(12) UK Patent (19) GB (11) 2 144 122 B

(54) Title of invention

Triglycerine monoalkyl ether compounds, a process for preparing the compounds, and cosmetics comprising them

(51) INT CL[4]; C07C 43/13 43/15

(21) Application No
8418025

(22) Date of filing
16 Jul 1984

(30) Priority data

(31) **58/135421**

(32) **25 Jul 1983**

(33) **Japan (JP)**

(43) Application published
27 Feb 1985

(45) Patent published
4 Feb 1987

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(52) Domestic classification
(Edition I)
C2C 1300 1492 200 20Y 215 21X 246 247 253 25Y 28X 30Y 314 31Y 339 360 361 362 364 36Y 382 43X 440 442 445 500 503 509 50Y 561 606 607 623 624 634 643 644 652 67Y 73Y 772 777 808 80Y 819 AA AB HC WA WJ YA YB YL
U1S 1343 1427 C2C

(56) Documents cited
None

(58) Field of search
C2C

GB 2 144 122 B

"TRIGLYCERINE MONOALKYL ETHER COMPOUNDS, A PROCESS FOR PREPARING THE COMPOUNDS, AND COSMETICS COMPRISING THEM"

This invention relates to novel ether compounds, i.e. 1,3-bis-o-(2,3-dihydroxypropyl)-2-o-alkyl(meaning a saturated or unsaturated group) glycerine (which may be hereinafter referred to simply as triglycerine monoalkyl ether). It also relates to a process for producing such ether compounds and cosmetics comprising the compounds.

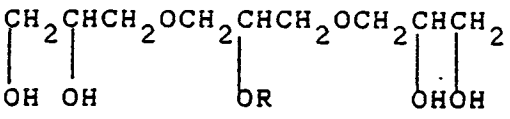
As is known, a great number of polyhydric alcohol derivatives having ether bonds exist in natural fields, of which monoalkyl ethers of glycerine (hereinafter referred to simply as glyceryl ethers) are most popular. For example, lipids of fishes contain palmityl glyceryl ether (hereinafter referred to simply as chimyl alcohol), stearyl glyceryl ether (hereinafter referred to simply as batyl alcohol), and oleyl glyceryl ether (selakyl alcohol).

The glyceryl ethers have a w/o type emulsifying characteristic and thus wide utility as cosmetic substrates (Japanese Laid-open Patent Application Nos. 49-87612, 49-92239 and 52-12109, and

Japanese Patent Publication No. 57-36260). It is also known that the glyceryl ethers have the pharmaceutical actions such as an acceleration effect for the blood cells formulation in the marrow, the antiphlogistic action, and the antitumor activity (Japanese Patent Publication Nos. 49-10724 and 52-18171).

In view of the fact that glyceryl ethers which have a number of characteristics are the unique type of surface active agent, attempts have been made to prepare, from polyhydric alcohols, polyol ether compounds similar in molecular structure (i.e. ether bonds and hydrophilic OH groups are contained in the molecule thereof) to glyceryl ethers (United States Patent No. 2,258,892, Japanese Patent Publication No. 52-18170, and Japanese Laid-open Patent Application Nos. 53-137,905 and 54-145,224). The resulting polyol ether compounds which have a w/o type emulsification characteristic are utilized as cosmetic substrates (German Laid-open Patent Publication No. 2,455,287), or are used, aside from an ordinary emulsifier, as an antibacterial agent or antimold agent.

According to the present invention, triglycerine m onoalkyl ethers of the general formula (I), which are novel polyol ether compounds,



(I)

in which R represents a saturated or unsaturated, linear or branched aliphatic hydrocarbon group having from 8 to 24 carbon atoms, have been found to exhibit excellent surface activity.

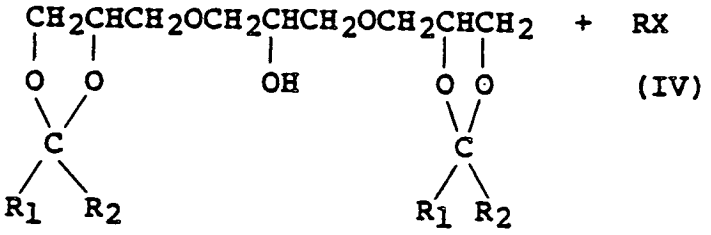
Accordingly, an object of the invention is to provide novel polyol ether compounds of the formula (I)>

Another object of the invention is to provide a process for producing the compounds (I).

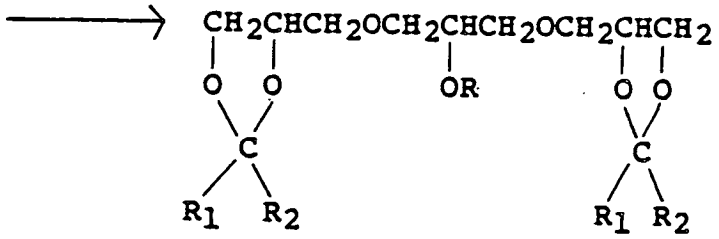
The invention also provides cosmetics comprising the compounds (I).

Glycerine polymers or esters thereof were proposed for use as a surface active agent (e.g. Journal of American Oil Chemist's Society, Vol. 56, pp. 835A - 840A, (1979). However, these glycerine polymers or esters thereof are found to be irregular in linkages of glycerine, or to be complicate mixtures having a wide distribution of molecular weight. In contrast, the polyol ether compounds according to the invention have a clear structure in which the ether bond exists at the center of the main chain of a linear trimer of glycerine and are thus novel compounds which completely different from the compounds described in the above literature.

The triglycerine monoalkyl ethers (I) of the present invention are prepared from a known compound of 1,3-bis-o-(2,3-o-isopropylideneglyceryl)glycerine (Journal f. Prakt. Chemie, Vol. 316, pp. 325-326 (1974) according to the process described below in high yield and high purity.

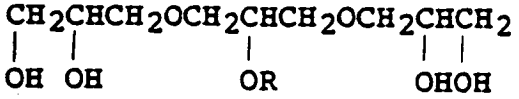


(II) (IV)



(III)

Hydrolysis →



in which R has the same meaning as defined before and R_1 and R_2 independently represent a hydrogen atom, a C_1 to C_5 alkyl group, and aryl group or an aralkyl group, respectively, and X represents a halogen atom or the like.

More particularly, the known compound of 1,3-bis-o-(2,3-o-isopropylideneglyceryl)glycerine (II) is etherifying in the presence of an alkaline substance and a catalytic amount of a quatenary onium salt (Williamson's ether synthesis), thereby giving 1,3-bis-o-(2,3-o-isopropylideneglyceryl)-2-o-alkylglycerine

(III), and hydrolyzing the alkylglycerine to obtain an intended triglyceryl monoalkyl ether (I).

