April 1999 Notes Chem. Pharm. Bull. **47**(4) 557—560 (1999)

Five New *cis*-Himachalane-Type Sesquiterpenes from the Heartwood of *Juniperus chinensis* var. *tsukusiensis*

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The following constituents were isolated from the heartwood of *Juniperus chinensis* var. *tsukusiensis*: *ar*-himachalene (1), 2-himachalen-6-ol (2), 3-himachalen-6-ol (3), 2α,6α-epoxy-3-himachalene (4), 2α,6α-epoxyhimachalan-3β-ol (5), and chinensiol (6). Compounds 2—6 are new *cis*-himachalane-type sesquiterpenes, and their structures were elucidated on the basis of spectral and chemical evidence. Himachalane-type sesquiterpenes were isolated for the first time in *Juniperus* species.

Key words *Juniperus chinensis*; Cupressaceae; *cis*-himachalane sesquiterpene; 2α,6α-epoxy-3-himachalene; 2α,6α-epoxyhimachalen-3-ol

The components of *Juniperus* species (Cupressaceae) contain many natural products with various skeletons.[1)] We have examined the chemical principles of the heartwood of *J. squamata* LAMB. var. *morrisonicola* HAY.,[2)] the heartwood of *J. formosana* HAY.,[3)] the roots of *J. chinensis* LINN.,[4)] bark of *J. chinense* LINN. var. *kaizuca* HORT. *ex* ENDL.,[5)] and the bark and heartwood of *J. formosana* HAY. var. *concolar* HAY.,[6)] which are all indigenous to Taiwan. Recently, we have investigated other indigenous species of *Juniperus*, including *J. chinensis* LINN. var. *tsukusiensis* MASAM.,[7)] and found two new sesquiterpene alcohols, 12-hydroxy-α-longipinene and 15-hydroxyacora-4(14),8-diene. We have now reinvestigated the same extract from the heartwood of the same plant, and found six himachalane-type sesquiterpenes, one known *ar*-himachalene (**1**)[8)] together with five new: 2-himachalen-6-ol (**2**), 3-himachalen-6-ol (**3**), 2α,6α-epoxy-3-himachalene (**4**), 2α,6α-epoxyhimachalan-3β-ol (**5**), and chinensiol (**6**) isolated in that elution order. In this paper we describe the structural elucidation of the five new *cis*-himachalane-type sesquiterpenes **2**—**6**.

Chinensiol (**6**),[4b)] reported in the previous communication, was elucidated in detail as follows. It has the molecular formula $C_{30}H_{50}O_3$ on the basis of elemental analysis. The electron impact mass spectrum (EI-MS) shows fragmentation peaks at 220 (16%) and 202 (20%). However, the FAB-MS (positive) exhibits a quasi-molecular ion peak at 459 [$(M+H)^+$, 2%] and fragment peaks at 333 (12%), 285 (35%), 221 (100%), 203 (221-H_2O, 80%). The structures of fragment ions at 220 and 202 were proposed to be structures **7** and **8**, respectively. The IR spectrum expresses absorptions at 3322 (OH), 3010 (=C–H), 1650 and 829 (–C=CH–), and 1040 cm^{-1} (C–O); and the ^{1}H-NMR spectrum (Table 1) exhibits signals at δ 0.90 and 1.15 (s, each 3H), 1.01 (d, 3H, J=6.9 Hz), 4.06 (br s, 2H, CH_2OH), and 5.72 (br d, 1H, J=2.2 Hz, H-2). Due to the fact that only three methyl groups and one hydroxymethyl group, together with about 24 protons, are estimated from the ^{1}H-NMR spectrum, chinensiol (**6**) was considered to be a dimeric sesquiterpenoid. The acetylation of chinensiol (**6**) with acetic anhydride in pyridine at room temperature gave the acetate **9** (amorphous; ν_{max} 1735, 1231, and 1026 cm^{-1}; no hydroxyl group absorption band was observed). The ^{1}H-NMR spectrum of acetate **9**

