Syntheses of Sesquiterpene Epoxides and Alcohols from γ-Gurjunene

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γ-Gurjunene, a natural sesquiterpene isolated from gurjun balsam, is obtained by isomerization of α-gurjunene in acidic medium. Oxidation of γ-gurjunene by reaction with *m*-chloroperbenzoic acid yielded a mixture of two monoepoxides and two diepoxides. Reduction reaction of a mixture of diepoxides with 4 equiv of lithium aluminum hydride or lithium triethylborohydride allowed isolation of a single diol in 93% yield. Four diols were obtained when reduction was realized with 2 equiv of reducing agent, including an epoxy alcohol, two enediols, and a dienol. The structure formulas of the compounds were determined using one- and two-dimensional NMR and gas chromatography−mass spectrometry.

INTRODUCTION

Gurjun balsam is a natural oleoresin exuded from the trees of the *Dipterocarpus* species growing in the forests of southeast Asia (Arctander, 1960). It is a pathological product formed only after incisions or other damage to the trunk of these tall trees. Gurjun balsam contains 60−80% of a viscous essential oil used in perfumery for its sweet, woody, balsamic, or pinelike odor. This oil has always had a reputation of being a material for adulteration of some essential oils like ylang-ylang, patchouli, vetiver, etc.

Gurjun essential oil is characterized by a high content of α-gurjunene, in addition to several sesquiterpenes including calarene, alloaromadendrene, and γ-gurjunene (2% of the oil) (Ehret and Ourisson, 1969). γ-Gurjunene is particularly obtained by isomerization of α-gurjunene in acidic medium. Therefore, oxidation reaction of α-gurjunene elicited more studies (Streith and Ourisson, 1963; Richardson *et al.*, 1991). Only oxidation of 11,12-dihydro-γ-gurjunene with *p*-nitroperbenzoic acid was studied by Ehret and Ourisson (1969). They isolated corresponding β- and α-epoxides with 55% and 5% yields, respectively. The purpose of this study was to obtain new oxidation and reduction products from γ-gurjunene having potential olfactory threshold.

MATERIALS AND METHODS

General Oxidation Procedure. *m*-Chloroperbenzoic acid (MCPBA; Fluka Chemicals, Buchs, Switzerland, 65% purity) was used as the oxidant. In the different experiments a solution of γ-gurjunene (Fluka Chemicals, 204 mg, 1 mmol) in methylene chloride (10 mL) was stirred at various temperatures (0 °C to reflux of solvent) during the addition of small aliquots of MCPBA (1−2 equiv, with regard to MCPBA purity) in methylene chloride. The reaction mixture was allowed to stand from 1 to 24 h. Unreacted MCPBA and byproduct *m*-chlorobenzoic acid were removed using first an aqueous solution containing 10% sodium sulfite and then 10% sodium

bicarbonate. The organic layer was dried over magnesium sulfate and then concentrated under vacuum on a rotary evaporator.

Synthesis of Compounds 2−5. Reaction is realized with 204 mg (1 mmol) of γ-gurjunene [**1**, (3*R*,6*R*,7*R*,10*R*)-6,10-dimethyl-3-isopropenylbicyclo[5.3.0]dec-1-ene] and 345 mg (1.3 mmol) of MCPBA. The reaction mixture contained compounds **2−5**. A 235 mg portion of a mixture containing 20% **2** [(3*R*,6*R*,7*R*,10*R*)-1β,2β-epoxy-6,10-dimethyl-3-isopropenylbicyclo[5.3.0]decane], 19% **3** [(3*R*,6*R*,7*R*,10*R*)-6,10-dimethyl-3-(11β,-12-epoxy)isopropylbicyclo[5.3.0]dec-1-ene], 11% **4** [(3*R*,6*R*,7*R*,-10*R*)-1β,2β-epoxy-6,10-dimethyl-3-(11β,12-epoxy)isopropylbicyclo[5.3.0]decane], and 30% **5** [(3*R*,6*R*,7*R*,10*R*)-1β,2β-epoxy-6,10-dimethyl-3-(11α,12-epoxy)isopropylbicyclo[5.3.0]decane] is submitted to column chromatography over silica gel (CC), with eluent pentane−diethyl ether (90:10 v/v, 400 mL). We isolated in tubes (14−16) 36 mg of monoepoxide **2** (R_f 0.80), in tubes (19−22) 24 mg of monoepoxide **3** (R_f 0.60), in tubes (42−43) 13 mg of diepoxide **4** (R_f 0.30), and in tubes (45−48) 56 mg of diepoxide **5** (R_f 0.28). Better yields of diepoxides **4** and **5** (24% and 76%, respectively) can be obtained with 2 equiv of MCPBA (4 h, ambient temperature).

