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Structure Elucidation of Oxidation–Reduction Products of Isolongifolene

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Three alcohol isomers have been synthesized in high yield from isolongifolene to provide easy-to-make and cheap odorants. Oxidation of isolongifolene by reaction with *m*-chloroperbenzoic acid yielded a mixture of the corresponding epoxide, ketone, and alcohol. Two other alcohols were obtained from the reduction of the epoxide and the ketone, respectively. An herbal, spicy, and earthy odor was detected from the ketone and alcohols. The structural formulas of the compounds were determined using one- and two-dimensional NMR and gas chromatography–mass spectrometry.

INTRODUCTION

Essential oils are commonly used in perfume, cosmetics, and household products. The chemical compositions of natural essential oils (Masada, 1976) indicate the presence of an oxygenated fraction which exhibits interesting odors for perfume purposes and a hydrocarbon fraction of lower commercial values. Ylang extra or first, which contains 70% of oxygenated compounds, is used in many perfume formulations, and ylang third, which is composed of 70% of sesquiterpene hydrocarbons (Gaydou *et al.*, 1986, 1988), is generally used in toiletry products. Since some essential oils are deterpenated (fennel, clove, lemongrass, lime, orange, thymus, and vetiver), finding an economically profitable use for the hydrocarbon fraction or synthetic terpenes has been investigated for many years.

Earlier studies of oxidation products of isolongifolene have shown that these compounds are potential perfume compounds (Amano *et al.*, 1976; Sakuma and Ban, 1976; Takasago Perfumery, Co. Ltd., 1982; Tan, 1987; Nomura and Fujihara, 1988; Nayak *et al.*, 1988). On the other hand, Ferber (1987) reviewed some reactions (epoxidation, Prins reaction, and allylic oxidation) of isolongifolene producing aroma chemicals. Classification and characterization of the fragrance isolongifolene properties have been done for their use in perfumes and cosmetics.

The purpose of this study was to obtain oxidation products of isolongifolene through efficient chemical syntheses and to evaluate their fragrances. Although some of these compounds are already known, the complete ^{1}H and ^{13}C nuclear magnetic resonance (NMR) chemical shift assignments have not yet been reported. Introduction of various two-dimensional NMR techniques allowed unambiguous assignment of ^{1}H and ^{13}C of various sesquiterpenic compounds (Faure *et al.*, 1986, 1987, 1991; Gaydou *et al.*, 1989), and these techniques were applied to the synthesized compounds.

MATERIALS AND METHODS

Oxidation of Isolongifolene (1). *m*-Chloroperbenzoic acid (MCPBA; Fluka Chemicals) was used as the oxidant.

Table I. Reaction Conditions of Isolongifolene (1) Oxidation and Yields of Various Products

				yield,[b] %			
expt	1:MCPBA[a]	temp, °C	time, h	1	2	3	4
a	1:1.3	−30	0.5	38	50	6	nd[c]
b	1:1.3	0	1.5	nd	71	15	6
c	1:1.3	25	12	nd	65	25	8
d	1:1.3	reflux[d]	24	nd	<1	76	1
e	1:1[e]	0	3.5	nd	78	11	1

[a] Mole ratio. [b] Relative percent obtained by GC on a Carbowax 20 M column. [c] Not detected. [d] Reflux of methylene chloride. [e] Biphasic experiment, methylene chloride–sodium bicarbonate (10%) (70:30 v/v).

