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LINOLEOYLATED POLYACETYLENES FROM THE ROOT OF *PANAX GINSENG**

KAZUHIRO HIRAKURA, MAKOTO MORITA, KAZUAKI NIITSU, YUKINOBU IKEYA, MASAO MARUNO

Tsumura Central Laboratories, Tsumura and Co., 3586 Yoshiwara, Ami-machi, Inashiki-gun, Ibaraki, Japan

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Key Word Index—*Panax ginseng*; Araliaceae; acetylenic compound; linoleoyl ester; panaxynol; panaxydol; ginsenoyne A; panaxyne epoxide.

Abstract—Three new linoleoylated acetylenic compounds were isolated from the methanol extract of the roots of *Panax ginseng*. The structures were determined by spectral and chemical methods.

INTRODUCTION

Panax ginseng C. A. Meyer is one of the most important oriental medicinal plants in Japan, Korea and China [2]. Many polyacetylenes e.g. panaxynol (**4**) [3] and panaxydol (**5**) [4] have been isolated from this plant. Previously, we have reported the structures of three new acetylenic compounds named ginsenoynes I–K [1]. In our further studies on the constituents of *P. ginseng*, we have isolated three new linoleoylated polyacetylenes along with panaxyne epoxide (**6**) [5, 6] from this plant, and the structures were elucidated by spectral and chemical methods.

RESULTS AND DISCUSSION

Compound **1** was obtained as an oil. The UV spectrum of **1** showed typical absorption bands for a conjugated diyne chromophore [7]. The IR spectrum of **1** showed the presence of triple bonds, an ester carbonyl and double bonds. The molecular formula of **1** was determined to be $C_{35}H_{54}O_2$ by HR-FAB mass spectrometry. The ^{1}H NMR spectrum of **1** was similar to that of **4**, except for the signals of the unsaturated fatty acid. The H-3 proton signal of **1** showed a downfield shift of +1.00 ppm if compared with that of **4** (Table 1). Methanolysis of **1** with HCl–MeOH gave **4** and methyl linoleate. This showed that **1** is the compound with the linoleoyl moiety linked to the C-3 hydroxyl group of **4**. From these results, **1** was determined as panaxynol linoleate [(9*Z*)-1,9-heptadecadiene-4,6-diyn-3-ol 3-linoleate].

Compound **2** was obtained as an oil. The UV spectrum of **2** showed typical absorption bands for a conjugated diyne chromophore. The IR spectrum of **2** showed the presence of triple bonds, an ester carbonyl and double bonds. The molecular formula of **2** was determined to be $C_{35}H_{54}O_3$ by HR-FAB mass spectrometry. The ^{1}H and ^{13}C NMR spectra of **2** were similar to those of **5**, except that the H-3 and C-3 signals apeared downfield if compared with those of **5** (Table 1), and additional signals appeared for a C_{18} unsaturated fatty acid (Tables 1 and 2). Methanolysis of **2** with HCl–MeOH gave methyl linoleate and two chlorohydrin derivatives **2a** and panaxydol chlorohydrin (**2b**) [4, 8]. The production of chlorohydrin derivative **2a** showed the presence of an epoxy ring moiety in **2**. These facts suggested that **2** is linoleoylated panaxydol. Finally, the structure of **2** was confirmed by treatment of **5** with linoleic anhydride to give **2**. From the above results, **2** is determined as panaxydol linoleate (9,10-epoxy-1-heptadecene-4,6-diyn-3-ol 3-linoleate). Compound **3** was obtained as an oil. The UV spectrum of **3** showed typical absorption bands for a diyne chromophore. The IR spectrum of **3** showed the presence of triple bonds, an ester carbonyl and double bonds. The molecular formula of **3** was determined to be $C_{35}H_{52}O_3$ by HR-FAB mass spectrometry. The ^{1}H and ^{13}C NMR spectra of **3** were similar to those of ginsenoyne A (**7**), except for the presence of a linoleoyl moiety. The treatment of **7** with linoleic anhydride gave **3**. From these results, **3** is determined as ginsenoyne A linoleate (9,10-epoxy-1,16-heptadecadiene-4,6-diyn-3-ol 3-linoleate).