General Reduction Procedure. Sesquiterpene diepoxides **4** and **5** (1:3, 236 mg, 1 mmol) were reduced with lithium aluminum hydride (LiAlH₄, Fluka Chemicals, 76 mg, 2 equiv), in refluxing THF (10 mL) during 12 h. The complex LiAl alcoholate was hydrolyzed with 10% sulfuric acid, and reduction products were isolated by diethyl ether extraction.

Reduction reaction using lithium triethyl borohydride (commercial name Super Hydride, Et₃BHLi, Aldrich Chemical Co., Inc.) was achieved using the method of Brown *et al.* (1980). The reaction was carried out under helium atmosphere. Sesquiterpene diepoxides **4** and **5** (1:3, 236 mg, 1 mmol) in 3 mL of tetrahydrofuran (THF) were added with a syringe to a solution containing 2 mL (2 mmol, 2 equiv) of a 1 mol L⁻¹ solution of LiEt₃BH in 1 mL of THF. The mixture was stirred vigorously 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 vacuum, the crude material was analyzed by GC and then by NMR and GC−MS.

Caution: Lithium hydride compounds are extremely reactive, and safety precautions must be taken.

Synthesis of Diol 6. A mixture of diepoxides **4** and **5** (81

Scheme 1. Oxidation Products from γ-Gurjunene (1) with MCPBA and Carbon Numbering Used for NMR Analyses
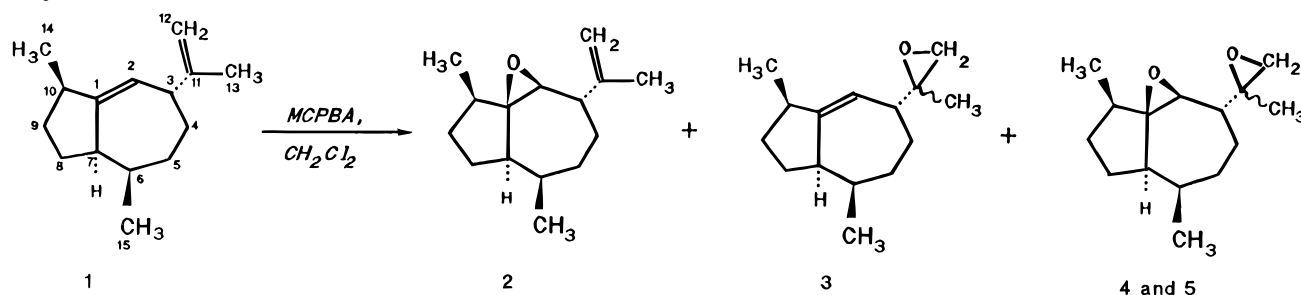
Table 1. γ-Gurjunene (1) Oxidation Conditions and Yields of Different Products[a]

entry	1: MCPBA[b]	temp (°C)	time (h)	yield (%)[c]					
				1	**2**	**3**	**4 or 5**	**5 or 4**	ni[d]
a	1:1	25	12	24.5	23	23	5	16	8.5
b	1:1	reflux[e]	24	28	23	10	5	16	18
c	1:1.3	0	2	3	19	18	11	35	14
d	1:1.3	25	12	nd[f]	20	19	11	30	20
e	1:2	0	2	nd	nd	nd	21.5	68	10.5
f	1:2	25	4	nd	nd	nd	24	76	0

[a] For compound identification, see Scheme 1. [b] Mole ratio with regard to MCPBA purity. [c] Relative percentage obtained by GC on a Carbowax 20M column. [d] Not identified. [e] Reflux of methylene chloride (38 °C). [f] Not detected.

mg, 0.34 mmol) was reduced by LiAlH₄ (52 mg, 4 equiv, 1.36 mmol). Diol **6** was formed in 93% yield (R_f 0.42, eluent pentane–diethyl ether, 30:70 v/v).

Synthesis of Epoxy Alcohol 7. Reduction of a mixture of **4** and **5** (70 mg, 0.3 mmol) by 2 equiv of Super Hydride (300 μL, 1 mol L⁻¹ solution) allowed us to isolate epoxy alcohol **7** in 95% yield (R_f 0.68, eluent pentane–diethyl ether, 30:70 v/v).

Syntheses of Compounds 8–10. A mixture of diepoxides **4** and **5** (43 mg, 0.18 mmol) was reduced by 28 mg (2 equiv, 0.36 mmol) of LiAlH₄. The reaction mixture contained 10% **8**, 34% **10**, and 20% **9**. Purification by CC, with eluent pentane–diethyl ether (30:70 v/v), allowed us to isolate in tubes (13–15) 6 mg of **10** (90% purity by GC, R_f 0.61), in tubes (24–38) 12 mg of **8** (86% purity by GC, R_f 0.58), and in tubes (42–45) 2 mg of **9** (88% purity by GC, R_f 0.26).

