Phytochemistry, Vol. 27, No. 2, pp. 435–438, 1988.
Printed in Great Britain.

0031-9422/88 $3.00+0.00

DITERPENES FROM THE RHIZOMES OF *ALPINIA FORMOSANA*

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(*Received* 26 *May* 1987)

Key Word Index—*Alpinia formosana*; Zingiberaceae; labdane; (*E*)-labda-8(17), 12-diene-15-ol-16-al; (*E*)-15,16-bisnorlabda-8(17),11-diene-13-one; chemotaxonomy.

Abstract—A new labdane-type diterpene, (*E*)-labda-8(17),12-diene-15-ol-16-al was isolated from the rhizomes of *Alpinia formosana* together with a bisnorlabdane-type diterpene, (*E*)-15,16-bisnorlabda-8(17),11-diene-13-one, two known sesquiterpenes and three known phenolic compounds. The chemotaxonomic significance of these findings is discussed briefly.

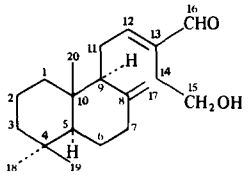
INTRODUCTION

We have studied many Alpinia genus plants with respect to the structure and biological activities [1–15]. That is, sesquiterpenes [4–8] from *A. japonica* and *A. intermedia*, diterpenes [9, 10] from *A. galanga* and *A. speciosa*, and diarylheptanoids [11–15] from *A. officinarum*, *A. Katumadai* and *A. oxyphylla* were isolated. The investigation of constituents of *A. formosana* led us to isolate a new labdane-type diterpene (**1**) together with six known compounds (**2–7**). In this paper, we report the isolation and characterization of one new and six known compounds, and discuss the chemotaxonomic usefulness of these compounds.

RESULTS

The aqueous methanol extracts of the fresh rhizomes of *A. formosana* were shaken with *n*-hexane. The *n*-hexane soluble fraction was then repeatedly separated by chromatography to give seven compounds (**1–7**).

Compound **1**, $C_{20}H_{32}O_2$, an unstable colourless oil, $[\alpha]_D^{20}+20.0°$ showed hydroxyl (3640 cm^{-1}), α,β-unsaturated carbonyl (1685 cm^{-1}) and exomethylene (3080 and 895 cm^{-1}) bands in the IR spectrum. The ^1H NMR spectrum suggested the presence of primary hydroxyl group (δ3.54, 2H, *t*, *J* = 6.5 Hz), exomethylene protons (4.42 and 4.85) and three tertiary methyl groups (0.75, 0.83 and 0.89). Furthermore, the ^1H NMR (δ9.23



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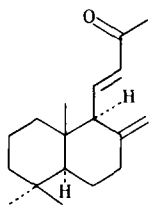

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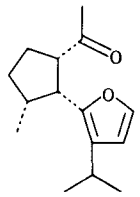

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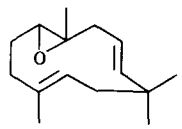

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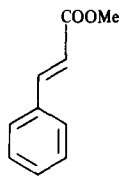

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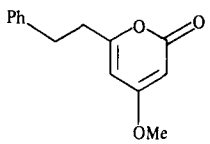

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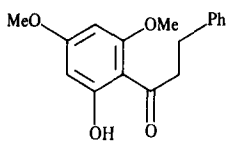

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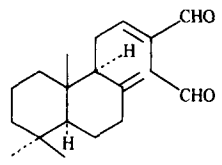

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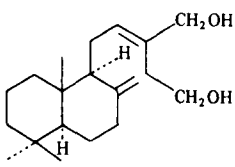

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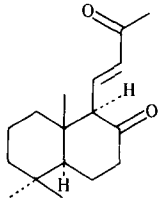