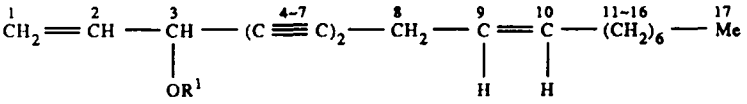
EXPERIMENTAL

General. See refs [1, 9]. Prep. reversed HPLC used a 2 × 30 cm packed column YMC S-343. GC-MS was measured using fused silica column: DB-1(15 m × 0.55 mm i. d., film thickness 0.25 μm); detector: EI-MS(mass range *m/z* 40 ~ 600); temp.: programmed 180 to 200° at 1° min^{-1}; injection temp.: 250°; interface: 250°; carrier gas: He 15 ml min^{-1}.

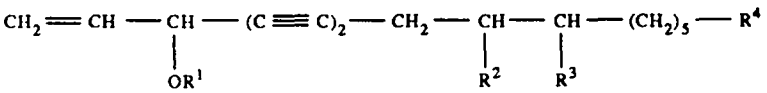
Plant material. The roots of *P. ginseng* were collected in Gunma prefecture, Japan, and were cultivated.

Isolation of compounds. Dried and crushed roots (60 kg) were divided into 10 parts and each part was extracted × 3 by refluxing with MeOH (100 l). The MeOH soln was

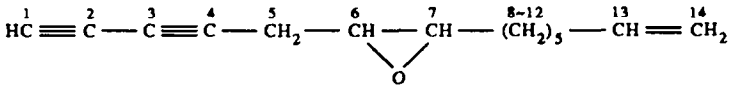
*Part 4 in the series 'The Constituents of *Panax ginseng*', for Part 3 see ref. [1].



	R^1
1	linoleoyl
4	H



	R^1	R^2	R^3	R^4
2	linoleoyl	—O—		CH_2Me
2a	linoleoyl	OH	Cl	CH_2Me
2b	H	OH	Cl	CH_2Me
3	linoleoyl	—O—		$CH=CH_2$
5	H	—O—		CH_2Me
7	H	—O—		$CH=CH_2$



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concd to 50% under red. pres. and H_2O added. The MeOH–H_2O soln was extracted with petrol to give a petrol extract (1.4 kg). This petrol extract was chromatographed on a silica gel column (4 kg), eluting with a hexane–EtOAc mixt. of increasing polarity.

The eluates were divided into 7 frs: F-1 (119 g), F-2 (87 g), F-3 (166.6 g), F-4 (229.4 g), F-5 (121.0 g), F-6 (29.2 g) and F-7 (14.8 g). A part of F-1 (14 g) was sepd by prep. HPLC with hexane–EtOAc (50:1) to give 3 frs as follows, F-1-1 (6.9 g), F-1-2 (1.4 g) and F-1-3 (4.9 g). The F-1-2 was rechromatographed on prep. reversed phase HPLC, eluted with THF–MeCN (1:5) to give **1** (83 mg). F-2 was sepd by prep. HPLC with hexane–EtOAc (18:1), hexane–C_6H_6 (1:2) successively to give **2** (490 mg), **3** (170 mg) and panaxyne epoxide (**6**, 110 mg).

Panaxynol linoleate (**1**). Oil $[\alpha]_D$ +18.7° ($CHCl_3$; *c* 6.8). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3012, 2260 (C≡C), 1744 (C=O), 1644 (C=C), 974, 938. UV λ_{max}^{EtOH} nm (log ε): 232 (2.93), 244 (2.88), 258 (2.65). FDMS *m/z*: 506[M]$^+$. HR-FABMS (positive, *m*-nitrobenzyl alcohol, at 7 kV, Xe) *m/z*: 505.4040 (Calcd for $C_{35}H_{53}O_2$ [M−H]$^+$: 505.4046).