Table 1. ^{1}H-NMR Data for **2**—**6**

δ_H	**2**[a)]	**3**[a)]	**4**[a)]	**5**[b)]	**6**[a)]
1	1.90 (α)[c)] (br s)	1.60 (α)[d)]	1.67 (α) (s)	1.78 (α) (s)	2.01 (α) (d, 2.2)
2	5.41 (br s)	2.00 (β)[d)] 1.86 (α)[d)]	3.78 (β) (s)	2.95 (β) (s)	5.72 (br d, 2.2)
4	1.97 (α) (m) 1.74 (β) (m)	5.32 (br m)	5.38 (br s)	1.81 (m)	2.14 (m)
5	1.57 (α) (m) 2.00 (β) (m)	2.33 (β) (br m) 1.80 (α) (br m)	2.12 (β) (m) 2.05 (α) (m)	1.54 (m)	1.83 (α) (m) 1.66 (β) (m)
7	2.03 (α) (m)	1.82 (α) (m)	2.05 (α) (m)	2.01 (α)	2.07 (α) (m)
8	1.51 (α) (m) 1.32 (β) (m)	1.84 (m) 1.60 (m)	1.67 (m)	1.68 (m) 1.33 (m)	1.48 (β) (m) 1.38 (β) (m)
9	1.55 (m)	1.82 (m)	1.67 (m) 1.52 (m)	1.56 (m) 1.28 (m)	1.60 (m)
10	1.56 (α) (m) 1.44 (β) (m)	1.76 (m)	1.65 (m) 1.52 (m)	1.58 (m) 1.30 (m)	1.53 (α) (m) 1.50 (β) (m)
12	0.85 (s)	1.24 (s)	1.10 (s)	1.06 (s)	0.90 (s)
13	1.07 (s)	1.30 (s)	0.63 (s)	1.26 (s)	1.15 (s)
14	0.99 (d, 6.8)	0.81 (d, 6.8)	0.95 (d, 6.8)	0.98 (d, 7.2)	1.01 (d, 6.9)
15	1.69 (s)	1.59 (s)	1.84 (s)	1.27 (s)	4.06 (br s)

a) 400 MHz in $CDCl_3$, (mult, J=Hz); assignment from ^{1}H, ^{13}C, DEPT, COSY, HMQC, and HMBC. *b*) 400 MHz in acetone-d_6. *c*) Stereochemistry assigned from the NOESY spectra. *d*) Obscured by other signals.

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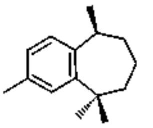
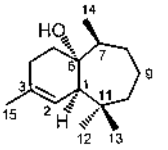
Table 2. ^{13}C-NMR Data for **2**—**6**

δ_C	**2**$^{a)}$	**3**$^{a)}$	**4**$^{a)}$	**5**$^{b)}$	**6**$^{a)}$
1	59.3 (d)	57.5 (d)	60.9 (d)	57.3 (d)	58.8 (d)
2	123.5 (d)	27.7 (t)	72.1 (d)	62.2 (d)	124.9 (d)
3	134.2 (s)	133.3 (s)	136.7 (s)	58.2 (s)	137.3 (s)
4	27.6 (t)	121.6 (d)	119.6 (d)	28.0 (t)	23.3 (t)
5	27.7 (t)	33.5 (t)	30.5 (t)	31.2 (t)	26.6 (t)
6	75.9 (s)	73.9 (s)	78.0 (s)	74.4 (s)	76.3 (s)
7	40.7 (d)	41.0 (d)	40.8 (d)	44.4 (d)	41.3 (d)
8	29.7 (t)	30.1 (t)	31.9 (t)	32.2 (t)	29.8 (t)
9	23.8 (t)	26.0 (t)	19.7 (t)	28.4 (t)	24.2 (t)
10	38.8 (t)	31.7 (t)	40.3 (t)	39.0 (t)	38.6 (t)
11	37.2 (s)	44.4 (s)	35.1 (s)	37.2 (s)	37.1 (s)
12	25.7 (q)	30.6 (q)	34.2 (q)	32.5 (q)	31.4 (q)
13	32.0 (q)	30.9 (q)	22.5 (q)	28.6 (q)	26.6 (q)
14	17.9 (q)	18.0 (q)	16.8 (q)	18.3 (q)	17.8 (q)
15	23.5 (q)	23.3 (q)	21.0 (q)	22.4 (q)	67.1 (q)

a) 100 Hz in $CDCl_3$, (mult); assignment from ^{1}H, ^{13}C, DEPT, COSY, HMQC, and HMBC. *b)* 100 Hz in acetone-d_6.



