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(21) International Application Number: PCT/EP93/03172 (22) International Filing Date: 11 November 1993 (11.11.93) (30) Priority Data: 981,972 25 November 1992 (25.11.92) US (71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors: RAHMAN, Mohammad, Abdur; 159 Bogert Road, River Edge, Bergen County, NJ 07661 (US). WU, Shang-Ren; 80 Glenmere Terrace, Mahwah, NJ 07430 (US). GARRETT, Peter, Robert; Charlesville, Cilcain Road, Pantymwyn, Clwyd CH7 5EH (GB). (74) Agent: FRANSELLA, Mary, Evelyn; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: ALKYLGLYCERAMIDES AND THEIR USE AS SURFACTANTS (57) Abstract Surface-active N-alkylglyceramides of formula (I), wherein R is a C₈₋₂₄ hydrocarbon radical, are effective surfactants and foaming agents, useful in detergent and personal product compositions. They may advantageously be used as a cosurfactant or foam enhancer in combination with another surfactant, especially an anionic surfactant, for example, primary alcohol sulphate or alkylbenzene sulphonate. $\begin{array}{c} \text{CH}_2 \text{ --- } \text{CH} \text{ --- } \text{C} \text{ --- } \text{NH} \text{ --- } \text{R} \\ \qquad \qquad \\ \text{OH} \qquad \text{OH} \end{array} \qquad \qquad \text{O} \\ \qquad \qquad \qquad$ (I)		

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ALKYLGLYCERAMIDES AND THEIR USE AS SURFACTANTSFIELD OF THE INVENTION

The present invention relates to novel surface-active N-alkylglyceramide compounds and to their use as
5 surface-active and/or foaming agents, for example, in detergent or personal product compositions. The compounds may advantageously be used in combination with other surfactants to give enhanced foaming and detergency.

BACKGROUND AND PRIOR ART

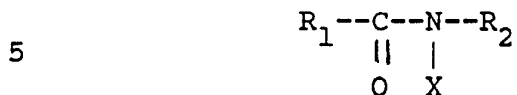
10 Glyceric acid, $\text{CH}_2\text{OH}-\text{CHOH}-\text{COOH}$, is a readily available material. It would therefore be a great advantage to design a surfactant based on the material, particularly a surfactant which can enhance and stabilise foam. Unexpectedly, it has
15 been found that the N-alkylglyceramides of the invention, especially when used in combination with other surfactants, meet this criterion.

The compounds of the invention have the formula $\text{CH}_2\text{OH}-\text{CHOH}-\text{CO}-\text{NHR}$, where R is a hydrocarbon group (defined below). There are compounds disclosed in the art which have
20 some structural similarities to the alkylglyceramides of the invention.

N-alkanolamides, for example, form a well-known class of compounds which have, of course, both an alcohol and an amide functional group. These compounds both enhance and stabilise
25 foam. However, these compounds are structurally different from the N-alkylglyceramides of the invention, in that the hydroxylic group is attached directly to the amine nitrogen atom rather than via the carbonyl carbon atom.

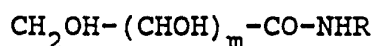
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US 5 009 814 (Kelkenberg et al/Hüls) teaches N-polyhydroxyalkyl fatty acid amide compounds having the formula



wherein R_1 is alkyl, R_2 is hydrogen, an alkyl group or an alkylene oxide group and X is a polyhydroxyalkyl group. Again, in these compounds, the polyhydroxyalkyl group is attached to the nitrogen atom rather than to the carbonyl group.

FR 2 523 962A (Centre Nationale de Recherche/Monsigny) teaches amides having the formula



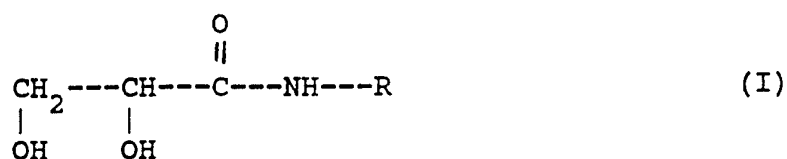
in which m is 2 to 6 and R is a linear or branched alkyl group having 6 to 18 carbon atoms. In these compounds, m must equal at least 2 and, therefore, these are not amides of glyceric acid. Also, there is also no teaching or suggestion that alkylamides may be used as cosurfactants with other detergent-active compounds.