In the different experiments a solution of 302 mg (1.5 mmol) of isolongifolene (1) [(1*R*)-2,2,7,7-tetramethyltricyclo[6.2.1.0^{1,6}]undec-5-ene)] (Fluka Chemicals) in 5 mL of methylene chloride was stirred at various temperatures (−30 °C to reflux of solvent) during the addition of small portions of MCPBA (519 mg, 1.3 equiv) in methylene chloride (2 mL). The reaction mixture was allowed to stand for 1–24 h. Unreacted MCPBA and byproduct *m*-chlorobenzoic acid were removed by extracting the methylene chloride solution with 10% sodium sulfite and 10% sodium bicarbonate. The biphasic experiments [methylene chloride/sodium bicarbonate (0.3 N), 70:30 v/v, 10 mL] with 75 mg of 1 and 128 mg of MCPBA were done at 0 °C during 1.5 h. The organic layers were then removed under vacuum on a rotavapor. The crude products contained isolongifolene epoxide (2) [(1*R*)-5,6-epoxy-2,2,7,7-tetramethyltricyclo[6.2.1.0^{1,6}]undecane)], isolongifolene ketone (3) [(1*R*)-2,2,7,7-tetramethyltricyclo[6.2.1.0^{1,6}]-undec-5-one)], and isolongifolene alcohol (4) (5,5,11,11-tetramethyltricyclo[6.2.1.0^{1,6}]undec-6-en-2-ol). The relative percentages were determined by gas chromatography (GC). The reaction conditions and yields of oxidation products 2–4 are given in Table I.

Purification of Epoxide 2. Reaction mixture (100 mg) containing 78% epoxide 2 and 11% ketone 3 was submitted to column chromatography (CC) over silica gel 60 (50 g, 230–400 Mesh, E. Merck) using a column of 30 cm (25 mm i.d.). Elution was carried out with 80:20 (v/v) pentane–diethyl ether (200 mL) and collected in 20 tubes. Tubes 11–13 (56 mg) contained epoxide 2 (95% purity by CG).

Purification of Alcohol 4. Reaction mixture (223 mg) containing 65% epoxide 1, 25% ketone 3, and 8% alcohol

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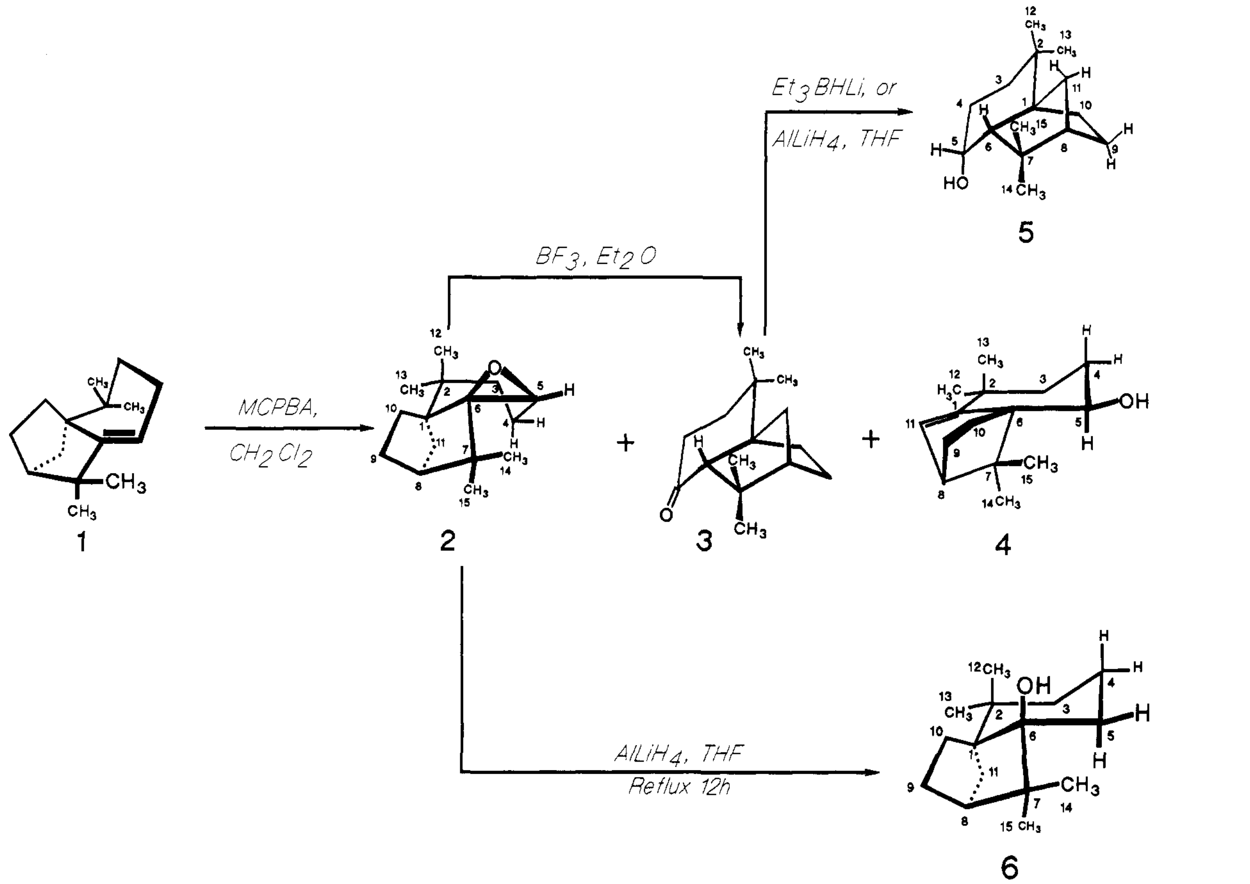

