

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
8 June 2006 (08.06.2006)

PCT

(10) International Publication Number  
**WO 2006/058450 A2**

(51) International Patent Classification: Not classified

(21) International Application Number:  
PCT/CH2005/000715(22) International Filing Date:  
30 November 2005 (30.11.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0426376.0 2 December 2004 (02.12.2004) GB  
0507925.6 20 April 2005 (20.04.2005) GB

(71) Applicant (for all designated States except US): GIVAUDAN SA [CH/CH]; Chemin de la Parfumerie 5, CH-1214 Vernier (CH).

(72) Inventor; and

(75) Inventor/Applicant (for US only): GOEKE, Andreas [DE/CN]; Song Tao Road, Alley 200, No 46, appartement 102, Shanghai 201203 (CN).

(74) Agent: MCSTEAN, John, Anthony; Ueberlandstrasse 138, CH-8600 Duebendorf (CH).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

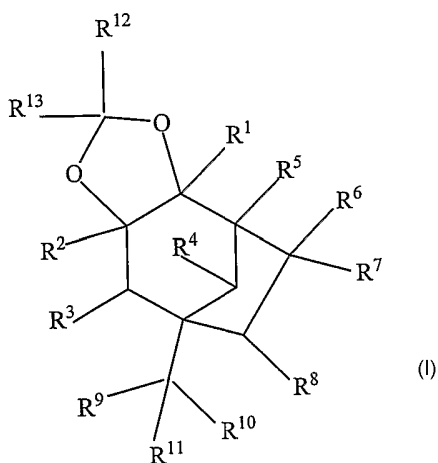
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPOUNDS

(57) Abstract: A compound of the formula (I) in which the moieties  $R^1$ - $R^{13}$  are independently selected from the following moieties:  $R^1$ ,  $R^5$ ,  $R^6$ ,  $R^8$ ,  $R^{11}$  - H, methyl, ethyl, propyl, isopropyl;  $R^3$  - H, methyl, ethyl, propyl, isopropyl, vinyl;  $R^4$  - H, methyl, ethyl;  $R^2$ ,  $R^7$ ,  $R^9$  - H, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl;  $R^{10}$  - H, methyl, ethyl, propyl, isopropyl, t-butyl;  $R^{12}$ ,  $R^{13}$  - H,  $C_{1-6}$  linear or branched alkyl; or  $R^4$  and  $R^{11}$  together with the carbon atoms to which they are attached form a 5- or a 6-membered cycloalkyl ring; or  $R^5$  and  $R^7$  together with the carbon atoms to which they are attached form a cycloalkyl ring having 3, 4, 5 or 6 members. The compounds have strong odours and are useful in fragrances and fragrance applications.

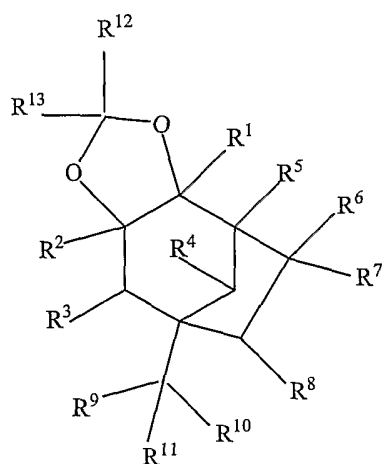
## COMPOUNDS

This invention relates to chemical compounds, and more particularly to chemical compounds having novel or enhanced odour properties, and to compositions including such compounds.