1



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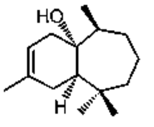

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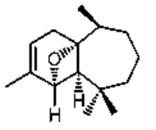

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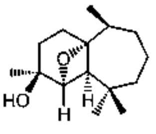

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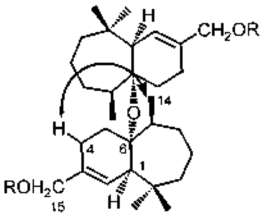
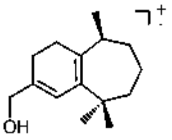
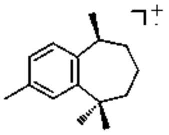


6 R=II
9 R=Ac



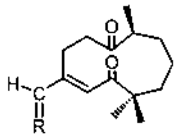
7

m/z 220



8

m/z 202



10 R=O
11 R=H, OH

showed one acetoxymethylene absorption signal [δ 2.05 (s, 3H) and 4.52 (br s, 2H)]. From the above evidence, we took two oxygen atoms into account as two primary alcohols; the remaining oxygen atom was considered to be an ether linkage. This conclusion was confirmed by the ^{13}C-NMR (Table 2) spectrum of chinensiol (**6**). The absorption signals at δ 67.1 [CH_2: by distortionless enhancement by olarization transfer (DEPT) method] and 76.3 (C) concern two carbons bearing one oxygen atom each. By the DEPT method, the chinensiol (**6**) is shown to contain three primary carbons, six secondary carbons, three tertiary carbons, and three quaternary carbons. Twenty-five hydrogen atoms (including one hydrogen atom from the hydroxyl group) on chinensiol (**6**) were estimated from the above carbon state. The result confirmed that chinensiol (**6**) is a dimeric sesquiterpene with ether linkage. The structure of chinensiol was deduced, as shown in formula **6** by interpretation of the ^{1}H–^{13}C correlation spectroscopy (COSY) spectrum of chinensiol and heteronuclear multiple-bond correlation spectroscopy (HMBC) correlations. In addition, **6** gave *ar*-himachalene (**1**) in acidic acetone solution. Chinensiol is a dimeric himachalene-type sesquiterpene. Irradiation of H_3-14 (at δ 1.03) caused nuclear Overhauser enhancements on H_b-4 (19%); this experiment indicates two results. One is that a himachalene-type sesquiterpene is a *cis*-fused ring. The second is that the secondary methyl group (H_3-14) was considered to be on the β-face (*trans* to ether linkage). The dimeric himachalene-type sesquiterpene was observed for the first time, and this type of himachalene sesquiterpene was isolated for the first time in *Juniperus* species.

We tried to oxidize the chinensiol (**6**) with pyridinium chlorochromate (PCC) in dichloromethane, and **6** yielded an unexpected product, **10** [mp 84—85 °C; $\nu_{\max}$ 1690; $\lambda_{\max}^{\mathrm{MeOH}}$: 206, 230, 280 nm; δ 0.97 (d, 3H, J=7.8 Hz), 1.10 and 1.21 (s, each 3H), 7.20 (br s, 1H) and 9.50 (s, 1H)]. The structure of the eleven-member ring product **10** was confirmed by an X-ray diffraction.[4b)] The formation pathway of product **10** is that the first intermediate **7** obtained from **6** *via* acidic elimination was subsequently oxidized with PCC to yield product **11**. The dione alcohol **11** was subsequently oxidized with PCC to obtain **10**. If the primary alcohol was first oxidized with PCC, the double bond would not be converted to a dione. The oxidation of enol ether with PCC was reported by Piancatelli,[9)] but the oxidation of tetraalkyl-substituted olefin with PCC has not been observed.