In the first step of the process of the invention, the 1,3-bis-o-(2,3-o-isopropylideneglyceryl)-2-o-alkylglycerine (III) is prepared from the 1,3-bis-o-(2,3-o-isopropylideneglyceryl)glycerine (II) and an etherifying agent (IV). This reaction is the so-called Williamson's ether synthesis reaction, which is preferably carried out in the presence of an alkaline substance and a catalytic amount of a quaternary onium salt.

The etherifying agent (IV: RX) used in the practice of the invention includes, for example, alkyl halides, alkylsulfonates, alkylsulfates, and the like. These agents should have a saturated or unsaturated, linear or branched fatty hydrocarbon group having from 8 to 24, and preferably 8 to 18 carbon atoms. More particularly, the agents include alkyl halides such as alkyl chlorides, alkyl bromides, alkyl iodides and the like, alkylparatoluenesulfonates, alkylmethanesulfonates, alkylbenzenesulfonates, and the like. Of these, preferable examples are alkyl bromides. The alkyl moieties of the etherifying agents (IV) include linear fatty hydrocarbon groups such as n-octyl,

n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, n-octadecenyl (oleyl), n-dococyl and the like, branched fatty hydrocarbon groups such as 2-ethylhexyl, 2-hexyldecyl, 2-octyldodecyl, 2-heptylundecyl, 2-(1,3,3-trimethylbutyl)octyl, 2-decyltétradecyl, 2-tetradecyloctadecyl, 5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octyl, and methyl-branched isostearyl groups represened by the following formula

$$CH_3(CH_2)_m\underset{\displaystyle CH_3}{\underset{|}{CH}}(CH_2)_n-$$

in which m is an integer from 4 to 10, n is an integer from 5 to 11, and m + n is from 11 to 17, with a distribution having a peak at m = 7 and n = 8. Further, sec-decyl, sec-octyl, sec-dodecyl and the like may be further included. The amount of the etherifying agent may not be critically limited and is generally from 1 to 5 moles, preferably 1 to 2 moles per mole of 1,3-bis-o-(2,3-o-isopropylidene-glyceryl)glycerine (II).

The quaternary onium salts are preferably ammonium salts because of the ease in industrial availability. Examples of the quaternary ammonium salts include: tetraalkylammonium salts such as, for example, tetrabutylammonium chloride, tetrabutylammonium

hydrogensulfate, trioctylmethylammonium chloride, lauryltrimethylammonium chloride, stearyltrimethylammonium chloride, benzyltrimethylammonium chloride and the like; a group of alkylammonium salts having a polyoxyalkylene group such as tetraoxyethylene stearyldimethylammonium chloride, bistetraoxyethylene stearylmethylammonium chloride and the like; and betaine compounds, amine oxide compounds, and ion-exchange resins.

These quaternary onium salts may be used in a catalytic amount, or may be used in amounts ranging from 0.005 to 0.5 mole, preferably 0.05 to 0.20 mole, per mole 1,3-bis-o-(2,3-o-isopropylidene-glyceryl)glycerine (II).

In the reaction of the first step, 1.0 mole of 1,3-bis-o-(2,3-o-isopropylideneglyceryl)glycerine (II) is subjected to the reaction in the presence of an aqueous solution of 1 to 10 moles, preferably 3 to 6 moles of an alkaline substance (10 to 80%, preferably 30 to 60% aqueous solution) in an inert hydrocarbon reaction solvent (e.g. hexane, benzene, toluene, xylene or the like) at a temperature from 30 to 70°C, preferably 40 to 60°C. The alkaline substances include, for example, sodium hydroxide, potassium hydroxide,

lithium hydroxide or the like. Industrially, sodium hydroxide is preferred.

Next, the resulting 1,3-bis-o-(2,3-o-isopropylideneglyceryl)-2-o-alkylglycerine (III) is subjected to hydrolysis.

The hydrolysis may be conducted by any known techniques. It is preferred to heat the alkylglycerine in an aqueous solution of a protonic acid such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, p-toluenesulfonic acid or the like.

The amount of the protonic acid is from 0.005 to 0.2, preferably from 0.05 to 0.1 mole, per mole of 1,3-bis-o-(2,3-o-isopropylideneglyceryl)-2-o-alkylglycerine (III).

The hydrolysis may proceed in the absence of any reaction solvent, but it is favorable to heat under reflux at a temperature of from 50 to 100°C using an water-soluble solvent including, for example a lower alcohol, a cylic ether such as THF, dioxane or the like.

In this manner, an intended triglycerine monoalkyl ether (I) can be obtained in high yield.

The triglycerine monoalkyl ether according to the invention is chemically stable because no linkages susceptible to decomposition, e.g. ester bond, are

contained in the molecular structure of the ether. Moreover, the ethers give a reduced degree of stimulus to the skin and have the surface activity, so that they are useful as an emulsifier, oil (emolient), humectant, thickener and particularly as a component of cosmetics.

Properties of typical compounds of the present invention are shown below.

