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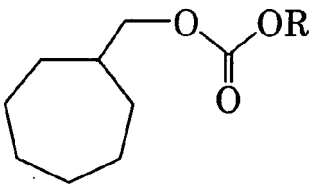
(54) Alkyl cycloheptylmethyl carbonates and perfume compositions

(57) The prevent invention relates to an alkyl cycloheptylmethyl carbonate represented by the general formula (1):



(1)

wherein R is methyl or ethyl.

The alkyl cycloheptylmethyl carbonates have a floral fruity jasmine scent.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to alkyl cycloheptylmethyl carbonates and perfume compositions containing the same.

BACKGROUND OF THE INVENTION

[0002] There are conventionally known several useful perfume compounds as carbonate compounds having a flowery scent. For example, it is known that methyl cyclooctyl carbonate (tradename: "JASMACYCLAT" available from Kao Corporation) has a herbal jasmine-like scent, and ethyl 2-tert-butyl cyclohexyl carbonate (tradename: "FLORAMAT" available from Kao Corporation) has a woody fruity scent. Further, it is also known that methyl 3 (or 4)-cyclooctenyl carbonate (tradename: "VIOLIFF" available from International Flavor & Fragrances Inc. (IFF)) has a floral violet and banana-like scent.

[0003] In addition, US Patent No. 4,080,309 describes that carbonate compounds such as cyclohexyl carbonate have a persistent natural comfortable scent and are useful as perfumes. For example, in US Patent No. 4,080,309, there are described ethyl cyclooctyl carbonate having a flowery sweet fruity scent, methyl trans-3,3,5-trimethylcyclohexyl carbonate having an earthy fruity natural scent, ethyl trans-3,3,5-trimethylcyclohexylcarbonate having fruity camphoric scent, methyl cis-3,3,5-trimethyl cyclohexyl carbonate having a fresh metallic scent, methyl 1-ethynylcyclohexyl carbonate having a fruity herbal scent, methyl 2-tert-butylcyclohexyl carbonate having a camphoric fruit scent, ethyl 2-tert-butylcyclohexyl carbonate having a woody fruity scent, methyl 4-tert-butylcyclohexyl carbonate having a fruity spicy woody scent, and ethyl 4-tert-butylcyclohexyl carbonate having a fruity woody scent.

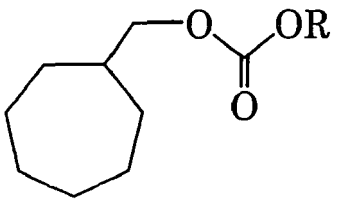
[0004] US Patent No. 4,397,789 describes methyl 4-cyclooctenyl carbonate having a sweet fruity violet scent and a cucumber-like green scent, and ethyl 4-cyclooctenyl carbonate having a minty strawberry-like scent.

[0005] Further, US Patent No. 5,100,872 describes that alkyl cyclohexylmethyl carbonates or alkyl cyclohexenylmethyl carbonates are useful as perfumes.

SUMMARY OF THE INVENTION

[0006] The present invention relates to:

(1) An alkyl cycloheptylmethyl carbonate represented by the general formula (1):



(1)

wherein R is methyl or ethyl; and

(2) a perfume composition containing the alkyl cycloheptylmethyl carbonate as defined in the above (1).

BRIEF DESCRIPTION OF THE DRAWINGS

[0007]

Fig. 1 is a chart showing results of ^{1}H-NMR measurement of methyl cycloheptylmethyl carbonate obtained in Example 1.

Fig. 2 is a chart showing results of FT-IR measurement of methyl cycloheptylmethyl carbonate obtained in Example 1.