Gas Chromatography (GC). 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 or 60 to 220 °C at 4 °C min⁻¹). Detector and inlet temperatures were 250 °C. Helium was used as carrier gas at an inlet pressure of 0.4 bar. The injections averaged 1 μL of a 2% solution of crude mixtures in pentane.

Gas Chromatography–Mass Spectrometry (GC–MS). Combined GC–MS was recorded on a Delsi gas chromatograph linked to a Ribermag R-10-10C mass spectrometer equipped with a quadrupolar sonde of 15.6 mm i.d. × 350 mm (chamber pressure, 10⁻⁶ mmHg) and coupled with a Sidar data computer. The GC column was a 0.32 mm i.d. × 25 m fused silica capillary column coated with Wax 51 (0.20 μm phase thickness). The column temperature was 150–220 °C, 3 °C min⁻¹; carrier gas, helium; ion source, 220 °C; ionizing voltage, 70 eV.

Column Chromatography (CC). Analytical CC was performed over silica gel 60 F₂₅₄ (230–400 mesh, Merck) with eluent pentane–diethyl ether.

Thin-Layer Chromatography. Analytical TLC was performed on precoated plates (5 × 10 cm, silica gel 60 F₂₅₄, 0.25 mm, Merck). Spots were visualized by examination under ultraviolet light (254 nm) and/or sulfuric acid spray reagent (5% solution of sulfuric acid in diethyl ether), followed by brief heating (100 °C).

Nuclear Magnetic Resonance Spectroscopy. All spectra were recorded on a Bruker AMX-400 spectrometer. The NMR spectra were measured as solutions in chloroform-d in 5 mm o.d. tubes for ¹³C and ¹H. Tetramethylsilane was used as internal standard in both measurements. Proton–proton

coupling constants were extracted from high-field resolution-enhanced ¹H spectra using the Gaussian multiplication technique (Ferridge and Lindon, 1978). Standard Bruker pulse sequences were used for homonuclear and heteronuclear correlation experiments. For other experimental details, see Faure *et al.* (1991).

RESULTS AND DISCUSSION

Oxidation Reaction of γ-Gurjunene. In continuation of our studies on sesquiterpene epoxidation by *m*-chloroperbenzoic acid (MCPBA) to provide new olfactory substances (Bombarda *et al.*, 1994, 1995), we have oxidized γ-gurjunene (**1**) with MCPBA. We have isolated four compounds, including two monoepoxides, **2** and **3**, and two diepoxides, **4** and **5** (Scheme 1).

Yield was low when we worked with 1 equiv of peracid. After 24 h reflux of methylene chloride, 28% of the γ-gurjunene had not reacted (Table 1, entry b). With an excess of peracid, temperature effect is insignificant: at ambient temperature, reaction is as rapid as that at 0 °C (entries c and d). Monoepoxides **2** and **3** were always isolated together. Oxidation reaction of γ-gurjunene is not regioselective. Therefore, only two monoepoxides were isolated among the four possibilities. The presence of other monoepoxides has never been shown; that shows the stereoselectivity of the reaction. The two diepoxides **4** and **5** were formed solely in the 1:3 ratio when we worked with 2 equiv of peracid (entries e and f). The retention times and mass spectral data of compounds **2–5** are given in Table 2. The ¹H and ¹³C chemical shifts and the ¹H–¹H coupling constants are given in Tables 3 and 4.

Structure of Compounds 2–5. Examination of epoxide **2** structure by the Alchemy program (Evans and Sutherland, 1988) shows that the heptanoic ring adopts a quasi boat conformation (Chart 1). According to this conformation, the H–C₂–C₃–H dihedral angle value is 102° for β-epoxide and 60° for α-epoxide. Taking into consideration that the ¹H NMR signal of 2-H (δ = 3.07 ppm) is a singlet, we concluded from the Karplus curve (Günther, 1993) that the corresponding dihedral angle value is near 100°. This result is in agreement with a β-epoxide, since molecular modeling gives 102° for its dihedral angle. The presence of an α-epoxide has never