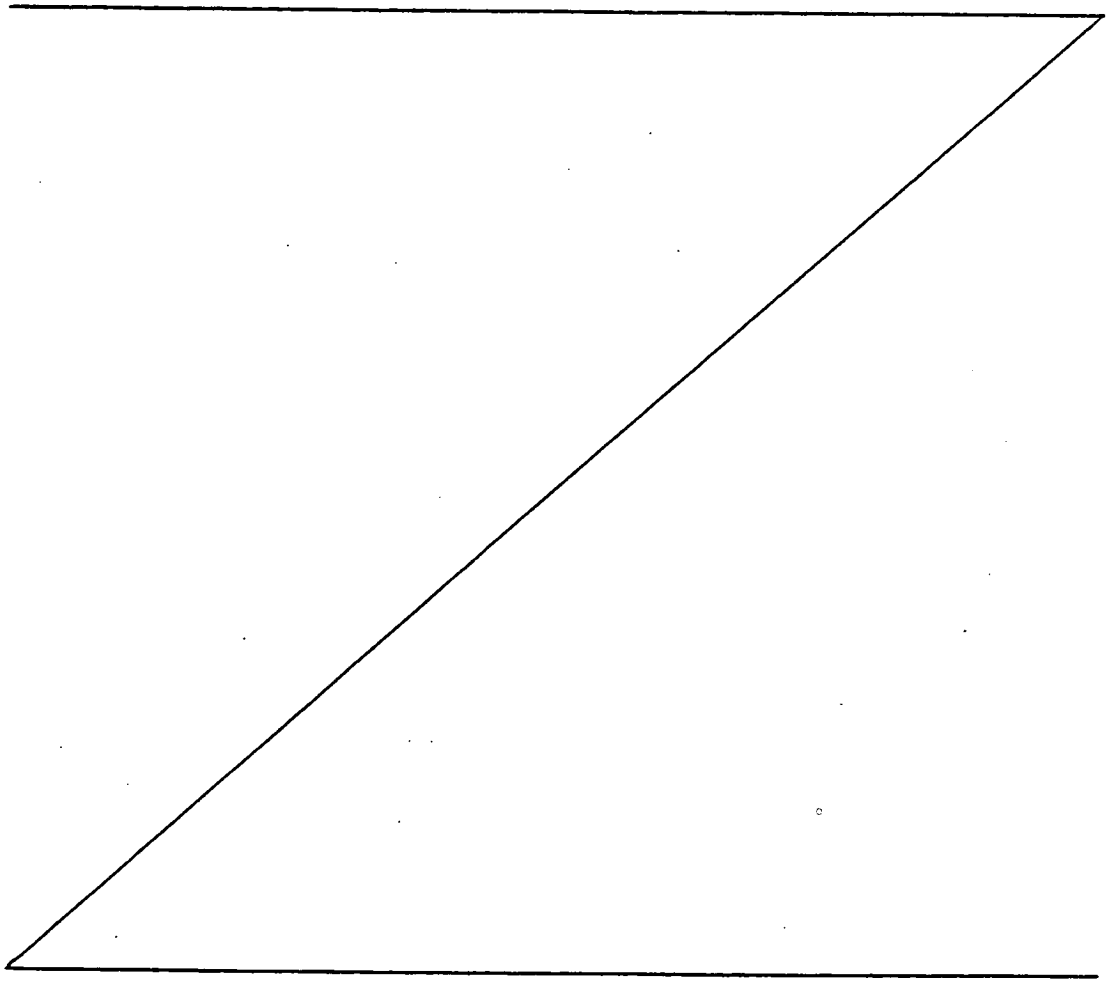


Table 1

R in Formula (I)	Color and State (25°C)	Solubility in Water (25°C)	
		[30%]*	[70%]*
$n\text{-}C_8H_{17}$	transparent liquid	uniform dissolution	uniform dissolution
$n\text{-}C_{12}H_{25}$	white solid	uniform dissolution	formation of liquid crystal
$n\text{-}C_{16}H_{33}$	white solid	uniform dissolution	formation of liquid crystal
$C_{18}H_{35}$ (Oleyl)	light yellow semi-solid	uniform dissolution	formation of liquid crystal
iso-$C_{18}H_{37}$ (methyl-branched isostearyl)	light yellow semi-solid	uniform dissolution	formation of liquid crystal

* Concentrations of the compounds of the invention

The triglycerine monoalkyl ethers are very hydrophilic and have solubility in water, though nonionic, comparable to ordinary ionic active agents. Because they have the glycerine structure, the compounds of the invention all exhibit high moisture absorptivity but are likely to form liquid crystal because of the long alkyl chain thereof. As a result, once the

compound contain water therein, the water is unlikely to be released. Especially, compounds of the formula (I) in which R represents a group containing from 8 to 18 carbon atoms have the well-balanced susceptibility to moisture absorption and unsusceptibility of releasing the moisture. Thus, they have a high moisture effect and are very useful as a humectant of cosmetics.

Of triglycerine alkyl ethers of the invention, those ethers of the formula (I) in which R represents a group having from 14 to 18 carbon atoms have higher emulsifying ability and are thus excellent when used as an emulsifier of emulsion-type cosmetics.

The amount of the ether compounds in cosmetics varies depending on various factors. When used as an emulsifier, the amount is from about 0.2 to 15 wt% and when used as a humectant, the amount is conveniently from 5 to 50 wt%.

The present invention is described in more detail by way of examples and references. The present invention is by no means limited to these examples, which are described for illustration only.

Reference 1

Synthesis of 1,3-bis-o-(2,3-o-isopropylideneglyceryl) glycerine (II)

(i) Into a 5 liters reactor equipped with a reflux condenser, dropping funnel, thermometer, and agitator were charged 1008 g of a 50% sodium hydroxide aqueous solution (504 g [12.6 mole] as NaOH), 555 g (4.2 moles) of 1,2-o-isopropylidene glycerine, and 1 liter of hexane, followed by agitation. Subsequently, 71.3 g (0.21 mole) of tetrabutylammonium hydrogensulfate was further added and the resulting reaction mixture was kept at 30°C. From the dropping funnel, 583 g (6.3 moles) of epichlorohydrin was dropped portion by portion whereupon heat was generated from the reaction mixture. After cooled appropriately, the reaction mixture was kept at a temperature from 45 to 50°C. The dropping of epichlorohydrin was completed in about 2 hours. The reaction mixture was agitated for further 2 hours at 45 to 50°C. The gas chromatograph of the reaction mixture revealed a disappearance of the 1,2-o-isopropylidene glycerine. Thereafter, the mixture was cooled, from which the hexane phase was collected by separation. The hexane phase was distilled off under reduced pressure to remove the hexane therefrom. By further distillation under reduced pressure, here was obtained 500 g of 1-o-(2,3-epoxypropyl)-2,3-o-isopropylidene glycerine which was a colorless, transparent liquid.

Yield: 63%

Boiling point: 83 to 85°C/1.3 mmHg (a value in literature: 92 to 93°C/2.5 mmHg)

(Literature: Journal f. Prakt. Chemie., Vol. 316, pp. 325 to 336 [1974])

(ii) Into a 3 liters reactor equipped with the instruments used in (i) of Reference (1) were charged 1653 g (12.5 moles) of 1,2-o-isopropylidene glycerine and 6.8 g (0.125 mole) of sodium methylate, followed by heating and agitating at a temperature of 85 to 100°C. Thereafter, 471 g (2.5 moles) of the 1-o-(2,3-epoxypropyl)-2,3-o-isopropylidene glycerine obtained in (i) of Reference (1) was dropped from the dropping funnel portion by portion in about 3 hours. During the dropping, the reaction mixture was maintained at about 100°C. After completion of the dropping, the mixture was agitated for further 5 hours at the above-indicated temperature. The gas chromatograph of the reaction mixture revealed disappearance of the 1-o-(2,3-epoxypropyl)-2,3-o-isopropylidene glycerine, after which the product was cooled. Subsequently, the 1,2-o-isopropylidene glycerine used in excess was distilled off under reduced pressure, followed by further

distillation under reduced pressure to obtain 600 g of colorless, transparent liquid 1,3-bis-o-(2,3-o-isopropylideneglyceryl)glycerine.