Our copending European Patent Application EP 550 277A, published on 7 July 1993, having an application date of 30 December 1992 and a priority date of 31 December 1991, describes and claims alkylglycerates (alkyl esters of glyceric acid) and their use as surfactants and cosurfactants in detergent compositions.

DEFINITION OF THE INVENTION

The present invention provides a surface-active and/or foaming and/or foam enhancing N-alkylglyceramide of the formula I:

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5 wherein R is a straight- or branched chain aliphatic or aliphatic/aromatic saturated or unsaturated hydrocarbon radical optionally interrupted by one or more oxygen, nitrogen or sulphur atoms, and containing from 8 to 24 aliphatic carbon atoms.

10 The invention further provides the use of a compound as defined above - an N-alkylglyceramide - as a surfactant and/or foaming agent and/or foam enhancer in a surface-active and/or foaming composition.

15 The invention also provides a detergent or personal product composition comprising a surface-active and/or foaming and/or foam-enhancing amount of a compound as defined above.

DETAILED DESCRIPTION OF THE INVENTION

The compounds and their preparation

20 In the formula I, R is a hydrocarbon group having 8 to 24 aliphatic carbon atoms. The R group may be aliphatic or mixed aliphatic/aromatic, straight-chain or branched-chain, saturated or unsaturated. The carbon chain may be interrupted by a heteroatom such as oxygen, nitrogen or sulphur.

25 In preferred compounds of the invention, R is a straight-chain or branched-chain aliphatic hydrocarbon group, more especially an alkyl or alkenyl group. Especially preferred are linear and branched C₈ to C₁₆ alkyl groups, for example, a linear C₈ or C₁₀ alkyl group.

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The compounds of the invention have surface-active and/or foaming and/or foam-enhancing properties. Depending on chain length, some compounds will be especially useful as surfactants in their own right, while others will be most valuable as cosurfactants or foam enhancers when used in combination with other surfactants: generally in significant amounts when used as cosurfactants, and in relatively small amounts when used as foam enhancers.

The novel surfactants of the present invention are based on a readily available material, glyceric acid. They may be prepared by reacting together a lower (eg C₁₋₄) ester of glyceric acid, for example, methyl glycerate, with an amine of the formula RNH, where R is as defined previously. This may be carried out, for example, in anhydrous methanol at a moderately elevated temperature under an atmosphere of nitrogen.

Detergent compositions

The novel surfactants of the present invention may be incorporated in detergent compositions of all physical types, for example, powders, liquids, gels and solid bars.

A detergent composition in accordance with the invention may suitably contain from 5 to 70 wt% of a surfactant system which includes or consists of an N-alkylglyceramide in accordance with the invention. The amount of N-alkylglyceramide in the composition may suitably range from 1 to 70 wt%, the lower end of the range representing compositions in which the N-alkylglyceramide is functioning as a foam enhancer to another surfactant present in a much larger amount.

N-Alkylglyceramides as cosurfactants

Especially preferred are detergent compositions containing a surfactant system comprising from 5 to 95 wt% of an N-alkylglyceramide of the invention and from 5 to 95 wt% of one or more other surfactants selected from soap, anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactant and zwitterionic surfactants.

The N-alkylglyceramide of the invention have been found to enhance foam stability when used as a cosurfactant, particularly when comprising from 25 to 90 wt%, more preferably from 40 to 80 wt%, of the surfactant system.

The other surfactant may be chosen from the many suitable detergent-active compounds available. These are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred surfactants that can be used are soaps and synthetic non-soap anionic and nonionic compounds; especially preferred are non-soap anionic surfactants.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15} ; primary and secondary alkyl sulphates, particularly $C_{12}-C_{15}$ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more

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especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

Especially preferred surfactants for use in combination with the N-alkylglyceramides of the invention are non-soap surfactants, more especially anionic sulphonate or sulphate-type surfactants, notably alkylbenzene sulphonates and primary alcohol sulphates.

N-alkylglyceramides as foam enhancers

The N-alkylglyceramides are also useful for incorporation in relatively small amounts, as foam enhancers, in high-foaming detergent compositions, for example, those intended for washing fabrics by hand. Such compositions typically contain a relatively high level of anionic surfactant, for example, alkylbenzene sulphonate or primary alcohol sulphate.

