Sesquiterpenes from the Rhizomes of *Ligularia dentata* Hara[1)]

Keizo NAYA,* Tohru OKAYAMA, Masaaki FUJIWARA, Makoto NAKATA, Tsutomu OHTSUKA, and Seiko KURIO
Department of Chemistry, Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo 662
(Received January 29, 1990)

From the rhizomes of *Ligularia dentata* Hara two new compounds, a phenolic norsesquiterpene ligudentatol (**2**), and a eudesmanoid ligucyperonol (**6**), have been isolated in addition to the known caryophillene (**1**) and additional three phenolic norsesquiterpenes (**3**, **4**, and **5**). The structures and stereochemistries of **2** and **6** have been established by a combination of spectroscopic and chemical methods, and by correlation with known ligujapone (**4**) and (+)-α-cyperone (**11**), respectively.

Ligularia dentata Hara (Marubadakebuki in Japanese) is a perenial herb that grows in subalpine grassland. The *ligularia* species have been extensively investigated by Takahashi,[2)] Bohlmann,[3-6)] and others;[7)] though they are thought to be rich sources of furanoeremophilanes, these molecules could not be found in this plant. The present paper reports on the isolation and structural elucidation of six sesquiterpenes from the title plant. The four known compounds among them were identified as being caryophyllene (**1**),[8)] and three norsesquiterpene phenols, (liguhodgsonal (**3**),[3,4)] ligujapone (**4**),[3)] and 2-hydroxyplatyphillide (**5**)[4,6)]) isolated previously from *Ligularia* and *Senecio* species by Bohlmann. The two new compounds were another phenolic norsesquiterpene and a eudesmane derivative, named ligudentatol (**2**) and ligucyperonol (**6**), respectively. Bohlmann and his colleagues have already studied the same plant,[3)] but reported only liguhodgsonal **3** as a common component with ours.

A structural elucidation of the new compounds, **2** and **6**, were performed as follows.

The structure of ligudentatol **2** ($C_{14}H_{18}O$, a colorless oil, $[\alpha]_D$ +82°) was readily deduced by a detailed comparison of the spectral data with those of the norsesquiterpene constituents; the constituents were found to be closely related with each other. They showed various characteristic common features: (i) a C_{14} compound (based on elemental analysis or HRMS); (ii) a phenolic OH group (positive color test to diazotized sulfanilic acid-Na_2CO_3 aqueous solution, and IR spectra in the 3600—3200 and 1600—1500 cm^{-1} regions); (iii) an isopropenyl group (IR ca. 1645 and 895 cm^{-1}; ^1H NMR: CH_3 and *exo*-methylene groups with allyl coupling); (iv) CH_3 or its oxygenated substituent attached to a trisubstituted phenol ring (UV 260—310 nm; ^1H NMR: two aromatic protons with *o*- or *m*-coupling). Also, the ^{13}C NMR spectra well illustrate the above features (Table 1 and Exptl.). Furthermore, **4** exhibits IR 1665 cm^{-1}; ^{13}C NMR δ=197.3; ^1H NMR δ=7.88 and 6.79 (each d, *J*=8.6 Hz) attributable to a conjugated system including 9-oxo and two aromatic protons (1-H and 2-H with *o*-coupling). Compound **2** also shows *o*-coupling, δ=6.82 and 6.57 (each d, *J*=8.4 Hz, 1-H and 2-H).[9)] In addition, acetylations of **2** and **4** showed induced upfield shifts of 14-Me signals (δ=2.12 to 2.02 in **2a** and 2.21 to 2.13 in **4a**) in ^1H NMR, indicating the presence of the phenolic OH at the *o*-position to the methyl group. In ^{13}C NMR, acetylation effects[10)] can be observed upon the chemical shifts of 2-C, 3-C, and 4-C in **2a** and **4a** (See Table 1). Further, the ^{13}C chemical shifts and the ^{13}C-^1H splittings in **4** [δ=41.8 (d) 7-CH, 43.1 (t) 8-CH_2] would be suited to the isopropenyl group[11)] attached to the β-carbon of the 9-keto group[12)] based on the ^{13}C NMR spectrum of 6-methoxy-1-tetralone.[13)]

Thus, the above observations revealed that ligudentatol **2** should be the 9-deoxy derivative of ligujapone **4**. In order to clarify the structural relationship

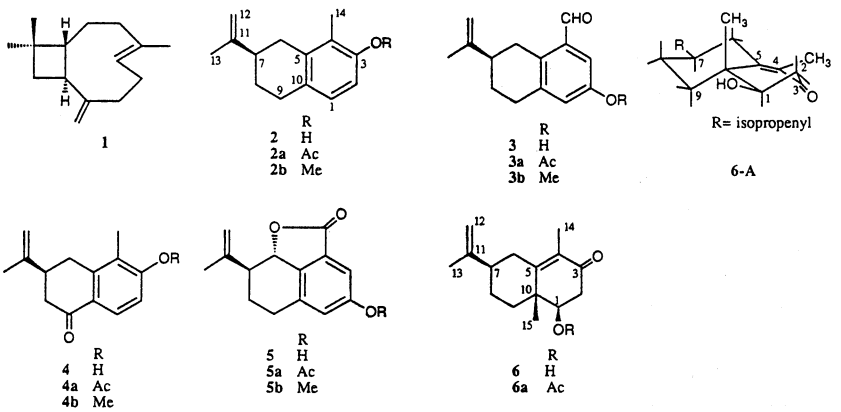
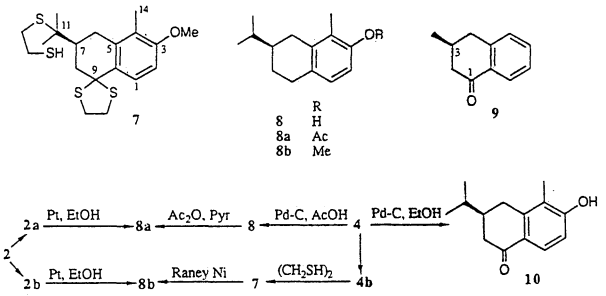


Fig. 1. Formula **1—6**

Table 1. ^{13}C NMR Chemical Shifts of Ligudentatol (**2**) and the Related Compounds (**2a**, **4**, **4a**, **4b**, **8**, **8a**, and **8b**)