2-Himachalen-6-ol (**2**) was isolated as a viscous liquid. Its molecular formula $C_{15}H_{26}O$ derived from HR-EI-MS, indicated three degrees of unsaturation. It shows an IR absorption bonds at 3478 (–OH) and the ^{1}H-NMR spectrum (Table 1) suggests that **2** has two singlet methyl groups [δ 0.85 and 1.07 (s, 3H each)], one doublet methyl group [δ 0.99 (d, 3H, J=6.8 Hz)], a methyl group attached to olefin [δ 1.69 (s, 3H)], and a trisubstituted olefinic proton [δ 5.41(br s, 1H)]. The ^{13}C-NMR data (Table 2) of **2** show that it contains four methyl groups (δ 17.9, 23.5, 25.7, 32.0), a trisubstituted olefin (δ 123.5, 134.2), five secondary carbons, two tertiary carbons, and two quaternary carbons (δ 75.9, with one carbon bearing a hydroxy group), based on a DEPT experiment. From the above evidence, **2** is a bicyclic sesquiterpene containing an endocyclic double bond. Comparison of the ^{1}H- and ^{13}C-NMR data of **2** with chinensiol (**6**) suggests that **2** possesses the same carbon skeleton of the monomer as **6** with a methyl group instead of a hydroxymethyl group. The structure of **2** was deduced to be as shown (2-himachalen-6-ol) on the basis of heteronuclear multiple-quantum coherence (HMQC), HMBC (Fig 1) and ^{1}H–^{1}H COSY spectra (^{1}H–^{1}H COSY correlation between H-4 and H-5, H-7 and H-14, and H-9 and H-8, H-10). The nuclear Overhauser effect (NOE) correlations (Fig. 2) of **2** confirmed the stereochemistry. According to the nuclear Overhauser enhancement and exchange spectroscopy (NOESY) experiment, the himachalene-type sesquiterpene is *cis* fused ring (not *trans*),[10)] and the secondary methyl group was considered to be on the β-face (*trans* to the hydroxy group).

3-Himachalen-6-ol (**3**), a viscous liquid, has the molecular formula $C_{15}H_{26}O$ on the basis of the exact mass of *m*/*z* 222.1992. It shows an IR absorption band at 3356 (–OH),

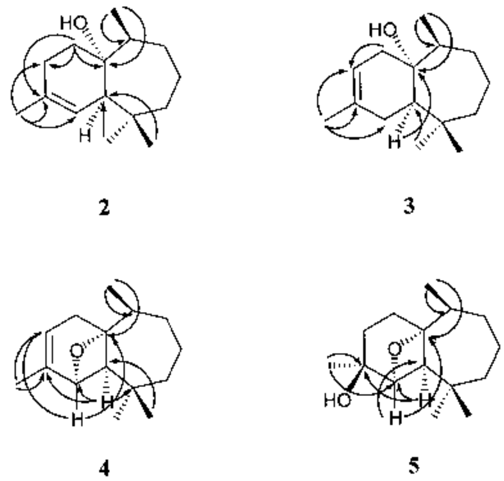

2 3 4 5

Fig. 1. Major HMBC of **2**, **3**, **4** (300 MHz in $CDCl_3$) and **5** (400 MHz in Acetone-d_6)

