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Santalane and isocampherenane sesquiterpenoids from *Illicium tsangii*

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Abstract

Six novel santalane and three novel isocampherenane sesquiterpenes have been isolated from *Illicium tsangii* and their structures determined by 2D-NMR spectroscopy. The santalanes may be derived from (−)-α-santalene by oxidation reactions.

Keywords: Illicium tsangii; Illiciaceae; Sesquiterpene; Santalane; Isocampherenane; Hydroperoxides; 2D-NMR; Autoxidation; Biosynthesis

1. Introduction

Illicium tsangii A.C. Sm. is a poisonous shrub found in southern China, which is used in traditional medicine for treating pain (Lin, 1997). No previous phytochemical investigations of *I. tsangii* have been reported, although the Illicium family is known to be characterized by oligomeric neolignans (Kouno, Hashimoto, Kawano, & Yang, 1989c; Kouno, Morisaki, Hara, & Yang, 1991; Kouno, Iwamoto, Kameda, Tanaka, & Yang, 1994; Sy & Brown, 1996; Sy, Saunders, & Brown, 1997), prezizaane sesquiterpenes (Yamada, Takada, Nakamura, & Hirata, 1965, 1968; Manabe, Wakamatsu, Hirata, & Yamada, 1979; Kouno, Irie, Kawano, & Katsube, 1983; Kouno, Irie, & Kawano, 1984; Wong, Gulbis, Mackay, Craik, & Andrews, 1988; Kouno, Kawano, & Yang, 1988; Yang, Kouno, Kawano, & Sato, 1988; Kouno et al., 1990; Kouno et al., 1989a, 1989b; Kouno, Mori, Akiyama, & Hashimoto, 1991; Fukuyama, Shida, & Kodama, 1993; Okuyama, Nakamura, & Yamazaki, 1993; Sy & Brown, 1998) and cycloartane triterpenes (Sy et al., 1997).

2. Results and discussion

Extraction of *I. tsangii* with dichloromethane followed by CC and HPLC yielded twelve santalene and isocampherenane sesquiterpenes (**1**–**12**). Compounds **1**–**3** were suggested to be isomeric sesquiterpene hydroperoxides from the results of high resolution mass spectroscopy (which showed the molecular formula $C_{15}H_{24}O_2$), infrared spectroscopy (which showed an –OH peak from a hydroperoxide at ca. 3300 cm^{-1}) and 1D-NMR spectra (δ_H 7–8 ppm for –OO*H* and δ_C 80–90 ppm for *C*–OOH). The tricyclic santalene skeleton of allylic tertiary hydroperoxide **1** was established by 2D-NMR experiments such as HSQC (Table 1 and 2), HMBC (Fig. 1) and ^1H–^1H COSY (Fig. 2). ^{13}C and ^1H signals for positions 1/5 and 2/4 of **1** are expected to be very similar since their chemical environment differs only in the relative proximity of either a methyl or an alkyl side-chain substituent at C-7. Since chemical shift arguments are considered to be unreliable and it is impossible to distinguish the two sides of the santalene system on the basis of connections between C and H atoms established through bonds using the afore-mentioned 2D-NMR techniques, we determined the NMR assignments of positions 1/5 and 2/4 on the basis of correlations observed through space in NOESY spectroscopy (thus, the H-1β proton gave an enhancement with the H-14 methyl group whilst the H-5β proton showed an enhancement to both H-8 protons). Structures and NMR assignments for all other compounds reported in this paper were rigorously determined using the same 2D-NMR methodology.