DETAILED DESCRIPTION OF THE INVENTION

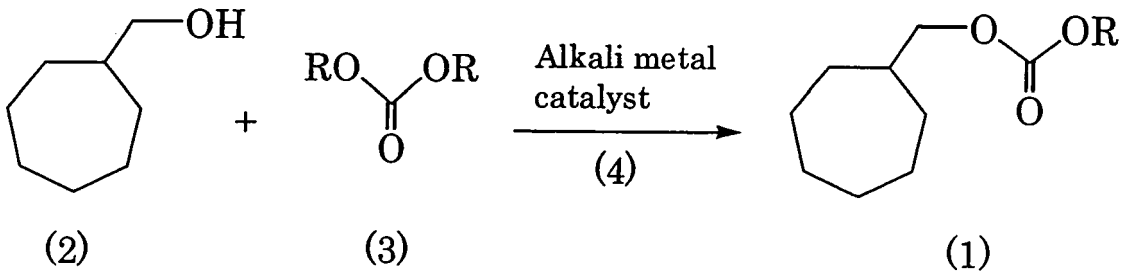
[0008] The present invention relates to alkyl cycloheptylmethyl carbonates having a floral fruity jasmine scent as well

as perfume compositions containing the same.

[0009] Scents or fragrances as required are changed with the times, and various perfumes having various scents or fragrances have been, therefore, demanded. In general, scents of perfume compounds considerably vary even by a slight difference in structure therebetween. For this reason, in order to obtain novel perfumes having various scents, it is extremely important to synthesize various compounds which are slightly different in structure from each other and examine scents thereof.

[0010] The present inventors have synthesized novel alkyl cycloheptylmethyl carbonates, and as a result of study on scents or fragrances thereof, have found that the compounds exhibit a floral fruity jasmine scent.

[0011] The alkyl cycloheptylmethyl carbonates of the present invention may be produced, for example, according to the reaction represented by the following formula:



(2) (3) (1)

wherein R is methyl or ethyl.

[0012] More specifically, the alkyl cycloheptylmethyl carbonate (1) of the present invention may be produced by reacting cycloheptyl methanol (2) (available from Sigma-Aldrich Inc.; catalogue number: R278173) with dimethyl carbonate or diethyl carbonate (3) in the presence of an alkali metal catalyst (4).

[0013] The alkali metal catalyst (4) used in the above reaction is not particularly limited, and is preferably an alkali metal alcoholate in view of a good yield. Examples of the alkali metal contained in the alkali metal alcoholate include sodium, potassium and lithium. Examples of the alkoxy residual group of the alkali metal alcoholate include lower alkoxy groups having 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy and tert-butoxy. Among these alkali metal alcoholates, preferred are sodium methylate and sodium ethylate.

[0014] Examples of the solvent used in the above reaction include hydrocarbon-based solvents such as hexane, cyclohexane, benzene, toluene and xylene, and ether-based solvents such as diethyl ether, dibutyl ether and tetrahydrofuran. In view of a good productivity, the reaction is preferably conducted under a solvent-free condition.

[0015] The dimethyl carbonate or diethyl carbonate (3) may be used in the reaction in an amount of 1 to 20 mol and preferably 2 to 10 mol per mol of cycloheptyl methanol (2).

[0016] The alkali metal catalyst (4) may be used in the reaction in an amount of 0.1 to 20 mol% and preferably 1 to 10 mol% on the basis of cycloheptyl methanol (2).

[0017] The temperature used in the above reaction varies depending upon kind of solvent to be used, etc., and is usually 20 to 150°C and preferably 60 to 120°C. The reaction is preferably performed while removing methanol or ethanol generated with progress of the reaction out of the reaction system. The pressure used in the above reaction may be either normal pressure or reduced pressure.

[0018] When the reaction reaches a desired equilibrium condition, the alkali metal catalyst (4) is neutralized using an acid to terminate the reaction. Examples of the acid include inorganic acids such as hydrochloric acid and phosphoric acid, and organic acids such as acetic acid, citric acid and tartaric acid. Among these acids, preferred are the inorganic acids.

[0019] An excess amount of dimethyl carbonate or diethyl carbonate (3) used in the reaction is distilled off under reduced pressure or normal pressure. The obtained reaction product may be purified by ordinary precision distillation, column chromatography, etc., to obtain a perfume having a purity suitable upon use.

[0020] The thus obtained alkyl cycloheptylmethyl carbonate of the present invention has a novel floral fruity jasmine scent, and may be used alone or in combination with the other perfume substances ordinarily used for cosmetics, as an aromatizing component.

[0021] The perfume composition of the present invention contains the alkyl cycloheptylmethyl carbonate represented by the above general formula (1). The alkyl cycloheptylmethyl carbonate has a novel scent in itself, and may be used in combination with various perfume substances to thereby readily produce perfumes having novel scents.