Methanolysis of **1** *with* HCl–MeOH. A mixt. of **1** (33 mg), 5%HCl–MeOH (2 ml) and C_6H_6 (1 ml) was stirred at 50° for 150 min. To the reaction mixt. was added 2% $NaHCO_3$ soln and it was then extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with H_2O, dried over $MgSO_4$ and concd under red. pres. The residue was purified by prep. HPLC, eluted with hexane–acetone (6:1) to give **4** (6.4 mg) and methyl linoleate. The methyl linoleate was identified with an authentic sample by GC-MS (R_t 5'04").

Panaxydol linoleate (**2**). Oil. $[\alpha]_D$ −14.3° ($CHCl_3$; *c* 11.0). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3008, 2260 (C≡C), 1746 (C=O), 1642 (C=C), 976, 938. UV λ_{max}^{EtOH} nm (log ε): 220 (*infl.* 3.03), 231 (3.09), 244 (3.07), 257 (2.83). FDMS *m/z*: 522 [M]$^+$. HR-FABMS *m/z* 523.4155 (Calcd for $C_{35}H_{55}O_3$ [M+H]$^+$: 523.4151).

Methanolysis of **2** *with* HCl–MeOH. A mixt. of **2** (52 mg), 5%HCl–MeOH (2 ml) and C_6H_6 (1 ml) was worked-up by the above method and purified by prep. HPLC, eluted with hexane–acetone (10:1) to give **2a** (15 mg), **2b** (24 mg) and methyl linoleate. The methyl linoleate was identified by GC-MS.

The compound **2b** was identified as panaxydol chlorohydrin by comparison with the physical data of the authentic sample [7]. The compound **2a** was identified as 10-chloro-1-heptadecen-4,6-diyne-3,9-diol 3-linoleate by the following physical data. Oil. $[\alpha]_D$ +4.4° ($CHCl_3$; *c* 2.3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (*br* OH), 3004, 2928, 2260 (C≡C), 1736 (C=O), 1648 (C=C), 974, 944. UV λ_{max}^{EtOH} nm (log ε); 232 (3.08), 245 (3.04), 258 (2.87). FABMS *m/z*: 559, 557 (each [M]$^+$). ^{1}H NMR (500 MHz, $CDCl_3$): δ0.88 (3H, *br t*, *J* = 7 Hz, H-17 or H-18'), 0.89 (3H, *br t*, *J* = 7 Hz, H-17 or H-18'), 1.25 ~ 1.39 (22H, *m*, H-13 ~ H-16, H-4' ~ H-7' and H-15' ~ H-17'), 1.40 ~ 1.45 and 1.50 ~ 1.58 (each 1H, *m*, H-12), 1.64 (2H, *br qui*, *J* = 7 Hz, H-3'), 1.79 ~ 1.85

Table 1. ^{1}H NMR spectral data for **1**~**5** and **7** (δ in $CDCl_3$, 500 MHz)