Compounds **2** and **3** were shown to be diastereoisomeric secondary allylic hydroperoxides by 2D-NMR. All three hydroperoxides **1**–**3** would appear to be derived from the ene-type addition of molecular oxygen to the known compound α-santalene (**4**) (Hodgson, MacSweeney, & Money, 1973; Monti & Larsen, 1978; Bohlmann, Knoll, King, & Robinson, 1979; Wu, Niwa, & Furukawa, 1984). In support of this, Kaiser and

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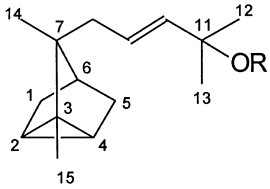

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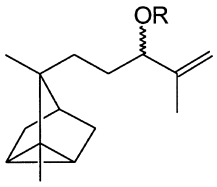

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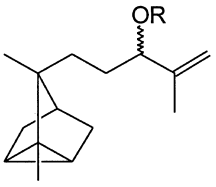

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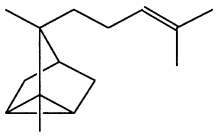

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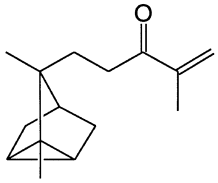

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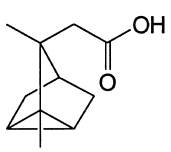

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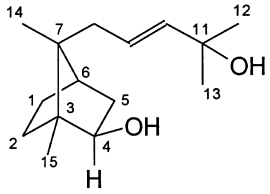

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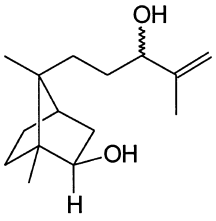

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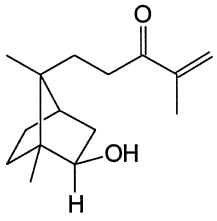

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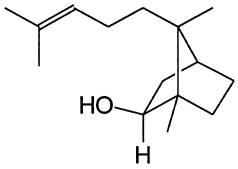

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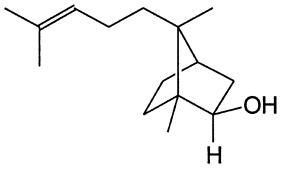

14 isoepicampherenol

Lamparsky (1977) have reported that in the presence of light and a photosensitizer, (+)-α-santalene ($[\alpha]_D$ +15.4°) undergoes autoxidation, and were able to isolate the tertiary hydroxide (−)-α-photosantolol A ($[\alpha]_D$ −22.2°) and a secondary hydroxide, following reduction of the autoxidation products. The same authors also reported the enantiomers of these two compounds, i.e. (+)-α-photosantolol A $[\alpha]_D$ (+31.4°), as natural products from an extract of *Lavandula officinalis* which also contained (−)-α-santalene ($[\alpha]_D$ −15.3°) (Kaiser & Lamparsky, 1977). Wu has reported (−)-α-photosantolol ($[\alpha]_D$ −20.7°) as a natural product from an extract of *Severinia buxifolia*, which also contained (+)-α-santalene ($[\alpha]_D$ +12.0°) (Wu et al., 1984). The optical rotation for **4** from our sample was negative, and the absolute stereochemistry for compounds **1**–**3** from *I. tsangii* is assumed to be as shown on the assumption that they are derived from **4** by oxidation as discussed above. Fortunately, quite large amounts of α-photosantolol A (**5**) were also obtained from the extract of *I. tsangii*: the optical rotation recorded for **5** ($[\alpha]_D$ +22.4°) was entirely consistent with its derivation from the autoxidation of (−)-α-santalene. In addition, the secondary allylic alcohols **6** and **7**, which may be derived by reduction of the corresponding secondary allylic hydroperoxides **2** and **3**, were also isolated from the extract in significant amounts.

Compound **8** possesses an α,β-unsaturated ketone group in the santalane side-chain and is formally the 11,12-dehydro derivative of dihydro-α-santalen-10-one (Wu et al., 1984): it is tempting to speculate that **8** is formed by elimination of the elements of water from either of the secondary allylic hydroperoxides **2** or **3**. Further oxidation of the side-chain would account for formation of the minor constituent norecasantalic acid (**9**) (Demole, Demole, & Enggist, 1976).