[0022] Examples of the other perfume substances usable in combination with the alkyl cycloheptylmethyl carbonate include hydrocarbons, alcohols, phenols, esters, carbonates, aldehydes, ketones, acetals, ethers, nitriles, carboxylic acids and lactones as well as other natural essential oils or natural extracts.

[0023] Examples of the hydrocarbons include limonene, α-pinene, β-pinene, terpinene, cedrene, longifolene and valencene.

[0024] Examples of the alcohols include linalool, citronellol, geraniol, nerol, terpineol, dihydromyrcenol, ethyl linalool, farnesol, nerolidol, cis-3-hexenol, cedrol, menthol, borneol, phenylethyl alcohol, benzyl alcohol, dimethylbenzyl carbinol, phenylethyldimethyl carbinol, phenyl hexanol, 2,2,6-trimethylcyclohexyl-3-hexanol and 1-(2-t-butylcyclohexyloxy)-2-butanol.

[0025] Examples of the phenols include guaiacol, eugenol, isoeugenol, thymol and vanillin.

[0026] Examples of the esters include formic esters, acetic esters, propionic esters, butyric esters, nonenoic esters, benzoic esters, cinnamic esters, salicylic esters, brassilic esters, tiglic esters, jasmonic esters, glycidic esters and anthranilic esters.

[0027] Specific examples of the formic esters include linalyl formate, citronellyl formate and geranyl formate. Specific examples of the acetic esters include n-hexyl acetate, cis-3-hexenyl acetate, linalyl acetate, citronellyl acetate, geranyl acetate, neryl acetate, terpinyl acetate, nopyl acetate, bornyl acetate, isobornyl acetate, o-t-butylcyclohexyl acetate, p-t-butylcyclohexyl acetate, tricyclodecenyl acetate, benzyl acetate, stearyl acetate, cinnamyl acetate, diemethylbenzylcarbinyl acetate, phenylethylphenyl acetate and 3-pentyltetrahydropyran-4-yl acetate. Specific examples of the propionic esters include citronellyl propionate, tricyclodecenyl propionate, allylcyclohexyl propionate, ethyl 2-cyclohexyl propionate and benzyl propionate. Specific examples of the butyric esters include citronellyl butyrate, dimethylbenzylcarbinyl n-butyrate and tricyclodecenyl isobutyrate.

[0028] Specific examples of the nonenoic esters include methyl 2-nonenoate, ethyl 2-nonenoate and ethyl 3-nonenoate. Specific examples of the benzoic esters include methyl benzoate, benzyl benzoate and 3,6-dimethyl benzoate. Specific examples of the cinnamic esters include methyl cinnamate and benzyl cinnamate. Specific examples of the salicylic esters include methyl salicylate, n-hexyl salicylate, cis-3-hexenyl salicylate, cyclohexyl salicylate and benzyl salicylate.

[0029] In addition, specific examples of the brassilic esters includes ethylene brassilate; specific examples of the tiglic esters include geranyl tiglate, 1-hexyl tiglate and cis-3-hexenyl tiglate; specific examples of the jasmonic esters include methyl jasmonate and methyl dihyrojasmonate; specific examples of the glycidic esters include methyl 2,4-dihydroxyethylmethylphenyl glycidate and 4-methylphenylethyl glycidate; and specific examples of the anthranilic esters include methyl anthranilate, ethyl anthranilate and dimethyl anthranilate.

[0030] Examples of the other esters include commercially available products such as "FRUITATE" (tradename: available from Kao Corp.; ethyltricyclo [5,2,1,$0^{2,6}$]decane-2 carboxylate).

[0031] Examples of the carbonates include commercially available products such as "JASMACYCLAT" (tradename: available from Kao Corp.), "FLORAMAT" (tradename: available from Kao Corp.), and "VIOLIFF" (tradename: available from IFF Inc.).