5

It has been found that certain dioxo-tricyclo-undecane compounds have desirable olfactory properties and can therefore be used in applications where such properties are desirable. The invention therefore provides a compound of the formula I

10



I

15 in which the moieties  $R^1$ – $R^{13}$  are independently selected from the following moieties:

$R^1, R^5, R^6, R^8, R^{11}$  - H, methyl, ethyl, propyl, isopropyl;

$R^3$  - H, methyl, ethyl, propyl, isopropyl, vinyl;

$R^4$  - H, methyl, ethyl;

20  $R^2, R^7, R^9$  - H, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl;

$R^{10}$  - H, methyl, ethyl, propyl, isopropyl, t-butyl;

$R^{12}, R^{13}$  - H,  $C_{1-6}$  linear or branched alkyl;

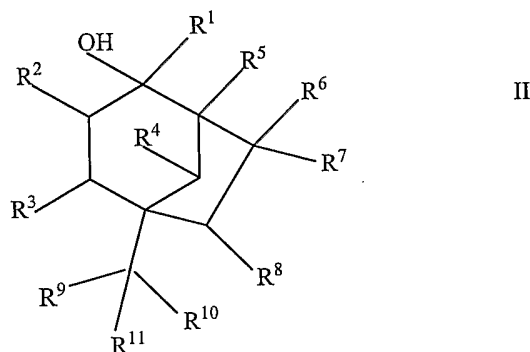
or  $R^4$  and  $R^{11}$  together with the carbon atoms to which they are attached form a 5- or a 6-membered cycloalkyl ring;

25 or  $R^6$  and  $R^7$  together with the carbon atoms to which they are attached form a cycloalkyl ring having 3, 4, 5 or 6 members.

The definition hereinabove given encompasses all stereochemical forms of the compound. The compound hereinabove described may be a mixture of isomers, or, if desired, it may be resolved by known methods into individual isomers. However, as such resolution inevitably adds to the cost of the process and therefore of the final materials, it is preferred to use the compound as a mixture.

A preferred compound is 8-isopropyl-2,4,4,10,10-pentamethyl-3,5-dioxatricyclo[6.2.1.0<sup>2,6</sup>]undecane.

The compounds of the invention may be prepared by known methods, starting from the known compounds II



in which the moieties R<sup>1</sup>–R<sup>10</sup> have the significances hereinabove defined.

The compounds of the invention have strong ambery woody and substantive odours and are useful in the preparation of fragrances and fragrance compositions. The invention therefore provides the use as a fragrance of a compound as hereinabove defined.

The invention further provides the use in a fragrance composition of a compound as hereinabove defined.

The compounds may be used in a broad range of fragrance applications, such as fine and functional fragrances, including perfumes, cosmetics, body care products and household products, for example, laundry, dishwashing and dishwasher products, polishes and cleaners, and so on. The invention therefore also provides a fragrance application comprising at least one compound as hereinabove defined.

The invention is further described with reference to the following non-limiting examples.

#### Example 1

##### **5-Isopropyl-2,7,7-trimethyl-bicyclo[3.2.1]oct-2-ene**

A solution of 5-isopropyl-7,7-dimethyl-bicyclo[3.2.1]octan-2-ol (18.5 g, 88 mmol) and KHSO<sub>4</sub> (100 mg) in toluene (250 ml) was heated 36h in a Dean-Stark apparatus. The solution was cooled and washed once with water and brine, dried (MgSO<sub>4</sub>) and concentrated in vacuo to yield 5-isopropyl-2,7,7-trimethyl-bicyclo[3.2.1]oct-2-ene (13.77 g, 81%). <sup>1</sup>H-NMR (100 MHz, CDCl<sub>3</sub>): 140.4 (s), 118.7 (d), 52.1 (d), 51.5 (t), 46.1 (s), 46.0 (s), 39.1 (t), 37.6 (d), 37.4 (t), 31.5 (q), 26.9 (q), 24.6 (q), 18.2 (q), 18.0 (q) ppm. GC/MS (EI): 192 (M<sup>+</sup>, 17), 177 (4), 149 (22), 136 (21), 121 (15), 107 (18), 93 (100), 77 (28), 57 (17), 41 (23). IR (ATR): 2957s, 2933s, 2869m, 1468m, 1452m, 1366m cm<sup>-1</sup>.