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and 6.17, 1H, *dd*, $J = 6.3$ and 6.6 Hz) and UV spectra (235 nm, ε 12400) indicated the presence of an α,β-unsaturated aldehyde. The ^{13}C NMR spectral data, except for the signal at δ61.4, showed a great resemblance to the labdane-type diterpene, (*E*)-labda-8(17),12-diene-15,16-dial (**8**), which was reported in our previous work [9, 10] (Table 1). Furthermore, the labdane-type skeleton was supported by the base peak at *m/z* 137 in the mass spectrum (Scheme 1). Reduction of **1** with $NaBH_4$ afforded labda-8(17),12-diene-15,16-diol (**9**), which was completely identical with the compound produced by reduction of **8**. Also 26.0% NOE between the aldehyde proton and the olefinic proton was observed. From the above results, it is reasonable to conclude that the absolute structure of **1** was (*E*)-labda-8(17),12-diene- 15-ol-16-al.

Compound **2**, $C_{18}H_{28}O$, mp 146.0–147.0°, $[\alpha]_D^{20} + 6.6°$, was identified as (*E*)-15,16-bisnorlabda-8(17),11-diene-13-one by comparison of its physical and spectral properties with those of the compound isolated from *Alpinia speciosa* [10]. To determine the absolute structure, the Octant rule was applied to compound **10** which was obtained by ozonolysis of **2**. The CD spectrum of **10** showed the negative Cotton effect ($\Delta\varepsilon_{290} = -2.71$). Therefore the absolute structure of **2** was determined to be as shown.

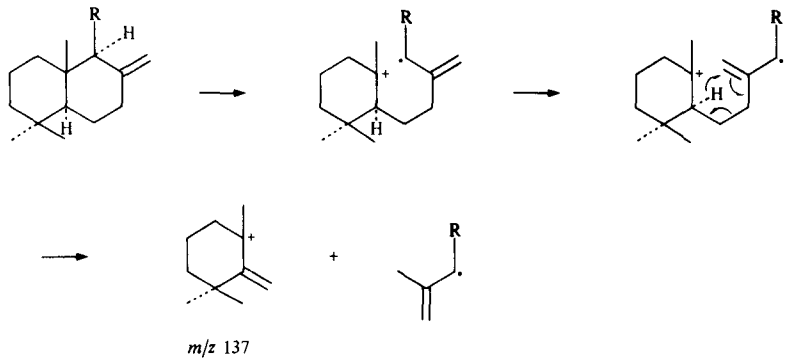
Compounds **3** and **4** were identified as furopelargone B

Table 1. ^{13}C chemical shifts of labdane-type diterpenes **1**, **2**, **8** and **9** [100 MHz, $CDCl_3$, TMS as int. standard]

C	1	2	8	9
1	39.4 *t*	36.6 *t*	39.2 *t*	39.2 *t*
2	19.4 *t*	19.0 *t*	19.3 *t*	19.4 *t*
3	42.1 *t*	42.0 *t*	42.0 *t*	42.2 *t*
4	33.6 *s*	33.6 *s*	33.6 *s*	33.6 *s*
5	55.6 *d*	54.4 *d*	55.4 *d*	55.5 *d*
6	24.2 *t*	23.2 *t*	24.1 *t*	24.3 *t*
7	38.0 *t*	40.9 *t*	39.3 *t*	38.1 *t*
8	148.2 *s*	148.5 *s*	148.0 *s*	148.6 *s*
9	56.8 *d*	60.8 *d*	56.5 *d*	57.2 *d*
10	39.7 *s*	39.3 *s*	39.6 *s*	39.6 *s*
11	24.4 *t*	146.5 *d*	24.7 *t*	22.4 *t*
12	159.1 *d*	133.5 *d*	159.8 *d*	132.4 *d*
13	140.2 *s*	197.9 *s*	134.7 *s*	135.5 *s*
14	28.3 *t*	27.2 *q*	37.8 *t*	32.8 *t*
15	61.4 *t*	—	197.1 *d*	66.6 *t*
16	195.9 *d*	—	193.4 *d*	61.6 *t*
17	107.8 *t*	108.6 *t*	107.8 *t*	107.4 *t*
18	33.6 *q*	33.6 *q*	33.6 *q*	33.6 *q*
19	21.8 *q*	21.9 *q*	21.7 *q*	21.8 *q*
20	14.5 *q*	15.1 *q*	14.4 *q*	14.5 *q*