[0032] Examples of the aldehydes include n-octanal, n-decanal, n-dodecanal, 2-methyl undecanal, 10-undecenal, citronellal, citral, hydroxycitronellal, benzaldehyde, phenyl acetaldehyde, phenylpropionic aldehyde, cinnamaldehyde, dimethyltetrahydrobenzaldehyde, 4(3)-(4-hydroxy-4-methylpentyl)-3-cyclohexen-1-carboaldehyde ("LYRAL" (tradename) available from IFF Inc.), 2-cyclohexyl propanal, p-t-butyl-α-methylhydrocinnamaldehyde, p-isopropyl-α-methylhydrocinnamaldehyde, p-ethyl-α,α-dimethylhydrocinnamaldehyde, α-amyl cinnamaldehyde, α-hexyl cinnamaldehyde, heliotropin and α-methyl-3,4-methylenedioxyhydrocinnamaldehyde.

[0033] Examples of the ketones include α-ionone, β-ionone, γ-ionone, α-methyl ionone, β-methyl ionone, γ-methyl ionone, methyl heptenone, 4-methylene-3,5,6,6-tetramethyl-2-heptenone, amyl cyclopentanone, 3-methyl-2-(cis-2-penten-1-yl)-2-cyclopenten-1-one, methyl cyclopentenolone, rose ketone, carvone, menthone, camphor, acetyl cedrene, isolongifolanone, nootkatone, benzyl acetone, anisyl acetone, methyl β-naphthyl ketone, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, maltol, muscone, civetone, cyclopentadecanone and cyclohexadecenone.

[0034] Examples of the acetals include formaldehyde cyclodecylethyl acetal, acetaldehyde ethylphenylpropyl acetal, citral diethyl acetal, phenyl acetaldehyde glycerol acetal and ethyl acetoacetate ethylene glycol acetal.

[0035] Examples of the ethers include cedryl methyl ether, anethole, β-naphthyl methyl ether, β-naphthyl ethyl ether, limonene oxide, rose oxide, nerol oxide, 1,8-cineole, rose furan and decahydro-3a,6,6,9a-tetramethylnaphtho[2.1-b]furan.

[0036] Examples of the nitriles include geranyl nitrile, citrollenyl nitrile and dodecane nitrile.

[0037] Examples of the carboxylic acids include benzoic acid, phenylacetic acid, cinnamic acid, hydrocinnamic acid, butyric acid and 2-hexenoic acid.

[0038] Examples of the lactones include γ-decalactone, δ-decalactone, γ-valerolactone, γ-nonalactone, γ-undecalactone, δ-hexalactone, γ-jasmolactone, whisky lactone, coumarin, cyclopentadecanolide, cyclohexadecanolide, ambrettolide, ethylene brassilate, 11-oxahexadecanolide and butylidene phthalide.

[0039] Examples of the natural essential oils or natural extracts include orange, lemon, lime, bergamot, vanilla, mandarine, peppermint, spearmint, lavender, camomile, rosemary, eucalyptus, sage, basil, rose, rockrose, geranium, jasmine, ylang ylang, anise, clove, ginger, nutmeg, cardamon, cedar, cypress, vetyver, patchouli, lemongrass and labdanum.

[0040] The content of the alkyl cycloheptylmethyl carbonate in the perfume composition of the present invention varies depending upon kinds of perfume substances to be used in combination therewith, kinds and strength of scents as aimed, etc., and is usually 0.001% by mass or higher, preferably 0.01% by mass or higher and more preferably 0.2% by mass or higher in view of effectively imparting a floral scent with a natural feeling to resultant perfumes, although not limited thereto.

[0041] Also, the method for producing the perfume composition of the present invention is not limited, and the perfume composition may be produced by mixing the alkyl cycloheptylmethyl carbonate of the present invention with the other perfume substances under stirring by ordinary methods.

[0042] The thus obtained perfume composition of the present invention can be suitably used as an aromatizing component for perfumes, soaps, shampoos and rinses, detergents, cosmetics, aromatic agents, etc.

EXAMPLES

EXAMPLE 1: Synthesis of Methyl Cycloheptylmethyl Carbonate

[0043] A 50-mL two-necked flask equipped with a cooling tube coupled to a thermometer and a vigoureux tube was charged with 1.9 g (0.0148 mol) of cycloheptyl methanol, 14.05 g (0.156 mol) of dimethyl carbonate and 0.12 g (0.62 mmol) of a solution of 28% by mass sodium methylate in methanol, and the contents of the flask were stirred by a magnetic stirrer. The resultant mixture was heated to 90°C in a 100°C oil bath and continuously heated for 2 hr while gradually distilling off methanol as produced together with a part of dimethyl carbonate out of the reaction system. As a result, after the elapse of 2 hr, the amount of distillates removed was 7 g.