Yield: 80%

Boiling point: 162 to 168°C/0.7 mmHg

Boiling point in literature: 173 to 176°C/0.8 mmHg

(Same literature as indicated in (i))

Reference 2

Synthesis of methyl-branched isostearyl alcohol:

Into a 20 liters autoclave were charged 4770 g of isopropyl isostearate [Emery 2310, commercially available from Emery Co., Ltd. U.S.A.] and 239 g of copper-chromium catalyst (product of Nikki Co., Ltd.). Hydrogen gas was charged into the reactor under a pressure of 150 kg/cm^2 and the reaction mixture was heated up to 275°C. After hydrogenation under 150 kg/cm^2/275°C for about 7 hours, the reaction product was cooled, followed by removing the catalyst residue by filtration to obtain 3500 g of crude product. The crude product was distilled under reduced pressure thereby obtaining 3300 g of colorless transparent isostearyl alcohol as a fraction of 80 to 167°C/0.6 mmHg. The thus

obtained isostearyl alcohol (monomethyl-branched isostearyl alcohol) had an acid value of 0.05, a saponification value of 5.5, and a hydroxyl value of 181.4. IR analysis (liquid film) revealed absorptions at 3340 and 1055 cm^{-1} and NMR analysis (CCl_4 solvent) revealed an absorption at (δ) = 3.50 (broad triplet, $-CH_2-OH$). According to the gas chromatograph, the alcohol was chiefly composed of about 75% of an alcohol whose number of carbon atoms in the alkyl group was 18, with the remainder being made of alcohols having alkyl groups with 14 and 16 carbon atoms. The branched methyl group was located substantially at the center of the main alkyl chain in all the alcohol components.

Reference 3

Synthesis of methyl-branched isostearyl bromide

Into a 5 liters container equipped with a thermometer, reflux condenser, and agitator were charged 813 g (3 moles) of the methyl-branched isostearyl alcohol obtained in Reference 2, 1032 g (6.1 moles) of a 47% hydrogen bromide aqueous solution, and 50.1 g (0.15 mole) of trimethylstearylammonium chloride, followed by heating to 100 to 120°C in a mantle heater under

agitation. After agitation for about 6 hours at the temperature, it was confirmed from gas chromatograph that the peak of the methyl-branched isostearyl alcohol disappeared. The reaction product was cooled and the organic phase was collected by phase separation. To the lower phase (aqueous phase) was added ether (1.5 liters) for ether extraction. The ether phase was collected by phase separation, followed by combining with the organic phase obtained before and adding a hydrogen bicarbonate aqueous solution to neutralize a remaining acid therewith. By phase separation, the ether phase was collected, to which was added Glauber's salt for drying, followed by distilling off the ether under reduced pressure and further distillation under reduced pressure to obtain 800 g of methyl-branched isostearyl bromide.

Yield: 80%

Boiling point: 145 to 169°C (0.3 mmHg)

IR (liquid film, cm^{-1}): 1200 to 1300, 720, 640, 560

NMR (CCl_4, δ, TMS internal standard): 3.30

(triplet, J=7.0 Hz, $-C\underline{H}_2Br$)

Elementary analysis: found and in parentheses,

calculated for $C_{18}H_{37}Br$

C 64.7% (64.85%); H 11.2% (11.19%);

Br 24.4% (23.97%)

Average molecular weight (VPO method/$HCCl_3$):

327 (333 as calculated)

Example 1

Synthesis of 1,3-bis-o-(2,3-dihydroxypropyl)-2-o-methyl-branched isostearyl glycerine:

(i) 192 g of a 50% sodium hydroxide solution (96 g [2.4 moles] as NaOH), 128 g (0.4 mole) of the bisdioxolane compound obtained in (ii) of Reference 1 and 400 ml of hexane were charged into a 2 liters reactor equipped with a reflux condenser, thermometer, dropping funnel and agitator, and agitated. To the mixture was further added 13.6 g (0.04 mole) of tetrabutylammonium hydrogensulfate. The reaction mixture was maintained at a temperature of 30°C, followed by dropping 133.4 g (0.4 mole) of the methyl-branched isostearyl bromide obtained in Reference 3 from the dropping funnel portion by portion in about 20 minutes. After completion of the dropping, the reaction mixture was kept at a temperature of 45 to 50°C and agitated for about 48 hours as it is. From the gas chromatograph of the reaction mixture, it was recognized that the methyl-branched isostearyl bromide disappeared. Thereafter, 500 ml of water was added to the reaction

mixture and agitated. The hexane phase was collected by phase separation. The hexane was distilled off under reduced pressure, followed by further distillation under reduced pressure, thereby obtaining 30 g of a fraction having a boiling point of 60°C to 240°C/1.0 mmHg. This fraction was not an intended compound as confirmed by the gas chromatography, IR and ^{1}H-NMR spectrum analyses.

As the distillation residue, there was obtained 200 g of 1,3-bis-o-(2,3-o-isopropylideneglyceryl)-2-o-methyl-branched isostearyl glycerine which was a colorless, transparent liquid.

Yield: 87%

Elementary analysis: found and in parentheses, calculated for $C_{33}H_{64}O_7$

C: 69.3% (69.19%),

H: 11.2% (11.26%)

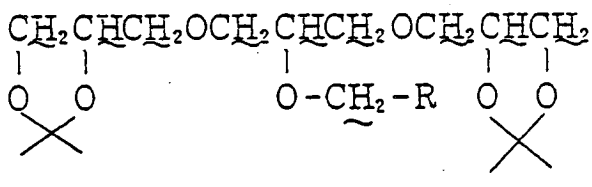
O: 19.5% (19.55%)

IR (liquid film, cm^{-1}): 3100 to 2800, 1460, 1380, 1375, 1255, 1215, 1180-1000, 845

^{1}H-NMR (δ in $CDCl_3$, TMS internal standard)

1.40 (s) } four isopropylidenemethyl
1.45 (s) } group

3.45 to 4.45 (m, 17H,



(ii) Into a 2 liters reactor equipped with the same reaction instruments as in (i) of Example 1 were charged 400 ml of ethanol and 400 ml of tap water, followed by further adding 4 g (0.04 mole) of concentrated sulfuric acid. From the dropping funnel, 164.4 g (0.287 mole) of the bisdioxolane obtained in (i) of Example 1 was dropped in about 30 minutes while agitating. After completion of the dropping, the reaction mixture was heated and refluxed. The reaction mixture was opaque at the initial stage of the reaction but are gradually changed into a transparent uniform solution as the hydrolysis proceeded. At about 70°C a uniform, transparent solution was obtained. Furthermore, the mixture was refluxed at 80°C for about 3 hours. The reaction product was cooled to room temperature, to which were added 500 ml of ether and then 300 g of a saturated saline solution for ether extraction. The ether phase was collected and the ether was distilled off under reduced pressure. At the time, a viscous gel-like substance was found to be produced

simultaneously with violent foaming. Thereafter, the substance was heated and dried at 80 to 90°C/1.0 mmHg. As a result, there was obtained 138g of 1,3-bis-o-(2,3-dihydroxypropyl)-2-o-methyl-branched isostearylglycerine (triglycerine isostearyl ether) in the form of a light yellow viscous paste.