Figure 1. Reaction scheme of oxidation and reduction products from isolongifolene (1) and carbon numbering used for NMR analyses.

Table II. Retention Times and Mass Spectra of Oxidation–Reduction Products of Isolongifolene (1)

compd[a]	I_R[b]	mass spectral data[c]
2	1787	M+ 220, 41 (100), 108 (63.4), 205 (61.6), 43 (54.7), 107 (50.7), 55 (43.3), 91 (38.6), 93 (36.7), 121 (34.6), 69 (33.8), 109 (33.8), 149 (31.3), 95 (26.7), 79 (26.6), 29 (25.9), 105 (25.2), 83 (24.2)
3	1990	M+ 220, 41 (100), 191 (82.7), 55 (70.8), 43 (58.9), 83 (48.5), 107 (48.5), 121 (48.2), 205 (41.7), 29 (43.1), 149 (42.8), 164 (38.3), 91 (36.1), 109 (36.1), 39 (34.5), 93 (32.1), 177 (30.7), 27 (27.6), 79 (27.3), 53 (25.3), 77 (25.0), 67 (24.3)
4	2032	M+ 220, 164 (100), 177 (96.3), 43 (78.2), 41 (75.6), 55 (38.0), 91 (34.9), 121 (28.8), 29 (26.2), 105 (25.6), 39 (24.7), 108 (23.5), 79 (22.7), 77 (21.7), 149 (21.1), 107 (19.5), 27 (18.9), 103 (18.1)
5	2108	M+ 222, 41 (100), 189 (64.3), 43 (60.8), 55 (49.4), 161 (34.8), 91 (34.3), 105 (33.3), 29 (30.4), 133 (30.1), 119 (24.7), 123 (23.9), 69 (23.7), 109 (23.7), 204 (22.0), 67 (21.9), 125 (21.3)
6	2047	M+ 222, 41 (100), 43 (77.1), 69 (52.1), 139 (42.4), 109 (41.8), 98 (37.6), 95 (32.5), 67 (25.6), 179 (20.7), 29 (19.4)

[a] See Figure 1 for structural formula. [b] Determined on a Carbowax 20 M silica capillary column. I_R of isolongifolene, 1479. [c] m/z (relative intensity).

4 was fractionated by CC using 70:30 (v/v) pentane–diethyl ether (300 mL) and collected in 35 tubes. Tubes 28–30 contained 20 mg of alcohol 4 (80% purity by GC).