The foaming of anionic surfactants such as alkylbenzene sulphonate can be quite badly affected by the presence of fatty soil which acts as an antifoam. The presence of quite small amounts of N-alkylglyceramide, eg 5-10 mole% based on the anionic surfactant, has been found to counteract this loss of foaming capacity successfully.

Other ingredients

Detergent compositions of the invention may also, depending on the purpose for which they have been formulated, contain various ancillary ingredients. For example, fabric washing compositions may contain detergency builders such as phosphates, aluminosilicates, polycarboxylate polymers,

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citrate; bleach components such as sodium perborate or percarbonate, bleach activators and bleach stabilisers; sodium carbonate; sodium silicate; antiredeposition agents such as cellulosic polymers; fluorescers; inorganic salts
 5 such as sodium sulphate; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; fabric softening compounds. This list is not intended to be exhaustive.

Table 1 below shows a typical outline formulation.

Table 1: heavy duty fabric washing powder

10	<u>Ingredient</u>	<u>Weight percentage range</u>
	Surfactant	5 to 70 wt%, preferably 5 to 40 wt%
	Builder	5 to 80 wt%, preferably 10 to 60 wt%
	Persalt bleach	5 to 35 wt%, preferably 10 to 25 wt%
	Bleach activator	1 to 8 wt%, preferably 2 to 5 wt%
15	Sodium carbonate	0 to 60 wt%, preferably 2 to 40 wt%
	Sodium silicate	0 to 15 wt%
	Fatty acid soap	0 to 5 wt%.
	Optional minor ingredients, salts and water.	

The optional minor ingredients may include
 20 antiredeposition agents such as cellulosic polymers; fluorescers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; foam controllers; and fabric softening compounds. This list
 25 is not intended to be exhaustive.

The N-alkylglyceramides are also suitable for incorporation into aqueous (both isotropic and lamellar) and non-aqueous liquid detergent compositions for washing fabrics. Suitable formulations are disclosed, for example, in
 30 US 4 244 840, EP 38 101A, EP 160 342A and EP 140 452A. Structured lamellar liquids may contain a deflocculating polymer as described and claimed in EP 346 995A (Unilever).

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The compositions of the invention are also suitable for incorporation into light-duty (non-bleaching, and generally unbuilt) high-foaming liquid detergent compositions, for example, those used for hand washing of dishes or of delicate
5 fabrics.

Other compositions

The compounds of the invention are also suitable for other applications in which surfactant and/or foaming and/or foam-enhancing properties are useful; in particular, for
10 personal product (personal care) formulations of various types.

Personal product compositions of the invention may be, for example, toilet bar compositions, facial or body cleansing compositions, shampoos for hair or body, conditioners or
15 conditioning shampoos, shower gels, cosmetic compositions, shaving preparations, or dental care compositions.

Toilet bar compositions

Typical toilet bar compositions are those comprising fatty acid soaps used in combination with a detergent other than
20 fatty acid soap and free fatty acids; however, the composition may comprise no fatty acid soap and may be based on actives other than fatty acid soap. Mildness-improving salts, such as alkali metal salts of isethionate, are also typically added. In addition other ingredients, such as
25 germicides, perfumes, colorants, pigments, suds-boosting salts and anti-mushing agents may also be added.

A typical outline formulation might be as shown in Table 2 below.

Facial or body cleansing compositions

N-alkylglyceramides may also be present in a facial or body cleansing composition. Examples of such cleaning compositions are described, for example, in US 4 812 253 (Small et al) and US 4 526 710 (Fujisawa).

Typically, cleansing compositions will comprise a fatty acid soap together with a non-soap surfactant, preferably a mild synthetic surfactant; a moisturiser or emollient; and polymeric skin feel and mildness aids. The compositions may further optionally include thickener (eg magnesium aluminium silicate, Carbopol (Trade Mark), water soluble polymers (eg carboxymethylcellulose), dyes, hydrotropes, brighteners, perfumes and germicides.

A typical outline formulation might be as in Table 3 below.

Shampoo compositions

The N-alkylglyceramide surfactant of the invention may be used, for example, in a hair or body shampoo. Examples of such compositions are described in US 4 854 333 (Inman) and US 4 526 710 (Fujisawa).