[0044] Next, the obtained reaction solution was cooled to 60°C, and 0.305 g of a 20% by mass phosphoric acid aqueous solution was added thereto for neutralization thereof. After completion of the neutralization, the resultant reaction solution was heated while reducing the pressure from 101 kPa to 1.3 kPa to distil off an excess amount of dimethyl carbonate. The distillation under reduced pressure was continued until finally reaching a pressure of 1.3 kPa and a temperature of 115°C.

[0045] After cooling, the resultant reaction solution was mixed with 3 g of hexane and 1 g of water, and the mixture was stirred for 10 min. Thereafter, the resultant reaction mixture was allowed to stand, and separated into a hexane layer and a water layer to recover the hexane layer. The water layer was extracted with 2 g of hexane one time to obtain an organic layer. The hexane layer together with the organic layer was subjected to distillation under reduced pressure to remove the solvent therefrom, thereby obtaining 2.7 g of a crude reaction product.

[0046] The thus obtained crude reaction product was purified by a silica gel column chromatography using an eluent containing hexane and ethyl acetate at a mixing ratio of 9:1, thereby obtaining 2.3 g of methyl cycloheptylmethyl carbonate at a yield of 78.8%.

[0047] The resultant methyl cycloheptylmethyl carbonate was subjected to ^{1}H-NMR analysis using an NMR apparatus available from Varian Inc., and FT-IR analysis using Fourier transform infrared spectrophotometer "Model: FT-710" available from Horiba Seisakusho Co., Ltd., to determine a structure thereof. The results are shown below.

(1) ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm)
1.70-1.90 (m, 1.3H), 3.76 (s, 3H), 3.92 (d, J=6.5 Hz, 2H)
(2) FT-IR (NaCl) (cm^{-1})
3911, 3811, 3791, 3662, 3639, 3510, 3483, 2925, 2856, 2692, 2387, 2349, 1749, 1587, 1529, 1460, 1442, 1389, 1267, 1115, 1059, 1009, 964, 908, 856, 793, 735,544,503,403
(3) Odor: Floral fruity jasmine scent; excellent residual scent
Fig. 1 shows a chart of ^{1}H-NMR measurement, and Fig. 2 shows a chart of FT-IR measurement.

EXAMPLE 2 AND COMPARATIVE EXAMPLE 1: Orange Flowery Perfume

[0048] Using the methyl cycloheptylmethyl carbonate produced in Example 1, there was prepared perfumes having compositions shown in Table 1.

[0049] More specifically, in Example 2, 10 parts by mass of methyl cycloheptylmethyl carbonate was added in place of 10 parts by mass of dipropylene glycol used in the orange flowery perfume obtained in Comparative Example 1, thereby obtaining a novel orange flowery perfume having an emphasized comfortable natural flowery scent.

[0050] Meanwhile, the commercial products described in Table 1 are as follows.
HERBAVERT: (tradename) available from Kao Corp.;

3,3,5-trimethylcyclohexyl ethyl ether.
Ligustral: (tradename) available from Quest International Inc.
AMBER CORE: (tradename) available from Kao Corp.;
1-(2-t-butylcyclohexyloxy)-2-butanol.

TABLE 1

	Example 2	Comparative Example 1
HERBAVERT *1	10	10
Ligustral SB *2	10	10
Linalool	370	370
Dimethylbenzyl carbinol	50	50
Terpineol	50	50
Phenylethyl alcohol	200	200
Phenylethyl dimethyl carbinol	100	100
Nerolidol	50	50
Phenyl hexanol	50	50
Phenylacetaldehyde glycerol acetal	40	40
Lyral SB 50DPG *3	20	20
AMBER CORE *1	40	40
Methyl cycloheptylmethyl carbonate	10	0
Dipropylene glycol	0	10
Total	1000	1000
Note *1: Tradenames of products available from Kao Corp. *2: Tradename of product available from Quest International Inc. *3: "Lyral" (tradename) available from IFF Inc.		

