to enhance not only the moisturizing and conditioning properties of the skin care compositions but the tactile properties as well. Such skin care compositions will normally contain
5 from 0.5% to 15% by wt. of an alkyl polyoxyalkylene carboxylate ester, preferably from 1% to 13%, and more preferably from 1.5% to 12%. The alkyl polyalkoxyalkylene carboxylate esters are preferably employed as the sole emollient component, totally replacing conventional fatty ester emollients such as isopropyl myristate,
10 isopropyl palmitate and similar compounds. Alternatively, the carboxylate esters may be employed in combination with conventional fatty ester emollients, thereby reducing the amount of conventional fatty ester emollient that needs to be employed.

The skin care compositions can contain other ingredients
15 commonly found in such compositions. For example, fatty alcohols may be employed to assist in stabilizing the composition and in providing a cosmetically acceptable viscosity. In general, a C₁₄ to C₂₂ substantially saturated alkanol is employed. Typical examples of suitable fatty alcohols are cetyl alcohol and stearyl alcohol.

20 Emulsifiers may also be employed and such may be cationic e.g., quaternary ammonium compounds such as dimethyl distearyl ammonium chloride, amphoteric such as betaines or sulfobetaines and nonionic such as polyethylene glycol monostearate.

In order to improve the lubricity of the skin care
25 compositions, a lubricant is generally employed. This may be a silicone oil such as dimethylpolysiloxane or other conventional polysiloxane or olive oil.

If desired, a humectant may be present in the skin care compositions. Typical humectants which may be employed include
30 propylene glycol and polyethylene glycol.

The amount of water or aqueous vehicle to be included depends upon the desired consistency of the final product. It is possible to

vary the amount of water present to formulate, for example, a thick-flowing liquid or lotion, a semi-liquid thick cream, or a paste.

5 The skin care compositions, in general, comprise from 1.5% to 10%, preferably from 2% to 8.5% of a fatty alcohol; from 1.5% to 12%, preferably from 2% to 10% of an emulsifying agent; and from 0.75% to 50%, preferably from 1% to 35% of a lubricant, all percentages being by weight.

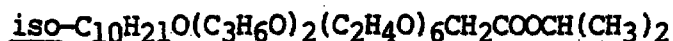
10 Other conventional additives typically employed in skin care compositions may be utilized. Fragrance oils, which mask the odor and provide cosmetic appeal, can be employed. Non-toxic and compatible dyes may be utilized to colour the compositions, as desired. Preservatives, such as methyl paraben, propyl paraben and formaldehyde may be utilized.

15 In addition, other ingredients can be employed beneficially to provide skin-care compositions tailored to a specific use. For example, a sun screen additive such as octyl dimethyl para-aminobenzoic acid can be employed. To provide skin protection, a skin protectant such as zinc oxide and the like can be employed. As a medicament, an essential oil such as menthol can be employed.

20 The skin care compositions of the invention exhibit good consistency, apply evenly to the skin, are absorbed rapidly and dry quickly, leaving the skin with a soft and smooth appearance. On application they have good tactile properties without feeling oily or greasy to the touch.

25 The following examples in which all parts are by weight and all temperatures in degrees centigrade illustrate the invention.

EXAMPLE 1 : Isodecyl-dipropoxy-hexaethoxymethyl carboxylic acid,
isopropyl ester



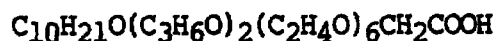
A) Preparation of dipropoxy-hexaethoxy isodecyl alcohol

5 To a reaction vessel is added, with stirring, 705 parts of
decyl alcohol (a mixture of primary, aliphatic alcohols, at least 70
mol % of which is branched 1-decanols, a boiling range of 216° to
223°, a specific gravity @ 20/20° of 0.838, a refractive index, n_D^{20} ,
of 1.400, a pour point of -53°, a viscosity @ 20° of 22.5 centistokes
10 and a solubility in water @20° of < 0.05 g/100 g and available
commercially from Exxon Chemical Co.), 10.6 parts of potassium
hydroxide (in pellet form) and 0.12 parts of sodium borohydride. The
system is evacuated and purged with nitrogen three times at 60°, then
heated to 100°. 260 Parts propylene oxide are then added over 60 min.
15 the reaction temperature rising to 155°. After allowing the reaction
mixture to react further until the pressure in the reaction system
falls to approx. 10 mbar, the procedure described above is repeated
with an additional 257 parts of propylene oxide, added over a period
of sixty minutes. After allowing the propoxylated alcohol reaction
20 mixture to react further until the pressure in the reaction system
again falls to approx. 10 mbar, the procedure described above is
repeated with 1178 parts of ethylene oxide, added over a period of
sixty minutes. When reaction is complete, the reaction system is
purged with nitrogen, cooled to 85° and an additional 0.12 parts of
25 sodium borohydride is added. The reaction system is then kept under a
nitrogen atmosphere for 2 hours, at 80°-90°, the catalyst present is
neutralised with glacial acetic acid and the product filtered to
yield a translucent, pale yellow liquid of the formula