C	2	2a	4	4a	4b	8	8a	8b
1	126.7	127.0	126.9	126.2	126.9	121.9	126.9	124.7
2	112.6	118.1	113.8	120.6	108.5	112.4	118.7	108.3
3	151.3	147.0	158.8	153.2	161.6	151.3	146.9	155.5
4	121.8	128.1	121.6	128.3	123.8	126.6	128.2	126.3
5	136.4	136.1	144.0	143.9	143.1	137.0	137.3	136.7
6	32.8	32.8	32.3	32.4	32.3	31.1	31.0	31.1
7	42.1	41.8	41.8	41.6	41.8	41.0	40.7	41.0
8	27.8	27.6	43.1	43.2	43.3	26.2	25.8	26.3
9	29.6	30.0	198.2	197.3	197.3	30.1	30.3	30.0
10	128.8	134.4	125.8	130.5	125.8	129.6	135.0	129.5
11	149.8	149.6	147.0	146.7	147.0	32.6	32.6	32.6
12	109.1	109.3	110.0	111.0	110.7	19.7[a)]	19.7[a)]	19.7[a)]
13	20.6	20.6	20.6	20.5	20.6	19.8[a)]	19.8[a)]	19.8[a)]
14	10.9	12.0	11.2	12.2	11.2	10.4	11.9	11.0
MeCO		169.7		168.7			169.7	
MeCO		20.8		20.8			20.9	
MeO					55.6			55.8

a) Assignments may be interchanged in each column.



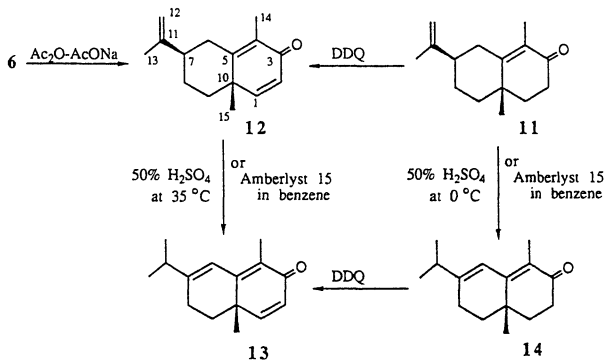
Scheme 1.

between **2** and **4**, both compounds were interconverted by the following routes (Scheme 1). 3-*O*-Methyligujapone (**4b**) was treated with 1,2-ethanedithiol-BF_3 to furnish a substitution-addition compound, $C_{19}H_{28}OS_4$ (**7**), which showed new ^1H NMR signals (δ=1.43, s and 1.32, s), thus indicating the presence of a sulfur atom attached to 11-C, as in the formula **7**. Subsequent desulfurization with Raney nickel afforded 3-*O*-methyldihydroligudentatol (**8b**) which was identical to **8b** converted from 3-*O*-methylligudentatol (**2b**) by hydrogenation with Adams' catalyst in EtOH. In another attempt, hydrogenation of **4** with 5% Pd-C in AcOH gave a tetrahydro derivative (**8**) accompanied by a reduction of the keto group. This showed a disappearance of the IR band due to the 9-keto group (1665 cm^{-1}) in **4**. The acetate of **8** was identical in all respects with **8a** transformed from **2a** by hydrogenation with Adams' catalyst in EtOH.

Finally, the stereochemistry of **4** and, accordingly, of **2** was drawn from the CD spectra. The absolute configuration and the CD spectra of substituted tetralone and tetralin were studied by Snatzke et al.[14] They reported that (*S*)-(+)-3-methyl-1-tetralone (**9**) showed a positive CD maximum in the n→π^* transition region ($\Delta\varepsilon_{321}$=+1.3), which has a preferred sofa-type conformation with an equatorial alkyl substituent. Both ligujapone **4** and its dihydro derivative (**10**) also showed positive Cotton effects in a similar region due to the n→π^* transition ($\Delta\varepsilon_{313}$=+2.81 in **4** and $\Delta\varepsilon_{316}$=+1.99 in **10**). These positive CD maxima seem to be controlled by equatorial (*S*)-oriented alkyl substituents.

Thus, ligudentatol can be represented by stereoformula **2**.

Ligucyperonol (**6**)[15,16] (colorless needles, mp 123.5—124.5 °C, $[\alpha]_D$ +85°) showed the following absorption spectra: UV (MeOH) 249 nm (ε 19200) attributable to a ketone conjugated with a trisubstituted double bond; IR ($CHCl_3$) 3600, 3420 (OH), 1660, 1610 (α,β-unsaturated C=O), 895 cm^{-1} (terminal methylene); ^1H NMR ($CDCl_3$) a vinyl methyl (δ=1.78, s, 14-Me), a quaternary methyl (1.18, s, 15-Me), a paired signals due to an isopropenyl group (δ=1.77, d, J=1.1 Hz and 4.78, d, J=1.1 Hz, 13-Me and 12-CH_2), an axial proton signal attached to a carbon bearing a hydroxyl group coupled with an adjacent isolated methylene group (δ=3.84, ddd, J=11, 7.1, 5.2 Hz, 1-H; 2.70, dd, J=7.1, 18 Hz, 2α-H; 2.50, dd, J=11, 18 Hz, 2β-H).



Scheme 2.

Table 2. ^{13}C NMR Chemical Shifts of Ligucyperonol (**6**) and the Related Compounds (**6a**, **11**, **12**, **13**, and **14**)

C	6	6a	11	12	13	14
1	74.4	75.4	37.5	156.4	154.8	37.2
2	42.5	40.1	33.8	126.2	118.4	33.9
3	197.3	195.5	198.7	186.2	186.8	199.0
4	129.5	130.0	128.9	129.4	127.4	126.4
5	161.7	160.4	161.8	159.4	154.6	156.1
6	37.8	37.5	33.0	38.0	127.2	118.3
7	45.2	45.0	46.0	46.6	153.4	155.9
8	26.6	26.4	27.0	26.3	23.7	23.7
9	32.9	32.7	42.0	32.9	32.5	36.5
10	41.4	39.2	35.9	40.2	37.6	33.2
11	148.9	148.7	149.0	148.5	35.8	36.1
12	109.4	109.4	109.2	109.6	21.6	21.1
13	20.6	20.6	20.6	20.8	21.3	21.1
14	10.9	11.0	10.9	10.5	10.0	10.1
15	16.3	17.6	22.6	23.6	25.2	21.5
MeCO		170.1				
MeCO		21.0				

Coupling constant J=5.2 Hz was exchangeable with D_2O, and disappeared upon acetylation of **6** (δ=5.05, dd, J=11.6, 6.2 Hz, 1-H). In addition, ligucyperonol **6** exhibited a CD maxima, $\Delta\varepsilon_{245}$=+11.4 and $\Delta\varepsilon_{317.8}$=−2.5, due to $\pi\rightarrow\pi^*$[17] and $n\rightarrow\pi^*$[18] transitions, respectively. The CD signs suggest that **6** preferentially adopts a half-chair conformation with a right-handed helix regarding the transoid enone system. Consequently, the (1*R*)-configuration can be assigned to the preferred conformation (cf. **6-A**).