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Table 2. Retention Time and Mass Spectra of Oxidation−Reduction Products of γ-Gurjunene

compound[a]	I_R[b]	mass spectral data[c]
2	1727	M+ 220 (3.0), 41 (100), 55 (62.0), 81 (44.0), 67 (41.1), 107 (37.1), 110 (36.2), 39 (35.0), 43 (34.8), 122 (31.7), 53 (30.7), 29 (30.1), 109 (29.0), 95 (25.7), 138 (25.2), 69 (24.8), 68 (24.1), 79 (21.4), 27 (21.0)
3	1809	M+ 220 (24.3), 41 (100), 107 (96.8), 55 (73.0), 43 (68.3), 81 (56.6), 29 (53.5), 105 (52.3), 91 (47.6), 93 (41.6), 161 (37.8), 39 (37.1), 79 (36.9), 95 (33.7), 67 (31.2), 147 (31.2), 162 (30.2), 53 (28.7), 119 (28.3), 189 (28.3), 133 (27.7), 27 (26.3), 77 (25.5), 121 (24.3)
4	2073	M+ 236 (0.8), 43 (100), 41 (92.4), 55 (70.0), 81 (55.3), 29 (43.9), 107 (34.9), 109 (33.9), 39 (33.7), 125 (33.7), 53 (32.2), 98 (28.5), 95 (27.5), 97 (27.3), 67 (26.7), 12 (26.2), 27 (25.6), 93 (25.0), 79 (23.1), 69 (22.0), 105 (20.3)
5	2083	M+ 236 (0.5), 43 (100), 41 (89.4), 55 (67.7), 81 (47.3), 29 (40.2), 39 (31.2), 53 (31.2), 109 (29.2), 107 (27.9), 67 (26.6), 125 (25.1), 27 (23.6), 97 (23.1), 95 (21.5), 69 (20.8), 121 (20.8), 79 (20.3)
6	2377	M+ 240 (0.3), 43 (100), 41 (95.3), 55 (78.4), 39 (75.1), 81 (50.4), 95 (41.0), 107 (38.9), 107 (38.7), 69 (35.9), 93 (31.4), 189 (29.4), 125 (28.8), 105 (27.6), 161 (25.0), 24 (25.0), 126 (24.5), 67 (23.4), 29 (22.8), 108 (21.9), 79 (21.4), 91 (21.3), 149 (18.7)
7	2117	(M+ − H2O) 220 (2.4), 43 (100), 41 (68.7), 81 (59.5), 59 (53.3), 105 (40.8), 109 (37.8), 95 (33.6), 55 (33.2), 91 (29.7), 67 (22.7), 39 (22.5), 93 (21.5), 138 (20.4), 82 (20.2), 137 (19.3), 79 (18.7)
8	1970	M+ 238 (0.3), 105 (100), 43 (93.4), 162 (62.4), 41 (60.9), 59 (59.1), 91 (59.7), 147 (54.1), 138 (46.1), 55 (34.7), 119 (29.8), 82 (29.5), 81 (26.9), 120 (25.4), 93 (24.5), 79 (23.0), 39 (22.3), 133 (21.3), 77 (19.2)
9	2237	(M+ − H2O) 220 (1.0), 59 (100), 43 (60.4), 41 (35.9), 105 (25.7), 55 (24.8), 91 (23.8), 162 (22.6), 95 (20.0), 147 (19.6), 180 (17.7), 109 (15.3), 205 (14.7), 93 (13.7), 79 (13.3)
10	1953	(M+ − H2O) 220 (10.9), 59 (100), 94 (74.4), 162 (71.1), 91 (57.4), 41 (53.3), 105 (50.0), 81 (39.6), 43 (39.4), 119 (37.0), 147 (36.8), 133 (31.8), 55 (23.8), 106 (23.6), 93 (22.5), 107 (21.5), 159 (19.4), 161 (18.1), 67 (18.1)

[a] See Scheme 1 for structural formula. [b] Determined on a Carbowax 20M silica capillary column. I_R of **10**, 1953. [c] m/z (relative intensity).

Table 3. ¹H and ¹³C NMR Chemical Shifts of Compounds 2 and 3

		2				**3**	
δ ¹³C[a]	group[b]	assignment[c]	δ ¹H[a]	δ ¹³C[a]	group[b]	assignment[c]	δ ¹H[a]
149.98	C	C-11		150.83	C	C-1	
110.09	CH₂	C-12	4.80 and 4.68	119.53	CH	C-2	
71.06	C	C-1		60.22	C	C-11	
63.19	CH	C-2	3.07	54.59	CH₂	C-12	2.64 and 2.57 [f]
47.36	CH	C-3	2.54[e]	47.68	CH	C-3	2.92
44.68	CH	C-7	2.42[e]	43.87	CH	C-7	
40.86	CH	C-10		40.91	CH	C-10	2.44
34.03	CH	C-6		34.59	CH	C-6	
33.56	CH₂	C-5		33.76[d]	CH₂	C-9	
31.13	CH₂	C-9		33.51[d]	CH₂	C-5	
27.62	CH₂	C-8		29.81	CH₂	C-8	
25.60	CH₂	C-4		25.86	CH₂	C-4	
20.99	CH₃	C-15	0.97[e]	19.72	CH₃	C-14	0.97 [f]
20.66	CH₃	C-13	1.75	18.29	CH₃	C-13	1.22
15.87	CH₃	C-14	0.85[e]	17.46	CH₃	C-15	0.78 [f]

[a] In ppm relative to TMS. [b] Determined from DEPT analyses. [c] Determined from 2D-NMR experiments. [d] Assignments could be reversed. [e] H-3 (dm, J = 11 Hz), H-7 (dt, J = 3.0, 8.7, 8.7 Hz), H-14 (d, J = 7.0 Hz), H-15 (d, J = 7.3 Hz). [f] H-12 (AB, J = 5.0 Hz), H-14 (d, J = 6.8 Hz), H-15 (d, J = 7.1 Hz).