In addition to the santalanes **1**–**9**, three campherenanes

Table 1
^{13}C NMR assignments for compounds **1**–**12**

Assignment[a]	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1 (CH_2)	31.3	31.5	31.5	31.6	31.2	31.4	31.5	31.5	31.6	27.1	27.1	28.1
2 (CH)	19.7	19.6	19.6	19.6	19.5	19.6	19.6	19.6	19.3	34.2 (CH_2)	34.4 (CH_2)	34.3 (CH_2)
3 (C)	27.0	27.4	27.4	27.4	26.9	27.4	27.4	27.3	27.1	49.8	49.1	49.2
4 (CH)	19.6	19.5	19.5	19.6	19.6	19.5	19.5	19.5	19.4	79.7	79.8	79.6
5 (CH_2)	31.0	30.9	31.0	31.1	31.0	31.0	31.0	31.0	31.3	39.8	40.0	40.0
6 (CH)	38.6	38.2	38.1	38.3	38.4	38.2	38.2	38.2	39.0	42.0	42.0	42.1
7 (C)	46.3	45.6	45.6	45.9	46.3	45.4	45.6	45.7	45.7	49.4	49.9	50.1
8 (CH_2)	37.4	30.2	30.0	34.6	37.0	29.9	29.8	29.3	38.8	35.6	28.5	27.2
9 (CH_2)	129.3 (CH)	25.9	25.8	23.4	124.1 (CH)	29.8	29.8	33.2	177.8 (C)	124.8 (CH)	30.5	33.8
10 (CH)	134.6	90.6	90.6	125.6	139.5	76.7	76.9	202.9 (C)	–	139.4	76.7	203.0 (C)
11 (C)	82.3	143.7	143.6	130.6	70.7	147.5	147.4	144.5	–	70.8	147.6	144.6
12 (CH_2)	24.38[b] (CH_3)	114.5	114.6	25.7 (CH_3)	29.90[b] (CH_3)	111.2	111.4	124.2	–	29.9 (CH_3)	111.1	124.2
13 (CH_3)	24.43[b]	17.1	17.0	17.6	29.92[b]	17.4	17.3	17.8	–	29.9	17.5	17.8
14 (CH_3)	17.5	17.4	17.4	17.5	17.4	17.5	17.5	17.4	17.8	16.8	16.8	16.7
15 (CH_3)	10.7	10.7	10.6	10.7	10.7	10.7	10.7	10.6	10.5	11.4	11.4	11.4

[a] Multiplicity determined from DEPT.
[b] Assignments interchangeable within column.

Table 2
^{1}H NMR assignments for compounds **1**–**12**

Assignment[a]	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1α	1.06	1.06	1.06	1.05	1.06	1.05	1.06	1.08	1.11	1.02	1.01	1.30
1*β*	1.61	1.59	1.59	1.61	1.60	1.59	1.60	1.61	1.66	1.62	1.62	1.35
2	0.88	0.83	0.84	0.82	0.86	0.83	0.83	0.86	0.89	0.97 (α) 1.50 (*β*)	0.95 (α) 1.51 (*β*)	0.97 (α) 1.53 (*β*)
4	0.88	0.83	0.84	0.82	0.84	0.83	0.83	0.86	0.89	3.67	3.63	3.66
5α	1.06	1.03	1.02	1.03	1.03	1.02	1.03	1.04	1.13	1.74	1.69	1.66
5*β*	1.63	1.56	1.49	1.59	1.64	1.57	1.52	1.57	1.71	1.74	1.74	1.76
6	1.52	1.53	1.53	1.59	1.53	1.54	1.55	1.54	1.91	1.82	1.83	1.83
8	1.95	1.31	1.18	1.23	1.97	1.29	1.18	1.50	2.27	2.70	2.01	2.28
	1.85	1.07	1.15	1.13	1.84	1.02	1.10	1.47	2.20	1.80	1.00	1.42
9	5.66	1.46	1.54	1.90	5.59	1.52	1.52	2.61	–	5.64	1.64	2.66
		1.43	1.35	1.88		1.44	1.48	2.61			1.47	2.66
10	5.52	4.25	4.25	5.11	5.59	3.99	3.99	–	–	5.64	4.00	–
12	1.34	5.03	5.04	1.67	1.31	4.92	4.92	5.95	–	1.32	4.94	5.97
		5.02	5.02			4.83	4.83	5.76			4.83	5.76
13	1.34	1.73	1.73	1.60	1.31	1.72	1.72	1.88	–	1.32	1.73	1.87
14	0.81	0.79	0.81	0.83	0.80	0.81	0.82	0.83	0.99	0.81	0.82	0.84
15	1.02	0.99	1.00	1.00	1.01	1.00	1.00	1.02	1.02	0.93	0.92	0.94

[a] ^{1}H attached to ^{13}C determined from the results of HSQC.

