Pergamon

PII: S0031-9422(97)00606-7

Phytochemistry, Vol. 47, No. 6, pp. 1117–1123, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

STILBENES, MONOTERPENES, DIARYLHEPTANOIDS, LABDANES AND CHALCONES FROM *ALPINIA KATSUMADAI*

KOON-SIN NGO and GEOFFREY D. BROWN*

Chemistry Department, The University of Hong Kong, Pokfulam Rd., Hong Kong

(*Received in revised form* 10 *June* 1997)

Key Word Index—*Alpinia katsumadai*; Zingiberaceae; stilbenes; menthane monoterpenoids; diarylheptanoids; chalcones; labdane diterpenes; mixed metabolites.

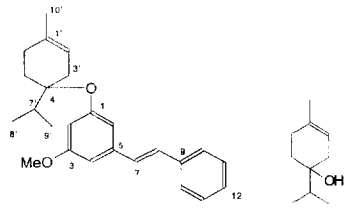
Abstract—The aerial parts of *Alpinia katsumadai* yielded six novel compounds, including 1-(1-terpinen-4-olyl)-3-methoxystilbene (*E*) (**1**), a mixed metabolite comprising elements from the stilbene and menthane monoterpene classes; the stilbenes 3-methoxy-5-hydroxystilbene (*Z*) (**7**) and 3,5-dihydroxystilbene (*Z*) (**8**); the diarylheptanoids 5-hydroxy-1-(4′-hydroxyphenyl)-7-phenyl-hepta-6-en-3-one (**10**) and *trans*-3,5-dihydroxy-1,7-diphenyl-hept-1-ene (**12b**); and a mixed metabolite (**13**) comprising elements from the chalcone and labdane diterpene classes of natural products. Several known representatives of each of these classes of natural product were also isolated. The structures of the novel compounds were determined by 2D NMR spectroscopy and NMR assignments of several of the known compounds, deduced by the same methodology, are reported for the first time.

INTRODUCTION

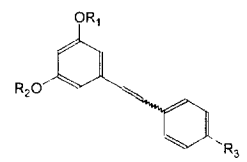
Alpinia katsumadai Hayata is native to Hainan Island in Southern China, but is widely distributed in shaded woodland in Hong Kong. It is used in traditional Chinese medicine as an antiemetic and for treatment of stomach disorders [1]. Previous investigations of *A. katsumadai* have reported a variety of diarylheptanoids [2], chalcones and flavonoids [3], monoterpenes and sesquiterpenoids [4, 5].

RESULTS AND DISCUSSION

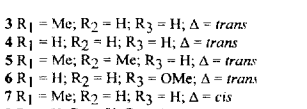
Extraction of the aerial parts of *A. katsumadai* with dichloromethane followed by CC and HPLC yielded compounds **1**–**8** and **10**–**18**. Accurate mass spectroscopy of novel compound **1** established the molecular formula $C_{25}H_{30}O_2$. The mass spectrum was dominated by two major fragments corresponding to stilbene (*m/z* 226) and the monoterpene (*m/z* 136) portions of the molecule. The structures of these two moieties in compound **1**, one containing 10 and the other 15 carbons, were deduced from the 2D NMR experiments HSQC and HMBC. HSQC showed carbons and protons connected by one bond (Tables 1 and 2) whilst HMBC correlations (Fig. 1), determined 2- and 3-bond carbon–proton couplings in each of the two portions. Correlations observed in ^1H–^1H COSY spectra confirmed the structure of **1**.



1 **2**



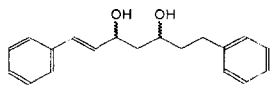
3 R_1 = Me; R_2 = H; R_3 = H; Δ = *trans*
4 R_1 = H; R_2 = H; R_3 = H; Δ = *trans*
5 R_1 = Me; R_2 = Me; R_3 = H; Δ = *trans*
6 R_1 = H; R_2 = H; R_3 = OMe; Δ = *trans*
7 R_1 = Me; R_2 = H; R_3 = H; Δ = *cis*
8 R_1 = H; R_2 = H; R_3 = H; Δ = *cis*
9 R_1 = Me; R_2 = Me; R_3 = H; Δ = *cis*



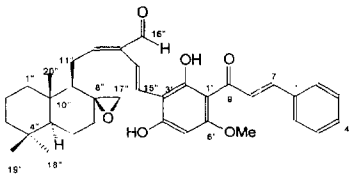
10 R = OH
11 R = H

The structure of the monoterpene and stilbene moieties of compound **1** were confirmed by isolation of

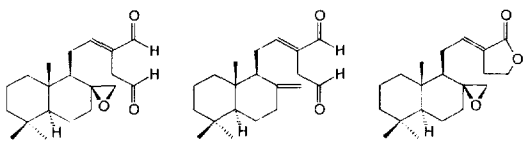
* Author to whom correspondence should be addressed.



