Sesquiterpenic Epoxides and Alcohols Derived from Hydrocarbons of Vetiver Essential Oil

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Increasing the value of the hydrocarbon fraction of Bourbon vetiver essential oil (BVEO) was attempted by oxidation and reduction reactions to obtain odorous sesquiterpenic alcohols. Oxidation of this sesquiterpenic fraction of BVEO with *m*-chloroperbenzoic acid afforded three new oxidized products, including a zizaene monoepoxide and two diepoxides derived from zizanene and valencene. Reduction reaction of sesquiterpenic epoxides of BVEO led to three sesquiterpenols, including two zizanol epimers and an epoxialcohol derived from valencene, which have been synthesized in high yields (85–100%). Structural determination of these derivatives followed from one- and two-dimensional NMR spectroscopy and gas chromatography–mass spectrometry techniques.

INTRODUCTION

Some oils have a high content of terpenes and are proposed as "monoterpeneless oil" for perfumery and aromatic industries because these components change oil quality. The oxygenated fraction of these oils exhibits interesting odors for perfumery purposes, whereas the hydrocarbon fraction is of lower commercial value. Ylang extra or first, which contains 70% oxygenated compounds, is used in many perfumery formulations and ylang third, which contains 70% sesquiterpenic hydrocarbons (Gaydou *et al.*, 1986, 1988), is generally used in toiletry products. To minimize deterioration of oil quality and increase oil stability, several methods have been developed, in particular for *Citrus* essential oils that are rich in limonene (Ferrer and Matthews, 1987; Moyler and Stephens, 1992; Tzamtzis *et al.*, 1990). In our case, we took an interest in the terpenic hydrocarbon fraction that is a by-product of aromatic industries. With this aim in view, we first performed an oxidation reaction and then a reduction reaction of this hydrocarbon fraction to obtain sesquiterpenols, which should have potentially interesting fragrances for perfumery.

Several reagents have been used to oxidize sesquiterpenic compounds into sesquiterpenols, particularly molecular oxygen (Shieh and Matsubara, 1981; Ter Heide *et al.*, 1988; Kazuo and Masaaki, 1979) or metal acetate (Haruo *et al.*, 1978; Iwamuro *et al.*, 1981; Tkachev *et al.*, 1983). But these methods lead to many by-products, and yields are generally low. Sesquiterpene oxidations are also done with carboxylic peracids, in particular with *m*-chloroperbenzoic acid. This method offers many advantages because epoxides were obtained in high yields (Tressl *et al.*, 1983; Bombarda *et al.*, 1994). Good regioselectivity was obtained in the case of β-cur-

cumene, germacrene D, and α-humulene (Weyerstahl *et al.*, 1986; Maurer and Hauser, 1982; Iwamuro *et al.*, 1981). Furthermore, good stereoselectivity was obtained in the case of prezizaenes, β-selinene, and α-gurjunene (Nagashima and Yoshida, 1981; Richardson *et al.*, 1991; Palmade *et al.*, 1963).

Bourbon vetiver essential oil (BVEO), considered as the best vetiver essential oil in the world for its exceptional olfactory qualities, is used in many perfumes known as "top quality goods" (Ganguly *et al.*, 1978; Garnero, 1971). From a chemical point of view, this oil is extremely complex and particularly rich in sesquiterpenes. More than 150 compounds, with 11 different sesquiterpene skeletons, have been characterized (Nguyen and Fetizon, 1963; Sabetay and Trabaud, 1939, 1942; Smadja, 1991). In this work, we describe an oxidation of the resulting hydrocarbon fraction of vetiver oil.

MATERIALS AND METHODS

Sampling and Origin of BVEO. All BVEO samples were obtained from a local distillery near Manapany-les-Hauts (south of Reunion Island, France).

Fractionation of BVEO. The hydrocarbon fraction was obtained by column chromatography (CC) of BVEO. The BVEO (5–10 g) was submitted to CC over silica gel 60 (215 g, 230–400 mesh, E. Merck) using an 80-cm column (30 mm i.d.). Elution of the hydrocarbon fraction containing compounds **1–3** was carried out with 450 mL of pentane (yield 30%). The oxygenated fraction was eluted with 600 mL of diethyl ether.

