

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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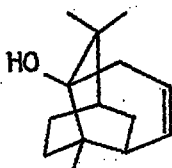
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(54) TRICYCLIC NORSESQUITERPENE ALCOHOL

(71) We, SOCIETE ANONYME DES ETABLISSEMENTS ROURE-BERTRAND FILS & JUSTIN DUPONT, a French company of 17Bis rue Legendre, Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel nor-sesquiterpene compound. In particular it relates to a hitherto unknown, tricyclic nor-sesquiterpene alcohol having the structural formula



This compound of formula I is referred to herein as 'nor-dehydropatchoulol', the name being chosen by analogy with the name patchoulol, which is also referred to as Patchouli alcohol (See Proc. Chem. Soc. 1963 p. 383).

Nor-dehydropatchoulol is a hitherto unknown compound which exists in the essential oil known as Patchouli Oil (See J.A.C.S. 83 p. 927). However, this compound is only present in natural Patchouli Oil to the extent of from about 3 to 10 parts per thousand by weight. We have now extracted nor-dehydropatchoulol from Patchouli Oil and have found that nor-dehydropatchoulol is the compound which is principally responsible for the characteristic odour properties of Patchouli Oil.

The present invention also relates to a process for extracting nor-dehydropatchoulol from Patchouli Oil, nor-dehydropatchoulol free from impurities such as those found in Patchouli Oil and perfume compositions to which nor-dehydropatchoulol has been added. The present invention does not cover natural Patchouli Oil.

According to one aspect of the invention there is thus provided a process for the extraction of nor-dehydropatchoulol, having the structural formula I given above, which comprises extracting said nor-dehydropatchoulol from Patchouli Oil by physical extraction methods.

The extraction is conveniently carried out using conventional methods, usually with the aid of several conventional physical methods, Chemical separation methods may also be employed. Extraction methods which may be used include fractional distillation, thin layer chromatography, gas - liquid partition chromatography, adsorption chromatography, sublimation and/or by combinations of these methods. One preferred method involves fractional distillation of natural Patchouli Oil, collection of the relevant fractions, adsorption chromatography of these fractions on a silica gel column followed by preparative gas-liquid partition chromatography.

Nor-dehydropatchoulol, extracted as described above, followed by purification, e.g. by sublimation, is a white crystalline solid having a melting point of 180 to 183°C, an $[\alpha]_D$ in chloroform of +61.5° and which has the infra-red spectrum and other physical characteristics set out in the following Example. The structure has been confirmed to be that set out in formula I given above by a variety of methods, including chemical degradation and X-ray analysis of derivatives.

Natural Patchouli Oil contains numerous other compounds, including a wide variety of hydrocarbons, epoxides, alcohols and sesquiterpene ketones many of which are also odouriferous compounds. The odour of all these extraneous compounds is of course absent from the odour of pure nor-dehydropatchoulol. Nor-dehydropatchoulol free from these other compounds thus constitutes a further feature of the present invention.

Nor-dehydropatchoulol has, both in the solid state and in solution in organic solvents such as are normally used in perfumery, an intense odour which is basically of the same type as the odour of natural Patchouli

Oil, but is free from the odours of the other odoriferous components of Patchouli Oil and in particular from the odours of the terpenes present in Patchouli Oil. The odour of the pure compound of this invention thereby avoids many of the nuances of the natural essential oil, the odour is furthermore much more stable, and the compound thus constitutes a valuable addition to the arsenal of the perfumer. Nor-dehydropatchoulol gives a more accentuated musty note and a better light woody note to perfumes than can be obtained with the use of Patchouli Oil. Furthermore, very much smaller amounts of nor-dehydropatchoulol need be added to a perfume formulation as compared with the amount of natural Patchouli Oil which would be needed to obtain the same effect. This latter point is of great importance when the formulation of perfumes and the perfuming of products such as soaps and other toilet products is considered.