B) Preparation of isodecyl-dipropoxy-hexaethoxy-methyl
carboxylic acid

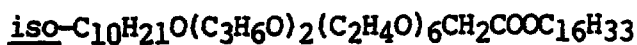
To 957.6 parts of the compound prepared in A) above, is
alternately added, in small portions over a period of 3 1/2 hours at
5 a temperature range of 25°-50°, equimolar amounts of sodium hydroxide
(71.2 parts) and sodium monochloroacetate (207.7 parts). Upon
completion of the addition, the temperature of the resulting reaction
mixture is maintained at 50° for 30 minutes, after which time the
temperature is raised to 75° over a period of 30 minutes. After
10 keeping the reaction mixture at a temperature of 75° for 90 minutes,
it is cooled to 50° and acidified with 175 parts of sulphuric acid
(50% conc.) in 600 parts of water, after which time separation of the
water soluble salt yields an oil of the formula



15 C) Preparation of the title compound

158.7 Parts of the compound prepared in B) above are heated to
60° under vacuum in a reaction vessel. After 12.7 parts of water are
collected, the reaction vessel is cooled and the vacuum broken. 100
Parts of anhydrous isopropanol (mole ratio alcohol:acid approx. 8:1)
20 are then added to the reaction vessel, after which time a catalytic
amount (25 drops) of 98% sulphuric acid is added to the reaction
mixture. The resultant mixture is then heated to reflux temperature
and maintained at this temperature for a period of 24 hours. After
removal of isopropanol and water by distillation, decantation yields
25 the title compound.

EXAMPLE 2: Isodecyl-dipropoxy-hexaethoxymethyl carboxylic acid, cetyl
ester



158.7 Parts of the compound prepared in Example 1 B) above are heated to 50° under vacuum in a reaction vessel. After 14 parts of water are collected, the reaction vessel is cooled and the vacuum broken. An equimolar amount (48.2 parts) of cetyl alcohol is then added to the reaction vessel and the mixture heated until the alcohol completely melts. A catalytic amount (~5 drops) of 98% sulphuric acid is then added and the resultant mixture heated to 130° under vacuum. After 3 hours, 3.9 parts of water are collected. The mixture is cooled to 5° and the title compound recovered by decantation.

10 EXAMPLE 3 Lauryl-hexaethoxymethyl carboxylic acid, cetyl ester



A) Preparation of hexaethoxy lauryl alcohol

To a reaction vessel is added, with stirring, 664.7 parts of lauryl alcohol and 8.5 parts of potassium hydroxide (in pellet form). The system is purged with nitrogen at 100° then heated to 160°, at which point the addition of 1059 parts of ethylene oxide to the reaction mixture is commenced. The temperature of the resulting reaction mixture is kept at 160°-170° throughout the gradual addition of ethylene oxide. Upon completion of the ethylene oxide addition, the reaction mixture is cooled to yield a compound of the formula



B) Preparation of lauryl-hexaethoxy-methyl carboxylic acid

Following essentially the procedure of Example 1 B), and using in place of the compound prepared in Example 1 A), an approximately equivalent amount of the compound prepared in A) above, a compound of the formula

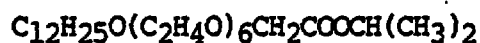


is obtained.

C) Preparation of the title compound

Following essentially the procedure of Example 2, using 101.6 parts of the compound prepared in B) above in place of the 158.7 parts of the compound of Example 1 B), the title compound is obtained.

5 EXAMPLE 4: Lauryl-hexaethoxymethyl carboxylic acid, isopropyl ester



Following essentially the procedure of Example 1 C), and using in place of the compound of Example 1 B) an approximately equivalent amount of the compound of Example 3 B), the title compound is
10 obtained.