Table 4. ¹H and ¹³C NMR Chemical Shifts of Compounds 4 and 5

|		**4**				**5**	
δ ¹³C[a]	group[b]	assignment[c]	δ ¹H[a]	δ ¹³C[a]	group[b]	assignment[c]	δ ¹H[a]
70.76	C	C-1		71.05	C	C-1	
60.83	C	C-11		60.37	CH	C-2	3.08
60.51	CH	C-2	3.34	60.37	C	C-11	
54.87	CH₂	C-12	2.61 and 2.58[d]	54.70	CH₂	C-12	2.71 and 2.62[e]
46.71	CH	C-3		46.16	CH	C-3	
44.75	CH	C-7	2.39[d]	44.44	CH	C-7	2.37[e]
40.83	CH	C-10		40.93	CH	C-10	
33.83	CH	C-6		33.86	CH	C-6	
33.32	CH₂	C-5		33.18	CH₂	C-5	
31.11	CH₂	C-9		31.16	CH₂	C-9	
27.65	CH₂	C-8		27.89	CH₂	C-8	
23.36	CH₂	C-4		22.17	CH₂	C-4	
20.80	CH₃	C-15	0.92[d]	20.79	CH₃	C-15	0.89[e]
17.72	CH₃	C-13	1.30	18.24	CH₃	C-13	1.26
15.84	CH₃	C-14	0.87[d]	15.83	CH₃	C-14	0.83[e]

[a] In ppm relative to TMS. [b] Determined from DEPT analyses. [c] Determined from 2D-NMR experiments. [d] H-7 (dt, J = 2.9, 8.4, 8.4 Hz), H-12 (AB, J = 4.9 Hz), H-14 (d, J = 7.0 Hz), H-15 (d, J = 7.3 Hz). [e] H-7 (dt, J = 2.8, 8.8, 8.8 Hz), H-12 (AB, J = 4.8 Hz), H-14 (d, J = 6.9 Hz), H-15 (d, J = 7.3 Hz).

been observed to our knowledge. The C_1−C_2 double-bond epoxidation takes place exclusively on the β-face. When we worked with 2 equiv of peracid, diepoxides **4** and **5** were exclusively isolated in the ratio of 1:3 (entries e and f). For these compounds, oxidation of the C_1−C_2 double bond results from an attack of the peracid on the β-face. The two diepoxides differ from the absolute configuration at carbon 11-C.

In conclusion, we can say that the oxidation reaction of γ-gurjunene is stereoselective since only a β-epoxide resulting from epoxidation of the C_1−C_2 double bond was obtained.