Oxidation of the Hydrocarbon Fraction. *m*-Chloroperbenzoic acid (MCPBA; Fluka Chemicals, Switzerland) was used as the oxidant. In the different experiments, a solution of BVEO sesquiterpenic fraction (100 mg−1 g) in methylene chloride (2–20 mL) was stirred at 0 °C during the addition of small aliquots of MCPBA (1 equiv) in methylene chloride. The reaction mixture was allowed to stand for 20 min to 1 h. Unreacted MCPBA and byproduct *m*-chlorobenzoic acid were removed by addition first of an aqueous solution containing 10% sodium sulfite and then 10% sodium bicarbonate. The organic layer was then concentrated under reduced pressure on a rotavapor. The crude products contained epoxides **4** [(1*S*,2*S*,5*S*,8*R*)-6α,13-epoxy-2,7,7-trimethyltricyclo[6.2.1.0[1,7]]-undecane; 7−9%] and **5** [(1*S*,2*S*,5*S*,8*R*)-6β,12-epoxy-2,7,7-trimethyltricyclo[6.2.1.0[1,7]]undecane; 6.5−13%] and diepoxides **6** [(1*R*,6*R*,10*S*)-(2α,3α),(7β,8β)-diepoxy-3,7-dimethyl-10-isopro-

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pylbicyclo[4.4.0]decane; 7−9%] and **7** [(5*S*,6*R*)-5,6-dimethyl-1α,2α-epoxy-8(13,13-dimethyl-8α,13α-epoxy) isopropylbicyclo-[4.4.0]decane; 5−7%]. [Relative percentages are obtained by gas chromatography (GC), *vide infra*.] After purification, the products were submitted to NMR spectroscopy and GC-MS.

Purification of Epoxide 5. The crude epoxide mixture (643 mg) was submitted to CC over silica gel 60 (50 g, 230−400 mesh, E. Merck) using a 30-cm column (25 mm i.d.). Elution was carried out with 90:10 (v/v) pentane:diethyl ether (500 mL) and collected in 50 tubes. Tubes 23−25 (tube volume, 10 mL) contained 17 mg of epoxide **5** (72% purity by GC; R_f 0.68).

Purification of Diepoxide 6. A solution of BVEO sesquiterpenic fraction (150 mg, 0.74 mmol) was reacted with MCPBA (257 mg, 1 equiv) at 0 °C for 20 min. The reaction mixture (120 mg) containing 7% of **4**, 6.5% of **5**, 9% of diepoxide **6**, and 6% of **7** was fractionated by CC with 70:30 (v/v) pentane:diethyl ether (500 mL) and collected in 50 tubes. Tubes 20−21 (tube volume, 10 mL) contained 9 mg of diepoxide **6** (80% purity by GC; R_f 0.65).

Purification of Diepoxide 7. A solution of BVEO sesquiterpenic fraction (650 mg, 2.92 mmol) was reacted with MCPBA (786 mg, 1 equiv at −30 °C for 30 min. The crude product containing 11.2% of **4**, 28.5% of **5**, 11.6% of **6**, and 10.5% of **7**, was submitted to CC. Elution of the monoepoxide fraction containing **4** and **5** was carried out with 300 mL of pentane:diethyl ether (90:10, v/v). The diepoxide fraction was eluted with 100% diethyl ether (400 mL). This second fraction (181 mg), containing 9% of **6** and 23% of diepoxide **7**, was submitted to CC. Elution was carried out with 60:40 (v/v) pentane:diethyl ether (500 mL) and collected in 50 tubes (tube volume, 10 mL). Tubes 37−41 (42 mg) contained 20% of diepoxide **6** and 63% of diepoxide **7**. This mixture was submitted to a new purification by CC with 50:50 (v/v) pentane:diethyl ether (150 mL) as eluant. Tubes 16−17 (10 mg) contained diepoxide **7** (75% purity by GC; R_f 0.55).

Reduction Procedures. The sesquiterpene epoxides or oxidized hydrocarbon fraction (220 mg; 1 mmol) were reduced with lithium aluminium hydride (LiAlH$_4$; Fluka Chemicals, Switzerland; 152 mg, 4 equiv) in refluxing tetrahydrofuran (THF; 10 mL) for 12 to 36 h. The complex LiAl−alcoholate was hydrolyzed with 10% sulfuric acid, and reduction products were obtained by extraction of the solution with diethyl ether.

The reduction reaction with lithium triethyl borohydride (LiEt$_3$BH, Aldrich Chemical Company Inc.) was achieved by the method of Brown *et al.* (1980) under helium atmosphere. Sesquiterpene epoxides (220 mg, 1 mmol) in 3 mL of THF were added with a syringe to a solution containing 2 mL (2 mmol, 2 equiv) of a 1 mol L^{-1} solution of LiEt$_3$BH in 1 mL of THF. The mixture was vigorously stirred at room temperature. After 12 h, the reaction mixture was hydrolyzed with 1 mL of water. The triethylborane formed was oxidized with 1 mL of 30% hydrogen peroxide. The aqueous phase was extracted with 2 × 5 mL of diethyl ether. After volatile material evaporation under reduced pressure, the crude material was analyzed by GC and then by NMR and GC-MS.