Table 2. ^{1}H NMR spectral data of the labdane-type diterpenes **1**, **2**, **8** and **9** [400 MHz, C_6D_6 (**1**) or $CDCl_3$ (**2**, **8** and **9**) TMS as int. standard, *J*(Hz) in parentheses]

H	1	2	8	9
9	1.60 (*dd*, 3.0, 11.1 Hz)			
11	2.21 (*ddd*, 6.6, 11.1, 16.1 Hz)	6.87 (*dd*, 10.3, 15.8 Hz)	2.33 (*ddd*, 6.5, 11.3, 16.7 Hz)	2.05 (*ddd*, 6.4, 11.2, 15.7 Hz)
	2.35 (*ddd*, 3.0, 6.3, 16.1 Hz)		2.50 (*ddd*, 3.0, 6.5, 16.7 Hz)	2.30 (*ddd*, 2.5, 6.4, 15.7 Hz)
12	6.17 (*dd*, 6.3, 6.6 Hz)	6.07 (*d*, 15.8 Hz)	6.07 (*t*, 7.0 Hz)	5.51 (*t*, 6.4 Hz)
14	2.43 (*dt*, 13.2, 6.5 Hz)	2.27 (*s*)	3.39 (*d*, 16.7 Hz)	2.42 (*dt*, 15.0, 6.4 Hz)
	2.49 (*dt*, 13.2, 6.5 Hz)		3.46 (*d*, 16.7 Hz)	2.47 (*dt*, 15.0, 6.4 Hz)
15	3.54 (*t*, 6.5 Hz)	—	9.40 (*s*)	3.75 (*td*, 6.4, 1.6 Hz)
16	9.23 (*s*)	—	9.63 (*s*)	4.02 (*br s*)
17	4.42 (*br s*)	4.41 (*d*, 1.6 Hz)	4.37 (*d*, 1.0 Hz)	4.44 *d*, 1.5 Hz)
	4.85 (*br s*)	4.79 (*d*, 1.6 Hz)	4.86 (*d*, 1.0 Hz)	4.82 (*d*, 1.5 Hz)
18	0.75 (*s*)	0.85 (*s*)	0.73 (*s*)	0.71 (*s*)
19	0.83 (*s*)	0.89 (*s*)	0.82 (*s*)	0.81 (*s*)
20	0.89 (*s*)	0.90 (*s*)	0.89 (*s*)	0.88 (*s*)



Scheme 1. The characteristic mass spectral fragmentation of labdane-type diterpenes.

[16] and humulene epoxide II [17], respectively. Compounds **5**, **6** and **7** were readily identified as methyl *trans*-cinnamate, dihydro-5,6-dehydrokawain and dihydroflavokawin B, respectively, by direct comparison of authentic specimens.

DISCUSSION

Only a few instances have been recorded of the isolation of diterpenes from Zingiberaceous plant [18–20]. The similar labdane-type diterpenes to **1** and **2** have also been isolated from *A. speciosa* and *A. galanga* and this structural feature seems to be characteristic of the diterpenic constituents in these three species of genus *Alpinia*. Furopelargone B has already been isolated from *A. japonica* [4–7] and *A. intermedia* [8], but hanalpinol which is assumed to be the direct precursor of furopelargone B was not isolated this time. Compound **4** has also been isolated from *A. speciosa* (unpublished results). The phenolic compounds (**5–7**) were identical with those which have been isolated from *A. speciosa* [21]. Therefore, *A. formosana* and *A. speciosa* are closely related plants in the genus *Alpinia*.