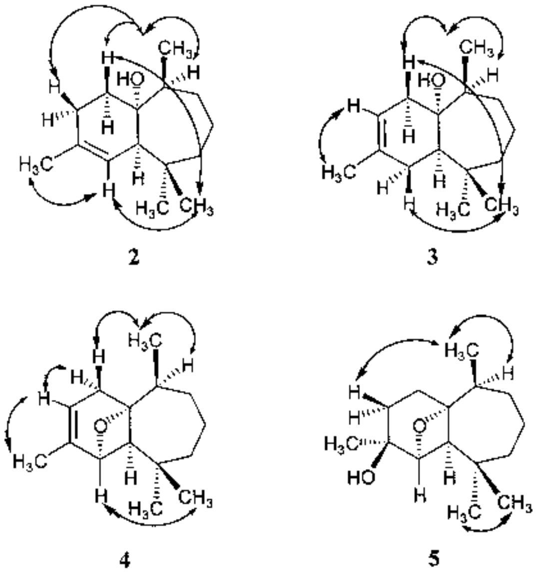

2 3 4 5

Fig. 2. Major NOE's Observed in the NOESY Spectra of **2**, **3**, **4** (400 MHz in $CDCl_3$) and **5** (400 MHz in Acetone-d_6)

and the ^{1}H-NMR spectrum (Table 1) indicates that **3** has two singlet methyl groups [δ 1.24 and 1.30 (s, each 3H)], one doublet methyl group [δ 0.81 (d, 3H, J=6.8 Hz)], a methyl group attached to olefin [δ 1.59 (s, 3H)], and a trisubstituted olefinic proton [δ 5.32 (m, 1H)]. The ^{13}C-NMR data (Table 2) of **3** show that it contains four methyl groups (δ 18.0, 23.3, 30.6, 30.9), a trisubstituted olefin (δ 121.6, 133.3), five secondary carbons, two tertiary carbons, and two quaternary carbons (δ 73.9, concerns one carbon bearing a hydroxy group), based on a DEPT experiment. From the above evidence, **3** is a bicyclic sesquiterpene containing an endocyclic double bond. Comparison of the ^{1}H- and ^{13}C-NMR data of **3** with that of **2** suggested that **3** possesses the same carbon skeleton as **2** with an olefin positioned from C-2 to C-3. The structure of **3** was deduced to be as shown (3-himachalen-6-ol) on the basis of HMQC, HMBC (Fig 1) and ^{1}H–^{1}H COSY spectra (^{1}H–^{1}H COSY correlation between H-1 and H-2, H-4 and H-5, H-7 and H-14, and H-9 and H-8, H-10). The NOE correlations (Fig. 2) of **3** confirmed the stereochemistry as **2**.

2α,6α-Epoxy-3-himachalene (**4**), a viscous liquid, has the molecular formula $C_{15}H_{24}O$ based on HR-MS. It shows an IR absorption band at 1027 (C–O). The ^{1}H-NMR spectrum (Table 1) indicates that **4** has two singlet methyl groups [δ 0.63 and 1.10 (s, each 3H)], one doublet methyl group [δ 0.95 (d, 3H, J=6.8 Hz)], a methyl group attached to an olefin [δ 1.84 (s, 3H)], and a trisubstituted olefinic proton [δ 5.38 (br s, 1H)]. The ^{13}C-NMR data (Table 2) of **4** showed that it contains four methyl groups (δ 16.8, 21.0, 22.5, 34.2), a trisubstituted olefin (δ 119.6, 136.7), four secondary carbons, three tertiary carbons, and two quaternary carbons (δ 72.1 and 78.0 concern two carbons bearing one oxygen atom), based on a DEPT experiment. On the basis of the above spectra and molecular formula, **4** appears to be a tricyclic sesquiterpene containing an endocyclic double bond. Compound **4** exhibited the same carbon skeleton as **3** except for a four-member ring epoxy group instead of a hydroxyl group. The relative stereochemistry of **4** was deduced from a NOESY (Fig. 2) study. In addition, the complete HMQC, HMBC (Fig. 1), and ^{1}H–^{1}H COSY spectra (^{1}H–^{1}H COSY correlation presented between H-4 and H-5, H-7 and H-14, and H-9 and H-8, H-10) data suggested the overall structure to be as shown.