Reduction Reaction of Epoxides 4 and 5. A mixture of epoxides containing 25% of **4** and 55% of **5** was reduced with LiAlH$_4$ (4 equiv) in refluxing THF for 24 h or with LiEt$_3$BH (2 equiv, ambient temperature, 12 h). Alcohols **8** [(1*S*,2*S*,5*S*,8*R*)-2,7,7-trimethyltricyclo[6.2.1.0^{1,7}]undecan-6α-ol)] and **9** [(1*S*,2*S*,5*S*,8*R*)-2,7,7-trimethyltricyclo[6.2.1.0^{1,7}]undecan-6β-ol] were obtained (25% and 46% yields, respectively). This mixture was fractionated by CC with 40:60 (v/v) pentane:diethyl ether (250 mL, collected in 30 tubes). Tubes 15−16 contained 6 mg of alcohol **8** (91% purity GC; R_f 0.78) and tubes 18−19 contained 21 mg of alcohol **9** (94% purity by GC, R_f 0.75).

Pure epoxide **5** (31 mg, 0.14 mmol) was reduced with LiAlH$_4$ (22 mg, 4 equiv) in refluxing THF for 24 h. Alcohol **9** was obtained with 85% purity by GC.

Reduction Reaction of Diepoxide 7. Diepoxide **7** (20 mg, 0.08 mmol) was reduced with LiEt$_3$BH (2 equiv, ambient temperature, 12 h). Epoxialcohol **10** [17 mg, 5,6-dimethyl-8-(13,13-dimethyl-8α,13α-epoxy)isopropylbicyclo[4.4.0]decan-1α-ol] was obtained with 91% purity by GC (89% yield). Purifi-
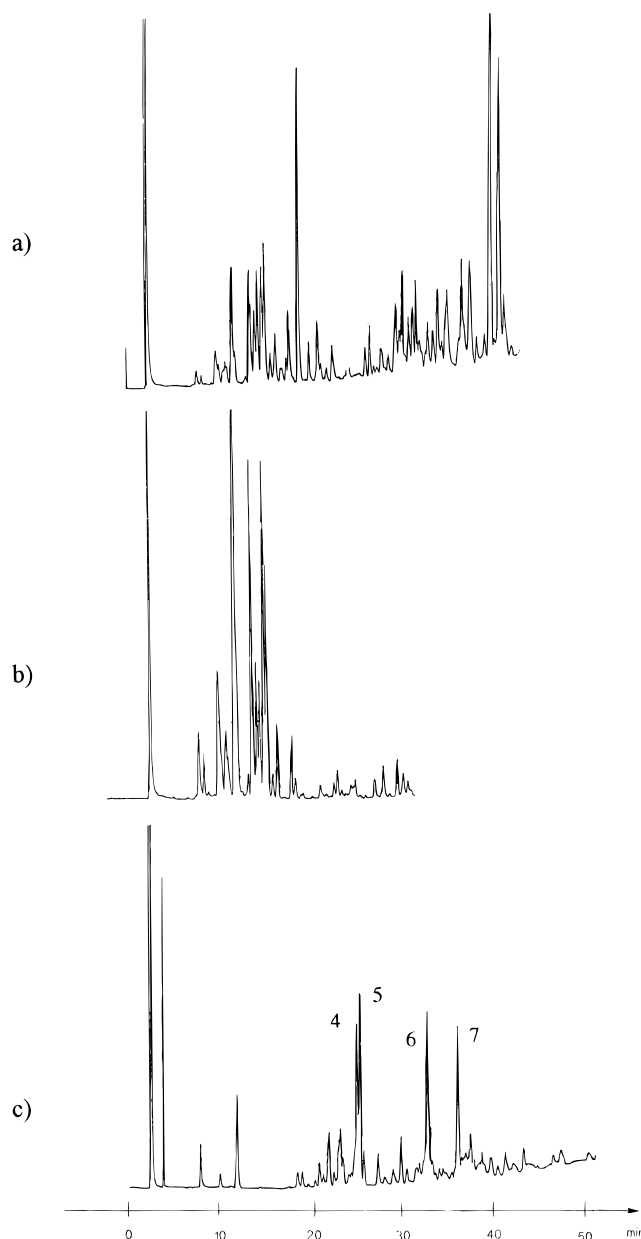

Figure 1. Gas chromatogram of (a) BVEO, (b) hydrocarbon fraction of BVEO, and (c) oxygenated hydrocarbon fraction of BVEO, obtained by GC on Carbowax 20 M column.

cation was by CC with 40:60 (v/v) pentane:diethyl ether (100 mL collected in 20 tubes) as the eluent. Tubes 12−13 contained 14 mg of epoxialcohol **10** (95% purity by GC; R_f 0.50).