EXPERIMENTAL

General procedures. Mps: uncorr; ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz): $CDCl_3$ or C_6D_6, with TMS as int. standard; CC: silica gel (Wakogel C-200 or Kieselgel 60) at amounts equivalent to 50–100 times the sample amount; prep. HPLC: glass 22 mm i.d. × 30 cm CIG column (Kusano Scientific Co., Tokyo) packed with Iatrobeads (60 μm spherical silica gel, Iatron Co., Tokyo) or RP-18 (25–45 μm); TLC: 0.25 mm silica gel ($60F_{254}$, Merck) or RP-18 plates (F_{254S}, Merck). Spots were detected by UV light (254 nm) and spraying with 10% H_2SO_4 and heating.

Extraction of Alpinia formosana. The fresh rhizomes (50 kg) of *A. formosana* collected in Satamisaki, Kagosima, in October 1985 were crushed and extracted with MeOH (× 2) at room temp. The MeOH extracts were diluted with H_2O to about 10% aq. MeOH and these were extracted with *n*-hexane. The *n*-hexane layer was evapd to give a brown oil (90.1 g).

Isolation of compounds **1–7**. A portion of the *n*-hexane extract (50.0 g) was subjected to CC on silica gel eluted with *n*-hexane–EtOAc. The fraction eluted with *n*-hexane–EtOAc (50:1) was subjected to HPLC on silica gel using *n*-hexane–EtOAc (20:1) and on RP-18 using MeOH–H_2O (9:1) to give **4** (245 mg). The fraction eluted with *n*-hexane–EtOAc (20:1) was subjected to HPLC on silica gel using *n*-hexane–EtOAc (9:1) and C_6H_6–EtOAc (50:1) and on RP-18 using MeOH–H_2O (9:1). When the procedures were repeated a few times, **2** (50 mg), **3** (100 mg), **5** (400 mg) and **7** (60 mg) were isolated. The fraction eluted with *n*-hexane–EtOAc (4:1) was subjected to HPLC on silica gel using *n*-hexane–$CHCl_3$–CH_3CN (6:3:1) and then HPLC on RP-18 using MeOH and on silica gel using C_6H_6–EtOAc (4:1) led to the isolation of **1** (100 mg). Repeated recrystallizations of the *n*-hexane–EtOAc (3:2) eluate furnished **6** (5.0 g). Compound **1** [(*E*)-labda-8(17), 12-diene-15-ol-16-al]. A colourless oil, $[\alpha]_D^{20}$ + 20.0° ($CHCl_3$; *c* 0.10); EIMS *m/z* (rel. int.): 304 $[M]^+$ (17), 286 (9), 273 (19), 216 (18), 201 (12), 275 (12), 249 (25), 137 (100), 123 (39), 95 (65), 81 (74), 69 (69); HRMS: Calc. 304.2401 Found 304.2409; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640 (OH), 3080, 895 (C=CH_2), 1685 (C=O), 1640 (C=C); UV λ_{max}^{EtOH} nm (ε): 235 (12400); ^{1}H NMR, $CDCl_3$: δ0.76 (3H, *s*), 0.83 (3H, *s*), 0.89 (3H, *s*), 3.69 (1H, *t*, *J* = 5.8 Hz), 3.70 (1H, *t*, *J* = 5.8 Hz), 4.41 (1H, *d*, *J* = 1.1 Hz), 4.86 (1H, *d*, *J* = 1.3 Hz), 6.58 (1H, *t*, *J* = 6.5 Hz), 9.36 (1H, *s*).

Compound **2**. (*E*)-15,16-bisnorlabda-8(17),11-diene-13-one. Colourless needles, mp 146.0–147.0°, $[\alpha]_D^{20}$ + 6.6° ($CHCl_3$; *c* 0.23); EIMS *m/z* (rel. int.): 260 $[M]^+$ (14), 245 (4), 150 (31), 137 (31), 121 (45), 69 (53), 43 (100); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3070, 890 (C=CH_2), 1675 (C=O), 1640, 1620 (C=C); UV λ_{max}^{EtOH} nm (ε): 228 (10000).