Shampoo compositions typically comprise a further surfactant; a compound for treating dandruff, eg selenium sulphide; a suspending agent; a thickening agent, eg cross-linked polyacrylate; a nonionic polymer; a nonvolatile silicone fluid; a preservative; a cationic surfactant; a pH adjusting agent; a perfume; a dye; a sequestering agent, such as disodium ethylenediamine tetraacetate.

A typical outline shampoo composition might be as in Table 4 below.

Toothpaste compositions

In yet another embodiment of the invention, the surfactant may be used in a toothpaste composition such as is taught and is described in US 4 935 227 (Duckworth).

5 Such compositions generally comprise abrasive gels (eg calcium carbonate), oral therapeutic agents (for example, fluorine containing compound), cosurfactants, flavouring agents, sweetening agents, humectants and binding or thickening gels.

10 A typical outline formulation might be as shown in Table 5 below.

Table 2: toilet bar composition

	<u>Ingredient</u>	<u>Weight %</u>
	C ₈ to C ₂₄ fatty acid	5-60
15	N-alkylglyceramide	1-45
	Cosurfactant other than	
	N-alkylglyceramide	0-50
	Alkyl or aryl sulphate or sulphonate	0-5
	Moisturiser (eg sorbitol or glycerol)	0.1-10
20	Water soluble polymer	0-10
	eg cellulose or polyacrylate)	
	Sequestering agent eg citrate	0.1-0.5
	Dyestuff	<0.1
	Optical brightener	<0.1
25	Whitening agent	0.1-0.4
	Fragrance	0.1-2.0
	Water	Balance

Table 3: facial or body cleansing composition

	<u>Ingredient</u>	<u>Weight %</u>
	C ₈₋₂₄ fatty acid salt (eg triethanolamine salt)	1-45
5	N-alkylglyceramide	10-75
	Alkyl or aryl sulphate or sulphonate	0-20
	Cosurfactant (eg cocoamidobetaine)	1-15
	Moisturiser (eg sorbitol)	0.1-15
	Refatting alcohol	0.5-5
10	Water soluble polymer	0-10
	Thickener	0-15
	Conditioner (eg quaternised cellulose)	0.1-15
	Sequestering agents (eg citrate)	0.1-0.4
	Dyestuff	<0.1
15	Optical brighteners	<0.1
	Whitening agents	0.1-0.4
	Fragrance	0.1-3.0
	Preservatives	0-0.2
	Water	Balance

20

Table 4: shampoo composition

	<u>Ingredient</u>	<u>Weight %</u>
	N-alkylglyceramide	5-15
	Anionic surfactant	0-10
	Amphoteric surfactant	0-10
25	Lauric monoethanolamide	0-5
	Thickener	0-5
	Fragrance	0-2
	Preservative	0-1
	Water	Balance

Table 5: toothpaste composition

<u>Ingredient</u>	<u>Weight %</u>
Synthetic surfactant (eg sodium lauryl sulphate)	1.5
5 N-alkylglyceramide	1-10
Alkyl or aryl sulphate or sulphonate	0-1
Abrasive (eg silicic acid/CaCO ₃)	20-55
Active ingredients (eg pyrophosphate)	0.1-2
Humectant (eg glycerin, sorbitol)	10-45
10 Thickener (eg cellulose derivative)	0-3
Sequestering agent (eg citrate)	0.1-0.4
Flavouring agent	0.5-2
Sweetener	<0.5
Dyestuff	<0.1
15 Water	Balance

EXAMPLES

The invention is illustrated greater detail in the following non-limiting Examples.

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Example 1: Synthesis of N-decylglyceramide

A solution of methyl glycerate (8.18 g, 0.068 mol) and decylamine (13.6 ml, 0.068 mol) in anhydrous methanol (50 ml) was heated at 60°C under nitrogen for 3 h. The solvent was removed on a rotary evaporator and the residue was crystallised from ethyl acetate which gave the pure compound, melting point 82-90°C (15.32 g, 92%).

The compound showed the following characteristics:

IR (nujol): 3270, 2920, 1640, 1470 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): delta 0.89 (t, CH₃), 1.27 (br, CH₂), 1.52 (m, CH₂), 2.78 (t, OH), 3.24 (m, CH₂) 3.88 (dd, CH), 4.15 (m, OH), 6.97 (t, NH).