Scheme 2. Reduction Products from γ-Gurjunene Diepoxides 4 and 5
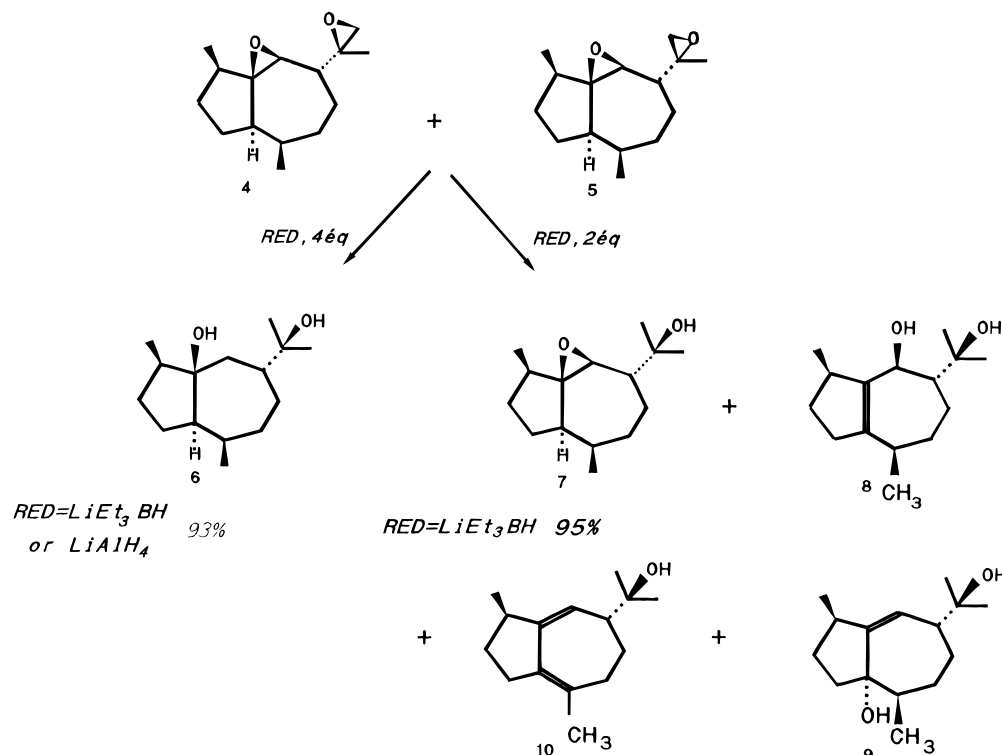
Chart 1. γ-Gurjunene Epoxide 2 Conformation Determined Using the Alchemy Program
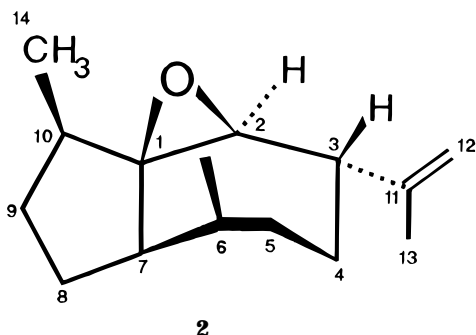
Reduction Reactions. We next studied the reduction reaction of epoxides. Two reducing agents retained our attention: first, lithium aluminum hydride (LiAlH₄), commonly used for reduction of sesquiterpene epoxides (aromadendrene, alloaromadendrene, or δ-cadinene epoxides) (Tressl *et al.,* 1983), and second, lithium triethylborohydride (LiEt₃BH), a superior reagent for reduction of epoxides that are relatively unreactive or prone to rearrangement (Brown *et al.,* 1980).

Reduction reaction of a mixture of diepoxides **4** and **5** by 4 equiv of reducing agent (LiAlH₄ or LiEt₃BH) allowed isolation of a single diol (**6**) in 93% yield. Hydride attack arose on the less substituted carbon for both epoxy groups (Scheme 2). When reduction reaction was carried out with 2 equiv of LiEt₃BH, epoxy alcohol **7**, corresponding to a selective reduction of the exocyclic double bond, was formed in 95% yield. If we worked with 2 equiv of LiAlH₄, four alcohols were isolated, including the epoxy alcohol **7**, two enediols **8** and **9**, and dienol **10** (Scheme 2). The retention times and mass spectral data are given in Table 2. The ¹H and ¹³C NMR chemical shifts and the ¹H–¹H coupling constants of **6**–**10** are given in Tables 5–7.

Formation of **9** and **10** can be explained by taking into account that isomerization product **8** of epoxy alcohol **7**

Table 5. ¹H and ¹³C NMR Chemical Shifts of Compound 6

δ ¹³C[a]	group[b]	assignment[c]	δ ¹H[a]
82.20	C	C-1	
72.96	C	C-11	
55.79	CH	C-7	1.92
47.60	CH	C-10	1.85
45.53	CH	C-3	1.55
34.00	CH	C-6	1.93
30.43	CH₂	C-8[d]	1.74 and 1.61
30.38	CH₂	C-2[d]	1.91 and 1.57
29.44	CH₂	C-5	1.34
28.96	CH₃	C-12	1.18
28.73	CH₂	C-9	1.75 and 1.10
27.90	CH₃	C-13	1.13
23.05	CH₃	C-15	0.84[e]
20.15	CH₂	C-4	1.61 and 1.38
13.61	CH₃	C-14	0.93 [f]

[a] In ppm relative to TMS. [b] Determined from DEPT analyses. [c] Determined from 2D-NMR experiments. [d] Assignments could be reversed. [e] H-15 (d, *J* = 6.8 Hz). [f] H-14 (d, *J* = 6.7 Hz).

was formed in the first step. Hydrolysis in acidic medium of enediol **8** leads to isolation of the second enediol, **9**. Dehydration of **9** leads to dienol **10** (Scheme 2).

Stereochemistry of Compounds 6–10. Comparison of ¹³C chemical shifts of methyl groups 10-Me and 6-Me for **6** and γ-gurjunene (**1**) showed that hydroxy group 1-OH induced an intense γ-effect on carbon 14-C (Δδ = 6.34 ppm) and a γ-effect on carbon 15-C (Δδ = 4.98 ppm) (Chart 2). Therefore, hydroxy group 1-OH is necessary in a β-position, taking into account the stereochemistry of 6-Me and 10-Me and their chemical ¹³C shift effects.