GC and GC-MS. A Delsi 300 gas chromatograph equipped with a flame ionization detector (FID) was used for compound separations with a fused silica capillary column (0.32 mm i.d.) coated with Carbowax 20 M (25 m; phase thickness, 0.20 μm; column temperature, 170 °C or 60 to 220 °C, 4 °C·min^{-1}). Detector and inlet temperatures were 250 °C. Helium was used as carrier gas at an inner pressure of 0.4 bar. The injections averaged 1 μL of a 2% solution of crude mixtures in pentane. Combined GC-MS was recorded on a Delsi gas chromatograph linked to a Ribermag R-10−10C mass spectrometer equipped with a quadrupole mass analyzer (15.6 mm i.d. × 350 mm, 10^{-6} mmHg) and coupled to a Sidar data computer. The GC column was a 0.32 mm (i.d.) × 25 m fused capillary column coated with Wax 51 (0.20 μm phase thickness). The column temperature was changed from 150 to 220 °C, at a rate of 3 °C min^{-1}, the carrier gas was helium, the ion source was 220 °C, and the ionizing voltage was 70 eV.

Thin-Layer Chromatography (TLC). Analytical TLC was performed on precoated plates (5 × 10 cm, silica gel 60
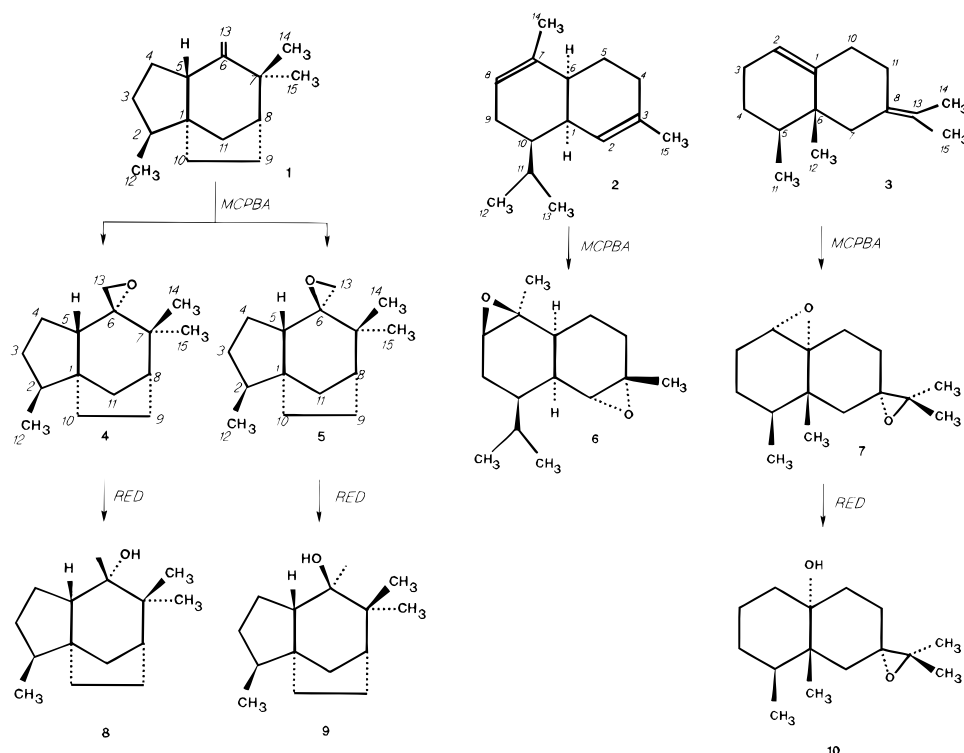
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Figure 2. Structures and carbon numbering for NMR analysis of sesquiterpenes **1**−**3**, epoxides **4**−**7**, and corresponding reduction compounds **8**−**10**.

F_{254}, 0.25 mm, Merck). Spots were visualized by examination under UV light and/or sulfuric acid spray reagent (5% solution of sulfuric acid in diethyl ether) followed by brief heating.