The fifth new himachalane derivative, 2α,6α-epoxyhimachalan-3β-ol (**5**), was isolated as a viscous liquid. It had the molecular formula $C_{15}H_{26}O_2$ based on HR-MS and contained a hydroxyl group due to a discernible absorption band at 3436 cm^{-1}. Comparing the ^{1}H- and ^{13}C-NMR spectral data of **5** with those of **4**, the main skeleton of **5** was in accord with **4** except that the olefinic function in **4** was hydrated in **5**. Compound **5** was completely converted to **4** in $CDCl_3$ solution at room temperature for 7 d. This result proved that the axial orientation hydroxyl group in **5** was an easy dehydration axial orientation. Compound **4** or **5** was treated with p-TsOH in acetone solution under room temperature for one day to yield **1**. Compound **5** was assigned as 2α,6α-epoxyhimachalan-3β-ol on the basis of the above evidence. Further proof for the structure of **5** was deduced from HMQC, HMBC (Fig. 1) and ^{1}H–^{1}H COSY spectra (^{1}H–^{1}H COSY correlation between H-4 and H-5, H-7 and H-14, H-9 and H-8, H-10). The NOE correlations (Fig. 2) of **5** confirmed its stereochemistry.

Experimental

General Procedures All evaporations were carried out under reduced pressure. Merck 60 (70—230 mesh and 230—400 mesh) Si gels were used for column and flash chromatography. Precoated plates of Merck Si F_{254} were used for TLC. HPLC: Merck-LiChrosorb Si-60 (7 μm), in both cases with a 250×10 mm column; solvent flow 2 ml min^{-1}. Polarimetric data: JASCO-DIP-1000 digital polarimeter. IR spectra were recorded on a Perkin Elmer 983G spectrometer. NMR: ^{1}H- and ^{13}C-NMR spectra were run on a Varian-Unity plus 400 (^{13}C at 100 MHz, ^{1}H at 400 MHz), and Bruker DMX-300 (^{13}C at 75 MHz, ^{1}H at 300 MHz) in $CDCl_3$ or acetone-d_6 solution with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ-values, and coupling constants (J) in hertz (Hz). EIMS and FABMS high resolution MS (HRMS) were taken on a JEOL SX-102A mass spectrometer, respectively.

Plant Material The heartwood of *J. chinensis* var. *tsukusiensis* was collected at the altitude of 2200 m above sea level at Chinsuishan, Hualien, in Taiwan in 1990.

Extraction and Isolation The heartwood of *J. chinensis* var. *tsukusiensis* (2.5 kg) was extracted with methanol (30 l) four times (4 d for every time) at room temperature. The combined extracts were concentrated *in vacuo* to give a residue (98 g), which was subjected to chromatography on silica gel with a gradient solvent system (hexane–ethyl acetate) to give the following products: **1** (14 mg), **2** (6 mg), **3** (2 mg), **4** (8 mg), **5** (20 mg) (with 10% ethyl acetate in hexane) and **6** (35 mg) (with 20% ethyl acetate in hexane) with SiO_2 chromatography, in that order. Detailed purification was achieved with HPLC [Merck LichroCART 250-10 Cat. 1.50179 Lichrosorb Si 60 (7 μm)] by using the same solvent system as in open colume. The physical characteristics of the himachalane-type sesquiterpenes are as follows.

2-Himachalen-6-ol (**2**): viscous oil. $[\alpha]_D^{18}$ +116.7° (c=0.5, $CHCl_3$). IR ν_{max}^{neat} cm^{-1}: 3478, 3045, 1660, 1444, 1372, 1016, 815. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. EI-MS (70 eV) m/z (rel. int. %): 222 (M^+, 26), 204 (26), 189 (7), 161 (19), 151 (29), 119 (100), 109 (55), 100 (37), 82 (48), 69 (30), 55 (24). HR-EI-MS Calcd for $C_{15}H_{26}O$ 222.1984. Found 222.1992.

3-Himachalen-6-ol (**3**): viscous oil. $[\alpha]_D^{25}$ +2.2° (c=0.2, $CHCl_3$). IR ν_{max}^{neat} cm^{-1}: 3356 (OH), 3020 (CH, olefinic), 1665, 1438, 1374, 1362, 1014, 810. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. EI-MS (70 eV) m/z (rel. int. %): 222 (M^+, 16), 204 (20), 151 (25), 119 (100), 109 (55). HR-EI-MS Calcd for $C_{15}H_{26}O$ 222.1984. Found 222.1992.