EXAMPLE 3 AND COMPARATIVE EXAMPLE 2: Floral Musky Perfume

[0051] Using the methyl cycloheptylmethyl carbonate produced in Example 1, there were prepared perfumes having compositions shown in Table 2.

[0052] More specifically, in Example 3, 262.5 parts by mass of dipropylene glycol was used in place of 272.5 parts by mass of dipropylene glycol used in the floral musky perfume obtained in Comparative Example 2, and 10 parts by mass of methyl cycloheptylmethyl carbonate was further added thereto, thereby obtaining a novel floral musky perfume having an increased natural flowery scent as well as an emphasized light musky scent with a transparent feeling.

[0053] Meanwhile, the commercial products described in Table 2 are as follows.

ROMILAT: (tradename) available from Kao Corp.;
3-methyl-3-butenyl-2,2-dimethyl propionate.
Helional: (tradename) available from IFF Inc.;
α -methyl-3,4-(methylenedioxy) hydroxycinnamaldehyde
MDJ: (tradename) available from Kao Corp.;
methyl-(2-pentyl-3-oxocyclopentyl)acetate.
AMBER CORE: (tradename) available from Kao Corp.;
1-(2-t-butylcyclohexyloxy)-2-butanol.
Habanolide: (tradename) available from Firmenich International SA.
AMBROXAN: (tradename) available from Kao Corp.;
dodecahydro-3a,6,6,9a-tetramethyl-[3aR-(3a.α,5a. β,9a. α,9b.β)] naphtho[2,1-b]furan.

TABLE 2

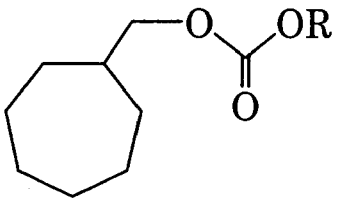
	Example 3	Comparative Example 2
Rose oxide	10	10
ROMILAT *1	20	20
Cis-3-hexenyl acetate	10	10
γ-Decalactone	5	5
Helional *2	10	10
Cis-3-hexenyl salicylate	20	20
MDJ *1	100	100
Phenylethylphenyl acetate	10	10
β-Ionone	20	20
γ-Methyl ionone	20	20
AMBER CORE *1	50	50
Benzyl cinnamate	10	10
Heliotropin	20	20
n-Hexyl salicylate	80	80
Benzyl salicylate	40	40
Ethylene brassilate	200	200
Habanolide *3	100	100
AMBROXAN *1	2	2
Ciste absolute (rockrose)	0.5	0.5
Methyl cycloheptylmethyl carbonate	10	0
Dipropylene glycol	262.5	272.5
Total	1000	1000
Note *1: Tradenames of products available from Kao Corp. *2: Tradename of product available from IFF Inc. *3: Tradename of product available from Firmenich International SA.		

INDUSTRIAL APPLICABILITY

[0054] The alkyl cycloheptylmethyl carbonates of the present invention have a floral fruity jasmine scent and are useful as an aromatizing component for perfumes, and can be extensively used in various products requiring a good fragrance such as perfumes, soaps, shampoos and rinses, detergents, cosmetics and aromatic agents.

Claims

1. An alkyl cycloheptylmethyl carbonate represented by the general formula (1):



(1)

wherein R is methyl or ethyl.

2. A perfume composition **characterized by** the alkyl cycloheptylmethyl carbonate as defined in claim 1.

3. The perfume composition according to claim 2, wherein a content of the alkyl cycloheptylmethyl carbonate in the composition is 0.001% by mass or higher.

4. The perfume composition according to claim 2 or 3, wherein the alkyl cycloheptylmethyl carbonate is methyl cycloheptylmethyl carbonate.