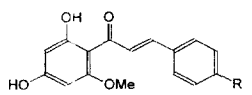
12a/12b



13



14 15 16



17 R=H
18 R=OH

free 1-terpinen-4-ol (**2**) and 3-methoxy-5-hydroxystilbene (*E*) (**3**) from the extract. The 2D NMR assignments for compound **2** agreed well with those obtained from the menthane monoterpene moiety of **1** (Tables 1 and 2). Similarly, NMR assignments for

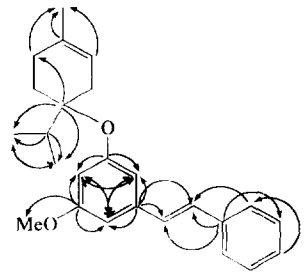


Fig. 1. HMBC correlations for **1** indicated by arrows from ^{13}C to ^{1}H.

the free stilbene **3** were consistent with assignments for the stilbene portion of mixed metabolite **1**. The free dihydroxystilbene pinosylvin (**4**) (previously isolated from *Pinus* spp. [6]) and 3,5-dimethoxystilbene (**5**) [7], which are both analogues of **3**, were also isolated from the extract and their complete NMR assignments are reported for the first time in Tables 1 and 2.

In addition to the known (*E*)-stilbenes **3**–**6**, the two (*Z*)-stilbene isomers **7** and **8** (i.e. the *cis* isomers of **3** and **4**) were also detected in the extract and are reported for the first time as natural products. The *cis* stilbenes were readily separated from their *trans* isomers by HPLC (*cis* isomers elute before the *trans* isomers). The *cis* isomer of compound **5**, 3,5-dimethoxystilbene (*Z*) (**9**), was not detected in the extract, but has been reported previously as a component of

Table 1. ^{13}C NMR data for mixed metabolite **1**, monoterpene **2** and stilbenes **3**–**8** ($CDCl_3$)

C	1	2	3	4	5	6	7	8
1	157.2		157.3	156.9	161.0	161.0	156.0	156.7
2	108.6		101.2	102.4	100.0	99.6	100.8	101.8
3	160.3		160.9	156.9	161.0	161.0	160.5	156.7
4	105.9		104.7	106.2	104.6	104.4	106.7	108.3
5	138.6		139.6	140.0	139.4	140.0	139.5	139.7
6	114.0		106.3	106.2	104.6	104.4	108.4	108.3
7	128.8		128.4	128.0	128.7	126.6	129.8	129.6
8	128.9		129.2	129.5	129.2	128.7	130.8	130.9
9	137.2		137.1	136.9	137.1	130.2	136.5	137.0
10/14	126.6		126.6	126.6	126.6	128.0	129.0	129.0
11/13	128.7		128.6	128.7	128.7	115.6	128.2	128.2
12	127.7		127.7	127.8	127.7	154.1	127.2	127.2
1-OMe	—		—	—	55.4	—	—	—
3-OMe	55.3		55.3	—	55.4	—	55.2	—
12-OMe	—		—	—	—	55.4	—	—
1′	134.0	133.9						
2′	118.3	118.4						
3′	31.1	34.6						
4′	83.6	72.0						
5′	28.5	30.8						
6′	27.9	27.1						
7′	33.2	36.8						
8′*	17.5	16.83						
9′*	17.6	16.85						
10′	23.2	23.3						

* Assignments interchangeable.

Table 2. ^{1}H NMR data for mixed metabolite **1**, monoterpene **2** and stilbenes **3–8** ($CDCl_3$)

H	1	2	3	4	5	6	7	8
2	6.47		6.37	6.26	6.40	6.38	6.27	6.21
4	6.74		6.60	6.54	6.67	6.64	6.36	6.29
6	6.74		6.62	6.54	6.67	6.64	6.31	6.29
7	6.98		6.93	6.88	7.02	6.88	6.49	6.45
8	7.05		6.99	6.97	7.09	7.02	6.59	6.57
10/14	7.50		7.42	7.42	7.50	7.39	7.30	7.25
11/13	7.35		7.30	7.30	7.36	6.82	7.22	7.22
12	7.28		7.21	7.22	7.26	—	7.19	7.19
1-OMe			—	—	3.83	—	—	—
3-OMe	3.81		3.74	—	3.83	—	3.63	—
12-OMe			—	—	—	3.83	—	—
2′	5.26	5.31						
3′	2.20	2.18						
	2.10	1.90						
5′	2.05	1.65						
	1.75	1.55						
6′	2.20	2.18						
	1.95	1.95						
7′	2.20	1.68						
8′*	0.99	0.93						
9′*	1.07	0.96						
10′	1.69	1.70						

* Assignments interchangeable.