Nor-dehydropatchoulol may be used for perfuming products which have hitherto been given an odour using natural Patchouli Oil. It may with advantage be used in many perfumes and also for perfuming industrial products, for example, solid and liquid detergents, synthetic washing agents, aerosols or cosmetic products of all kinds (e.g. soaps). The amount in which nor-dehydropatchoulol can usefully be used in odourant compositions such as for example perfumed products varies over a wide-range. Nor-dehydropatchoulol may thus for example be incorporated into products in an amount of from 1.0 to 20% by weight and preferably from 2.0 to 5.0% by weight.

The extraction of nor-dehydropatchoulol from natural Patchouli Oil and the use of nor-dehydropatchoulol in perfume formulations will now be illustrated with reference to the following Examples.

Example 1

5 kg of essential Patchouli Oil from Singapore obtained from the leaves of *Pogostemon cablin* Benth. (Syn. *P. patchouli* Pellet var. *suavis* Hook), were dissolved in 5 litres of diethyl ether. This solution was extracted nine times with 250 ml of 0.06N aqueous hydrochloric acid. The solution was then washed neutral with diethyl ether. The washed and dried oil which resulted was then carefully

fractionated under a reduced pressure of 0.2 to 0.5 mm of mercury using an efficient adiabatic column filled with metal pellets and equipped with a total condensation head. The first 35% of the total weight of distillate were rejected. The fractions rejected in this way had the following physical constants

b.p.=80—90°C (0.3 mm Hg)

$n_D^{15}=1.5010-1.5070$

$\alpha_D=-50^\circ$ at 0°C.

The next 15% by weight of the oil collected was the fraction required and had the physical constants

b.p.=90—100°C (0.3 mm Hg)

$n_D^{15}=1.5070-1.5090$

$\alpha_D=70^\circ$.

This latter fraction was then chromatographed on ten times its weight of silica gel (0.05—0.2 mm). The column was first eluted with petroleum ether in order to eliminate residual sesquiterpene hydrocarbons, and then with a mixture of petroleum ether and diethyl ether in ratio of 9:1 by volume.

Repeated chromatography according to the conditions set out above yielded a series of fractions enriched in nor-dehydropatchoulol. Traces of epoxy caryophyllene and patchoulol were amongst other constituents present which contaminated the product. Others are indicated on the accompanying chromatographic diagram. The separation on a silica column gel was followed by examination of the different fractions by thin layer chromatography on silica. Using an elution mixture of petroleum ether/ethyl acetate, 9/1 vol/vol, nor-dehydropatchoulol displayed an R_f of about 0.47.

Preparative gas chromatography effected on the previously enriched fractions obtained as above yielded a white crystalline product which was homogeneous both in gas and thin-layer chromatography.

The product displayed the following physical characteristics: Melting point=180—183°C; $[\alpha]_D$ in chloroform=61.5°; empirical formula by microanalysis $C_{14}H_{22}O$; molecular weight: 206. Mass spectrum analysis gave the following peaks: 206 (M), 191 (M—CH₃), 188 (M—H₂O), 173 (188—CH₃), 163 (M—C₃H₇), 145 (188—C₃H₇ or 163—H₂O), 119, 107 and 91.

Ultra-violet spectrum (EtOH): no absorption.

Spectrum in the far ultra-violet (n-hexane): $\lambda_{max}=180$ nm ($\epsilon=8200$).

I.R. spectrum:

$\nu_{max}^{(cm^{-1})}$: 3620 (ν OH free) }
 3500 (ν OH assoc.) } (HO—C—
 1050 (ν C—O) }
 1388—1370 (CH₃: gemdimethyl)
 1650 (ν C=C) } (—CH=CH—)
 1700 (γ CH strong) } C

Associated bands at 1420, 1362, 1288, 1185, 973, 852 and 845.

NMR spectrum at 100 MHz: (solvent CCl₄, internal reference TMS) δ (p.p.m.):

- 5 0.78 (3 H; S; $(\text{CH}_3-\text{C}-)$)
 $\text{CH}_3-\text{C}-\text{CH}_3$
 1.06 (2 $\times$ 3 H; S; $\text{CH}_3-\text{C}-\text{CH}_3$)
 $\text{CH}_3-\text{C}-\text{CH}_3$
 2.33 (1 H; doublet of doublet; $J_1 \sim 18\text{Hz}$, $J_2 \sim 4\text{Hz}$); $(-\text{CH}-\text{CH}=\text{CH}-)$
 C
 5.44—5.70 (2 H; J 10 Hz); $(\text{CH}=\text{CH}-)$

- 10 The structure of the compound was also confirmed as being that of formula I by means of X-ray analysis on a bromo derivative thereof.