The stereochemistry of epoxy alcohol **7** was confirmed by examination of its ¹H NMR spectra (coupling constants). In fact, ³*J*₂,₄ < 0.8 Hz (typical of a W coupling) was in agreement with a β-epoxide. For **8**, proton 2-H shows a signal at 4.71 ppm which appears as a singlet due to the noncoupling with proton 3-H. In fact, the

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Table 6. ^{1}H and ^{13}C NMR Chemical Shifts of Compounds 7 and 8

	7				8		
δ ^{13}C^a	group^b	assignment^c	δ ^{1}H^a	δ ^{13}C^a	group^b	assignment^c	δ ^{1}H^a
74.01	CH	C-11		146.76	C	C-7	
59.72	CH	C-2	3.43^d	141.12	C	C-1	
49.54	CH	C-3	1.87^d	74.27	C	C-11	
44.04	CH	C-7	2.39^e	67.43	CH	C-2	4.71
41.67	CH	C-10	1.91	50.67	CH	C-3	1.49
34.06	CH$_2$	C-5	1.76 and 1.19	43.41	CH	C-10	2.82
33.79	CH	C-6	1.84^d	35.00	CH$_2$	C-8	2.46 and 2.12
31.58	CH$_2$	C-9	1.91 and 1.36	34.42	CH	C-6	2.48
29.22	CH$_2$	C-8	1.91 and 1.55	34.27	CH$_2$	C-5	1.97 and 1.47
28.41	CH$_3$	C-12	1.25	31.13	CH$_2$	C-9	2.01 and 1.30
27.10	CH$_3$	C-13	1.24	29.90	CH$_3$	C-12	1.33
20.82	CH$_3$	C-15	0.95^f	28.42	CH$_3$	C-13	1.22
20.71	CH$_2$	C-4	1.36	22.33	CH$_2$	C-4	1.96 and 1.91
15.97	CH$_3$	C-14	0.88^f	19.95	CH$_3$	C-14	0.97^g
70.81	C	C-1		18.07	CH$_3$	C-15	1.01^g

^{a} In ppm relative to TMS. ^{b} Determined from DEPT analyses. ^{c} Determined from 2D-NMR experiments. ^{d} $^3J_{2-3} < 0.8$ Hz. ^{e} H-7 (dt, $J = 8.5, 8.5, 2.5$ Hz). ^{f} H-15 (d, $J = 7.0$ Hz), H-14 (d, $J = 7.0$ Hz). ^{g} H-14 ($J = 6.8$ Hz), H-15 ($J = 7.3$ Hz).

Table 7. ^{1}H and ^{13}C NMR Chemical Shifts of Compounds 9 and 10

	9				10		
δ ^{13}C^a	group^b	assignment^c	δ ^{1}H^a	δ ^{13}C^a	group^b	assignment^c	δ ^{1}H^a
154.18	C	C-1		145.97	C	C-1	
125.60	CH	C-2	5.57	133.52	C	C-6	
83.34	C	C-7		133.52	C	C-7	
73.18	C	C-11		121.63	CH	C-2	5.49
49.32	CH	C-3	2.40	73.46	C	C-11	
41.16	CH	C-6	1.47	51.33	CH	C-3	2.24
41.01	CH$_2$	C-8	1.47 and 1.77	41.61	CH	C-10	2.44^e
40.52	CH	C-10	2.30	37.76	CH$_2$	C-5	2.36
35.33	CH$_2$	C-5	1.68 and 1.86	32.26	CH$_2$	C-9	1.13 and 1.82
31.97	CH$_2$	C-9	1.29 and 1.74	31.17	CH$_2$	C-8	2.23 and 2.41
30.35	CH$_2$	C-4	1.85 and 1.88	27.91	CH$_2$	C-4	1.57 and 1.97
26.85	CH$_3$	C-12	1.19	27.64	CH$_3$	C-13	1.22
26.75	CH$_3$	C-13	1.18	26.90	CH$_3$	C-12	1.22
18.18	CH$_3$	C-14	1.09^d	22.97	CH$_3$	C-15	1.72
17.76	CH$_3$	C-15	0.92^d	19.09	CH$_3$	C-14	1.05^e

^{a} In ppm relative to TMS. ^{b} Determined from DEPT analyses. ^{c} Determined from 2D-NMR experiments. ^{d} H-14 (d, $J = 7.5$ Hz), H-15 (d, $J = 6.8$ Hz). ^{e} H-14 (d, $J = 6.6$ Hz).