The above observation regarding the functional groups and a biogenetic consideration caused us to postulate a eudesmane-type, with the stereoformulas **6** and **6-A** for ligucyperonol. This presumption was also supported by its ^{13}C NMR data (Table 2).

In order to confirm this assumption, the chemical correlation of **6** to (+)-α-cyperone (**11**)[19] with the known stereochemistry was performed by the following two routes (Scheme 2). Dehydrated ligucyperonol (eudesma-1,4,11-trien-3-one) (**12**)[20] and its isomer, eudesma-1,4,6-trien-3-one (**13**), were synthesized from both **6** and **11**, as shown in Scheme 2: that is, i) without migration of $\Delta^{11,12}$; and ii) with migration of $\Delta^{11,12}$ to $\Delta^{6,7}$, respectively.

The hydroxyl group of **6** was dehydrated with Ac_2O-AcONa under reflux to afford a dehydro derivative (**12**), which showed ^1H NMR signals due to a terminal methylene and a newly introduced double bond conjugated with the keto group, δ=4.81 (d, J=1.1 Hz, 12-CH_2, 6.77 and 6.23 (each d, J=9.9 Hz, 1- and 2-H). Compound **12** was also obtained from (+)-α-cyperone **11** by dehydrogenation with DDQ in dioxane.

Pure (+)-α-cyperone **11** was obtained via its semicarbazone (mp 209.0—210.0 °C[21]) from the commercial drug "Ko-bushi", dried rhizomes of *Cyperus rotundus* of Chinese origin. Compound **12** was isomerized to eudesma-1,4,6-trien-3-one (**13**) by stirring in dilute H_2SO_4,[22] or by heating with Amberlyst 15; it showed UV_{max} 315 nm (ε 17400) caused by a crossed conjugated trienone moiety, and ^1H NMR signal due to a newly observed olefinic proton at δ=6.41 (s, 6-H). Similarly, (+)-α-cyperone **11** was subjected to isomerization with dilute H_2SO_4,[16] or with Amberlist 15 in dry benzene at 70 °C; it afforded β-cyperone (**14**),[22,23] which showed a shifted olefinic proton, δ=6.29 (br s, 6-H) and an isopropyl signals, δ=1.12 (6H, d, J=6.8 Hz, 12- and 13-Me). The following dehydrogenation of **14** with DDQ in dry dioxane under reflux gave the same compound as the above **13**. The results of these interconversions are consistent with those of the ^{13}C NMR data in Table 2.

Thus, ligucyperonol can be represented by stereoformulas **6** and **6-A**.

The sesquiterpenes, hitherto found in *Ligularia* species, include a large number of eremophilanes;[2-7] however, little is known about the occurrence of a eudesmane-type derivative postulated as a biogenetic precursor of eremophilanes in those plants.

It would therefore be the first example that four phenolic norsesquiterpenes **2**—**5** and an additional eudesmane-type product **6** have been isolated from a *Ligularia* plant.

Experimental

All melting points are uncorrected. The IR, UV, CD, and MS spectra were taken with Hitachi 270-30, Cary 118, JASCO Model ORD/CD-5, and JEOL JMS-D300 spectrophotometers, respectively. The ^1H and ^{13}C NMR spectra were recorded with a JEOL FX-90Q (90 MHz and 22.5 MNz) spectrometer; the chemical shifts are reported in δ-values (with TMS as the internal reference). The optical rotations were measured with a Perkin-Elmer 141 polarimeter. The TLC were run on a Kieselgel G (Merck). Centrifugal preparative liquid chromatography was conducted with a Hitachi Model CLC-5. The analytical and preparative GLC were performed with a Hitachi 163 (ϕ=3 mm×2 m) and Varian aerograph Model 90-P (ϕ=6 mm×1 m).

Isolation of Constituents. The plant rhizomes of *Ligularia dentata* (A. Gray) Hara were collected at the foot of Mt. Goryu in Nagano Prefecture. Fresh rhizomes (30 kg) were extracted in the cold with MeOH for 2 weeks. The solvent was removed under reduced pressure, and the residue was suspended in H_2O and then extracted, successively, with hexane and ether. Both extracts were washed with a saturated $NaHCO_3$ aqueous solution and then with water; they were then dried over anhydous Na_2SO_4 and evaporated in vacuo, respectively, leaving dark oils [hexane extract (A): 70.5 g and ether extract (B): 62 g].

Extracts A and B were divided in a similar manner into the three crude fractions by column chromatography over silica gel with benzene (Fr. 1), benzene-AcOEt (20 : 1) (Fr. 2), and benzene-AcOEt (10 : 1) (Fr. 3), and finally with AcOEt (Fr. 4) as eluents. Further purification was achieved by GLC and repeated chromatography as follows.

A small amount (137 mg) of the ether-soluble hydrocarbons from Fr. 1 was subjected to vacuum distillation, bp 116 °C/0.08 mmHg (1 mmHg≈133.322 Pa), to afford a color-

less oil. The main fraction on GLC (FID: PEG-20M, column temp 120 °C, N_2 50 ml min^{-1}, retention time 8.8 min; ca. 80% of the total peak areas) was collected by preparative GLC (TCD: column temp 120 °C, H_2 80 ml min^{-1}, retention time 13 min) to afford caryophillene (**1**) (0.85% yield based on the crude extract). This was identical with the authentic sample by a comparison of the IR and ^{1}H NMR spectra with GLC analysis. The other hydrocarbons were not further investigated.

Fr. 2-A (4.64 g) was chromatographed on silica gel (200 g) with hexane-ether (50 : 1) and gave a pale-yellow oil (331 mg, 4.7% based on the crude extract A), which was positive to diazotized sulfanilic acid and purified by preparative TLC (hexane-ether 5 : 1) to furnish ligudentatol (**2**) (150 mg; R_f 0.56,benzene).