Pinus banksiana [7]. Literature NMR data for **9** were in good agreement with those obtained for compounds **7** and **8**. ^{13}C NMR assignments for the stilbene *cis* isomers relative to the *trans* consistently showed sizeable downfield shifts (2–2.5 ppm) for the aromatic carbons *ortho* to the alkene (i.e. C-4, 6, 10, 14) and for the alkene carbons themselves (*ca* 1.5 ppm). ^{1}H NMR assignments showed upfield shifts (0–0.5 ppm) at all positions for the *cis* isomers relative to the *trans*; the size of this shift diminished with distance away from the double bond.

Accurate mass spectroscopy established the composition of the novel diarylheptanoid **10** as $C_{19}H_{20}O_3$. The structure of **10** was deduced using the same methodology as for compound **1** and all the foregoing compounds and complete NMR assignments were made by HSQC (Table 3) and HMBC (Fig. 2). The structure of **10** received support from a comparison of complete NMR assignments of the known compound **11** (Table 3) which was also present in the extract. The absolute stereochemistry for compound **10** is assumed to be 5*R* as has been determined for **11** [2], since optical rotations for the two compounds were comparable (Lit. value for **11** +17.8° (*c* 0.67) [2]). A reduced form of **11** was also isolated as an inseparable mixture of diastereoisomers **12a** and **12b**. One of these diastereoisomers (**12a**) gave very similar NMR data to a 3,5-dihydroxy-1,7-diphenyl-1-heptene reported previously from *A. katsumadai* [2].

HREI mass spectrometry of novel compound **13** showed a weak $[M]^+$ corresponding to the molecular formula $C_{36}H_{42}O_6$. The structure of **13**, which is a conjugate between a labdane diterpene and a chalcone, was deduced by 2D NMR. Assignments for the labdane portion of **13** were rigorously made by HSQC (Table 4) and HMBC (Fig. 3) as previously and received confirmation from the NMR analysis of known labdanes **14** and **15**, which were also present in the extract. The dialdehyde **15** was first reported from *Alpinia speciosa* [8]; **14** was first reported from *Afromomum danielli* [9] (also in the Zingiberaceae). The optical rotation for **14** isolated from *A. katsumadai* agreed well with that cited in the literature (+28.1°, *c* 1.41) and the absolute stereochemistry for all labdanes reported herein has been assigned accord-

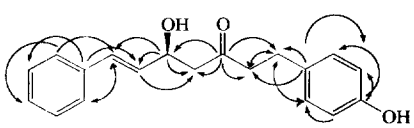


Fig. 2. HMBC correlations for **10** indicated by arrows from ^{13}C to ^{1}H.

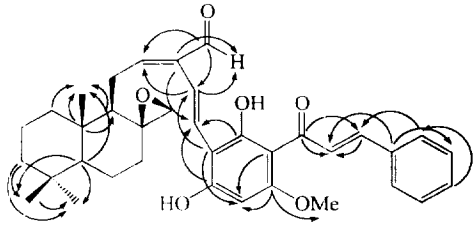


Fig. 3. HMBC correlations for **13** indicated by arrows from ^{13}C to ^{1}H.

Table 3. ^{13}C and ^{1}H assignments for diarylheptanoids **10–12b** ($CDCl_3$)

Assignment	δ_C 10	11	12a/12b	δ_H 10	11	12a/12b
1	28.7	29.5	31.12/31.72	2.85	2.93	2.70/2.80
2	45.5	45.2	39.70/39.24	2.75	2.80	1.84/1.80
3	210.5	210.1	70.69/68.93			3.95/4.00
4	49.3	49.3	43.38/42.67	2.70	2.70	1.77/1.84
5	68.6	68.6	73.76/71.73	4.74	4.75	4.55/4.66
6	130.1	130.1	131.85/131.76	6.16	6.17	6.23/6.28
7	130.5	130.5	130.19/130.13	6.60	6.62	6.63/6.60
1′	132.6	140.7	141.89/141.89			
2′/6′	129.4	128.6*	128.62/128.62	7.02	7.17	7.15–7.30*
3′/5′	115.4	128.3	128.47/128.47	6.74	7.20	7.15–7.30*
4′	154.1	126.2	125.92/125.92		7.20	7.15–7.30*
1″	136.5	136.5	136.50/136.55			
2″/6″	126.5	126.5	126.52/126.50	7.35	7.36	7.35/7.35
3″/5″	128.6	128.6*	128.44/128.41	7.30	7.31	7.30/7.30
4″	127.8	127.8	127.81/127.73	7.23	7.23	7.23/7.23

* Insufficient resolution to allow accurate assignment.