Yield: 98%

Elementary analysis: found and in parentheses, calculated for $C_{27}H_{56}O_7$

C: 65.7% (65.82%)

H: 11.2% (11.46%)

O: 22.8% (22.73%)

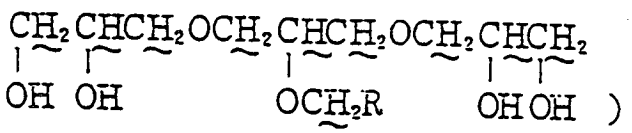
Hydroxyl value: 450 (455.5)

IR (liquid film, cm^{-1}):

3650-3050, 3000-2700, 1455, 1170-1000, 850

^{1}H-NMR (δ in $CDCl_3$, TMS internal standard):

3.20 to 4.0 (m, 17H,



4.0 to 4.4 (broad singlet, 4H, four OHs)

Examples 2 - 7

(i) Various 1,3-bis-o-(2,3-o-isopropylideneglyceryl)-2-o-alkylglycerines were prepared according to the procedure (i) of Example 1. The yield and physical values of these compounds are shown in Table 1.

(ii) Various 1,3-bis-o-(2,3-dihydroxypropyl)-2-o-alkylglycerines were prepared according to the procedure (ii) of Example 1. The yield of these compounds were quantitative, with physical values shown in Table 2.

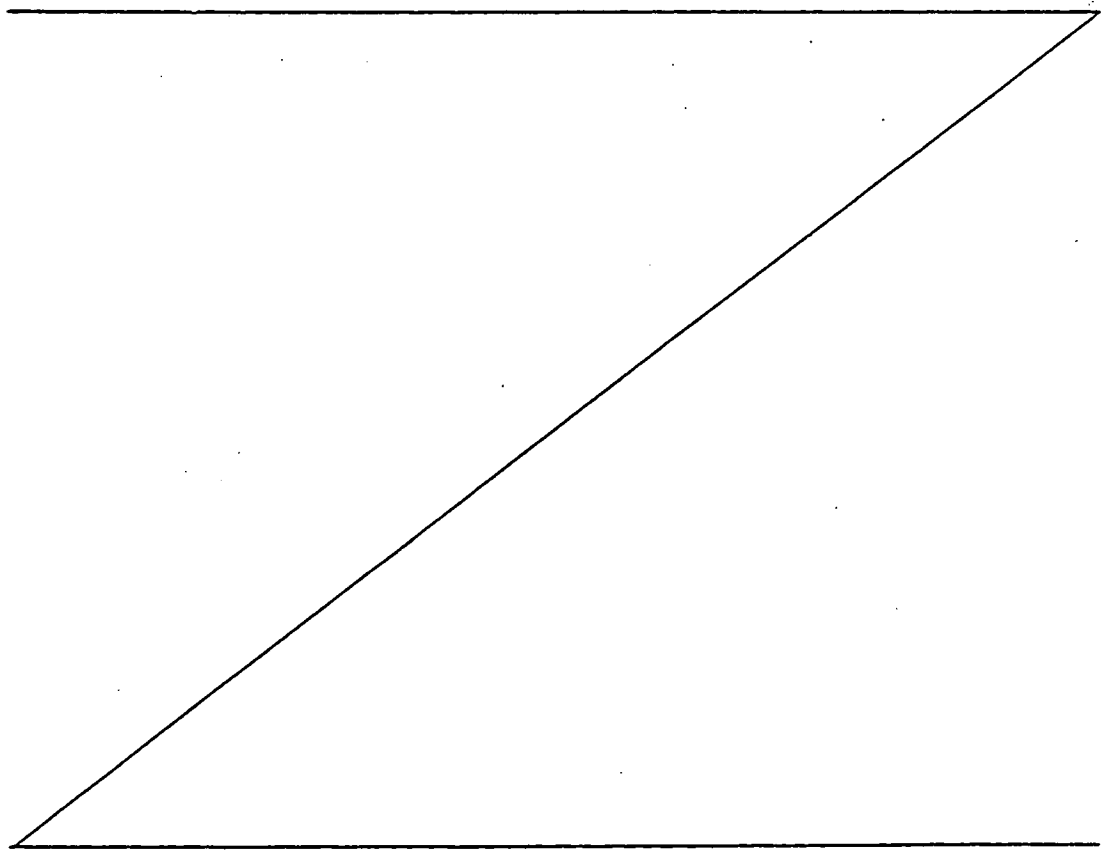
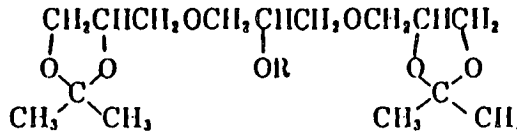