- 15 Examples 2 and 3 hereafter illustrate two odoriferous compositions according to the invention containing nor-dehydropatchoulol.

- The classical concentrate composition of Example 2 containing 1% by weight of nor-dehydropatchoulol has an odour which
 20 emphasises that nor-dehydropatchoulol is free from many unwanted perfumes notes which are present in natural Patchouli oil.

- In the composition of Example 3 the introduction of 5% by weight of nor-dehydropatchoulol gives entirely new effects which it
 25 would be impossible to obtain otherwise and particularly with natural Patchouli oil.

Example 2

	Parts by weight
30 Concentrate No. 1	
Bergamotte peel oil extra	30
Lemon peel oil	20
Yland Yland oil Nossi-Bé	50
Phenylethyl alcohol	266
35 Hydroxycitronellal	100
Cyclamen aldehyde, 10% in ethylphthalate (E.P.)	10
C.10 aldehyde 100%, 10% in E.P.	5
C.11 aldehyde 100%, 10% in E.P.	5
40 Lauraldehyde C.12, 50% in E.P.	20
Petitgrain oil Citronnier	10
Benzyl acetate	60
Phenylacetic acid 1%	10
Isoeugenol	20
45 Linalol	20
Rose oil Anatolian	30
Geraniol	20
Jasmine absolute	140
Liquid indolene 50% in E.P.	20
50 Oak moss absolute A	60
Forest moss absolute	20
Methyllionone	50
Florentine iris resinoid, washed	10
Phenylethyl acetate	10

Vetiver oil rectified	20	55
Vetiveryl acetate	100	
Caryophyllenyl acetate	60	
Guaiacum wood oil	60	
Musk ambrette	40	
Musk ketone	20	60
Coumarin	20	
Cyclohexadecanolide	50	
Kephalis (mixture of 1-ethoxy-4-(ethoxyvinyl)-3,3,5,5-tetramethylcyclo-1-hexane and 4-(1-ethoxyvinyl)-3,3,5,5-tetramethylcyclohexanone obtained according to Example 2 of the French patent 1,498,736)	10	
Sandalwood essence	20	70
Nor-dehydropatchoulol	14	
	1,400	

Example 3

	Parts by weight	
Concentrate No. 2		75
Ylang ylang oil Nossi-bé	40	
Bergamotte peel oil	240	
Lemon peel oil	120	
Benzyl acetate	100	
Hydroxycitronellal	140	80
Geranium oil Africa	60	
Petitgrain oil, Grasse	40	
Neroli oil, Grasse	10	
Phenylethyl alcohol	40	
Lauraldehyde C.12 50% 10 in E.P.	20	85
MNA aldehyde C.12 100%, 10% in E.P.	20	
Linalol	50	
C.11 aldehyde 100%, 10% in E.P.	20	
Rose in May absolute	40	90
Cyclamen aldehyde	10	
Oak moss absolute	60	
Musk ketone	60	
Coumarin	80	
Jasmine absolute	60	95
Hexylcinnamaldehyde	30	
Styrax resinoid No. 1, 50% in E.P.	30	
Kephalis	50	
Sandalwood oil East Indian	20	
Vetiver oil rectified	20	100
Methyllionone, gamma	40	
Musk ambrette	90	
Cyclohexadecanolide	30	
Nor-dehydropatchoulol	80	
	1,600	105

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that

WHAT WE CLAIM IS:—

1. A process for the extraction of nor-dehydropatchoulol having the structural formula

110

Associated bands at 1420, 1362, 1288, 1185, 973, 852 and 845.