Table 4. ^{13}C NMR assignments for mixed metabolite **13**, labdanes **14–16** and chalcones **17** and **18** ($CDCl_3$)

C	13	14	15	16	17	18 MeOH-d_4
1	135.5				135.6	126.9
2/6	128.4				128.4	129.8
3/5	128.9				128.9	115.4
4	130.1				130.1	159.6
7	142.4				142.4	142.3
8	127.6				127.5	124.0
9	192.8				192.8	192.5
1′	105.9				105.9	105.2
2′	166.4				167.9	167.1
3′	105.8				96.8	95.6
4′	161.0				162.8	164.9
5′	91.1				91.1	91.0
6′	162.1				163.3	163.2
6′-OMe	55.9				56.0	54.9
1″	39.4	39.3	39.2	39.3		
2″	18.5	18.5	19.3	18.6		
3″	41.9	41.8	42.0	41.9		
4″	33.5	33.5	33.6	33.5		
5″	55.1	54.9	55.4	54.9		
6″	20.1	20.0	24.1	20.0		
7″	35.9	35.7	37.9	35.8		
8″	58.1	57.5	148.0	57.6		
9″	53.3	52.6	56.5	52.4		
10″	39.9	39.8	39.6	39.6		
11″	22.6	22.3	24.7	22.8		
12″	157.6	160.3	160.0	142.9		
13″	138.5	135.0	134.9	124.8		
14″	121.1	39.3	39.4	25.4		
15″	126.4	196.7	197.4	65.4		
16″	194.6	192.8	193.6	171.4		
17″	49.1	48.8	107.9	49.1		
18″	33.5	33.5	33.6	33.5		
19″	21.7	21.7	21.7	21.8		
20″	14.7	14.6	14.4	14.6		

ingly. The ^{13}C NMR data for labdanes **14**–**16** (previously reported from *A. galanga* [10]) are given in Table 4 for purposes of comparison (N.B. some previously reported assignments [8–10] are in error). Assignments for the chalcone moiety of metabolite **13** were confirmed by 2D NMR investigation of the freely occurring compounds cardamonin (**17**) [3] and helichrysetin (**18**) [11], which were also present in the extract.

In addition to the foregoing compounds, the extract of *A. katsumadai* also contained the common compounds camphor, 1,8-cineole and methyl cinnamate (all previously identified from *A. katsumadai* [4]) as well as stigmasterol, sitosterol, β-selinene and pinocembrin which are reported for the first time.

Both stilbenes and monoterpenes are very common classes of natural product, and, as discussed above, are well documented from the genus *Alpinia*. However, compound **1** is the first example of a mixed metabolite containing both classes of natural product of which we are aware. Diarylheptanoids are particularly common in the genus *Alpinia* and are known from *A. officinarum* [12–16], *A. oxyphylla* [17, 18] and *A. conchigera* [19]. Chalcones and labdane diterpenes are also quite characteristic of *Alpinia* and have been reported from *A. speciosa* [8, 20–22], *A. galanga* [10, 23], *A. formosana* [24] and *A. javanica* [25]. The isolation of **13** is, we believe, the first report of a mixed metabolite involving a labdane and a chalcone. This tendency to form mixed metabolites is not unique to *A. katsumadai* within the genus; mixed metabolites containing diarylheptanoid and chalcone moieties have been previously reported from *A. blepharocalyx* [26].

EXPERIMENTAL

General. Chemical shifts are expressed in ppm (δ) relative to TMS as int. standard. All NMR experiments were run on Bruker DPX 300 or DRX 500 instruments. Two dimensional spectra were recorded with 1024 data points in F_2 and 256 data points in F_1. HREIMS were recorded at 70 ev on a Finnigan-MAT 95 MS spectrometer. IR: CCl_4; TLC: plates were developed using *p*-anisaldehyde; CC: silica gel 60–200 μm (Merck); HPLC: PREP-SIL 20 mm × 25 cm column, flow rate 8 ml min^{-1}.