Repeated chromatography of Fr. 3-A (14.6 g) and Fr. 2-B (4.74 g) on silica gel (hexane-ether 25 : 1) afforded liguhodgsonal (**3**) as amorphous solid [146 mg (A) and 87 mg (B); R_f 0.77, benzene-AcOEt 15 : 1]. A further elution of Fr. 3-A and repeated chromatography of Fr. 3-B (7.53 g) with hexane-ether (7 : 1) gave pale-yellow crystalls, 346 mg (A) and 402 mg (B), respectively, (total content: 0.56%), which were purified by recrystallization to afford ligujapone (**4**) (TLC: R_f 0.65, benzene-AcOEt 5 : 1). Further elution of the above chromatography with hexane-ether (5 : 1) gave pale greenish crystalls, 12.3 mg (A) and 224 mg (B), which were purified by recrystallization to furnish 2-hydroxyplatyphillide (**5**) (TLC: R_f 0.45, benzene-AcOEt 5 : 1).

Fr. 4-A (7.63 g) was chromatographed on silica gel (350 g) with hexane-ether (3 : 1) afforded ligucyperonol (**6**) (119 mg) (TLC: R_f 0.25, benzene-AcOEt 5 : 1).

The acetylation and methylation were performed with acetic anhydride-pyridine, and methyl iodide-K_2CO_3 in acetone or CH_2N_2-ether solution in the usual manner, respectively.

Ligudentatol (2). Colorless oil, $[\alpha]_D^{22}$ +82.4° (*c* 0.80, $CHCl_3$); UV (MeOH) 280 (ε 9700), 220sh nm (9000); IR ($CHCl_3$) 3600, 3330, 1645, 1600, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.82 (d, *J*=8.4 Hz, 1-H), 6.57 (d, *J*=8.4 Hz, 2-H), 4.78 (br s, 12-CH_2), 4.55 (s, OH), 2.12 (s, 14-Me), 1.82 (t, *J*=1.1 Hz, 13-Me); ^{13}C NMR (Table 1).

Found: *m/z* 202.1347. Calcd for $C_{14}H_{18}O$: M, 202.1353.

2a: Colorless oil, $[\alpha]_D^{22}$ +61.0° (*c* 0.59, $CHCl_3$); UV (MeOH) 265 nm (ε 600); IR (neat) 1765, 1645, 1640sh, 1600, 885 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.96 (d, *J*=8.4 Hz, 1-H), 6.76 (d, *J*=8.4 Hz, 2-H), 4.79 (m, 12-CH_2), 2.31 (s, OAc), 2.02 (s, 14-Me), 1.81 (t, *J*=1.1 Hz, 13-Me); ^{13}C MMR (Table 1); TLC: R_f 0.39 (hexane-ether 10 : 1).

Found: *m/z* 244.1457. Calcd for $C_{16}H_{20}O_2$: M, 244.1458.

2b: Colorless oil; $[\alpha]_D^{22}$ +42° (*c* 0.25, $CHCl_3$); IR ($CHCl_3$) 1645, 1600, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.92 (d, *J*=8.4 Hz, 1-H), 6.68 (d, *J*=8.4 Hz, 2-H), 4.78 (br s, 12-CH_2), 3.80 (s, OMe), 2.11 (s, 14-Me), 1.82 (t, *J*=1.1 Hz, 13-Me); TLC: R_f 0.26 (hexane).

Iiguhodgsonal (3): Colorless amorphous solid, $[\alpha]_D^{22}$ +108° (*c* 0.85, $CHCl_3$); UV (MeOH): 330 (ε 3600), 263 (9300), 225 nm (16000); IR ($CHCl_3$) 3580, 3320, 2730, 1690, 1650, 1615, 1595, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=10.25 (s, 14-H), 7.16 (d, *J*=2.7 Hz, 3-H), 6.86 (d, *J*=2.7 Hz, 1-H), 5.66 (s, OH), 4.78 (br d, *J*=0.8 Hz, 12-CH_2), 3.43 (dd, *J*=11.0, 3.9 Hz, 6α-H), 1.82 (br s, 13-Me); ^{13}C NMR ($CDCl_3$) δ=121.9 (1-C), 153.7 (2-C), 115.8 (3-C), 134.8 (4-C), 131.7 (5-C), 30.0 (6-C), 41.5 (7-C), 27.2 (8-C), 30.8 (9-C), 139.8 (10-C), 148.9 (11-C), 109.7 (12-C), 20.8 (13-C), 192.6 (14-C).

Found: *m/z* 216.1151. Calcd for $C_{14}H_{16}O_2$: M, 216.1146.

3a: Colorless oil, $[\alpha]_D^{23}$ +87.7° (*c* 0.52, $CHCl_3$); UV (MeOH) 255 (ε 9300), 306 nm (2200); IR (neat) 1770, 1695, 1650, 1605, 1590, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=10.24 (s, 14-H), 7.37 (d, *J*=2.4 Hz, 3-H), 7.06 (d, *J*=2.4 Hz, 1-H), 4.80 (m, 12-CH_2), 2.31 (s, OAc), 1.83 (br s, 13-Me); ^{13}C NMR ($CDCl_3$) δ=127.5 (1-C), 148.5 (2-C), 122.8 (3-C), 134.9 (4-C), 136.8 (5-C), 31.4 (6-C), 41.2 (7-C), 26.9 (8-C), 29.9 (9-C), 139.8 (10-C), 148.7 (11-C), 109.8 (12-C), 21.0 (13-C), 191.6 (14-C), 169.3 ($CH_3\underline{C}O$), 20.7 ($\underline{C}H_3CO$); TLC: R_f 0.87 (benzene-AcOEt 5 : 1).

Found: *m/z* 258.1261. Calcd for $C_{16}H_{18}O_3$: M, 258.1251.

3b: Colorless oil, $[\alpha]_D^{22}$ +101.3° (*c* 0.46, $CHCl_3$); IR ($CHCl_3$) 1690, 1650, 1610, 1580, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=10.28 (s, 14-H), 7.20 (d, *J*=3 Hz, 3-H), 6.88 (d, *J*=3 Hz, 1-H), 4.80 (m, 12-CH_2), 3.83 (s, OMe), 1.82 (s, 13-Me); ^{13}C NMR δ=120.7 (1-C), 157.4 (2-C), 113.7 (3-C), 139.5 (4-C), 131.6 (5-C), 30.0 (6-C), 41.4 (7-C), 27.1 (8-C), 30.7 (9-C), 139.9 (10-C), 149.0 (11-C), 109.5 (12-C), 20.7 (13-C), 192.2 (14-C), 55.4 ($O\underline{C}H_3$); TLC: R_f 0.63 (benzene).

Found: *m/z* 230.1296. Calcd for $C_{15}H_{18}O_2$: M, 230.1302.