Compound **3** (*furopelargone B*). A colourless oil, $[\alpha]_D$ + 44.1° ($CHCl_3$; *c* 0.12); EIMS *m/z* (rel. int.): 234 $[M]^+$ (100), 191 (52), 163 (86), 149 (56), 123 (43), 109 (51), 91 (40); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2960, 1715 (C=O), 1465, 1360, 1220, 1160, 1075, 890; UV λ_{max}^{EtOH} nm (ε): 222 (6500); ^{1}H NMR, $CDCl_3$: δ0.72 (3H, *d*, *J* = 6.8 Hz), 1.15 (6H, *d*, *J* = 6.7 Hz), 1.86 (3H, *s*), 2.80 (1H, *septet*, *J* = 6.7 Hz), 3.15 (1H, *m*), 3.59 (1H, *t*, *J* = 7.0 Hz), 6.20 (1H, *d*, *J* = 1.9 Hz), 7.20 (1H, *d*, *J* = 1.9 Hz); ^{13}C NMR, $CDCl_3$: δ16.1 (*q*), 23.6 (*q*), 24.3 (*q*), 24.5 (*d*), 24.7 (*t*), 28.6 (*q*), 31.8 (*t*), 40.3 (*d*), 43.8 (*d*), 57.8 (*d*), 108.0 (*d*), 128.4 (*s*), 140.9 (*d*), 147.2 (*s*), 208.2 (*s*).

Compound **4** (*humulene epoxide* II). A colourless oil, $[\alpha]_D^{20}$ − 9.8° ($CHCl_3$; *c* 0.25); EIMS *m/z* (rel. int.): 220 $[M]^+$ (22), 203 (38), 138 (100), 109 (87), 43 (49); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2970, 1445, 1385, 1070, 970, 820; ^{1}H NMR, $CDCl_3$: δ1.08 (3H, *s*), 1.11 (3H, *s*), 1.31 (3H, *s*), 1.56 (3H, *br s*), 4.99 (1H, *br t*), 5.16 (1H, *d*, *J* = 15.9 Hz), 5.28 (1H, *ddd*, *J* = 5.2, 10.0 and 15.9 Hz); ^{13}C NMR, $CDCl_3$: δ15.1 (*q*), 17.2 (*q*), 24.8 (*t*), 25.6 (*q*), 29.0 (*q*), 36.5 (*s*), 36.6 (*t*), 40.3 (*t*), 42.6 (*t*), 61.8 (*d*), 63.1 (*s*), 122.1 (*d*), 125.7 (*d*), 131.8 (*s*), 143.0 (*d*).

Compound **5** (*methyl* trans-*cinnamate*). Colourless needles, mp 32.0–33.0°; EIMS *m/z* (rel. int.): 162 $[M]^+$ (55), 131 (100), 103 (56), 77 (32); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 (C=O), 1638 (C=C), 1170, 985, 773; UV λ_{max}^{EtOH} nm (ε): 266 (21000); ^{1}H NMR, $CDCl_3$: δ3.78 (3H, *s*), 6.20 (1H, *d*, *J* = 16.0 Hz), 7.20–7.60 (5H, *m*), 7.62 (1H, *d*, *J* = 16.0 Hz). Compound **6** (dihydro-5, 6-dehydrokawain). Colourless needles, mp 98.5°; EIMS *m/z* (rel. int.): 230 $[M]^+$ (35), 202 (3), 125 (36), 91 (100), 69 (18); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (C=O), 1655, 1570, 1500, 1455, 1410, 1245, 1140, 1040, 700; UV λ_{max}^{EtOH} nm (ε): 277 (7200); ^{1}H NMR, $CDCl_3$: δ2.73 (2H, *t*, *J* = 7.5 Hz), 2.95 (2H, *t*, *J* = 7.5 Hz), 3.74 (3H, *s*), 5.40 (1H, *d*, *J* = 2.2 Hz), 5.71 (1H, *d*, *J* = 2.2 Hz), 7.15–7.29 (5H, *m*); ^{13}C NMR, $CDCl_3$: δ171.2 (*s*), 164.8 (*s*), 164.4 (*s*), 139.9 (*s*), 128.6 (*d*), 128.3 (*d*), 126.4 (*d*), 100.2 (*d*), 87.8 (*d*), 55.8 (*q*), 35.4 (*t*), 32.8 (*t*).