Isolation of **1**–**8**, **10**–**18**. Leaves and stems were collected from Pokfulam Country Park, Hong Kong Island. A voucher specimen of *A. katsumadai* Hayata is deposited in the University of Hong Kong herbarium (GDBROWN 97/1). The sample (1.25 kg) was immediately extracted with CH_2Cl_2 in a Soxhlet apparatus (8 hr). The organic extract was then dried and evapd. under red. pres. to yield a dark green solid (10.6 g; 0.85%). **1** (4 mg): CC (R_f 0.45, 5% EtOAc–hexane, staining pink), HPLC (R_t 14.2 min, 3% EtOAc–hexane); **2** (18 mg): CC (R_f 0.55, 15% EtOAc–hexane, staining violet), HPLC (R_t 18.2 min, 10% EtOAc–hexane); **3** (133 mg): CC (R_f 0.39, 32% EtOAc–hexane, staining brown), HPLC (R_t 12.7 min, 32% EtOAc–hexane); **4** (15 mg): CC (R_f 0.32, 50% EtOAc–hexane, staining violet), HPLC (R_t 14.4 min, 40% EtOAc–6% AcOH–hexane); **5** (8 mg): CC (R_f 0.50, 15% EtOAc–hexane, staining violet), HPLC (R_t 15.5 min, 10% EtOAc–hexane); **6** (6 mg): CC (R_f 0.30, 30% EtOAc–hexane, staining green), HPLC (R_t 16.0 min, 30% EtOAc–hexane); **7** (12 mg): CC (R_f 0.41, 28% EtOAc–hexane, staining green), HPLC (R_t 13.6 min, 25% EtOAc–hexane); **8** (5 mg): CC (R_f 0.39, 35% EtOAc–hexane, staining violet), HPLC (R_t 16.5 min, 33% EtOAc–hexane); **10** (9 mg): CC (R_f 0.32, 50% EtOAc–hexane, staining yellow), HPLC (R_t 20.8 min, 42% EtOAc–hexane); **11** (7 mg): CC (R_f 0.36, 30% EtOAc–hexane, staining violet), HPLC (R_t 17.9 min, 30% EtOAc–hexane); **12** (2 mg): CC (R_f 0.30, 50% EtOAc–hexane, staining violet), HPLC (R_t 26.4 min, 42% EtOAc–hexane); **13** (10 mg): CC (R_f 0.37, 50% EtOAc–hexane, staining pale yellow), HPLC (R_t 20.1 min, 45% EtOAc–hexane); **14** (34 mg): CC (R_f 0.28, 30% EtOAc–hexane, staining green), HPLC (R_t 14.6 min, 35% EtOAc–hexane); **15** (81 mg): CC (R_f 0.43, 15% EtOAc–hexane, staining violet), HPLC (R_t 20.8 min, 10% EtOAc–hexane); **16** (8 mg): CC (R_f 0.33, 35% EtOAc–hexane, staining pale yellow), HPLC (R_t 24.0 min, 29% EtOAc–hexane); **17** (5 mg): CC (R_f 0.38, 50% EtOAc–hexane, staining violet), HPLC (R_t 13.6 min, 42% EtOAc–hexane); **18** (20 mg): CC (R_f 0.35, 50% EtOAc–hexane, staining brown), HPLC (R_t 21.5 min, 45% EtOAc–hexane).

1-(1-*Terpinen*-4-*olyl*)-3-*methoxystilbene* (E) (**1**). Oil. HREIMS *m/z* (rel. int.): 362.2246 [$[M]^+$, $C_{25}H_{30}O_2$ requires 362.2246] (2), 319 (2), 299 (5), 226 (100), 136 (38); IR ν_{max} cm^{-1}: 2961, 2938, 2855, 1637, 1587, 1456, 1431, 1151; ^1H NMR ($CDCl_3$): δ 7.50 (2H, *d*, *J* = 7.1 Hz, H-10/14), 7.35 (2H, *t*, *J* = 7.1 Hz, H-11/13), 7.28 (1H, *m*, H-12), 7.05 (1H, *d*, *J* = 16.6 Hz, H-8), 6.98 (1H, *d*, *J* = 16.6 Hz, H-7), 6.74 (2H, *t*, *J* = 2.2 Hz, H-4/6), 6.47 (1H, *t*, *J* = 2.2 Hz, H-2), 5.26 (1H, *br s*, H-2′), 3.81 (3H, *s*, 3-OMe), 1.69 (3H, *s*, H-10′), 1.07 (3H, *d*, *J* = 6.5 Hz, H-8′ or H-9′), 0.99 (3H, *d*, *J* = 6.8 Hz, H-8′ or H-9′).