##### **8-Isopropyl-2,4,4,10,10-pentamethyl-3,5-dioxo-tricyclo[6.2.1.0<sup>2,6</sup>]undecane**

A solution of 5-isopropyl-2,7,7-trimethyl-bicyclo[3.2.1]oct-2-ene (1.00 g, 5.2 mmol), OsO<sub>4</sub> (0.052 mmol, 2.5% in t-BuOH) and N-morpholine-N-oxide (913.3 mg, 6.76 mmol) in aqueous acetone (10 ml) was stirred at room temperature for 40h. The mixture was diluted with MTBE, filtered, concentrated in vacuo and the residue purified by chromatography on silica (hexane:ethyl acetate = 7:3). To the resulting diol (0.4 g) was added 2,2-dimethoxy-propane (5 ml) and a catalytic amount of *p*-TsOH and the solution was stirred for 5h at room temperature. The mixture was now concentrated and the residue purified by chromatography on silica (hexane:ethyl acetate = 95:5) to yield a colorless oil (0.41 g, 30%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 4.12 (dd, *J* = 8.9 Hz, 8.5Hz, 1H, 6-H), 2.09 (dd, *J* = 12.0 Hz, 2.1 Hz, 1H, 11-H<sub>a</sub>), 1.84 (d, *J* = 5.1 Hz, 1H, 1-H), 1.80 (ddd, *J* = 14.2 Hz, 8.9 Hz, 2.5 Hz, 1H, 7-H<sub>a</sub>), 1.62 (ddd, *J* = 14.2 Hz, 6.1 Hz, 2.1 Hz, 1H, 7-H<sub>b</sub>), 1.53-1.48 (m, 1H, 11-H<sub>b</sub>), 1.52 (s, 3H), 1.48 (s, 6H), 1.46 (sept., *J* = 6.8 Hz, 1H, 8-CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (dd, *J* = 13.2 Hz, 2.0 Hz, 1H, 9-H<sub>a</sub>), 1.26 (dd, *J* = 13.2 Hz, 2.0 Hz, 1H, 9-H<sub>b</sub>), 1.16 (s, 3H), 1.10 (s, 3H), 0.86 (d, *J* = 6.8 Hz, 3H, 8-CH(CH<sub>3</sub>)<sub>a</sub>), 0.80 (d, *J* = 6.8 Hz, 3H, 8-CH(CH<sub>3</sub>)<sub>b</sub>) ppm. <sup>13</sup>H-NMR (100 MHz, CDCl<sub>3</sub>): 108.6 (s), 84.6 (s), 78.2 (d), 54.3 (d), 52.4 (t), 45.7 (s), 39.4 (s), 38.1 (t), 37.7 (d), 36.1 (t), 35.1 (q), 30.4 (q), 29.7 (q), 29.4 (q), 27.6 (q), 18.2 (q), 17.9 (q) ppm. GC/MS (EI): 266

( $M^+$ , 1), 251 (14), 209 (46), 165 (98), 137 (67), 109 (31), 95 (52), 81 (42), 69 (36), 55 (39), 43 (100), 41 (49). IR (ATR): 2958m, 2873m, 1466m, 1366m, 1229s, 1207m, 1074s, 1049m, 1014m  $\text{cm}^{-1}$ .

5

### Example 2

The following compounds were prepared according to example 1.

#### **5-sec-Butyl-2,7,7-trimethyl-bicyclo[3.2.1]oct-2-ene**

Mixture of 2 diastereomers:  $^1\text{H}$ -NMR (100 MHz,  $\text{CDCl}_3$ ): 140.4 (2s), 118.7, 118.6 (d), 52.7, 52.3 (t), 52.0, 51.9 (d), 46.7, 46.6 (s), 45.9, 45.8 (s), 45.8, 45.5 (d), 39.5, 39.3 (t), 37.6, 37.0 (t), 31.6, 31.5 (q), 26.9 (2q), 24.9, 24.8 (t), 24.6 (2q), 14.2, 14.1 (q), 18.0, 12.9 (q) ppm. GC/MS (EI): 206 ( $M^+$ , 14), 177 (4), 149 (38), 135 (4), 121 (24), 107 (19), 93 (100), 77 (18), 57 (35), 41 (17). IR (ATR): 2959s, 2930s, 2866m, 1451m, 1378m, 884m  $\text{cm}^{-1}$ .