(Hikino, Suzuki, & Takemoto, 1967; Eck, Hodgson, MacSweeney, Mills, & Money, 1974) were also isolated with structures suggestive of derivation from allylic hydroperoxides, as discussed above, viz.: the tertiary alcohol (**10**), the secondary alcohol (**11**) and the α,*β*-unsaturated ketone (**12**). The ^{1}H chemical shift and multiplicity for the well-resolved H-4 proton in compounds **10**–**12** (δ 3.63–3.67, t, $J=6$ Hz) is indicative of a *β*-relative configuration for the 4-OH group (Hodgson et al., 1973; Ranibai, Ghatge, Patil, & Bhattacharyya, 1986) as found for isocampherenol (**13**) and isoepicampherenol (**14**) (the chemical shift for this proton in the 4-epimers campherenol and epicampherenol is clearly distinct at ca. δ 4.00 ppm) (Hikino et al., 1967; Hodgson et al., 1973). NOESY correlations established the relative stereochemistry for **10**–**12**, as belonging to the isocampherenol

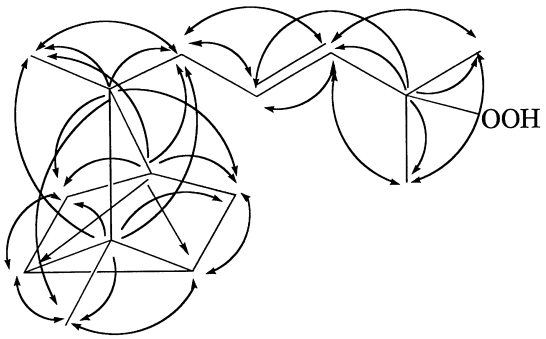

Fig. 1. Santalane skeleton of **1** as determined by correlations observed in HMBC (indicated by arrow from ^{13}C to ^{1}H; double-headed arrows indicate correlations observed in both directions).

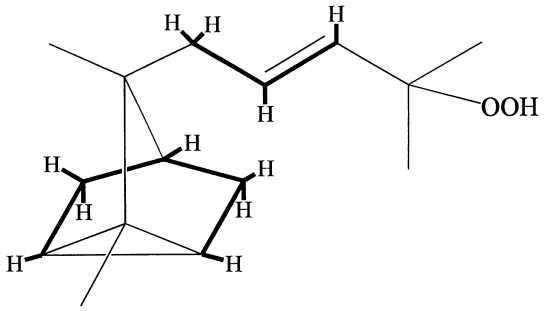

Fig. 2. Santalane skeleton of **1** as determined by correlations observed in ^{1}H–^{1}HCOSY (indicated by heavy lines in structure).

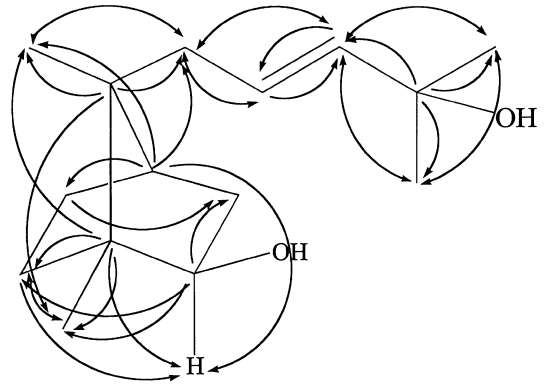

Fig. 3. Isocampherenane skeleton of **10** as determined by correlations observed in HMBC (indicated by arrows from ^{13}C to ^{1}H; double-headed arrows indicate correlations observed in both directions).

series since a strong correlation was observed from H-14 to H-1β/H-2β and from H-5β to H-8/9. The absolute stereochemistries of compounds **10**–**12** are not known.