¹³C NMR (50 MHz, CDCl₃): delta 14.05, 22.62, 26.94, 29.29, 29.42, 29.55, 31.85, 39.23, 64.47, 72.67, 172.59;

MS (CI, isobutane): MH⁺, 246.

Example 2: synthesis of N-octylglyceramide

N-octylglyceramide was prepared by the method of Example 1, using methyl glycerate and n-octylamine as starting materials.

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Example 3Foam Height

Foam is an important attribute in many consumer products (eg, consumer products). Foam is one of the dominant factors that determines the commercial value of products such as shampoo, soap, shower gel or dishwashing liquids. Also, acceptability of many consumer products is closely related to the quality and texture of the foam they produce (psychological aspect).

Since most foaming data on surfactants is typically obtained by the Ross-Miles method (Ross J and Miles G D, Am Soc for Testing Material Method D1173-53 Philadelphia, PA, (1953); Oil & Soap (1958) 62 : 1260) the foaming and foam enhancement ability of the surfactants of the invention was also assessed using this method.

In the Ross-Miles method, 200 ml of a solution of surfactant contained in a pipette of specified dimensions with a 2.9 mm internal diameter orifice is allowed to fall 90 cm onto 50 ml of the same solution contained in a cylindrical vessel maintained at a given temperature (often 60°C) by means of a water jacket. the height of the foam produced in the cylindrical vessel is read immediately after all the solution has run out of the pipette (initial foam height) and then again after a given amount of time (generally, 5 min).

Using this method, the foam production (measured initially) and foam stability (the height after 10 minutes) were measured for surfactant systems with and without an N-alkylglyceramide (C₈), the other surfactant being sodium dodecyl sulphate (SDS or C₁₂ PAS). All measurements were carried out at 45°C in water with 120 ppm hardness.

The results are set forth in Table 6 below.

Table 6: foam stability of PAS/C₈ glyceramide systems

<u>Surfactant system (weight %)</u>		<u>Foam height (mm)</u>	
C ₁₂ PAS	C ₈ glyceramide	Initial	After 10 minutes
100	0	145	78
5 90	10	165	108
75	25	158	134
50	50	169	151
25	75	172	153
10	90	155	127

10 It can be clearly observed from the numbers above that, when used in sufficient amounts, the N-alkylglyceramide compounds of the invention, clearly enhanced foam stability. Thus, though a 90:10 mixture of PAS/glyceramide showed a foam height of about 108 after 10 minutes, by the time 50:50
 15 mixtures and 25:75 mixtures (all percentages by weight) were used, foam height after 10 minutes was at 151-153 mm.

Thus, the N-alkylglyceramide of the invention enhances foam stability when used as a cosurfactant, particularly when comprising 25 to 90% the surfactant mixture, more preferably,
 20 when comprising 40 to 80% by weight of the mixture.

Example 4: foam enhancement of alkylbenzene sulphonate

This Example demonstrates that the N-alkylglyceramides of the present invention are also valuable when used in small amounts, to enhance or boost the foam of anionic surfactant in the presence of oily soil which acts as a foam suppressant. The anionic surfactant used was sodium dodecyl benzene sulphonate (C₁₂ LAS).

Solutions were prepared at 0.005 molar total surfactant in 1.2 g/litre sodium tripolyphosphate, 0.4 g/litre sodium carbonate and 0.002 molar calcium chloride; this electrolyte was chosen as a model for handwash conditions used in some overseas countries. After equilibration at 25°C, the solutions were clear and colourless.

Foamabilities were measured by the Ross-Miles test described above, at 25°C, in the presence and in the absence of a foam suppressant.