Ligujapone (4): Mp 178—179 °C, colorless needles (from diisopropyl ether); $[\alpha]_D^{22}$ +6.8° (*c* 0.71, $CHCl_3$); UV (MeOH) 232 (ε 16900), 288 nm (18100); CD (*c* 7.36×10^{-4}, MeOH) $[\theta]_{313}$ +9270; IR ($CHCl_3$) 3580, 3270, 1665, 1600sh, 1585, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.88 (d, *J*=8.6 Hz, 1-H), 6.79 (d, *J*=8.6Hz, 2-H), 6.55 (s, OH), 4.85 (m, 12-CH_2), 2.21 (s, 14-Me), 1.83 (m, 13-Me); ^{13}C NMR (Table 1).

Found: C, 77.71; H, 7.48%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

4a: Colorless oil; $[\alpha]_D^{22}$ +10.4° (*c* 0.78, $CHCl_3$); UV (MeOH) 256 (ε 18000), 290 nm (2700); CIMS *m/z* 259 (MH^+ base peak); IR ($CHCl_3$) 1765, 1685, 1650, 1600, 1590, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.96 (d, *J*=8.6 Hz, 1-H), 7.00 (d, *J*=8.6 Hz, 2-H), 4.87 (m, 12-CH_2), 2.35 (s, OAc), 2.13 (s, 14-Me), 1.83 (t, *J*=0.9 Hz, 13-Me); ^{13}C NMR (Table 1); TLC: R_f 0.53 (benzene-AcOEt 20 : 1).

4b: Mp 66.0—67.0 °C, colorless needles (from hexane); $[\alpha]_D^{22}$ +4.8° (*c* 0.48, $CHCl_3$); UV (MeOH) 229 (ε 18600), 282 nm (18200); CD (*c* 4.78×10^{-5}, MeOH) $[\theta]_{320}$+6000; EIMS: *m/z* 230 (M^+), 188 (M^+-42, base peak); IR ($CHCl_3$) 1665, 1590, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.96 (d, *J*=8.8 Hz, 1-H), 6.82 (d, *J*=8.8 Hz, 2-H), 4.84 (m, 12-CH_2), 3.88 (s, OMe), 2.17 (s, 14-Me), 1.83 (t, *J*=1.3 Hz, 13-Me); ^{13}C NMR (Table 1); TLC: R_f 0.59 (benzene-AcOEt 20 : 1).

Found: C, 78.23; H, 7.92%. Calcd for $C_{15}H_{18}O_2$: C,78.23; H, 7.88%.

2-Hydroxyplatyphyllide (5): Mp 214.0—216.0 °C (decomp), colorless prisms (from AcOEt); $[\alpha]_D^{25}$ −66.5° (*c* 0.43, MeOH); UV (MeOH) 239 sh (ε 6600), 313 nm (4900); EIMS: *m/z* 230 (M^+), 162 (base peak); IR (KBr) 3280, 1735, 1645, 1625, 1610sh, 895 cm^{-1}; ^{1}H NMR (methanol-d_4) δ=6.95 (d, *J*=2.0 Hz, 3-H), 6.91 (dd, *J*=2.0, 1.1 Hz, 1-H), 5.26 (d, *J*=9.4 Hz, 6-H), 4.94 (m, 12-CH_2), 1.87 (t, *J*=1.1 Hz, 13-Me); ^{13}C NMR (acetone-d_6) δ=119.4 (1-C), 153.2 (2-C), 103.9 (3-C), 133.9 (4-C), 127.9 (5-C), 88.0 (6-C), 55.0 (7-C), 34.8 (8-C), 35.8 (9-C), 143.4 (10-C), 148.7 (11-C), 115.9 (12-C), 28.0 (13-C), 167.5 (14-C).

Found: C, 72.95; H, 6.12%. Calcd for $C_{14}H_{14}O_3$: C,73.02; H, 6.13%.

5a: Mp 105.0—106.0 °C, colorless needles (from hexane); $[\alpha]_D^{22}$ −44° (*c* 1.01 $CHCl_3$); UV (MeOH) 231.5 (ε 7700), 292 nm

(2600); ElMS *m/z* 272 (M^+), 230, 162 (base peak); IR (KBr) 1765, 1760, 1650, 1635, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.36 (m, 3-H), 7.14 (m, 1-H), 5.26 (d, *J*=10.1 Hz, 6-H), 4.97 (m, 12-CH_2), 2.32 (s, OAc), 1.88 (t, *J*=1.1 Hz, 13-Me); ^{13}C NMR ($CDCl_3$) δ=125.8 (1-C), 152.2 (2-C), 116.1 (3-C), 135.1 (4-C), 126.0 (5-C), 80.3 (6-C), 46.3 (7-C), 26.0 (8-C), 26.7 (9-C), 143.9 (10-C), 146.2 (11-C), 112.5 (12-C), 20.6 (13-C), 169.2 (14-C), 169.2 ($CH_3\underline{C}O$), 21.0 ($\underline{C}H_3CO$); TLC: R_f 0.72 (benzene-AcOEt 5 : 1).

5b: Mp 92.0—93.0 °C, colorless leaflets (from hexane) $[\alpha]_D^{22}$ −50.4° (*c* 0.96, $CHCl_3$); UV (MeOH) 243 (ε 4200), 308 nm (3500); EIMS *m/z* 244 (M^+), 176 (base peak); IR ($CHCl_3$) 1755, 1640, 1630, 1605, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.09 (m, 3-H), 6.95 (m, 1-H), 5.16 (d, *J*=9.6 Hz, 6-H), 4.95 (m, 12-CH_2), 3.84 (s, OMe), 1.87 (t, *J*=1.1 Hz, 13-Me); ^{13}C NMR ($CDCl_3$) δ=120.0 (1-C), 161.8 (2-C), 105.8 (3-C), 134.9 (4-C), 125.8 (5-C), 80.3 (6-C), 46.6 (7-C), 26.1 (8-C), 26.9 (9-C), 141.7 (10-C), 112.2 (12-C), 20.7 (13-C), 170.1 (14-C), 55.9 ($O\underline{C}H_3$); TLC: R_f 0.58 (benzene-AcOEt 20 : 1).

Found: C, 73.85; H, 6.63%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

Ligucyperonol (6): Mp 123.5—124.5 °C, colorless needles (from diisopropyl ether-hexane); $[\alpha]_D^{22}$ +85° (*c* 1.10, $CHCl_3$); UV (MeOH) 249 nm (ε 19200); CD (*c* 2.98×10^{-4}, MeOH, 25 °C) $[\theta]_{245}$+37600, $[\theta]_{317.8}$−8300; EIMS *m/z* 234 (M^+), 216, 191, 190, 147 (base peak); IR ($CHCl_3$) 3600, 3420,1660, 1610, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.78 (d, *J*=1.1 Hz, 12-CH_2), 3.83 (ddd, *J*=11, 7.1, 5.2 Hz, 1-H), 2.70 (dd, *J*=7.1, 18 Hz, 2α-H), 2.50 (dd, *J*=11, 18 Hz, 2β-H), 1.78 (s, 14-Me), 1.77 (d, *J*=1.1 Hz, 13-Me), 1.18 (s, 15-Me); ^{13}C NMR (Table 2); TLC: R_f 0.25 (benzene-AcOEt 5 : 1).