1-*Terpinen*-4-*ol* (**2**). Oil. EIMS *m/z* (rel. int.): 154 (29), 111 (62), 109 (55), 93 (43), 71 (100); IR ν_{max} cm^{-1}: 3641, 3354 br, 2964, 2931, 2879, 1678; ^1H NMR ($CDCl_3$): δ 5.31 (1H, *dd*, *J* = 2.3, 0.7 Hz, H-2′), 1.70 (3H, *s*, H-10), 0.96 (3H, *d*, *J* = 6.9 Hz, H-8′ or H-9′), 0.93 (3H, *d*, *J* = 6.9 Hz, H-8′ or H-9′).

3-*Methoxy*-5-*hydroxystilbene* (E) (**3**). Gum. HREIMS *m/z* (rel. int.): 226.0986 [$[M]^+$, $C_{15}H_{14}O_2$ requires 226.0979] (100); IR ν_{max} cm^{-1}: 3408, 3059, 3022, 2960, 2941, 1678, 1609, 1595, 1499, 1456; ^1H NMR ($CDCl_3$): δ 7.42 (2H, *d*, *J* = 7.5 Hz, H-10/14), 7.30 (2H, *t*, *J* = 7.5 Hz, H-11/13), 7.21 (1H, *t*, *J* = 7.5 Hz, H-12), 6.99 (1H, *d*, *J* = 16.3 Hz, H-8), 6.93 (1H, *d*, *J* = 16.3 Hz, H-7), 6.62 (1H, *s*, H-6), 6.60 (1H, *s*, H-4), 6.37 (1H, *s*, H-2), 3.74 (3H, *s*, 3-OMe).

3-*Methoxy*-5-*hydroxystilbene* (Z) (**7**). Gum. IR ν_{max} cm^{-1}: 3300 (br), 3026, 2928, 2854, 1700, 1609; ^1H NMR ($CDCl_3$): δ 7.35–7.15 (5H, *m*, H-10-14), 6.59

(1H, *d*, J = 12.2 Hz, H-8), 6.49 (1H, *d*, J = 12.2 Hz, H-7), 6.36 (1H, *d*, J = 1.6 Hz, H-4), 6.31 (1H, *d*, J = 1.6 Hz, H-6), 6.27 (1H, *t*, J = 2.3 Hz, H-2), 3.63 (3H, *s*, -OMe).

3,5-*Dihydroxystilbene* (Z) (**8**). Oil. HREIMS *m/z* (rel. int.): 212.0836 [[M]$^+$, $C_{14}H_{12}O_2$ requires 212.0835] (100), 131 (72); IR ν_{max} cm^{-1}: 3300 (br), 3034, 2937, 1603; ^{1}H NMR ($CDCl_3$): δ 7.30–7.15 (5H, *m*, H-10-14), 6.57 (1H, *d*, J = 12.2 Hz, H-8), 6.45 (1H, *d*, J = 12.2 Hz, H-7), 6.29 (2H, *d*, J = 2.1 Hz, H-4/6), 6.21 (1H, *t*, J = 2.1 Hz, H-2).

5-*Hydroxy*-1-(4′-*hydroxyphenyl*)-7-*phenyl-hepta*-6-*en*-3-*one* (**10**). Oil, $[\alpha]_D$ = +10.7° (*c* 0.14, $CHCl_3$). HREIMS *m/z* (rel. int.) 296.1411 [[M]$^+$, $C_{19}H_{20}O_3$ requires 296.1410] (39), 278 (22), 164 (67), 131 (78), 107 (100); IR ν_{max} cm^{-1}: 3350 (br), 3022, 2924, 2853, 1709, 1614; ^{1}H NMR ($CDCl_3$): δ 7.35 (2H, *d*, J = 7.0 Hz, H-2″/6″), 7.30 (2H, *t*, J = 7.0 Hz, H-3″/5″), 7.23 (1H, *t*, J = 7.0 Hz, H-4″), 7.02 (2H, *d*, J = 8.4 Hz, H-2′/6′), 6.74 (2H, *d*, J = 8.4 Hz, H-3′/5′), 6.60 (1H, *d*, J = 15.9 Hz, H-7), 6.16 (1H, *dd*, J = 15.9, 6.2 Hz, H-6), 4.74 (1H, *m*, H-5), 2.85 (2H, *t*, J = 7.2 Hz, H-1), 2.75 (2H, *t*, J = 7.2 Hz, H-2), 2.70 (2H, *m*, H-4′).