The cooccurrence of santalenes and campherenanes in other species has been commented on previously and it has been suggested that the two skeleta are biosynthetically related (Eck et al., 1974). Both santalenes and campherenanes are very rare classes of sesquiterpenes; the majority of previous reports of santalenes have been associated with sandalwood oil (from *Santanalum album*) (Demole et al., 1976; Ranibai et al., 1986; Nikoforov, Jirovetz, Machatschek, Stanek, & Buchbauer, 1990; Alpha et al., 1996).

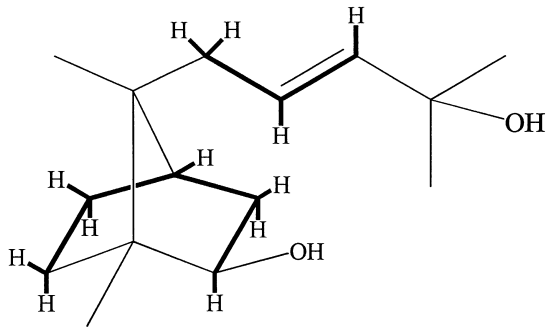

Fig. 4. Isocampherenane skeleton of **10** as determined by correlations observed in ^{1}H–^{1}H COSY(indicated by heavy lines in structure).

3. Experimental

3.1. General

Chemical shifts are expressed in ppm (δ) relative to TMS as int. standard. All NMR experiments were run on a Bruker DRX 500 instrument with $CDCl_3$ as solvent. HSQC and HMBC experiments were recorded with 2048 data points in F_2 and 128 data points in F_1. EIMS were recorded at 70 eV on a Finnigan-MAT 95 MS spectrometer; FTIR spectra were recorded in $CHCl_3$ on a Shimadzu FTIR-8201 PC instrument. TLC plates were developed using *p*-anisaldehyde. HPLC separations were performed using a PREP-SIL 20 mm $\times$ 25 cm column, flow rate 8 ml/min.

Leaf tissue of *I. tsangii* (750 g) was obtained from Conghua County, Guangdong province, China; a voucher specimen (Q. Lin and G. Hao 939) has been deposited in the herbarium of the University of Hong Kong (HKU) and the IBSC herbarium. The sample was ground to a fine powder under liq. N_2 and immediately extracted with CH_2Cl_2. The organic extract was then dried and evapd. under red. pres. to yield a dark green oil (16.7 g; 2.2% w/w) which was separated by column chromatography and HPLC. **1** (189 mg) (R_t 13.75 min in 10% EtOAc/hexane); **2** (57 mg) (R_t 46.4 min in 2% EtOAc/hexane); **3** (57 mg) (R_t 49.3 min in 2% EtOAc/hexane); **4** (391 mg) (R_f 0.72 in hexane, staining violet); **5** (364 mg) (R_t 16.9 min in 15% EtOAc/hexane); **6** (221 mg) (R_t 17.1 min in 10% EtOAc/hexane); **7** (190 mg) (R_t 18.3 min in 10% EtOAc/hexane); **8** (135 mg) (R_t 13.1 min in 2%EtOAc/hexane); **9** (5 mg) (R_t 8.4 min in 50% EtOAc/hexane/1% AcOH); **10** (9 mg) (R_t 34.5 min in 35% EtOAc/hexane); **11** (10 mg) (R_t 41.2 min in 37% EtOAc/hexane); **12** (16 mg) (R_t 22.4 min in 20% EtOAc/hexane).

*3.2. 11-Hydroperoxy-α-santal-9-ene (**1**)*

Oil. $[\alpha]_D$ +15.0° ($CHCl_3$, *c* 2.8). HREIMS *m/z* (rel. int.): 236.1777 ([M^+] calc. 236.1776 for $C_{15}H_{24}O_2$) (1), 203 (10), 121 (100), 93 (35). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3329 (br), 2982, 2945, 2930, 2873, 1456, 1379, 1364. ^1H NMR: δ 7.29 (1H, s, –OO*H*), 5.66 (1H, dt, *J*=15.7, 7.5 Hz), 5.52 (1H, d, *J*=15.7 Hz), 1.95 (1H, dd, *J*=13.9, 7.5 Hz), 1.85 (1H, dd, *J*=13.9, 7.5 Hz), 1.34 (6H, s), 1.02 (3H, s), 0.81 (3H, s).