NMR spectrum at 100 MHz: (solvent CCl_4 , internal reference TMS) δ (p.p.m.):

5 0.78 (3 H; S; $(\text{CH}_3-\text{C}-)$)

1.06 (2×3 H; S; $\text{CH}_3-\text{C}-\text{CH}_3$)

2.33 (1 H; doublet of doublet; $J_1 \sim 18\text{Hz}$,

$J_2 \sim 4$ Hz); $(-\text{CH}-\text{CH}=\text{CH}-)$
C

5.44—5.70 (2 H; J 10 Hz); $(\text{CH}=\text{CH}-)$

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	C.10 aldehyde 100%, 10% in E.P.	5
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40	Lauraldehyde C.12, 50% in E.P.	20
	Petitgrain oil Citronnier	10
	Benzyl acetate	60
	Phenylacetic acid 1%	10
	Isoeugenol	20
45	Linalol	20
	Rose oil Anatolian	30
	Geraniol	20
	Jasmine absolute	140
	Liquid indolene 50% in E.P.	20
50	Oak moss absolute A	60
	Forest moss absolute	20
	Methylionone	50
	Florentine iris resinoid, washed	10
	Phenylethyl acetate	10

Vetiver oil rectified	20	55
Vetiveryl acetate	100	
Caryophyllenyl acetate	60	
Guaiacum wood oil	60	
Musk ambrette	40	
Musk ketone	20	60
Coumarin	20	
Cyclohexadecanolide	50	
Kephalis (mixture of 1-ethoxy-4-(ethoxyvinyl)-3,3,5,5-tetramethylcyclo-1-hexane and 4-(1-ethoxyvinyl)-3,3,5,5-tetramethylcyclohexanone obtained according to Example 2 of the French patent 1,498,736)	10	65
Sandalwood essence	20	70
Nor-dehydropatchoulol	14	
	1,400	

Example 3

	Concentrate No. 2	Parts by weight	
	Ylang ylang oil Nossi-bé	40	75
	Bergamotte peel oil	240	
	Lemon peel oil	120	
	Benzyl acetate	100	
	Hydroxycitronellal	140	80
	Geranium oil Africa	60	
	Petitgrain oil, Grasse	40	
	Neroli oil, Grasse	10	
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	Kephalis	50	
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	Vetiver oil rectified	20	100
	Methylionone, gamma	40	
	Musk ambrette	90	
	Cyclohexadecanolide	30	
	Nor-dehydropatchoulol	80	
		1,600	105

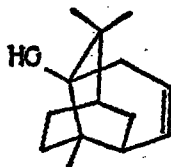
Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that

WHAT WE CLAIM IS:—

1. A process for the extraction of nor-dehydropatchoulol having the structural formula

110





which comprises extracting said nor-dehydropatchoulol from Patchouli Oil by physical extraction methods.

5 2. A process as claimed in claim 1, wherein fractional distillation is used as a physical extraction method.

3. A process as claimed in claim 1 or claim 2, wherein chromatography is used as a physical extraction method.

10 4. A process as claimed in claim 3, wherein thin layer chromatography, gas-liquid partition chromatography and/or adsorption chromatography is used.

15 5. A process for the extraction of nor-dehydropatchoulol from Patchouli Oil substantially as herein described with particular reference to the foregoing Example 1.

20 6. An odoriferous composition containing nor-dehydropatchoulol and which is free of natural Patchouli Oil.

7. An odoriferous composition to which substantially pure nor-dehydropatchoulol has been added.

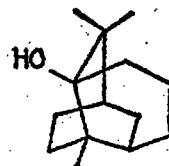
8. An odoriferous composition as claimed in claim 7 containing at least 1.0% by weight of nor-dehydropatchoulol.

9. An odoriferous composition as claimed in claim 7 or claim 8, containing from 2 to 5% by weight of nor-dehydropatchoulol.

10. Odoriferous compositions containing added nor-dehydropatchoulol substantially as hereinbefore described with reference to the foregoing Examples 2 and 3.

I 11. Nor - dehydropatchoulol whenever extracted from Patchouli Oil according to a process as claimed in any one of claims 1 to 5.

12. Nor-dehydropatchoulol having the structural formula



I 13. Nor-dehydropatchoulol, free from other hydrocarbons, epoxides, alcohols and sesquiterpene ketones occurring in Patchouli Oil.

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