Trans-3,5-*dihydroxy*-1,7-*diphenyl-hept*-1-*ene* (*inseparable mixture of diastereoisomers*) (**12b** *and* **12a**). Gum. ^{1}H NMR ($CDCl_3$): δ 7.35 (2H, *d*, J = 7.0 Hz, H-2″/6″); 7.30 (2H, *t*, J = 7.0 Hz, H-3″/5″); 6.63 (1H, *d*, J = 15.9 Hz, H-7)/6.60 (1H, *d*, J = 15.9 Hz, H-7); 6.28 (1H, *dd*, J = 15.9, 6.1 Hz, H-6)/6.23 (1H, *dd*, J = 15.9, 6.6 Hz, H-6); 4.66 (1H, *m*, H-5)/4.55 (1H, *m*, H-5); 4.00 (1H, *m*, H-3)/3.95 (1H, *m*, H-3).

Compound **13**. Gum, $[\alpha]_D$ = +22.7° (*c* 0.04, $CHCl_3$). HREIMS *m/z* (rel. int.): 570.2970 [[M]$^+$, $C_{36}H_{42}O_6$ requires 570.2958] (1), 310 (12), 270 (26), 232 (10), 193 (21), 153 (100), 136 (70), 107 (58), 77 (28); IR ν_{max} cm^{-1}: 3420 (br), 3022, 2928, 2860, 1717, 1616; ^{1}H NMR ($CDCl_3$): δ 14.97 (1H, *s*, 2′-OH), 9.49 (1H, *s*, H-16″), 7.83 (1H, *d*, J = 15.7 Hz, H-8), 7.72 (1H, *d*, J = 15.7 Hz, H-7), 7.60 (2H, *m*, H-2/6), 7.42 (1H, *d*, J = 17.7 Hz, H-15″), 7.38 (3H, *m*, H-3-5), 6.98 (1H, *d*, J = 17.7 Hz, H-14″), 6.35 (1H, *t*, J = 6.4 Hz, H-12″), 5.98 (1H, *s*, H-5′), 3.90 (3H, *s*, 6′-OMe), 2.52 (1H, *d*, J = 3.8 Hz, H-17a″), 2.32 (1H, *d*, J = 3.8 Hz, H-17b″), 0.98 (3H, *s*, H-20″), 0.92 (3H, *s*, H-18″), 0.88 (3H, *s*, H-19″).

8β(17)-*Epoxylabd*-12-*ene*-15,16-*dial* [E] (**14**). Oil, $[\alpha]_D$ = +34.0° (*c* 0.43, $CHCl_3$). HREIMS *m/z* (rel. int.) 318.2195 [[M]$^+$, $C_{20}H_{30}O_3$ requires 318.2195] (11), 303 (32), 289 (24), 271 (16), 220 (12), 207 (25), 194 (49), 179 (100), 163 (15), 137 (19); IR ν_{max} cm^{-1} 2930, 2907, 2068, 2844, 1732, 1690, 1641; ^{1}H NMR ($CDCl_3$): δ 9.64 (1H, *s*, H-15), 9.41 (1H, *s*, H-16), 6.67 (1H, *t*, J = 6.5 Hz, H-12), 3.45 (1H, *d*, J = 17.3 Hz, H-14a), 3.36 (1H, *d*, J = 17.3 Hz, H-14b), 2.42 (1H, *d*, J = 3.8 Hz, H-17a), 2.30 (1H, *d*, J = 3.8 Hz, H-17b), 0.93 (3H, *s*, H-20), 0.92 (3H, *s*, H-18), 0.88 (3H, *s*, H-19).

Cardamonin (*alpinetin chalcone*) (**17**). Gum. HREIMS *m/z* (rel. int.): 270.0892 [[M]$^+$, $C_{16}H_{14}O_4$ requires 270.0892] (100), 193 (77); IR ν_{max} cm^{-1}: 3230 (br), 3032, 2934, 2853, 1628, 1605; ^{1}H NMR ($CDCl_3$): δ 14.20 (1H, *s*, 2′-OH), 7.88 (1H, *d*, J = 15.6 Hz, H-8), 7.78 (1H, *d*, J = 15.6 Hz, H-7), 7.60 (2H, *m*, H-2/6), 7.42 (3H, *m*, H-3-5), 6.03 (1H, *d*, J = 2.1 Hz, H-3′), 5.95 (1H, *d*, J = 2.1 Hz, H-5′), 3.93 (3H, *s*, 6′-OMe).