Table 1

1,3-Bis-O-(2,3-O-Isopropylideneglyceryl)-2-O-Alkylglycerine

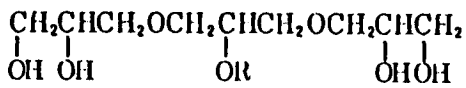


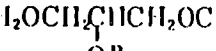
Example	R	Nature	Elementary Analysis (Calculated) C	H	O	IR (Liquid Film, cm^{-1})	^1H-NMR (δ in $CDCl_3$ TMS Internal Standard) a) Isopropylidene	$CH_2CHCH_2OCH_2CHCH_2OCH_2CHCH_2$ (OR)	Others	Yield (%)
2	C_8H_{17}	195~200℃ (0.6mmHg)	63.9% (63.86)	10.2% (10.25)	26.3% (25.89)	3050~2700, 1450, 1375, 1365, 1250, 1170~1000, 840	1.35(s) 1.40(s)	3.33~4.50(m)	—	85
3	$C_{12}H_{25}$	218~220℃ (0.7mmHg)	66.6 (66.36)	10.5 (10.73)	22.9 (22.92)	3050~2700, 1450, 1370, 1365, 1250, 1210 1175~1000, 840	1.33(s) 1.40(s)	3.35~4.50(m)	—	86
4	$C_{14}H_{29}$	liquid	67.4 (67.40)	10.8 (10.92)	21.2 (21.67)	3100~2700, 1460, 1380 1370, 1255, 1210, 1180 ~1000, 840	1.33(s) 1.37(s)	3.30~4.50(m)	—	84
5	$C_{16}H_{33}$	liquid	67.9 (68.34)	10.9 (11.10)	20.6 (20.56)	3050~2700, 1460, 1380 1370, 1250, 1210, 1180 ~1000, 840	1.35(s) 1.40(s)	3.35~4.50(m)	—	85
6	$C_{18}H_{37}$	liquid	69.3 (69.19)	11.2 (11.26)	19.9 (19.55)	3050~2700, 1450, 1370 1360, 1245, 1200, 1180 ~1000, 835	1.33(s) 1.40(s)	3.35~4.50(m)	—	88
7	$C_{18}H_{35}$ (Oleyl)	liquid	69.7 (69.43)	10.7 (10.95)	19.4 (19.62)	3100~2700, 1455, 1380 1370, 1250, 1210, 1180 ~1000, 845	1.35(s) 1.43(s)	3.35~4.50(m)	2.0(br. s, 4H) 5.40(t, 2H	85

a) s: singlet t: triplet m: multiplet br: broad

Table 2

1,3-Bis-O-(2,3-Dihydroxypropyl)-2-O-Alkylglycerine



Example	R	Nature	Elementary Analysis (Calculated) C	H	O	Hydroxyl Value (Calculated)	Yield (%)	IR (Liquid Film, cm^{-1})	^{1}H-NMR (δ in $CDCl_3$ TMS Internal Standard [a]) OH		Others
2	C_8H_{17}	liquid	57.6% (57.93)	10.2% (10.30)	31.7% (31.77)	633.4 (636.8)	95	3700~3050, 3000~2700, 1450, 1170~1000, 850	4.33 (br. s)	3.33~4.20 (m)	—
3	$C_{12}H_{25}$	liquid	61.6 (61.73)	10.5 (10.86)	27.0 (27.41)	543.7 (549.3)	96	3700~3050, 3000~2700, 1450, 1170~1000, 850	4.30 (br. s)	3.33~4.20 (m)	—
4	$C_{14}H_{29}$	mp 35℃	63.3 (63.27)	11.0 (11.08)	25.2 (25.65)	518 (514)	95	3700~3050, 3000~2700, 1450, 1170~1000, 850	4.10 (br. s)	3.35~4.0 (m)	—
5	$C_{16}H_{33}$	mp 40.5℃	64.8 (64.62)	10.9 (11.28)	23.5 (24.10)	480 (483)	95	3700~3050, 3000~2700, 1450, 1170~1000, 850	4.25 (br. s)	3.35~4.10 (m)	—
6	$C_{18}H_{37}$	mp 51℃	65.5 (65.82)	11.3 (11.46)	22.9 (22.73)	451.1 (455.5)	95	3700~3050, 3000~2700, 1455, 1180~1000, 855	3.90 (br. s)	3.45~3.85 (m)	—
7	$C_{18}H_{35}$ (Oleyl)	Paste	65.4 (66.09)	10.9 (11.09)	22.4 (22.82)	456.6 (457.4)	94	3700~3050, 3000~2700, 1455, 1180~1000, 850	4.15 (br. s)	3.30~4.0 (m)	1.95 (br. s 4H) 5.35 (t, 2H)

a) s: singlet, t: triplet m: multiplet br: broad

Example 8

Triglycerine alkyl ethers were subjected to a test of moisture absorptivity and retentivity (note 1) for evaluation as a humectant. The results are shown in Table 3.

Table 3

Compound Tested	Moisture Absorptivity (%)		Moisture Retentivity (%)	
	after 1 day	after 7 days	after 1 day	after 7 days
Products of Invention				
R in Formula (I)				
$n\text{-}C_8H_{17}$	9.5	28.5	35	10
$n\text{-}C_{12}H_{25}$	7.0	19.5	50	10
$n\text{-}C_{16}H_{33}$	5.5	17.0	65	35
$C_{18}H_{35}$ (Oleyl)	6.0	20.0	60	30
iso-$C_{18}H_{37}$ (Methyl-branched Isostearyl)	6.0	21.0	60	25
Comparative Products				
Sorbitol	10.5	54.0	10	0
Glycerine	22.5	82.5	20	5

(note 1) *Moisture absorptivity: 1.00 g of a compound being tested which had been dried was placed in a cylindrical glass contained with ø 2.0 cm x 2.0 cm and allowed to stand under constant temperature and humidity conditions of a relative humidity of 93% and a temperature of 25°C. The moisture absorptivity was calculated according to the following equation.

$$\text{Moisture Absorptivity (\%)} = \left(\frac{\text{weight of absorbed compound} - \text{weight of dried compound}}{\text{weight of dried compound}}\right) \times 100$$

* Moisture Retentivity: 1.00 g of a compound being tested which contained 10% of moisture was placed in a cylindrical glass container with ø 2.0 cm x 2.0 cm and allowed to stand under constant temperature and humidity conditions at a humidity of 20% and a temperature of 25°C. The variation in the weight was measured and the moisture retentivity was calculated according to the following equation.

$$\text{Moisture Retentivity (\%)} = \left(\frac{\text{weight of compound containing 10\% of moisture} - \text{weight of moisture released compound}}{\text{weight of compound containing 10\% of moisture} \times 0.1}\right) \times 100$$

From the results of this test, it will be seen that the triglycerine alkyl ethers have suitable degree of moisture absorptivity and retentivity and are thus suitable as a humectant of cosmetics.

Example 9

Triglycerine monoalkyl ethers and comparative compounds were each subjected to an emulsification test (note 2) to compare them with one another with respect to the performance as an emulsifier. The results are shown in Table 4.