Isomerization of Isolongifolene Epoxide (2) in Isolongifolene Ketone (3). The epoxide 2 (115 mg, 0.52 mmol) was dissolved in 4 mL of methylene chloride and then 13 μL of boron trifluoride etherate (1 mol L^{-1}) (Fluka Chemicals) was added with rapid stirring. After 1 min at ambient temperature, the reaction was quenched by the addition of an excess of aqueous 10% sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and the solvent removed under vacuum on a rotovap. The purity of 3 was determined by GC (97%) and then analyzed by NMR and GC–MS.

Reduction of Isolongifolene Epoxide (2) and Isolongifolene Ketone (3). The epoxide 2 (56 mg, 0.25 mmol) was reduced with lithium aluminum hydride ($LiAlH_4$, Fluka Chemicals) 19 mg (0.5 mmol) in refluxing THF (5 mL) over 12 h. The complex LiAl–alcoholate was hydrolyzed with 10% sulfuric acid, and the alcohol 6 [(−)-isolongifolan-7-α-ol or [(1*R*,6*S*)-2,2,7,7-tetramethyltricyclo[6.2.1.$0^{1,6}$]undecan-6-ol] was obtained by extraction of the solution with diethyl ether (67% purity by GC for the crude mixture). Purification by CC (pentane–diethyl ether, 80:20 v/v) yielded 6 (76%), which was submitted to NMR and GC–MS analyses and compared with an authentic commercial sample (Fluka Chemicals).

The reduction of 85 mg (0.39 mmol) of isolongifolene ketone (3) by 30 mg (0.78 mmol) of $LiAlH_4$ in the same conditions described above yielded the alcohol 5, [(1*R*,6*S*)-2,2,7,7-tetramethyltricyclo[6.2.1.$0^{1,6}$]undecan-5-ol] (82% purity by GC). Better yield was obtained using lithium triethylborohydride ($LiEt_3BH$, Aldrich Chemical Co. Inc.) following the method of Brown *et al.* (1980). The reaction was carried out under helium atmosphere. Thirty-seven milligrams (0.168 mmol) of 3 in 3 mL of tetrahydrofuran (THF) was added with a syringe to a solution containing 168 μL (0.168 mmol) of a 1 mol L^{-1} solution of $LiEt_3BH$ in 1 mL of THF. The mixture was vigorously stirred at room temperature. After 12 h, the reaction mixture was

Table III. ^{1}H and ^{13}C NMR Chemical Shifts of Isolongifolene Epoxide (2) and Isolongifolene Ketone (3)

compd 2				compd 3			
δ $^{13}C^{a}$	group[b]	assignment[c]	δ $^{1}H^{a,d}$	δ $^{13}C^{a}$	group[b]	assignment[c]	δ $^{1}H^{a,d}$
72.61	C	C-6		211.29	C	C-5	
57.12	CH	C-5	3.15	60.65	CH	C-6	2.24
52.41	C	C-1		60.03	C	C-1	
46.71	CH	C-8	1.74	49.09	CH	C-8	1.64
36.34	C	C-7		40.13	CH_2	C-4	2.27 (ax) and 2.08 (e)
36.70	CH_2	C-11	1.69 (s) and 1.21 (a)	38.37	C	C-7	
32.94	CH_2	C-3	1.19 and 1.07	37.91	CH_2	C-3	1.68 (ax) and 1.47 (e)
30.24	C	C-2		36.77	CH_2	C-11	1.48 (s) and 1.14 (a)
27.31[e]	CH_3	C-13	0.81	33.56	C	C-2	
26.71	CH_3	C-15	0.89	32.76	CH_3	C-15	0.94
25.36[e]	CH_3	C-12	0.81	26.61	CH_2	C-9	1.76 (n) and 1.27 (x)
25.04	CH_2	C-9	1.76 and 1.42	25.46	CH_3	C-13	0.97
24.62	CH_2	C-10	1.50 and 1.38	23.64	CH_2	C-10	1.52 (n) and 0.96 (x)
22.28	CH_2	C-4	1.76	23.43	CH_3	C-14	1.20
20.87	CH_3	C-14	0.75	23.21	CH_3	C-12	1.16

[a] In ppm with respect to TMS. [b] Determined from DEPT spectra. [c] Determined from 2D measurements. [d] an, anti; e, equatorial; a, axial; n, endo; x, exo; s, syn. [e] Assignments may be reversed.

hydrolyzed with 1 mL of water. The triethylborane formed was oxidized with 1 mL of 30% hydrogen peroxyde. The aqueous phase was extracted with 2 × 5 mL of diethyl ether. After the volatile materials were evaporated under vacuum, the crude material was analyzed by GC (97% purity) and then analyzed by NMR and GC–MS.