EXAMPLE 5:

A) Following essentially the procedure of Example 3 A) and employing the appropriate starting alcohol and the appropriate amount of ethylene oxide, the following compounds are obtained:

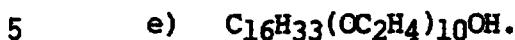
15 a) $\text{R}^a(\text{OC}_2\text{H}_4)_8\text{OH}$
where R^a is the residue of a mixture of C_{12} - C_{15} predominantly straight chain alcohols containing approximately 20% branching and available commercially from Shell Chemical Co.;

20 b) $\text{R}^b(\text{OC}_2\text{H}_4)_{12}\text{OH}$
where R^b is the residue of a mixture of C_{12} - C_{15} straight chain alcohols and available commercially from Union Carbide;

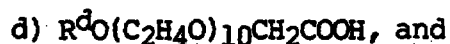
c) $\text{R}^c(\text{OC}_2\text{H}_4)_{11}\text{OH}$
where R^c is the residue of a mixture of primary, aliphatic
25 alcohols, at least 70 mol % of which is branched 1-decanols and available commercially from Exxon Chemical Co.;



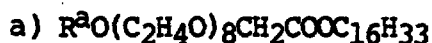
where R^d is the residue of a commercially available isostearyl alcohol containing a mixture of branched methyl isomers; and



B) Following essentially the procedure of Example 3 B), and using in place of the compound prepared in Example 3 A), an approximately equivalent amount of compounds 5 A) a) - e), there is obtained:



15 C) a) Following essentially the procedure of Example 2 and using in place of the compound prepared in Example 1 B), an approximately equivalent amount of compounds 5 B) a) - e), there is obtained:



EXAMPLES 6 - 10:

Following essentially the procedure of Example 1 C), and using in place of the compound prepared in Example 1 B), an approximately equivalent amount of the compounds of Example 5 B) a) - e), there are 5 obtained the isopropyl esters corresponding to the compounds 5 C) a) - e).

It should be understood that in all of the Examples above, the indicated number of propyleneoxy units and ethyleneoxy units are average values.

10 EXAMPLE 11:

A body cream formulation contains the following ingredients:

		<u>Weight Percent</u>
<u>Ingredients</u>		
	cetyl alcohol	2.5
15	stearyl alcohol	5.0
	light silicone oil	1.0
	Pationic SSL (amphoteric emulsifier) ¹	1.5
	water	82.6
20	propylene glycol	5.0
	compound of Example 1	2.0
(¹ Pationic SSL is a Trade Mark.)		

The above formulation is prepared by heating the water to 70°, heating the remaining ingredients to 70°, and after adding the water slowly, with stirring, to the heated mixture of ingredients, allowing 25 the resultant mixture to cool to room temperature.

EXAMPLES 12-14:

In the formulation of Example 11, the compound of Example 1 may be replaced by the compounds of Examples 7, 8 and 9.

EXAMPLE 15:

An oil-in-water body lotion formulation contains the following ingredients:

	<u>Ingredients</u>	<u>Weight Percent</u>
5	A. polyethylene glycol (400)	
	monostearate	2.5
	olive oil	47.5
	propyl paraben	0.15
10	Compound of Example 2	2.5
	B. methyl paraben	0.15
	water	46.8

The above formulation is prepared by combining and heating the components of A to 70°, combining and heating the components of B to 70°, and after adding A to B, with stirring, allowing the resultant mixture to cool to room temperature.

EXAMPLES 16-18:

In the formulations of Example 15, the compound of Example 2 may be replaced by the compounds of Examples 5 C) b), c) and d).

20 EXAMPLE 19:

An oil-in-water body lotion formulation contains the following ingredients:

	<u>Ingredients</u>	<u>Weight Percentage</u>
25	A. Arlacel 60 (non-ionic emulsifier) ²	2
	Tween 60 (polysorbate) ²	3
	Compound of Example 1	10
	B. water	85.
	(² Arlacel and Tween are Trade Marks.)	

The above formulation is prepared by combining and heating the components of A to 70°, heating the water to 72°, and after adding the water slowly, with stirring, to the heated mixture of ingredients, allowing the resultant mixture to cool to room
5 temperature.

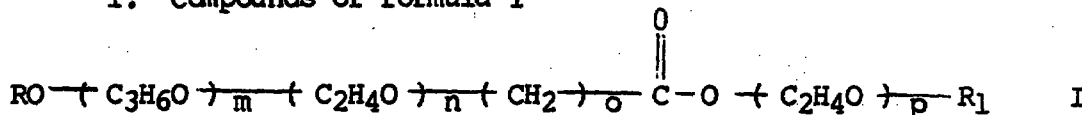
EXAMPLES 20-21:

In the formulation of Example 19, the compound of Example 2 may be replaced by the compounds of Examples 7 and 8.