NMR Spectroscopy. All NMR spectra were recorded on a Bruker AMX-400 spectrometer. The ^{13}C and ^{1}NMR spectra were measured as solutions in chloroform-*d* in 5-mm o.d. tubes. Tetramethylsilane was used as internal standard in both measurements. Proton−proton coupling constants were extracted from high-field resolution-enhanced ^{1}H NMR spectra by the Gaussian multiplication technique (Ferridge and Lindon, 1978). Resonance multiplicities for carbon-13 were established via the acquisition of DEPT spectra (Doddrell *et al.*, 1982) obtained for proton pulses, $P = 90°$ (CH only) and $P = 135°$ (CH and CH_3 differentiated from CH_2). Standard Bruker pulse sequence were used for homonuclear and heteronuclear correlation experiments. For other experimental details, see Faure *et al.* (1991).

RESULTS AND DISCUSSION

Hydrocarbon Fraction Oxidation of BVEO. A hydrocarbon fraction representing 30% of BVEO was obtained by fractionation of the oil by CC. The gas chromatograms of BVEO and hydrocarbon fraction are given in Figures 1a and 1b, respectively. The oxidation reaction of BVEO hydrocarbons was achieved with *m*-chloroperbenzoic acid (MCPBA) at various hydrocarbon:MCPBA ratios (1:1 to 1:3) because some of the hydrocarbons have more than one double bond. The gas chromatogram of the oxidized products were, similar for each experiment (Figure 1c). Among the reaction mixture, four oxidized compounds (**4**−**7**) were obtained in high yields. These oxidized compounds were isolated and their structures determined by NMR spectroscopy. The structures of the compounds isolated suggested that the more reactive sesquiterpenes contained in the hydrocarbon fraction were zizaene (**1**), zizanene (**2**), and valencene (**3**; Figure 2). These compounds represent the major sesquiterpenes as given by Garnero (1971). Zizaene is a sesquiterpene commonly found in vetiver essential oil (Nguyen and Fetizon, 1963), and is gener-

ally associated with prezizaene, a precursor of zizaene (Andersen and Falcone, 1970). Valencene is a common sesquiterpene of various essential oil (Masada, 1976), but zizanene is a typical sesquiterpene of vetiver (Garnero, 1971).

In the presence of MCPBA, zizaene (**1**) led to the two corresponding zizaene epoxide epimers **4** and **5** (Figure 2) in a ratio 0.9:1.1, as observed by GC analyses (Figure 1c). Among the four stereoisomer epoxides of zizanene (**2**) expected, the (2,3)α-(7,8)β-diepoxide **6** (Figure 2) was the main product, as confirmed by spectroscopic structure determinations (Figure 2). This compound corresponded to α and β attacks on 2,3 and 7,8 double bonds, respectively, by the oxidant reagent. The main attack site by MCPBA during epoxidation of valencene (**3**) is on the α face of two double bonds to yield the valencene diepoxide **7** (Figure 2). In fact, the β face is hindered by the CH_3-11 and CH_3-12 groups.

The retention time and mass spectral data of **5**, **6**, and **7** are given in Table 1. The ^{1}H and ^{13}C chemical shifts are given in Table 2 for **5**, Table 3 for **6**, and Table 4 for **7**, and the ^{1}H−^{1}H coupling constants are given in Table 5.

Reduction of Epoxides 4−7. Reduction of the oxidized hydrocarbon portion with lithium aluminum hydride ($LiAlH_4$) or lithium triethylborohydride (Et_3-BHLi) led to three major alcohols, **8**, **9**, and **10**, representing 25% of the mixture (Figure 1). Structures of these sesquiterpenols are given in Figure 2. Zizanene diepoxide **6** was not reduced by $LiAlH_4$ or Et_3BHLi, and only the 1,2-epoxide of valencene diepoxide was reduced in the corresponding α-ol **10**. Alcohols **9** and **10** had been isolated when a reduction reaction was achieved with pure **5** and **7**. Alcohol **8** was isolated from the reduction reaction of a mixture of **4** and **5**. The structure of **4**, which is zizaene epoxide (an epimer of **5**), has been specified on the basis of the structure determination of the sesquiterpenol **8**. This reaction was regioselective, with hydride attack on the less