Gas Chromatography (GC) and Gas Chromatography–Mass Spectrometry (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, 0.15 μm; column temperature, 170 °C). 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 and coupled with 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 150–220 °C, 3 °C min^{-1}; carrier gas, helium; ion source temperature, 220 °C; ionizing voltage, 70 eV.

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 ^{13}C and ^{1}H. Tetramethylsilane was used as internal standard in both measurements. Proton–proton coupling constants were extracted from high-field resolution-enhanced ^{1}H spectra using the Gaussian multiplication technique (Ferridge and Lindon, 1978). Resonance multiplicities for ^{13}C 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 sequences were used for homonuclear and heteronuclear correlation experiments. For other experimental details see Faure *et al.* (1991).

Odor Evaluation. Odor quality for the various ketone and alcohols (**3**, **4**, and **5**, 97, 80 and 82% purity by GC, respectively; **6**, authentic commercial sample) was determined by three aromaticians from the Reseach Centre of Nestec Ltd. The olfactory thresholds were determined at the opening of the flasks containing dried substances.

RESULTS AND DISCUSSION

Oxidation of Isolongifolene and Isomerization of the Corresponding Epoxide. Isolongifolene is an artifact from the acid-catalyzed hydration of longifolene (Nayak and Dev, 1960). Among the various oxidation reactions available in chemical synthesis, epoxidation using a peracid is a method of choice since byproduct formations are very low. This method was applied with success using sesquiterpenes such as aromadendrene and alloaromadendrene (Tressl *et al.*, 1983) and humulene (Lam and Deinzer, 1987). Products from chemical epoxidation of isolongifolene **1** with *m*-chloroperbenzoic acid are given in Figure 1. As shown in Table I, the yield in the corresponding epoxide **2**, using *m*-chloroperbenzoic acid, ranged from 1 to 78%. Better yields were obtained at low temperature and short time (experiments b and e, Table I). Although this epoxide **2** was first reported by Prahlad *et al.* (1964), the stereochemistry of this compound showing an *endo* configuration was proved later by X-ray analysis (McMillan and Paul, 1974). The retention time and mass spectral data of **2** are given in Table II. The ^{1}H and ^{13}C chemical shifts are given in Table III and the ^{1}H–^{1}H coupling constants in Table IV. The carbon numbering used for NMR analyses is given in Figure 1.

Table IV. ^{1}H–^{1}H Coupling Constants[a] of Compounds 2–5

	compd			
pairs[b]	2	3	4	5
3ax–3e		13.6	13.4	
3ax–4ax		13.6	13.0	
3ax–4e		5.2	3.1	
3e–4ax		6.8	3.3	
3e–4e		2.0	3.1	
4ax–4e		15.3	12.9	
4ax–5	3.8		11.5	2.6
4e–5	1.7		4.8	2.6
5–6				2.6
8–11			3.3	
8–11an	1.7	1.4		1.3
8–11s	2.4	2.3		2.5
8–9x		3.7	3.3	
9x–9n		12.3	11.4	12.0
9x–10x		6.7	3.3	5.7
9x–10n		12.3	8.0	12.6
9n–10n		2.3		2.3
9n–10x		9.2	9.6	9.3
9n–11s	2.4	2.3		2.6
10n–10x		12.4	11.8	12.6
10n–11s	2.4	2.3		2.5
11an–11s	10.0	9.7		

[a] *J* in Hz. [b] an, anti; e, equatorial; a, axial; n, endo; x, exo; s, syn.