Claims:

1. Compounds of formula I



in which R is C₈-C₂₂ alkyl;

R₁ is C₁-C₂₂ alkyl;

5 m is 0 or an integer 1 to 4;

n is an integer 3 to 20;

o is an integer 1 to 4; and

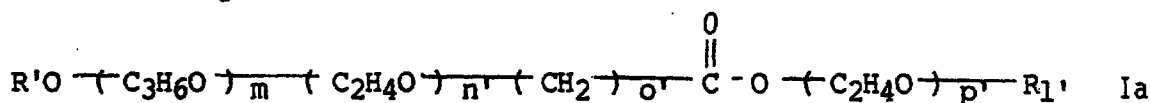
p is 0 or an integer 1 to 20, with the provisos that:

1) when R₁ is C₁-C₃ alkyl, then p is 0; and

10 2) when m is 0, n is an integer 6 to 20

and mixtures thereof.

2. Compounds as claimed in Claim 1 of formula Ia



in which R' is C₁₀-C₁₈ alkyl;

15 R₁' when p' is 0, is C₃-C₁₈ alkyl or, when p' is other than 0, is C₆-C₁₈ alkyl;

m is as defined in Claim 1,

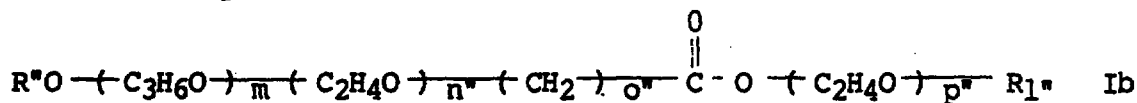
n', when m is 0, is an integer 6 to 18 or, when m is other than 0, is an integer 3 to 12;

o' is an integer 1 to 3;

20 and p' is 0 or an integer 1 to 16,

and mixtures thereof.

3. Compounds as claimed in Claim 2 of formula Ib

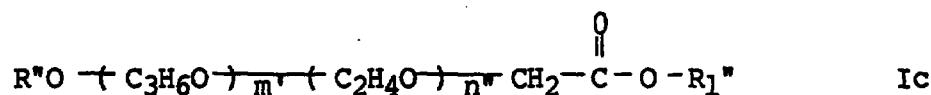


in which R'' is C₁₀-C₁₆ alkyl;



5 R_1'' when p'' is 0, is C_3 - C_{18} alkyl and, when p'' is other than 0, is C_{10} - C_{16} alkyl;
 m is as defined above;
 n'' , when m is 0, is an integer 6 to 14 or, when m is other than 0, is an integer 3 to 10;
 o'' is an integer 1 or 2;
and p'' is 0 or an integer 1 to 12,
and mixtures thereof.

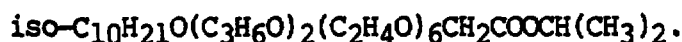
4. Compounds as claimed in Claim 3 of formula Ic



10 in which R'' , n'' and R_1'' are as defined in Claim 3
and m' is 0 or 2,
and mixtures thereof.

5. Compounds as claimed in Claim 4 in which R_1'' is isopropyl or cetyl, and mixtures thereof.

15 6. A compound of formula



7. A compound of formula



20 in which R^a is the residue of a mixture of C_{12} - C_{15}
predominantly straight chain alcohols containing approximately 20 %
branching.

8. A compound of formula



in which R^a is as defined in Claim 7.

9. A compound as claimed in Claim 1 as described in any one of Examples 2, 3 c), 4, 5 C b)- e) and 7 - 10.

5 10. A skin care composition comprising from 0.5 % to 15 % by weight of a compound as claimed in any one of Claims 1 - 9, or mixtures thereof.

10 11. A skin care composition as claimed in Claim 10 in which a compound or mixture of compounds as claimed in Claim 1 is the sole emollient component.

12. A skin care composition as claimed in Claim 10 or Claim 11 containing in addition from 1.5 % to 10 % of a fatty alcohol, from 1.5 % to 12 % of an emulsifying agent and from 0.75 % to 50 % of a lubricant, all percentages being by weight.

15 13. A skin care composition as described in any one of Examples 11 - 21.