*3.3. 10ξ-Hydroperoxy-α-santal-11-ene (**2**)*

Oil. $[\alpha]_D$ −2.8° ($CHCl_3$, *c* 0.58). HREIMS *m/z* (rel. int.): 236.1767 ([M^+] calc. 236.1776 for $C_{15}H_{24}O_2$) (12), 203 (6), 147 (8), 135 (15), 121 (95), 93 (100). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3329 (br), 2928, 2876, 1454, 1375, 1321. ^1H NMR: δ 7.77 (1H, s, –OO*H*), 5.03 (1H, t, *J*=1.5 Hz), 5.02 (1H, d, *J*=0.7 Hz), 4.25 (1H, t, *J*=6.7 Hz), 1.73 (3H, s), 0.99 (3H, s), 0.79 (3H, s).

*3.4. 10ξ-Hydroperoxy-α-santal-11-ene (**3**)*

Oil. $[\alpha]_D$ −17.0° ($CHCl_3$, *c* 0.58). HREIMS *m/z* (rel. int.): 220.1833 ([M^+–O] calc. 220.1827 for $C_{15}H_{24}O$) (25), 204 (13), 187 (5), 161 (9), 137 (23), 123 (43), 121 (97), 119 (56), 93 (100). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3306 (br), 2949, 1452, 1371, 1319. ^1H NMR: δ 7.75 (1H, s, –OO*H*), 5.04 (1H, t, *J*=1.6 Hz), 5.02 (1H, s), 4.25 (1H, t, *J*=6.9 Hz), 1.73 (3H, s), 1.00 (3H, s), 0.81 (3H, s).

*3.5. α-Santal-10-ene (α-santalene) (**4**)*

Liquid. $[\alpha]_D$ −12° ($CHCl_3$, *c* 0.35). HREIMS *m/z* (rel. int.): 204.1881 ([M^+] calc. 204.1878 for $C_{15}H_{24}$) (100), 189 (48), 161 (55), 121 (52), 119 (41), 107 (49), 105 (44), 94 (99), 93 (99). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 2928, 2874, 1456, 1377. ^1H NMR: δ 5.11 (1H, t, *J*=7.2 Hz), 1.67 (3H, s), 1.60 (3H, s), 1.00 (3H, s), 0.83 (3H, s).

*3.6. 11-Hydroxy-α-santal-9-ene (α-photosantalol A) (**5**)*

Oil. $[\alpha]_D$ +22.4° ($CHCl_3$, *c* 4.8). HREIMS *m/z* (rel. int.): 220.1815 ([M^+] calc. 220.1827 for $C_{15}H_{24}O$) (1), 202 (2), 162 (4), 121 (100), 93 (40). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3593, 2974, 2955, 2928, 2874, 1456, 1370. ^1H NMR: δ 5.59 (2H, m), 1.97 (1H, dd, *J*=15.9, 4.6 Hz), 1.84 (1H, dd, *J*=15.9, 4.0 Hz) 1.31 (6H, s), 1.01 (3H, s), 0.80 (3H, s).

*3.7. 10ξ-Hydroxy-α-santal-11-ene (α-photosantolol B diastereoisomer) (**6**)*

Oil. $[\alpha]_D$ +0.9° ($CHCl_3$, *c* 6.0). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3429 (br), 2945, 2880, 1454, 1375. ^1H NMR: δ 4.92 (1H, t, *J*=1.0 Hz), 4.83 (1H, t, *J*=1.6 Hz), 3.99 (1H, t, *J*=6.5 Hz), 1.72 (3H, s), 1.00 (3H, s), 0.81 (3H, s).