The low yield observed in experiment d was due to an isomerization of **2** into the ketone **3** (Figure 1). Good yield for **3** was obtained (97%) starting from **2** and boron trifluoride etherate according to a process described by Whitesell *et al.* (1981) in the total synthesis of an iridoid monoterpene. The mechanism of this rearrangement has

Table V. ^{1}H and ^{13}C NMR Chemical Shifts of Isolongifolene Alcohols 4 and 5

compd 4				compd 5			
δ ^{13}C[a]	group[b]	assignment[c]	δ ^{1}H[a,d]	δ ^{13}C[a]	group[b]	assignment[c]	δ ^{1}H[a,d]
154.18	C	C-1		68.22	CH	C-5	4.16
126.46	CH	C-11	5.60	54.67	C	C-1	
69.79	CH	C-5	3.80	52.24	CH	C-6	1.30
59.63	C	C-6		48.26	CH	C-8	1.67
55.87	C	C-7		37.98	CH_2	C-11	1.23 (s) and 1.08 (an)
51.33	CH	C-8	2.17	37.72	C	C-7	
37.80	CH_2	C-3	1.40 (e) and 1.34 (a)	33.74	C	C-2	
32.68	C	C-2		33.04	CH_3	C-15	0.92
30.51[e]	CH_3	C-13	0.99	32.17	CH_2	C-3	1.67 and 1.02
29.87	CH_2	C-4	1.75 (e) and 1.67 (a)	32.17	CH_2	C-4	1.62 and 1.58
29.81[e]	CH_3	C-12	1.05	27.63	CH_3	C-13	0.90
25.04	CH_2	C-9	1.83 (x) and 0.92 (n)	25.64	CH_2	C-9	1.70 (n) and 1.28 (x)
22.02	CH_2	C-10	2.02 (x) and 0.96 (n)	23.49	CH_3	C-14	0.92
21.35[f]	CH_3	C-14	0.89	22.75	CH_2	C-10	2.14 (x) and 1.41 (n)
20.31[f]	CH_3	C-15	0.81	22.75	CH_3	C-12	1.12

[a] In ppm with respect to TMS. [b] Determined from DEPT spectra. [c] Determined from 2D measurements. [d] an, anti; e, equatorial; a, axial; n, endo; x, exo; s, syn. [e,f] Assignments may be reversed.

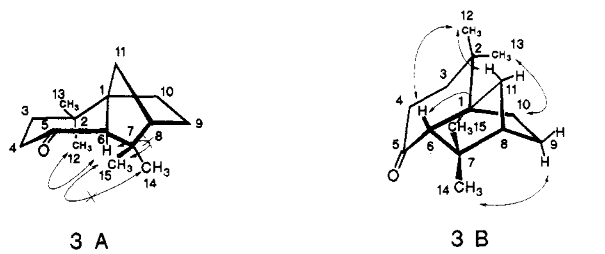

Figure 2. Two epimers of isolongifolene ketone 3 showing the NOE cross-peaks.

been previously investigated (Coxon *et al.*, 1970), showing that the intermediate carbocation involved the cleavage of the most substituted oxygen–carbon bond. As shown in Figure 2, two ketone epimers **3A** and **3B**, at the C-7 position, can be investigated. Since during the isomerization process only one epimer is formed, the stereochemistry of this ketone was a matter of some controversy in the 1970s (Eschinasi *et al.*, 1970; Ranganathan *et al.*, 1970; Lala, 1971; Metha and Kapoor, 1973). The stereochemistry of **3B** was unequivocally established using two-dimensional NMR experiment as discussed below.

Reduction of Isolongifolene Epoxide (2) and Isolongifolene Ketone 3B. Reduction of epoxide **2** using lithium aluminum hydride ($LiAlH_4$) was regioselective, with hydride attack on the less substituted carbon, and yielded the corresponding pure alcohol **6** with an axial hydroxy group (Figure 1). The reduction of the ketone **3B** was achieved with $LiAlH_4$, but better yield in alcohol **5** (98%) was obtained using lithium triethylborohydride ($LiEt_3BH$). This reaction was stereoselective, and the axial hydroxy group position resulted in a hydride attack on the less hindered side. Mass spectral and NMR data of these compounds are given in Tables II and IV–VI.