2α,6α-Epoxy-3-himachalene (**4**): viscous oil. $[\alpha]_D^{20}$ +2.5° (c=0.3, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3010 (CH, olefinic), 1660 (C=C), 1436, 1393, 1225, 1032, 983, 907, 810. 1H-NMR: Table 1. ^{13}C-NMR: Table 2. EI-MS (70 eV) m/z (rel. int. %): 220(M^+, 33), 177 (25), 149 (94), 135 (54), 109 (100), 95 (42), 81 (26), 69 (85), 55 (42), 43 (47). HR-EI-MS Calcd for $C_{15}H_{24}O$ 220.1827. Found 220.1837.

2α,6α-Epoxyhimachalan-3β-ol (**5**): viscous oil. $[\alpha]_D^{25}$ −56.4° (c=0.7, $CHCl_3$). IR ν_{max}^{neat} cm^{-1}: 3436 (OH), 1374, 1360, 1216, 1120, 1023, 957, 884, 854, 800. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. EI-MS (70 eV) m/z (rel. int. %): 222 [$(M-16)^+$, 8], 210 (47), 154 (38), 140 (71), 125 (63), 109 (100), 98 (57), 85 (52), 69 (63), 55 (38), 43 (78). HR-EI-MS Calcd for $C_{15}H_{26}O_2$ 238.1933. Found 238.1975.

Chinensiol (**6**): mp 122—123 °C, $[\alpha]_D^{13}$ +40.0° (c=1.0, $CHCl_3$). IR ν_{max}^{neat} cm^{-1}: 3322 (OH), 3010 (CH, olefinic), 1650 (C=C), 1040, 829. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. EI-MS (70 eV) m/z (rel. int. %): 220 (16), 202 (20). FABMS m/z (%): 459 [$(M+1)^+$, 2], 333 (12), 285 (35), 221 (100), 203 (221-H_2O, 80). *Anal*. Calcd for $C_{30}H_{50}O_3$: C, 78.55, H, 10.46. Found: C, 78.43, H, 10.54.

Acetylation of 6 Compound **6** (10 mg) in pyridine (0.5 ml) was treated with Ac_2O (0.5 ml). The reaction mixture stood at room temperature overnight and then was worked up by the usual method. The residue gave **9** (11 mg): amorphous, IR ν_{max}^{KBr} cm^{-1}: 1741 (AcO, ester), 1228, 1024 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 5.77 (br s, 1H, H-2), 4.49 (br s, 2H, H-15), 2.07 (s, 3H, AcO), 1.13, 0.89 (s, each 3H, H-12, H-13), 1.01 (d, 3H, J=7.0 Hz, H-14).

Oxidation of 6 with Pyridinium Chlorochromate (PCC) Compound **6** (20 mg) in 2 ml of CH_2Cl_2 was added to a suspension of powdered 4 Å molecular sieves (0.5 g) and PCC (210 mg) in 3 ml CH_2Cl_2. The reaction mixture was stirred at ambient temperature for 6 h. The suspension mixture was diluted with Et_2O (35 ml) and filtered with celite. Purification of the filtrate gave an aldehyde, **10**: mp 84—85 °C; UV λ_{max} nm (MeOH) (log ε) 206 (3.86), 230 (3.76), 280 (3.13). IR ν_{max}^{KBr} cm^{-1}: 1690 (C=O, conjugated aldehyde), 1240, 1080. ^{1}H-NMR ($CDCl_3$) δ 9.50 (s, 1H, –CHO), 7.20 (br s, 1H, H-2), 1.21, 1.10 (s, each 3H), 0.97 (d, 3H, J=7.8 Hz).

Reaction of 4, 5 or 6 with *p*-TsOH in Acetone Compound **4** (7 mg), **5** (8 mg), or **6** (8 mg) and p-TsOH (5 mg) were dissolved in 1 ml of acetone for one day under stirring. All reaction mixtures gave compound **1** (4 mg) after purification.

Acknowledgement This research was supported by the National Science Council of the Republic of China.

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