5. Use of the alkyl cycloheptylmethyl carbonate as defined in claim 1 for perfume.

Fig. 1

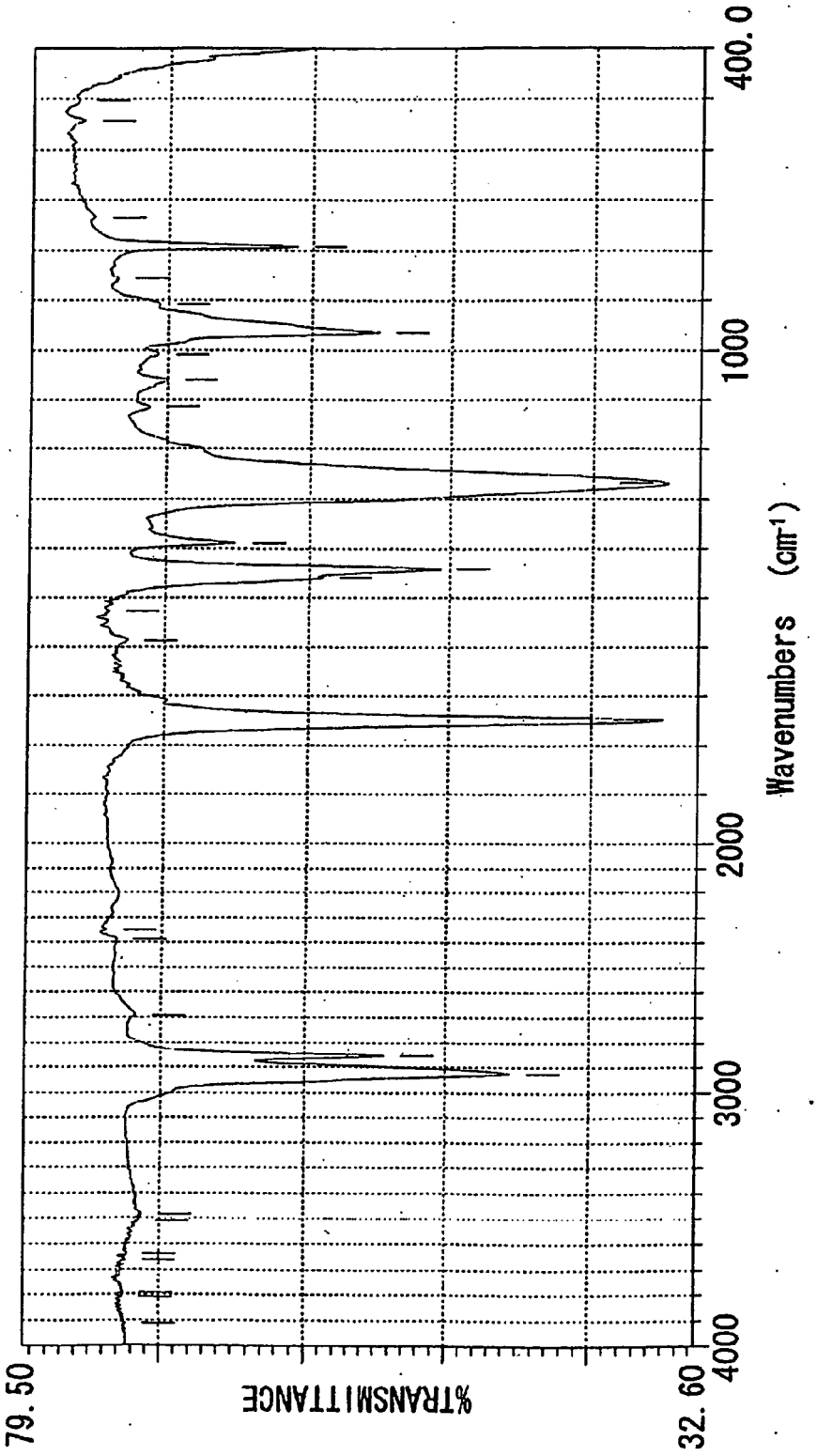
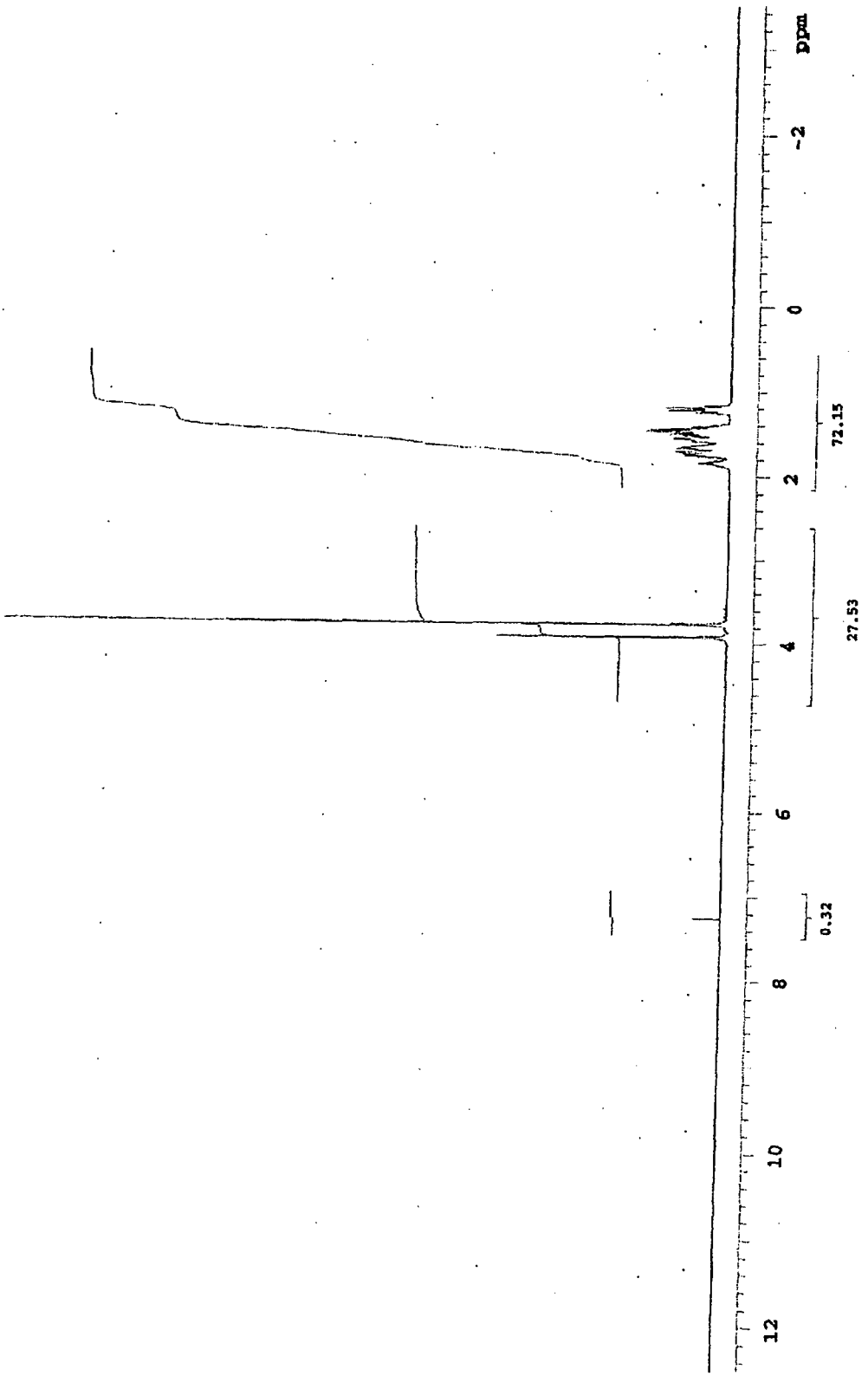

400.0
1000
2000
3000
4000
Wavenumbers (cm-1)
%TRANSMITTANCE
79.50
32.60

Fig. 2



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 00 4209

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,A	US 5 100 872 A (NARULA ET AL) 31 March 1992 (1992-03-31) * example XIX * -----	1-5	INV. C11B9/00
D,A	US 4 080 309 A (BRUNS ET AL) 21 March 1978 (1978-03-21) Abstract -----	1-5	
D,A	US 4 397 789 A (BODEN ET AL) 9 August 1983 (1983-08-09) Abstract -----	1-5	
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 06, 28 June 1996 (1996-06-28) & JP 08 053385 A (KAO CORP), 27 February 1996 (1996-02-27) * abstract * -----	1-5	

TECHNICAL FIELDS SEARCHED (IPC)

C11B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	12 June 2006	Saunders, T

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 00 4209

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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12-06-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5100872 A	31-03-1992	NONE	
US 4080309 A	21-03-1978	NONE	
US 4397789 A	09-08-1983	NONE	
JP 08053385 A	27-02-1996	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82