Chart 2. ^{14}C and ^{15}C NMR Chemical Shifts of 6 and 1
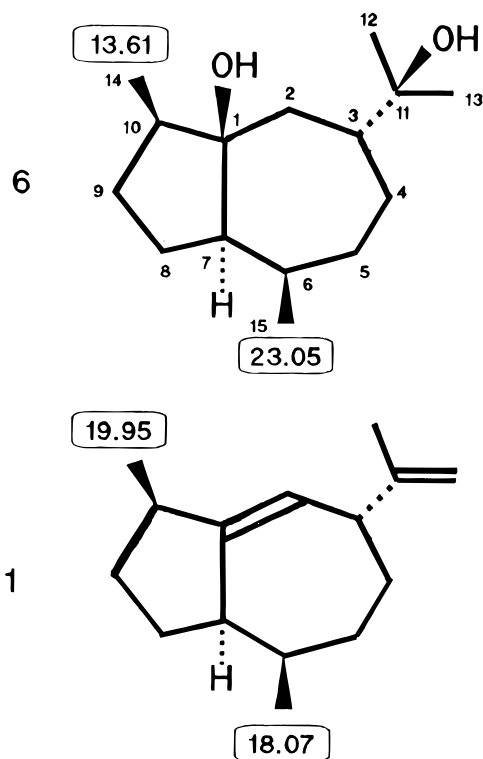
H$-$C$_2-$C$_3-$H dihedral angle is near 90°, and consequently, the hydroxy group is in the β-position as in the epoxide. We can note for **6** that the presence of a β-hydroxy group on carbon 1-C leads to a γ-effect on carbon 14-C and a δ-effect on carbon 15-C. For **9**, with a hydroxy group on carbon 7-C, these effects would be noted with a β-hydroxy group. But for carbons 14-C and 15-C, ^{13}C NMR chemical shifts give 18.18 and 17.76 ppm, values near those obtained for **1**. Therefore, hydroxy group 7-OH is in a β-position.

LITERATURE CITED

Arctander, S. In *Perfume and Flavor Materials of Natural Origin*; Elizabeth, NJ, 1960; p 285.

Bombarda, I.; Smadja, J.; Gaydou, E. M.; Conan, J.-Y.; Faure, R. Structure Elucidation of Oxidation−Reduction Products of Isolongifolene. *J. Agric. Food Chem.* **1994**, *42*, 138−142.

Bombarda, I.; Gaydou, E. M.; Smadja, J.; Faure, R. Synthèse de Composés Oxygénés Dérivés du Caryophyllène. (Synthesis of oxygenated compounds derived from caryophyllene). *Bull. Soc. Chim. Fr.* **1995**, *136*, 836−842.

Brown, H. C.; Kim, S. C.; Krishnamurphy, S. Selective Reductions. 26. Lithium Triethylborohydride as an Exceptionally Powerful and Selective Reducing Agent in Organic Synthesis. Exploration of the Reactions with Selected Organic Compounds Containing Representative Functional Groups. *J. Org. Chem.* **1980**, *45*, 1−12.

Ehret, C.; Ourisson, G. Le γ-Gurjunène, Structure et Configuration. Isomérisation de l'α-Gurjunène. (Structure and

confirmation of γ-gurjunene. Isomerization of α-gurjunene). *Tetrahedron* **1969**, *25*, 1785−1799.

Evans and Sutherland. *Alchemy II*; Tripos Associates, Inc., St. Louis, MO, 1988.

Faure, R.; Ramanoelina, A. R. P.; Rakotonirainy, O.; Bianchini, J. P.; Gaydou, E. M. Two-Dimensional Nuclear Magnetic Resonance of Sesquiterpenes. 4. Application to complete assignment of ^{1}H and ^{13}C NMR Spectra of some Aromadendrene Derivatives. *Magn. Reson. Chem.* **1991**, *29*, 969−971.

Ferridge, A. G.; Lindon, J. C. Resolution Enhancement in FT NMR through the Use of a Double Exponential Function. *J. Magn. Reson.* **1978**, *31*, 337−340.

Günther, H. *La spectroscopie de RMN*; Masson: Paris, 1993; pp 120−121.

Richardson, D. P.; Messer, A. C.; Newton, B. A.; Lindeman N. I. Identification and Preparation of Antiinsectan Dienols from *Dipterocarpus kerrii* Tree Resins. *J. Chem. Ecol.* **1991**, *17*, 663−685.

Streith, J.; Ourisson, G. L'α-Gurjunène. Quelques Réactions de l'α-Gurjunène (α-Gurjunene. II. Reactions of α-gurjunene). *Bull. Soc. Chim. Fr.* **1963**, *8−9*, 1960−1965.

Tressl, R.; Engel, K. H.; Kassa, M.; Koppler, H. Characterization of Tricyclic Sesquiterpenes in Hop (*Humulus lupulus, var. Hersbrucker Spät*). *J. Agric. Food Chem.* **1983**, *31*, 892−897.