Table 1. Retention Times and Mass Spectra of Oxidation−Reduction Products of BVEO

compd[a]	I_R[b]	mass spectral data[c]
5	1810	M+ 220, 41(100), 105(50.3), 91(47.4), 55(43.6), 205(42.6), 43(34.6), 177(34.6), 133(32.7), 124(31.9), 93(30.4), 79(30.0), 29(29.2), 39(26.9), 119(24.8), 67(24.3), 109(24.2), 95(23.5), 175(23.2), 107(23.1), 77(21.4), 220(20.1), 53(20.0)
6	2000	M+ 236, 43(100), 41(41.7), 55(23.9), 95(22.8), 193(22.3), 109(21.4), 105(20.8), 107(18.9), 93(15.5), 39(13.8), 53(12.0), 91(11.8), 81(11.7), 79(11.6), 29(11.3), 67(10.3)
7	2135	M+ 236, 41(100), 43(90.0), 221(64.5), 55(57.6), 93(51.1), 179(36.6), 81(32.6), 109(31.1), 53(30.7), 105(29.3), 79(25.9), 95(25.1), 119(25.0), 107(22.8), 67(22.3), 39(21.9), 29(20.6), 161(20.6)
8	1893	M+ 222, 43(100), 41(51.0), 71(50.8), 109(36.8), 95(30.6), 179(29.9), 82(28.4), 67(21.9), 55(21.5), 189(18.2), 69(17.4), 93(15.9), 107(15.6), 137(15.5), 81(14.3), 91(13.0), 79(12.1), 29(11.5), 135(11.3), 161(11.0)
9	1818	M+ 222, 43(100), 41(89.0), 109(55.6), 84(45.8), 69(45.4), 95(44.7), 179(41.5), 71(39.2), 55(30.3), 67(27.8), 93(27.8), 161(27.8), 207(27.2), 81(23.3), 91(22.0), 79(21.2), 107(20.8), 29(19.5), 105(17.6)
10	2309	M+ 238, 43(100), 41(91.4), 122(83.7), 55(61.9), 107(60.6), 109(50.2), 111(38.6), 81(36.5), 95(36.3), 105(28.4), 123(28.4), 93(27.0), 205(26.6), 91(26.0), 223(25.4), 29(24.6), 121(24.3), 147(24.1), 59(23.9), 67(23.6), 69(22.3), 106(21.6), 39(20.5)

[a] See Figure 2 for structure formula. [b] Determined on a Carbowax 20 M silica capillary column. [c] *m/z* (relative intensity).

Table 2. ¹H and ¹³C NMR Chemical Shifts of Compound 5

δ¹³C[a]	group[b]	assignment[c]	δ¹H[a]
64.00	C	C-6	—[d]
54.88	C	C-1	—
49.00	CH₂	C-13	2.82(a)[e] and 2.75(s)
48.25	CH	C-8	1.86
45.01	CH	C-5	2.28
40.27	CH	C-2	1.79
37.94	C	C-7	—
35.50	CH₂	C-11	1.77(β) and 1.30(α)
33.50	CH₂	C-4	1.57(α) and 1.06(β)
32.10	CH₂	C-3	1.90 and 1.13
25.37	CH₂	C-9	1.56
24.08	CH₃	C-14	1.04
23.22	CH₂	C-10	1.47(β) and 1.17(α)
22.25	CH₃	C-15	0.68
19.76	CH₃	C-12	0.91

[a] In ppm with respect to TMS. [b] Determined from DEPT spectra. [c] Determined from 2-D measurements. [d] —, Not determined. [e] a, anti; s, syn.

Table 3. ¹H and ¹³C NMR Chemical Shifts of Compound 6

δ¹³C[a]	group[b]	assignment[c]	δ¹H[a]
62.18	CH	C-8	3.02
58.89	CH	C-2	2.65
58.04	C	C-7	—[d]
57.56	C	C-3	—
38.49	CH	C-10	1.45
34.20	CH	C-1	2.04
34.13	CH	C-6	1.92
28.30	CH	C-11	1.68
27.01	CH₂	C-9	2.22(α) and 1.36(β)
26.82	CH₂	C-4	1.87 and 1.64
23.46	CH₃	C-15	1.29
21.84	CH₃	C-14	1.32
21.57	CH₂	C-5	1.62
21.39	CH₃	C-12	0.93
21.24	CH₃	C-13	0.94

[a] In ppm with respect to TMS. [b] Determined from DEPT spectra. [c] Determined from 2-D measurements. [d] —, Not determined.

Table 4. ¹H and ¹³C NMR Chemical Shifts of Compound 7

δ¹³C[a]	group[b]	assignment[c]	δ¹H[a]
65.13[d]	C	C-1	—[e]
65.10[d]	C	C-13	—
63.84	C	C-8	—
60.51	CH	C-2	3.01
38.55	CH₂	C-7	1.70
37.55	C	C-6	—
32.95	CH	C-5	1.79
29.92	CH₂	C-10	2.13(β) and 1.10(α)
28.37	CH₂	C-9	2.02(α) and 1.65(β)
24.34	CH₂	C-4	1.23 and 1.18
22.47	CH₂	C-3	1.99(β) and 1.88(α)
21.91	CH₃	C-14	1.34
20.90	CH₃	C-15	1.38
15.26	CH₃	C-11	0.68
15.04	CH₃	C-12	0.90

[a] In ppm with respect to TMS. [b] Determined from DEPT spectra. [c] Determined from 2-D measurements. [d] Assignment may be reversed. [e] —, Not determined.