Found: C, 76.78; H, 9.37%. Calcd for $C_{15}H_{22}O_2$: C,76.88; H, 9.46%.

6a: Colorless oil; $[\alpha]_D^{22}$ +23° (*c* 0.81, $CHCl_3$); UV (MeOH) 248 nm (ε 21000); IR ($CHCl_3$) 1745, 1670, 1610, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.05 (dd, *J*=11.6, 6.2 Hz, 1-H), 4.79 and 4.78 (each d, *J*=1.1 Hz, 12-CH_2), 2.77 (dd, *J*=6.2, 17 Hz, 2α-H), 2.56 (dd, *J*=11.6, 17 Hz, 2β-H), 2.08 (s, OAc), 1.78 (s, 14-Me), 1.77 (d, *J*=1.1 Hz, 13-Me), 1.24 (s, 15-Me); ^{13}C NMR (Table 2); TLC: R_f 0.72 (benzene-AcOEt 5 : 1).

Found: *m/z* 276.1685. Calcd for $C_{17}H_{24}O_3$: M, 276.1719.

3-*O*-Methyldihydroligudentatol 8b from 3-*O*-Methylligujapone 4b. a) To a mixture of **4b** (50 mg) and 1,2-ethanedithiol (0.5 ml), BF_3-etherate (0.5 ml) was added with ice cooling at 0 °C and under stirring. The mixture was kept at room temperature for 3.5 h, diluted with MeOH (2 ml) and concentrated under reduced pressure. The resulting pale-yellow oil was chromatographed over silica gel (20 g, hexane-ether 5 : 1) to afford a thioacetal (**7**) (55 mg, 82%); $[\alpha]_D^{22}$ +55° (*c* 1.72, $CHCl_3$); IR ($CHCl_3$) 1600, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.84 (d, *J*=8.8 Hz, 1-H), 6.77 (d, *J*=8.8 Hz, 2-H), 3.80 (s, OMe), 3.51 (m, acetal CH_2), 2.81 (m, acetal CH_2), 2.10 (s, 14-Me), 1.43 (s, 12-Me), 1.32 (s, 13-Me); TLC: R_f 0.61 (hexane-ether 5 : 1).

Found: *m/z* 400.1016. Calcd for $C_{19}H_{28}OS_4$: M, 400.1013.

b) The thioacetal **7** (40 mg) was heated under reflux with Raney Ni (2.5 g) in EtOH (30 ml) for 6 h. The combined filtrates were evaporated in vacuo to give a colorless oil (20 mg) which was purified by preparative TLC (elution with hexane, 4 times) to give 3-*O*-methyldihydroligudentatol (**8b**) (13 mg, 58%).

8b: Colorless oil, $[\alpha]_D^{22}$ +67° (*c* 1.25, $CHCl_3$); IR ($CHCl_3$) 1600, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.91 (br d, *J*=8.5 Hz, 1-H), 6.66 (d, *J*=8.5 Hz, 2-H), 3.79 (5, OMe), 2.12 (s, 14-Me), 0.97 and 0.96 (each d, *J*=6.4 Hz, 12- and 13-Me); ^{13}C NMR (Table 1); TLC: R_f 0.37 (hexane).

Found: *m/z* 218.1656. Calcd for $C_{15}H_{22}O$: M, 218.1665.

Hydrogenation of 3-*O*-Methylligudentatol 2b. A solution of **2b** (6 mg) in EtOH (0.2 ml) was hydrogenated at room temperature and under atmospheric pressure in the presence of Adams' catalyst (3 mg) for 40 min to quantitatively afford 3-*O*-methyldihydroligudentatol (**8b**) (6 mg) as a colorless oil; $[\alpha]_D^{24}$ +67° (*c* 0.25, $CHCl_3$). This was found to be identical in all respects ($[\alpha]_D$, IR, and ^1H NMR) with **8b** converted from 3-*O*-methylligujapone **4b** (described above).

Hydrogenation of Ligujapone 4. a) A solution of **4** (40 mg) in acetic acid (2 ml) was hydrogenated with 5% Pd-C (40 mg) for 16 h. The filtrate was evaporated in vacuo and the residual pale-yellow oil chromatographed on silica gel (10 g) to furnish dihydroligudentatol (**8**) as a colorless oil (37.6 mg, 92%); $[\alpha]_D^{23}$ +71.6° (*c* 0.19, $CHCl_3$); UV (MeOH) 281 nm (ε 3500); IR (neat 3400, 1600, 1490, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.82 (d, *J*=8.3 Hz, 2-H), 6.57 (d, *J*=8.3 Hz, 1-H), 4.50 (s, OH), 2.13 (s, 14-Me), 0.98 (d, *J*=5.5 Hz, 12-Me), 0.97 (d, *J*=6.4 Hz, 13-Me); ^{13}C NMR (Table 1).

Acetylation of **8** (11.9 mg) was carried out in the usual manner with Ac_2O (0.5 ml) and pyridine (0.25 ml) to give (**8a**) (10.7 mg, 77%).

8a: Colorless oil, $[\alpha]_D^{22}$ +45° (*c* 0.10, $CHCl_3$); UV (hexane) 228 (ε 1700), 256.5 (400), 265.3 (300), 275.0 nm (400); IR (neat) 1770, 1600, 1220, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.95 (d, *J*=8.9 Hz, 2-H), 6.75 (d, *J*=8.9 Hz, 1-H), 2.32 (s, OAc), 2.03 (s, 14-Me), 0.98 (d, *J*=5.3 Hz, 12- and 13-Me); ^{13}C NMR (Table 1).