Compound **7** (*dihydroflavokawin B*). Colourless needles, mp 104.0–105.0°; EIMS *m/z* (rel. int.): 286 $[M]^+$ (28), 181 (100), 154 (23), 83 (21); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1620 (C=O), 1600, 1420, 1220, 1210, 1160, 1120, 700; UV λ_{max}^{EtOH} nm (ε): 214 (infl. 23000), 288 (19000); ^{1}H NMR, $CDCl_3$: δ2.99 (2H, *t*, *J* = 7.0 Hz), 3.32 (2H, *t*, *J* = 7.0 Hz), 3.81 (3H, *s*), 3.82 (3H, *s*), 5.92 (1H, *d*, *J* = 2.4 Hz), 6.07 (1H, *d*, *J* = 2.4 Hz), 7.18–7.31 (5H, *m*), 14.00 (1H, *s*, disappeared with D_2O); ^{13}C NMR, $CDCl_3$: δ204.5 (*s*), 167.7 (*s*), 166.0 (*s*), 162.7 (*s*), 141.7 (*s*), 128.4 (*d*), 125.9 (*d*), 105.8 (*s*), 93.7 (*d*), 90.8 (*d*), 55.5 (*q*), 45.7 (*t*), 30.7 (*t*).

Reduction of compound **1**. A MeOH soln of **1** (20 mg) was treated with excess of $NaBH_4$. After work-up in the usual way, the product was subjected to HPLC (*n*-hexane–EtOAc, 1:1) to give a colourless oil, **9** (15 mg) whose spectral data including specific rotation were identical with those of **9** produced by reduction of (*E*)-8(17),12-diene-15,16-dial in the same manner. Compound **9**: A colourless oil, $[\alpha]_D$ + 20.0° ($CHCl_3$; *c* 0.3); EIMS *m/z* (rel. int.): 306 $[M]^+$ (2), 288(68), 273 (56), 257 (37), 215 (21), 137 (100); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 2940, 1640, 1600, 1460, 1440, 1385, 1260.

Ozonolysis of compound **2**. After a soln of **2** (22 mg) in MeOH (5 ml) was bubbled with O_3 for a few minutes at 0°, the reaction mixture was stirred for 1 hr at 30° with acetic acid (0.25 ml) and zinc powder (20 mg). Then the solvent was evapd and the product was subjected to HPLC (*n*-hexane–EtOAc, 7:3) to give colourless needles, **10** (10 mg), mp 83–84°; EIMS *m/z* (rel. int.): 262 $[M]^+$ (12), 244 (17), 219 (26), 205 (20), 137 (35), 111 (100); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2960, 1715 (C=O), 1680 (C=O), 1630 (C=C), 1460, 1425, 1390, 1360, 1250, 985; ^{1}H NMR $CDCl_3$: δ0.89 (3H, *s*), 0.91 (3H, *s*), 0.99

(3H, *s*), 2.30 (3H, *s*), 2.86 (1H, *d*, $J = 9.8$ Hz), 5.97 (1H, *d*, $J = 16.2$ Hz), 6.90 (1H, *dd*, $J = 9.8, 16.2$ Hz); CD: $\Delta\varepsilon_{290} = -2.79$.

Acknowledgement—We are grateful to Mr. Akira Seo and Mr. Shoichiro Seo, Seo Pharmacy, Kagoshima, for their kind co-operation in the collection of *A. formosana*. We are also grateful to Dr Tunao Ueki, Natural Park Instructor, National Institute of Environment, for identification of *A. formosana*.

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