*3.8. 10ξ-Hydroxy-α-santal-11-ene (α-photosantolol B diastereoisomer) (**7**)*

Oil. $[\alpha]_D$ +6.4° ($CHCl_3$, *c* 4.4). HREIMS *m/z* (rel. int.): 220.1833 ([M^+] calc. 220.1827 for $C_{15}H_{24}O$) (25), 204 (13), 187 (5), 161 (9), 137 (23), 123 (43), 121 (97), 119 (56), 93 (100). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3429 (br), 2945, 2872, 1458, 1375. ^1H NMR: δ 4.92 (1H, t, *J*=0.9 Hz), 4.83 (1H, t, *J*=1.5 Hz), 3.99 (1H, t, *J*=6.5 Hz), 1.72 (3H, s), 1.00 (3H, s), 0.82 (3H, s).

*3.9. α-Santal-11-ene-10-one (**8**)*

Oil. $[\alpha]_D$ −7.9° ($CHCl_3$, *c* 1.56). HREIMS *m/z* (rel. int.): 218.1661 ([M^+] calc. 218.1671 for $C_{15}H_{22}O$) (30), 203 (15), 175 (35), 160 (30), 134 (32), 121 (93), 119 (70), 93 (100). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 2947, 2928, 2876, 1672, 1456, 1375, 1328. ^1H NMR: δ 5.95 (1H, s), 5.76 (1H, t, *J*=0.7 Hz), 2.61 (2H, m), 1.88 (3H, s), 1.02 (3H, s), 0.83 (3H, s).

*3.10. Norecasantalic acid (**9**)*

Oil. $[\alpha]_D$ +12.2° ($CHCl_3$, *c* 0.25). HREIMS *m/z* (rel. int.): 180.1154 ([M^+] calc. 180.1150 for $C_{11}H_{16}O_2$) (28), 165 (5), 135 (10), 121 (31), 120 (31), 105 (35), 93 (100). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3400–2600 (br) 2930, 2880, 1701. ^1H NMR: δ 2.27 (1H, d, *J*=14.5 Hz), 2.20 (1H, d, *J*=14.5 Hz), 1.02 (3H, s), 0.99 (3H, s).

*3.11. 11-Hydroxy-isocampheren-9-ene (**10**)*

Oil. $[\alpha]_D$ +18.4° ($CHCl_3$, *c* 0.46). HREIMS *m/z* 220 [M^+–H_2O] (15), 205 (54), 193 (48), 175 (80), 147 (28), 135 (39), 121 (44), 109 (91), 95 (100). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3422 (br), 2959, 2876, 1458, 1373. ^1H NMR: δ 5.64 (2H, m), 3.67 (1H, t, *J*=6.0 Hz), 2.70 (1H, dd, *J*=14.8, 5.0 Hz), 1.32 (6H, s), 0.93 (3H, s), 0.81 (3H, s).

*3.12. 10ξ-Hydroxy-isocampheren-11-ene (**11**)*

Oil. $[\alpha]_D$ −11.6° ($CHCl_3$, *c* 0.1). HREIMS *m/z* (rel. int.): 220.1835 ([M^+–H_2O] calc. 220.1827 for $C_{15}H_{24}O$) (5), 205 (8), 176 (9), 164 (15), 139 (23), 137 (40), 107 (48), 95 (100). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3398, 2954, 2880, 1456, 1373. ^1H NMR: δ 4.94 (1H, s), 4.83 (1H, d, *J*=1.5 Hz), 4.00 (1H, t, *J*=6.4 Hz), 3.63 (1H, dd, *J*=7.7, 4.2 Hz), 1.73 (3H, s), 0.92 (3H, s), 0.82 (3H, s).

*3.13. Isocampheren-11-ene-10-one (**12**)*

Oil. $[\alpha]_D$ −4.4° ($CHCl_3$, *c* 0.37). HREIMS *m/z* (rel. int.): 236.1781 ([M^+] calc. 236.1776 for $C_{15}H_{24}O_2$) (6), 218 (5), 194 (11), 177 (14), 151 (30), 132 (67), 99 (56), 95 (100). IR $\upsilon_{max}^{CHCl_3}$ cm^{-1}: 3421 (br), 2959, 2877, 1670, 1456, 1375. ^1H NMR: δ 5.97 (1H, s), 5.76 (1H, s), 3.66 (1H, t,

$J = 6.0$ Hz), 2.66 (2H, m), 1.87 (3H, s), 0.94 (3H, s), 0.84 (3H, s).

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