Although the yield in alcohol **4** was relatively low (8% of the crude products), it has been possible to obtain this compound in pure form for spectral analyses (Tables IV and V) and for olfactive evaluation (Table VII).

Nuclear Magnetic Resonance Results. The ^{1}H and ^{13}C NMR spectral parameters were deduced from concerted application of heteronuclear and homonuclear chemical shift correlation diagrams. The establishment of the proton connectivity is easily available from the homonuclear correlation experiment (Aue *et al.*, 1976; Nagayama *et al.*, 1980), while the relationships between all of the carbon and hydrogen atoms were achieved from the ^{13}C–^{1}H shift correlation spectrum with proton decoupling in the F1 dimension (Bax, 1983; Rutar, 1984). The stereochemical assignment of the H-9 and H-10

Table VI. ^{13}C NMR Chemical Shifts of Isolongifolene Alcohol 6

δ ^{13}C[a]	group[b]	assignment
80.00	C	C-6
57.67	C	C-1
48.65	CH	C-8
43.10	C	C-7
39.53	CH_2	C-11
35.50[c]	CH_2	C-5
34.40[c]	CH_2	C-3
33.21	C	C-2
28.67	CH_3[d]	C-13
26.85	CH_3[d]	C-15
25.96	CH_2	C-9
25.00	CH_3	C-12
22.43	CH_3	C-14
22.35	CH_2	C-10
18.85	CH_2	C-4

[a] In ppm with respect to TMS. [b] Determined from DEPT spectra. [c,d] Assignment may be reversed.

methylene resonances follows from the close comparison of the vicinal and long-range (W) ^{1}H–^{1}H coupling constants with the previously reported data for norbornyl derivatives (Gaudemer, 1977). Moreover, with the exception of compound **3**, the spectral parameters for *gem*-dimethyl groups were not unambiguously determined. The ^{1}H and ^{13}C chemical shifts are given in Tables III, V, and VI and the coupling constants in Table IV. For some derivatives (compounds **2** and **5**), the high crowding of methylene resonances precludes the accurate determination of ^{1}H 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.

In this paper, the stereochemistry of **3** was unequivocally established using two-dimensional NMR experiment. Unambiguous determination of the methyl resonances could be obtained from the analysis of the phase-sensitive NOESY spectrum (Bodenhausen *et al.*, 1984). The H-14, H-13, and H-12 were easily located at 1.20, 0.97, and 1.16 ppm because of their NOE cross-peaks with the *endo*-H-9, *endo*-H-10, and *syn*-H-11 protons, respectively. Finally, the stereochemistry at C-6 was determined using the H-6 NOE cross-peaks with H-15 and H-12. Only the structure of **3B** (Figure 2) was consistent with the above results.

For alcohols **4** and **5**, the coupling constants of the proton on the carbon atom bearing the hydroxy group indicated that this function was equatorial and axial, respectively (Table IV). The ^{13}C chemical shifts of **6** (for which the structure was confirmed with a commercial sample) were

Table VII. Odor Properties of Oxidation-Reduction Products of Isolongifolene

compd	odor: main character	odor: secondary notes
3	woody	green/incense
4	pharmaceutical	sticking-plaster
5	medicinal	green/woody
6	camphorated	pungent

determined by comparison with the values for the other isolongifolene derivatives.

Odor Properties. Table VII reports the results of odor evaluation of the synthesized compounds. The ketone **3** showed a markedly woody odor different from that of the three alcohols, **4–6**. The alcohol **5**, characterized by a medicinal odor, shows also as secondary notes a green and woody odor, quite similar to that of alcohol **4**, and a slightly spiced odor like that of alcohol **6**.

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