15

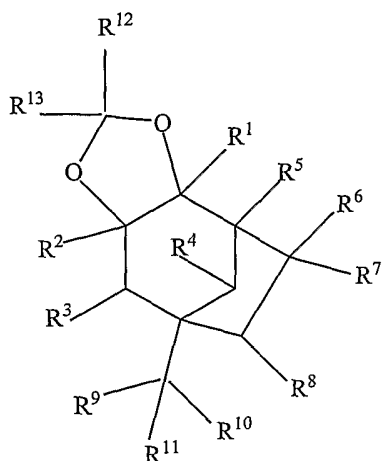
#### **8-sec-Butyl-2,4,4,10,10-pentamethyl-3,5-dioxo-tricyclo[6.2.1.0<sup>2,6</sup>]undecane**

Mixture of 2 diastereomers (in a ratio of 1:1):  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ): 4.10 (ddd,  $J = 2.5, 6.2, 8.7$  Hz, 1H), 2.18-2.11 (m, 1H), 1.85-1.81 (m, 1H), 1.79-1.26 (m, 6H), 1.52 (s, 3H), 1.48 (s, 6H), 1.15 (s, 3H), 1.10 (s, 3H), 0.88 (t,  $J = 7.4$  Hz, 3H), 0.85, 0.78 (2d,  $J = 6.8$  Hz, 3H) ppm.  $^{13}\text{H}$ -NMR (100 MHz,  $\text{CDCl}_3$ ): 108.6 (2s), 84.6 (2s), 78.2 (2s), 54.2, 54.1 (d), 53.3, 53.1 (t), 46.2 (2s), 45.9 (d), 45.6 (d), 39.4, 39.2 (s), 38.3, 38.1 (t), 36.4, 36.2 (t), 35.1 (2q), 30.4 (2q), 29.7 (2q), 29.4 (2q), 27.6 (2q), 24.9, 24.8 (t), 14.3, 14.0 (q), 13.0, 12.8 (q) ppm. GC/MS (EI): 280 ( $M^+$ , 2), 265 (35), 223 (96), 165 (31), 151 (100), 109 (24), 95 (33), 81 (18), 57 (33), 43 (35).

25

## Claims:

1. A compound of the formula I



I

in which the moieties  $R^1$ – $R^{13}$  are independently selected from the following moieties:

$R^1, R^5, R^6, R^8, R^{11}$  - H, methyl, ethyl, propyl, isopropyl;

$R^3$  - H, methyl, ethyl, propyl, isopropyl, vinyl;

$R^4$  - H, methyl, ethyl;

$R^2, R^7, R^9$  - H, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl;

$R^{10}$  - H, methyl, ethyl, propyl, isopropyl, t-butyl;

$R^{12}, R^{13}$  - H,  $C_{1-6}$  linear or branched alkyl;

or  $R^4$  and  $R^{11}$  together with the carbon atoms to which they are attached form a 5- or a 6-membered cycloalkyl ring;

or  $R^6$  and  $R^7$  together with the carbon atoms to which they are attached form a cycloalkyl ring having 3, 4, 5 or 6 members.

2. 8-isopropyl-2,4,4,10,10-pentamethyl-3,5-dioxo-tricyclo[6.2.1.0<sup>2,6</sup>]undecane.

3. The use as a fragrance of a compound according to claim 1.

4. The use in a fragrance composition of a compound according to claim 1.

5. A fragrance application comprising at least one compound according to claim 1.