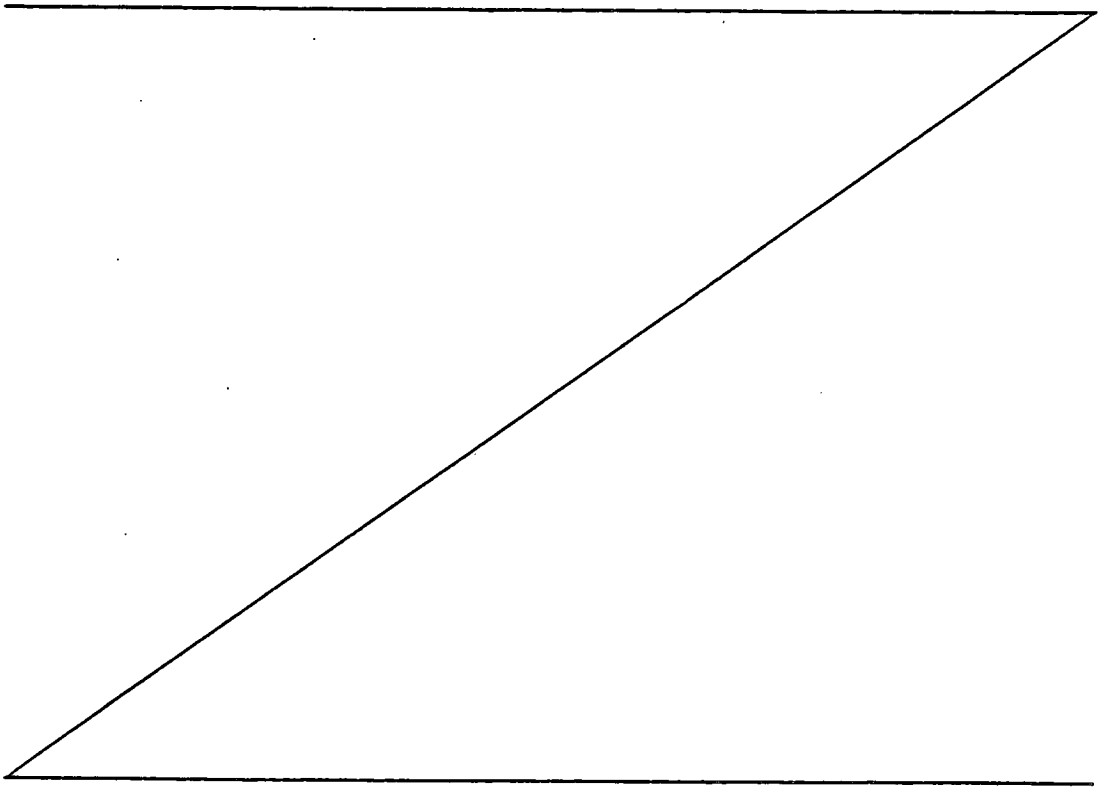


Table 4

Compounds Tested	State Immediately after Emulsification (Average Size ø)	Stability after 7 Days (%)	
		Oil Phase Separation Rate	Aqueous Phase Separation Rate
Products of Invention			
R in Formula (I)			
n-$C_{12}H_{25}$	Slightly nonuniform o/w cream (25 μm)	4	43
n-$C_{14}H_{29}$	Uniform o/w cream (6.5)	0	12
n-$C_{16}H_{33}$	Uniform o/w cream (8.5)	0	18
$C_{18}H_{35}$ (Oleyl)	Uniform o/w cream (3.8)	0	10
iso-$C_{18}H_{37}$ (Methyl-branched Isostearyl)	Uniform o/w cream (3.8)	0	8
Comparative Products			
Diglycerine Monooleate	Uniform w/o cream	38	0
Polyoxyethylene Oleyl Ether	Nonuniform o/w cream	75	88

(Note 2) Emulsification test: 5 g of a compound being tested was mixed with 45 g of liquid paraffin and heated at 75°C. Separately, 50 g of purified water was heated to 75°C and was added to the mixture of the liquid paraffin and the compound under agitation for emulsification, followed by cooling to room temperature while agitating. The emulsion obtained immediately after the emulsification was observed and the state of separation after preservation at 25°C for 7 days was also observed. The emulsion stability was calculated according to the following equation.

$$\text{separation rate of aqueous phase} = \frac{\text{amount of separated aqueous phase (ml)}}{50} \times 100$$

$$\text{separation rate of oil phase} = \frac{\text{amount of separated oil phase (ml)}}{50} \times 100$$

The above test results demonstrated that while the monoalkyl ester of diglycerine gave a w/o type emulsion, the triglycerine monoalkyl ethers of the invention permitted formation of o/w types emulsions and the emulsifying strength was the highest when the number of carbon atoms in R was from 14 to 18.

Example 10

Lotion:

Triglycerine monooctyl ether was used to prepare a lotion of the following composition.

(Composition)

(1)	Triglycerine monooctyl ether (product of invention)	7.0 (wt%)
(2)	Ethanol	15.0
(3)	Glycine	1.0
(4)	Sodium pyrrolidonecarboxylate	1.5
(5)	Polyoxyethylene lauryl ether	1.5
(6)	Perfume	0.2
(7)	Purified water	balance

(Preparation)

(1) to (7) were uniformly mixed under agitation. The resulting lotion was applied to skin. It was found that the lotion had good affinity for skin and was soft to the touch, thus being excellent as a cosmetic lotion.

Example 11

Emulsion:

Triglycerine monolauryl ether was used to prepare an emulsion of the following composition.

(Composition)

(1)	Squalane	5.0 (wt%)
(2)	Vaseline (registered trade mark)	2.0
(3)	Polyoxyethylene oleyl ether	1.2
(4)	Sorbitan sesquioleate	0.8
(5)	Ethanol	5.0
(6)	Triglycerine monolauryl ether (product of invention)	6.0
(7)	1% Carboxy vinyl polymer aqueous solution	20.0
(8)	Potassium hydroxide	0.1
(9)	Purified water	balance

(Preparation)

(5), (6), (8) and (9) were mixed and heated to 70°C, which was gradually added, for emulsification under agitation, to (1) to (4) previously mixed and heated. To the mixture was added (7), which was uniformly mixed, followed by uniform emulsification by the use of a homogenizer mixer and cooling to room temperature. The resulting emulsion was applied to skin and was found to give good softness after use. Thus, it had good properties as a cosmetic emulsion.

Example 12

Emulsion-type Lip Cream:

Triglycerine monocetyl ether was used to prepare an emulsion-type lip cream having the following composition.

(Composition)

(1)	Liquid paraffin	32 (wt%)
(2)	Carnauba	8
(3)	Microcrystalline wax	12
(4)	Jojoba oil	8
(5)	Vaseline (registered trade mark)	10
(6)	Triglycerine monocetyl ether (product of invention)	5
(7)	Glycerine	5
(8)	Purified water	balance

(Preparation)

(1) to (5) were heated to 85°C and uniformly mixed, to which was added a heated mixture of (6) to (8), followed by sufficiently agitating for emulsification. Immediately after the emulsification, the mixture was poured into a mold and cooled. The resulting emulsified product was a relatively soft solid w/o emulsion with a glossy, milky white color. When molded as a rod, the emulsion had properties excellent as a lipcream.