Table 5. ¹H−¹H Coupling Constants[a] of Compounds 5−7

pairs	5	6	7
1−9α		2.0	
2−3α			3.9
2−12	7.1		
5−4α	11.2		
5−4β	6.8		
5−11			6.9
5−13s	0.7		
8−9α		2.8	
8−11α	4.6		
9α-9β		−14.0	−13.0
9α-10α		2.0	4.0
9α-10β			14.0
9β-10α		12.0	3.1
9β-10β			4.0
10α-10β			−13.2
11β-11α	−11.5		
11−12		6.5	
11−13		6.5	
13a-13s[b]	−4.3		

[a] *J* in Hz. [b] a, anti; s, syn.

substituted carbon, and yielded to the corresponding pure alcohols **8**, **9**, and **10** (yields >85%). Retention time and mass spectral data of these compounds are given in Table 1 and NMR data are in Tables 6 and 7.

NMR Results. The strategy used in the assignment of spectra and determination of the structures requires the connecting together of individual fragments. As we have recently reported (Bombarda *et al.*, 1994; Aycard *et al.*, 1993; Faure *et al.*, 1991; Raharivelomanana *et al.*, 1993, 1994), the molecular framework of this kind of structure can be deduced from the concerted application of homonuclear and both direct and long-range ¹H-detected heteronuclear chemical shift correlation experiments. First, the establishment of the proton

connectivities is available from the COSY spectrum (Aue *et al.*, 1976; Nagayama *et al.*, 1980). Then, one bond proton−carbon chemical shift correlations were achieved by the proton-detected C,H correlation technique (HMQC; Bax and Subramanian, 1986). The CH$_n$ groups were assigned and assembled from the analysis of long-range correlation responses over two or three bonds (^2J or ^3J couplings) with the HMBC sequence (Bax and Summers, 1986). Finally, the stereochemistry of these rigid molecules was unequivocally established from the analysis of the phase-sensitive NOESY diagram (Bodenhausen *et al.*, 1984). Preliminary determination of structural units followed from the inspection of one-

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Table 6. ¹H and ¹³C NMR Chemical Shifts of Compounds 8 and 9

	8			**9**		
$\delta^{13}C^a$	group[b]	assign-ment[c]	$\delta^{13}C^a$	group[b]	assign-ment[d]	δ^1H^a
76.98	C	C-6	76.14	C	C-6	—[e]
52.78	C	C-1	53.22	CH	C-5	1.86
51.84	CH	C-5	53.17	C	C-1	—
50.79	CH	C-8	50.04	CH	C-8	1.75
40.37	CH	C-2	41.42	C	C-7	—
39.86	C	C-7	40.15	CH	C-2	1.74
36.08	CH₂	C-11	36.19	CH₂	C-11	1.68 and 1.19
33.18	CH₂	C-4	33.19	CH₂	C-4	1.64 and 1.04
32.08	CH₂	C-3	32.03	CH₂	C-3	1.94 and 1.05
27.34	CH₃	C-14	26.40	CH₃	C-14	0.99
26.31	CH₂	C-9	25.55	CH₂	C-9	1.55
23.88	CH₃	C-15	23.33	CH₂	C-10	1.64 and 1.87
23.60	CH₂	C-10	23.33	CH₃	C-15	0.88
21.35	CH₃	C-13	21.96	CH₃	C-13	1.11
19.86	CH₃	C-12	19.89	CH₃	C-12	0.88

[a] In ppm with respect to TMS. [b] Determined from DEPT spectra. [c] Determined from 2-D measurements. [d] Determined by comparison with ¹³C chemical shifts of **9** from 2-D measurements. [e] —, Not determined.
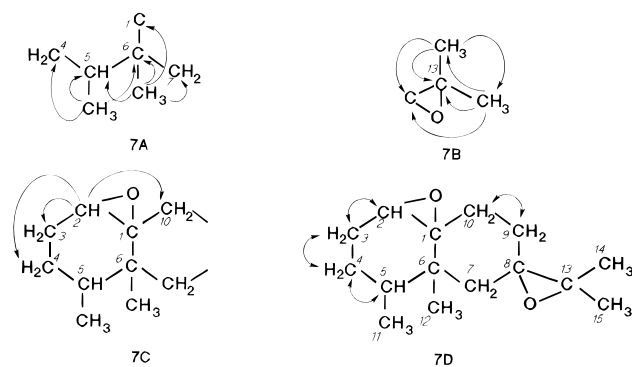
Table 7. ¹H and ¹³C NMR Chemical Shifts of Compound 10