Acknowledgements—We would like to thank the CRCG for funding this research. Dr R. Saunders and R. Cortlett of The Department of Ecology and Biodiversity, The University of Hong Kong, helped in identifying the plant material. The University of Hong Kong provided a postgraduate research studentship to Mr Ngo.

REFERENCES

1. Tang, W. and Eisenbrand, G., *Chinese Drugs of Plant Origin*, Springer, Berlin, 1992, p. 87.
2. Kuroyanagi, M., Noro, T., Fukushima, S., Aiyama, R., Ikuta, A., Itokawa, H. and Morita, M., *Chemical and Pharmaceutical Bulletin*, 1983, **31**, 1544.
3. Yushiro, K., Shuhichi, T. and Ikuo, Y., *Yakugaku Zasshi*, 1968, **88**, 239.
4. Saiki, Y., Ishikawa, Y., Uchida, M. and Fukushima, S., *Phytochemistry*, 1978, **17**, 808.
5. Lawrence, B. M., Hogg, J. W., Terhune, S. J. and Pichitakul, N., *Phytochemistry*, 1972, **11**, 1534.
6. Bachelor, F. W., Loman, A. A. and Snowdon, L. R., *Canadian Journal of Chemistry*, 1970, **48**, 1554.
7. Rowe, J. W., Bower, C. L. and Wagner, E. R., *Phytochemistry*, 1969, **8**, 235.
8. Itokawa, H., Morita, M. and Mihashi, S., *Chemical and Pharmaceutical Bulletin*, 1980, **28**, 3452.
9. Kimbu, S. F., Njimi, T. K., Sondengam, B. L., Akinniyi, J. A. and Connolly, J. D., *Journal of the Chemical Society, Perkin Transactions 1*, 1979, 1303.
10. Morita, H. and Itokawa, H., *Planta Medica*, 1988, **54**, 117.
11. Van Puyvelde, L., De Kimpe, N., Costa, J., Munyjabo, V., Nyirankuliza, S., Hakiamungu, E. and Schamp, N., *Journal of Natural Products*, 1989, **52**, 629.
12. Itokawa, H., Morita, M. and Mihashi, S., *Chemical and Pharmaceutical Bulletin*, 1981, **29**, 2383.
13. Itokawa, H., Morita, H., Midorikawa, I., Aiyama, R. and Morita, M., *Chemical and Pharmaceutical Bulletin*, 1985, **33**, 4889.
14. Uehara, S.-I., Yasuda, I., Akiyama, K., Morita, H., Takeya, K. and Itokawa, H., *Chemical and Pharmaceutical Bulletin*, 1987, **35**, 3298.
15. Kiuchi, F., Shibuya, M. and Sankawa, U., *Chemical and Pharmaceutical Bulletin*, 1982, **30**, 2279.
16. Inoue, T., Shinbori, T., Michiyo, F., Keiji, H. and Yoshiro, M., *Yakugaku Zasshi*, 1978, **98**, 1255.
17. Itokawa, H., Aiyama, R. and Ikuta, A., *Phytochemistry*, 1982, **21**, 241.
18. Shoji, N., Umeyama, A., Takemoto T. and Ohizhumi, Y., *Planta Medica*, 1984, **50**, 186.
19. Athamprasangsa, S., Buntrarongroj, U., Dam-

pawan, P., Ongkavoranan, N., Rukachaisirikul, V., Sethijinda, S., Sornnarintra, M., Sriwub, P. and Taylor, W. C., *Phytochemistry*, 1994, **37**, 871.
20. Itokawa, H., Morita, M. and Mihashi, S., *Phytochemistry*, 1981, **20**, 2503.
21. Krishna, B. M. and Chaganty, R. B., *Phytochemistry*, 1973, **12**, 238.
22. Lin, J.-H., *Kuo Li Chung-Kuo I Yao Yan Chiu So Yen Chiu Pao Kao*, 1982, 147.
23. Morita, H. and Itokawa, H., *Chemical Letters*, 1986, 1205.
24. Itokawa, H., Yoshimoto, S. and Morita, H., *Phytochemistry*, 1988, **27**, 435.
25. Sirat, H. M., Masri, D. and Rahman, A. A., *Phytochemistry*, 1994, **36**, 699.
26. Kadota, S., Hui, D., Basnet, P., Prosain, J. K., Xu, G.-J. and Namba, T., *Chemical and Pharmaceutical Bulletin*, 1994, **42**, 2647.