Found: *m/z* 246.1625. Calcd for $C_{16}H_{22}O_2$: M, 246.1614.

b): A soln of **4** (60.3 mg) in EtOH (1 ml) was hydrogenated with 5% Pd-C for 1.5 h. The filtrate was evaporated in vacuo to afford a semicrystalline product, which was crystallized from diisopropyl ether to give dihydroligujapone (**10**) as colorless prisms, mp 176.0—177.0 °C, $[\alpha]_D^{22}$ +21.3° (*c* 0.16, $CHCl_3$); UV (MeOH) 231 (ε 18000), 286 nm (20000); IR (KBr) 3150, 1650, 1580, 1290, 840 cm^{-1}; CD (*c* 3.93×10^{-4}, MeOH, 22 °C) $[\theta]_{316}$+6570; ^1H NMR ($CDCl_3$) δ=7.86 (d, *J*=8.6 Hz, 1-H), 6.73 (d, *J*=8.6 Hz, 2-H), 5.74 (d, *J*=2.0 Hz, OH), 2.21 (s, 14-Me), 1.00 (d, *J*=7.7 Hz, 12- and 13-Me).

Found: *m/z* 218.1336. Calcd for $C_{14}H_{18}O_2$: M, 218.1302.

Hydrogenation of Ligudentatol Acetate 2a. A soln of **2a** (40 mg) in EtOH (0.5 ml) was hydrogenated with Adams' catalyst (16 mg) for 2.5 h. The filtrate was evaporated in vacuo to afford dihydroligudentatol acetate (**8a**) as a colorless oil (26 mg, 89%). This sample was found to be identical in all respects ($[\alpha]_D$, IR, and ^1H NMR) with **8a** transformed from ligujapone **4** by hydrogenation and acetylation (described above).

Dehydration of Ligucyperonol 6. A mixture of **6** (16 mg) and AcONa (56 mg) in Ac_2O (1 ml) was refluxed for 11 h. The reaction mixture was decomposed with ice-water and then extracted with ether. Working-up as usual gave a pale-yellow oil (15 mg), which was purified by preparative TLC (benzene-AcOEt 30 : 1) to afford eudesma-1,4,11-trien-3-one (**12**) (14 mg, 95%).

12: Colorless oil, $[\alpha]_D^{22}$ −149° (*c* 0.52, $CHCl_3$); UV (MeOH) 240 (ε 11000), 265.5 nm (7700); IR (neat) 1660, 1625, 1610 cm^{-1} (α,β-unsaturated CO); ^1H NMR ($CDCl_3$) δ=6.77 (d, *J*=9.9 Hz, 1-H), 6.23 (d, *J*=9.9 Hz, 2-H), 4.81 (d, *J*=1.1 Hz, 12-CH_2), 1.92 (d, *J*=1.1 Hz, 14-Me), 1.80 (t, *J*=1.1 Hz, 13-Me), 1.25 (s, 15-Me); ^{13}C NMR (Table 2); TLC: R_f 0.31 (benzene-AcOEt

30 : 1).

Found: *m/z* 216.1513. Calcd for $C_{15}H_{20}O$: M, 216.1509.

Eudesma-1,4,11-trien-3-one 12 from (+)-α-Cyperone 11. a) Isolation of (+)-α-Cyperone 11: The commercial drug "Ko-bushi", the dried rizomes (5 kg) of *Cyperus rotundus* Linne of the Chinese origin, were powdered and extracted with ether at room temperature for 3 days. Removal of the solvent afforded a dark oil (50.6 g). The crude extract (6.7 g) was steam-distilled to give a light-brown oil (2.03 g), which was subjected to centrifugal chromatography (silica gel KT-2061, 100 g; hexane-ether 50 : 1) to furnish a pale-yellow oil (387 mg), including (+)-α-cyperone (**11**) as the main component (5.8% based on the crude extract). The above oil (2.57 g) was treated with semicarbazide acetate and the resulting solid was recrystallized from EtOH to afford (+)-α-cyperone semicarbazone (1.325 g) as colorless prisms; mp 209.0—210.0 °C. Pure (+)-α-cyperone (**11**) was obtained from the above semicarbazone by steam distillation with saturated aqueous oxalic acid, followed by redistillation, bp 120—125 °C (bath temp)/0.1 mmHg (ca. 13.3 pa), and preparative GLC: Thermon 1000, column temperature 170 °C, H_2-flow rate 80 ml min^{-1}, retention time 12.6 min; $[\alpha]_D^{22}$ +119° (*c* 1.32, $CHCl_3$); UV (MeOH) 250 (ε 8400), 299 nm (1450); IR (neat) 1660, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.78 (d, *J*=1.1 Hz, 12-CH_2), 1.78 (t, *J*=1.1 Hz, 13-Me), 1.78 (s, 14-Me), 1.22 (s, 15-Me); ^{13}C NMR (Table 2).

Found: *m/z* 218.1690. Calcd for $C_{15}H_{22}O$: M, 218.1665.

b) Dehydrogenation of (+)-α-Cyperone 11 with DDQ. A solution of **11** (399 mg) and DDQ (827 mg) in dry dioxane (30 ml) was refluxed for 20 h. After filtration and concentration of the filtrate, the residual oil was diluted with ether, then washed with aqueous 1% NaOH and water. Working-up the dried solution in the usual manner gave a brown oil (338 mg), which was chromatographed on silica gel (67 g) and eluted with benzene-AcOEt (100 : 1) to give dehydroligucyperonol (eudesma-1,4,11-trien-3-one) (**12**), as a pale-yellow oil (237 mg, 60%). Pure **12**, a colorless oil, $[\alpha]_D^{22}$ −167° (*c* 0.27, $CHCl_3$), was obtained by preparative GLC: Thermon 1000, column temperature 170 °C, H_2-flow rate 100 ml min^{-1}, retention time 13.2 min; analytical GLC: Thermon 1000, column temperature 180 °C, N_2-flow rate 50 ml min^{-1}, retention time 18.0 min. This sample was identical in all respects with **12** prepared by the dehydration of **6** (described above).

Preparation of Eudesma-1,4,6-trien-3-one 13. (A) By Isomerization of Eudesma-1,4,11-trien-3-one 12: a) A mixture of **12** (39 mg) in aqueous 50% H_2SO_4 (1 ml) was stirred at 35 °C for 2 h. Dilution with water, extraction with ether, and working up as usual gave a crude oil (25 mg), which was purified by preparative TLC (R_f 0.23, benzene-AcOEt 10 : 1) to afford eudesma-1,4,6-trien-3-one (**13**) (9 mg, 23%).

13: Colorless oil, $[\alpha]_D^{22}$ +321° (*c* 0.40, $CHCl_3$); UV (MeOH) 228 (ε 17800), 315 nm (17400); IR (neat) 1650, 1605^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.73 (d, *J*=9.7 Hz, 1-H), 6.41 (s, 6-H), 6.23 (d, *J*=9.7 Hz, 2-H), 1.13 (each d, *J*=6.8 Hz, 12- and 13-Me); ^{13}C NMR (Table 2).