Example 13

Hand Cream (o/w type)

Triglycerine mono(methyl-branched) isostearyl ether was used as an emulsifier to prepare a hand cream (o/w type) of the following composition.

(Composition)

(1)	Triglycerine mono(methyl-branched) stearyl ether (product of invention)	3.4 (wt%)
(2)	Stearic acid	8.0
(3)	Squalane	4.0
(4)	Stearyl alcohol	1.5
(5)	Butyl paraoxybenzoate	0.1
(6)	Methyl paraoxybenzoate	0.1
(7)	Propylene glycol	5.0
(8)	Sodium hydroxide	0.1
(9)	Purified water	balance

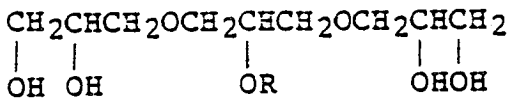
(Preparation)

(1) to (5) were mixed and heated to 75°C. Separately, a mixture of (6) to (9) was heated to 75°C and was gradually added to the mixture of (1) to (5) for emulsification, followed by cooling to room temperature.

The resulting emulsion was a glossy cream and had a high stability, with good affinity for skin. Thus, it was suitable as a hand cream.

CLAIMS:

1. A polyol ether compound of the general formula (I)

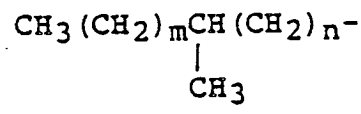


(I)

in which R represents a saturated or unsaturated, linear or branched aliphatic hydrocarbon group having from 8 to 24 carbon atoms.

2. The polyol ether compound according to Claim 1, wherein R is a linear aliphatic hydrocarbon group having from 8 to 18 carbon atoms.

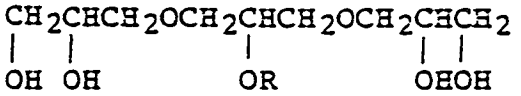
3. The polyol ether compound according to Claim 1, wherein R represents a methyl-branched isostearyl group represented by the following formula



in which m is an integer from 4 to 10, n is an integer from 5 to 11, and m + n is from 11 to 17, with a distribution having a peak at m = 7 and n = 8.

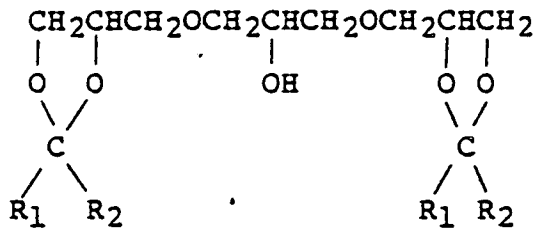
4. The polyol ether compound according to Claim 1, wherein R represents an oleyl group.

5. A process for preparing a polyol ether compound of the formula (I)



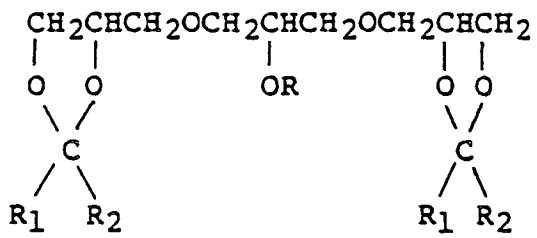
(I)

in which R represents a saturated or unsaturated, linear or branched aliphatic hydrocarbon group having from 8 to 24 carbon atoms, the process comprising the steps of etherifying 1,3-bis-o-(2,3-o-isopropylideneglyceryl) glycerine of the following general formula (II)



(II)

in which R_1 and R_2 independently represent a hydrogen atom, a C_1 to C_5 alkyl group, an aryl group or an aralkyl group, in the presence of an alkaline substance and a catalytic amount of a quaternary onium salt, thereby giving 1,3-bis-o-(2,3-o-isopropylideneglyceryl)-2-o-alkylglycerine of the general formula (III)



(III)

in which R_1, R_2 and R have the same meanings as defined above, respectively, and hydrolyzing the compound of the formula (III) to obtain the compound of the formula (I).

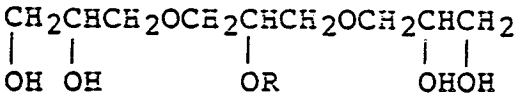
6. The process according to Claim 5, wherein said quaternary onium salt is a quaternary ammonium salt, quaternary phosphonium salt, betaine, amine oxide or ion-exchange resin.

7. The process according to Claim 5, the etherification is carried out with use of an alkyl halide.

8. The process according to Claim 5, wherein the hydrolysis is carried out in the presence of a protonic acid catalyst.

9. The process according to Claim 5, wherein the hydrolysis is carried out in water to which a water-soluble organic solvent is added.

10. A cosmetic composition comprising an effective amount of a polyol ether compound of the general formula (I)



(I)

in which R is a saturated or unsaturated, linear or branched fatty hydrocarbon group having from 8 to 24 carbon atoms.

11. A polyol ether compound as claimed in claim 1 and substantially as described in any one of the examples herein set forth.

12. A process as claimed in claim 5 and substantially as described in any one of the specific examples herein set forth.

THE PATENT OFFICE

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RENEWAL DETAILS

PATENT No 2144122

RENEWAL DATE 16.07.1990

RENEWAL FEE PAID FOR 6th YEAR ON 5.7.89

WM

FOR THE COMPTROLLER 25.01.90

NOTE: RENEWALS FILED WITHIN THE LAST FEW DAYS MAY NOT APPEAR IN THE RECORDS

REGISTER ENTRY FOR GB2144122

Form 1 Application No GB8418025.6 filing date 16.07.1984

Priority claimed:
25.07.1983 in Japan - doc: 58135421

Title NOVEL POLYOL ETHER COMPOUNDS PROCESS FOR PREPARING THE COMPOUNDS AND COSMETICS COMPRISING SAME

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Classified to
C2C U1S
C07C

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Publication No GB2144122 dated 27.02.1985

Examination requested 06.11.1984

Patent Granted with effect from 04.02.1987 (Section 25(1)) with title TRIGLYCERINE MONOALKYL ETHER COMPOUNDS A PROCESS FOR PREPARING THE COMPOUNDS AND COSMETICS COMPRISING THEM

**** END OF REGISTER ENTRY ****