The foam suppressant used was artificial sebum. It was dispersed at a concentration of 1 g/litre in 0.5 litre of surfactant/electrolyte solution at 60°C using a high-speed shear mixer, the solution then being cooled to 25°C before foam testing. The results were as follows:

<u>Surfactant system (weight %)</u>			<u>Foam height (mm)</u>	
LAS	C ₁₀ glyceramide		Without antifoam	With antifoam
25 100	0		137	64
96.34	3.66		137	89
92.67	7.33		139	108

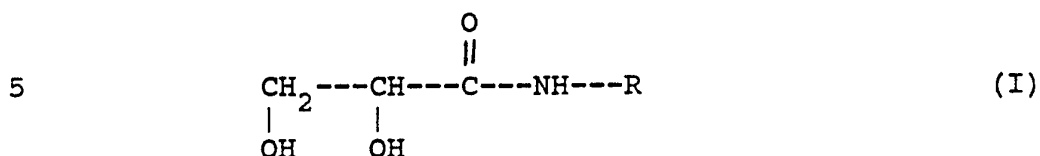
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CLAIMS

1 A compound which is an N-alkylglyceramide of the formula
I:



wherein R is a straight- or branched chain aliphatic or aliphatic/aromatic saturated or unsaturated hydrocarbon radical optionally interrupted by one or more oxygen, nitrogen or sulphur atoms, and containing from 8 to 24 aliphatic carbon atoms.

2 A compound as claimed in claim 1, wherein R represents a
straight- or branched chain alkyl or alkenyl group having from
15 8 to 24 carbon atoms.

3 A compound as claimed in claim 1, wherein R represents a
straight- or branched chain alkyl group having from 8 to 16
carbon atoms.

4 A compound as claimed in claim 1, wherein R represents a
20 linear C₈ or C₁₀ alkyl group.

5 A process for the preparation of a compound as claimed in claim 1, which comprises reacting a C₁₋₄ alkyl ester of glyceric acid with an amine of the formula RNH.

6 Use of a compound as claimed in claim 1 as a surfactant
5 and/or foaming agent and/or foam-enhancing agent in a surface-active and/or foaming composition.

7 A detergent composition comprising a surface-active and/or foaming and/or foam-enhancing amount of a compound as claimed in claim 1.

10 8 A detergent composition comprising from 5 to 70 wt% of a surfactant system comprising a compound as claimed in claim 1.

9 A detergent composition as claimed in claim 8, containing a surfactant system comprising from 5 to 95 wt% of a compound as claimed in claim 1 and from 5 to 95 wt% of
15 one or more other surfactants selected from soap, anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactant and zwitterionic surfactants.

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10 A detergent composition as claimed in claim 9, wherein the surfactant system comprises from 25 to 90 wt% of a compound as claimed in claim 1 and from 10 to 75 wt% of other surfactant.

5 11 A detergent composition as claimed in claim 9, wherein the other surfactant comprises an anionic sulphate or sulphonate type detergent.

12 A detergent composition as claimed in claim 9, wherein the other surfactant comprises a primary alcohol sulphate or
10 an alkylbenzene sulphonate.

13 A personal product composition containing a surface-active and/or foaming and/or foam-enhancing amount of a compound as claimed in claim 1, wherein the compositions is a toilet bar, a facial and/or body cleanser, a shampoo, a
15 conditioner, a conditioning shampoo, a shower gel, a cosmetic composition, an antiperspirant or deodorant composition, a shaving preparation, or a toothpaste composition.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/03172

A. CLASSIFICATION OF SUBJECT MATTER

C 07 C 235/06, C 07 C 235/08, C 11 D 1/66, A 61 K 7/50,
A 61 K 7/24, A 61 K 7/15

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 07 C 235/00, C 11 D 1/00, A 61 K 7/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 110, no. 1, issued 02 January 1989 (Columbus, Ohio, USA), T. MASE et al. "Saturated heterocyclic carboxamides, especially thiazolidinecar- boxamides, useful as PAF antagonists, their pharmaceu- tical compositions, and processes and intermediates for their preparation." page 552, abstract no. 23877v & Eur.Pat.Appl. EP 279 681 (YAMONOUCHI PHARMACEUTICAL) + Chemical Abstracts, Twelfth Collective Index vol. 106-115 (1987-1991) page 16618F, column 2, lines 53-56.	1

☐

Further documents are listed in the continuation of box C.

☐

Patent family members are listed in annex.

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Date of the actual completion of the international search
08 February 1994

Date of mailing of the international search report

25.02.94

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	-- FR, A1, 2 523 962 (CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE) 30 September 1983 (30.09.83), pages 1-4 (cited in the application). ----	1-10, 13

ANHANG

zum internationalen Recherchen-
bericht über die internationale
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ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
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PCT/EP 93/03172 SAE 82143

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