Found: *m/z* 216.1515. Calcd for $C_{15}H_{20}O$: M, 216.1509.

b) A mixture of **12** (47 mg) and Amberlist **15** (47 mg) in dry benzene (0.6 ml) was heated at 70 °C for 2 h. Filtration and removal of the solvent left a yellow oil (39 mg), which was subjected to preparative TLC (R_f 0.20, benzene-AcOEt 15 : 1) to give **13**, as a colorless oil (22 mg, 56.5%). This was identical in all respects with the above **13**.

(B) Isomerization and Dehydrogenation of (+)-α-Cyperone 11: a-i) A mixture of **11** (81.9 mg) in aqueous 50% H_2SO_4 (2 ml) was stirred at 0 °C for 10 h. Working-up as usual afforded an oil (83 mg), which was purified by preparative TLC (R_f 0.72, benzene-AcOEt 3 : 1), gave β-cyperone (**14**) as a colorless oil (56 mg, 67.5%).

a-ii) A mixture of **11** (93 mg) in dry benzene (0.6 ml) and Amberlist 15 (93 mg) was heated at 70 °C for 1.5 h. Filtration and removal of the solvent afforded β-cyperone (**14**) as a pale-yellow oil (88 mg, 95%), which was purified in a similar manner as above to afford a colorless oil; $[\alpha]_D^{20}$ +232° (*c* 0.505, $CHCl_3$); UV 299.5 nm (ε 7000); IR (neat) 1650, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.29 (br s, 6-H), 1.83 (s, 14-Me), 1.12 (each d, *J*=6.8 Hz, 12- and 13-Me), 1.09 (s, 15-Me); ^{13}C NMR (Table 2).

Found: C, 82.30; H, 10.25%. Calcd for $C_{19}H_{22}O$: C, 82.51; H, 10.16%.

b) A solution of β-cyperone **14** (12.6 mg) in dry dioxane (1.5 ml) and DDQ (26.2 mg) was refluxed for 20 h. After filtration and concentration of the solution, the residue was diluted with ether, then washed with aqueous 1% NaOH and water. Working up as usual gave a brown oil (13.2 mg), which was purified by preparative TLC (R_f 0.20, benzene-AcOEt 20 : 1) to furnish a colorless oil (3.2 mg, 25.4%). This product was identical in all repects (TLC, IR, and ^{1}H NMR) with the substance **13** prepared by method (**A**) (described above).

References

1) K. Naya, M. Fujiwara, T. Okayama, and S. Kurio, 30th Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics, Hiroshima, Sept. 1986, Symposium Papers, p. 152.

2) F. Patil, G. Ourisson, Y. Tanahashi, M. Wada, and T. Takahashi, *Bull. Soc. Chim. France*, **1968**, 1047; Y. Tanahashi, Y. Ishizuka, and T. Takahashi, *Tetrahedron Lett.*, **1968**, 3739; Y. Moriyama, T. Sato, H. Nagano, Y. Tanahashi, and T. Takahashi, *Chem. Lett.*, **1972**, 637; H. Nagano and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **45**, 1935 (1973); M. Tada, Y. Moriyama, Y. Tanahashi, and T. Takahashi, *Tetrahedron Lett.*, **1972**, 5251; H. Nagano, Y. Tanahashi, Y. Moriyama, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **46**, 2840 (1973); M. Tada, Y. Moriyama, Y. Tanahashi, and T. Takahashi, *ibid.*, **47**, 1999 (1974); H. Nagano and T. Takahashi, *ibid.*, **51**, 3335 (1978); Y. Ishizuka, Y. Tanahashi, T. Tsuyuki, T. Takahashi, and K. Tori, *ibid.*, **52**, 1182 (1979)

3) F. Bohlmann, D. Ehlers, C. Zdero, and M. Grenz, *Chem. Ber.*, **110**, 2640 (1977).

4) F. Bohlmann and K. H. Knoll, *Phytochemistry*, **18**, 877 (1979)

5) F. Bohlmann and C. Zdero, *Phytochemistry*, **19**, 1550 (1980)

6) F. Bohlmann and U. Fritz, *Phytochemistry*, **19**, 2471 (1980)

7) H. Ishii, T. Tozyo, and H. Minata, *Tetrahedron*, **21**, 2065 (1965); H. Ishii, T. Tozyo, and H. Minato, *J. Chem. Soc. C*, **1966**, 1545; H. Ishii, T. Tozyo, M. Nakamura, and H. Minato, *Tetrahedron*, **26**, 2911 (1970); T. Kurihara and S. Suzuki, *Yakugaku Zasshi*, **97**, 863 (1977); *ibid.*, **98**, 1441 (1978).

8) "Spectral Atlas of Terpenes and the Related Com-

pounds," ed by Y. Yukawa and S. Ito, Hirokawa, Tokyo (1973), p. 38.

9) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon, London (1969), p. 202.

10) M. Christl, H. J. Reich, and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 3463 (1971).

11) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

12) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 1347 (1970).

13) E. Breitmair and W. Voelter, "Carbon-13 NMR Spectroscopy," 3rd ed, VCH Verlag., Weinheim (1987), p. 54.

14) J. Barry, H. B. Kagan, and G. Snatzke, *Tetrahedron*, **27**, 4737 (1971).

15) D. L. Roberts, *Phytochemistry*, **11**, 2077 (1972): A formula "1-keto-α-cyperone" was assigned to a compound isolated from tobacco and the structure **6** was also given to its reduction product with Zn dust-AcOH. Later, the structure was revised to "1-keto-α-cyperone" in Ref. 16.

16) A. Murai, M. Ono, A. Abiko, and T. Masamune, *Chem. Lett.*, **1978**, 1005.

17) C. Djerassi, R. Records, E. Bunnenberg, K. Mislow, and A. Mocowitz, *J. Am. Chem. Soc.*, **84**, 870 (1962).

18) G. Snatzke, *Tetrahedron*, **21**, 413, 421, 439 (1965).

19) R. Howe and F. J. McQuillin, *J. Chem. Soc.*, **1955**, 2423.

20) A. Sannai, T. Fujimori, and K. Kato, *Phytochemisty*, **21**, 2986 (1982).

21) H. Hikino, K. Aota, and T. Takemoto, *Chem. Pharm. Bull.*, **14**, 894 (1966).

22) F. J. McQuillin, *J. Chem. Soc.*, **1955**, 528.

23) D. H. R. Barton and E. Tarlton, *J. Chem. Soc.*, **1954**, 3492.