$\delta\,^{13}C^a$	group[b]	assignment[c]	δ^1H^a
72.40	C	C-1	—[d]
65.26	C	C-13	—
64.29	C	C-8	—
41.68	C	C-6	—
35.31	CH₂	C-7	1.86 and 1.43
34.80	CH₂	C-2	1.74 and 1.37
34.46	CH	C-5	1.87
33.57	CH₂	C-10	1.63 and 1.27
29.39	CH₂	C-4	1.28 and 1.21
24.94	CH₂	C-9	2.15 and 1.52
21.97	CH₃	C-14	1.35
20.89	CH₃	C-15	1.30
20.88	CH₂	C-3	1.71 and 1.52
15.42	CH₃	C-11	0.73
14.54	CH₃	C-12	0.82

[a] In ppm with respect to TMS. [b] Determined from DEPT spectra. [c] Determined from 2-D measurements. [d] —, Not determined.

Figure 3. Long-range ¹³C—¹H connectivities for proton methyl shifts (**7A**, **7B**) and epoxide resonance (**7C**), and ¹H—¹H intercoupling network (**7D**) observed in the case of valencene diepoxide **7** (see text).
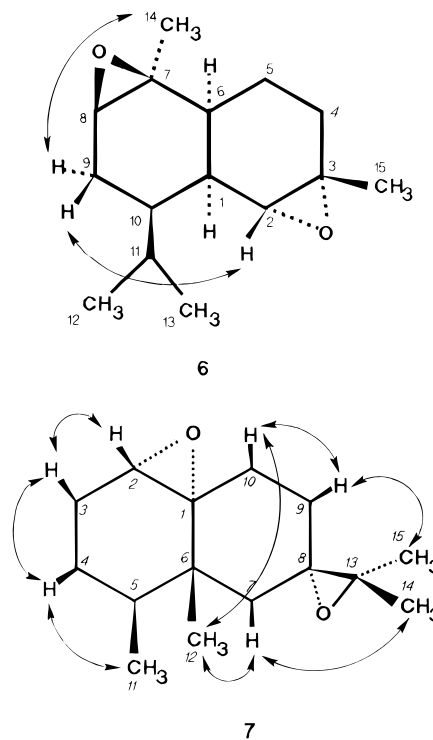
Figure 4. Selected through space interaction pathways deduced from the phase sensitive NOESY spectrum of ziza-nene and valencene diepoxides **6** and **7**.

dimensional spectra. In **5**—**7** and **10**, the occurrence of an epoxide ring was indicated by ¹H and ¹³C NMR data, and the evidence for quaternary aliphatic alcohols was clearly established from the ¹³C NMR chemical shifts. Further inspection of the remaining ¹H resonances showed signals for tertiary and secondary methyl groups for all compounds.

The strategy applied in this work is exemplified by the structural analysis of valencene diepoxide **7**. Utilizing the HMBC contour plot, structural fragments **7A** and **7B** (Figure 3), can be determined with the proton methyl shifts. Long-range correlation responses observed for the epoxide proton CH-2 lead to the substructure **7C** (Figure 3) and unambiguous assignments of methylene carbon C-5, CH₂-3, and CH₂-10. Finally, with the proton connectivities obtained from the COSY spectrum, the structure of **7D** (Figure 3) was determined, which corresponds to valencene diepoxide **7**. The stereochemistry of the two epoxide rings in **6** and **7** and the determination of methyl resonances CH₃-14 and CH₃-15 in **7** were unequivocally established on the basis of NOE cross-peaks obtained from the phase-sensitive NOESY experiment (Figure 4). For diepoxide **6**, correlation peaks between H-9α and H-14, and between H-9β and H-2, are in agreement with a (7,8)-β and a (2,3)-α epoxide because only this configuration allows

these correlations from Drieding model. As for **6**, correlation peaks for **7** between H-15 and H-9β, and between H-14 and H-7β, indicate that epoxide 8,13 is α. For some derivatives, the high crowding of methylene resonances preclude the accurate determination of ¹H chemical shifts and proton—proton coupling constants from one-dimensional measurements. These proton resonances, therefore, were assigned from the slices of the chemical shift heteronuclear correlation diagrams.

Odor Evaluation. These new constituents were submitted to olfactory evaluation. A characteristic precious wood- and root-like odor appear to be important for the head note of this oil and may have valuable synergistic effects with the other typical vetiver odor compounds.

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