H	1	2	3	4	5	7
1a	5.31 *dt* (9.9, 1.0)	5.32 *dt* (9.9, 1.0)	5.33 *dt* (9.8, 1.0)	5.24 *ddd* (10.2, 1.3, 0.9)	5.24 *ddd* (10.1, 1.5, 1.0)	5.23 *ddd* (10.3, 1.5, 1.0)
1b	5.52 *dt* (16.7, 1.0,)	5.53 *dt* (16.7, 1.0)	5.53 *dt* (16.7, 1.0)	5.46 *ddd* (17.1, 1.5, 0.9)	5.46 *ddd* (17.1, 1.5, 1.0)	5.45 *ddd* (17.0, 1.5, 1.0)
2	5.85 *ddd* (16.7, 9.9, 5.7)	5.86 *ddd* (16.7, 9.9, 5.7)	5.86 *ddd* (16.7, 9.8, 5.7)	5.94 *ddd* (17.1, 10.2, 5.4)	5.94 *ddd* (17.1, 10.1, 5.4)	5.93 *ddd* (17.0, 10.3, 5.4)
3	5.91 *dqui* (5.7, 1.0)	5.92 *dqui* (5.7, 1.0)	5.92 *dqui* (5.7, 1.0)	4.91 *br t* (6)	4.92 *br* (5)	4.90 *br d* (5.4)
8a	3.02 *d-like* (7)	2.38 *ddd* (17.3, 7.1, 1.0)	2.37 *ddd* (17.8, 7.1, 1.0)	3.03 *d*-like (6.9)	2.39 *ddd* (17.7, 7.1, 1.0)	2.38 *ddd* (17.7, 7.2, 1.0)
8b		2.68 *ddd* (17.3, 5.5, 1.0)	2.69 *ddd* (17.8, 5.5, 1.0)		2.70 *ddd* (17.7, 5.4, 1.0)	2.71 *ddd* (17.7, 5.5, 1.0)
9	5.30~5.41 *m*	3.13 *ddd* (7.1, 5.5, 4.1)	3.13 *ddd* (7.1, 5.5, 4.0)	5.38 *dtt* (10.6, 6.9, 1.6)	3.15 *ddd* (7.1, 5.5, 1.0)	3.15 *ddd* (7.2, 5.5, 4.1)
10	5.50 *dtt* (10.5, 7.3, 1.6)	2.95 *br td* (6, 4)	2.95 *ddd* (7.1, 5.3, 4.0)	5.52 *dtt* (10.6, 7.4, 1.6)	2.97 *br td* (6, 4.1)	2.98 *br td* (6, 4.1)
11	1.99~2.07 *m*			2.02 *qd* (7.2, 1.6)	1.45~1.55 *m*	
12			1.35~1.45 m	1.36 *br qui*		1.45~1.55 *m*
13			1.48~1.55 *m*	(7)		1.35~1.45 *m*
14	1.25~1.39 *m*	1.25~1.39 *m*	1.25~1.38 *m*	1.25~1.40 *m*	1.25~1.40 *m*	
15			2.06 *m*			2.06 *br qt* (6, 1.5)
16			5.81 *ddt* (17.0, 10.2, 6.6)			5.81 *ddt* (17.1, 10.2, 6.7)
17a	0.88[a] *br t* (7)	0.88[a] *br t* (7)	4.94 *ddt* (10.2, 2.1, 1.5)	0.88 *br t* (7)	0.89 *br t* (7)	4.94 *ddt* (10.2, 2.1, 1.5)
17b			5.00 *ddt* (17.0, 2.1, 1.5)			5.01 *ddt* (17.1, 2.1, 1.5)
2′	2.33 *t*-like (7.5)	2.34 *t*-like (7.8)	2.34 *t*-like (7.8)			
3′	1.63 *br qui* (7.5)	1.64 *br qui* (7.8)	1.64 *br qui* (7.8)			
4′,5′ 6′,7′ 15′	1.25~1.39 *m*	1.25~1.39 *m*	1.24~1.35 *m*			
8′,14′	1.99~2.07 *m*	2.05 *br q* (7)	2.06 *m*			
9′10′ 12′,13′	5.30~5.41 *m*	5.29~5.41 *m*	5.30~5.42 *m*			
11′	2.77 *br t* (7)	2.77 *br t* (7)	2.77 *br t* (7)			
18′	0.89[a] *br t* (7)	0.89[a] *br t* (7)	0.89 *br t* (7)			

Coupling constants (J) in Hz are given in parentheses.
Signal assignments were based on ^{1}H–^{1}H COSY experiments.
[a]Assignments may be interchanged in each column.

(2H, *m*, H-11), 2.05 (4H, *m*, H-8′ and H-14′), 2.11 (1H, *d*, J = 8.3 Hz, C-9-OH), 2.34 (2H, *t*-like, J = 7.5 Hz, H-2′), 2.63 (1H, *ddd*, J = 1.0, 6.4 and 17.3 Hz, H-8), 2.66 (1H, *ddd*, J = 1.0, 6.6 and 17.3 Hz, H-8), 2.77 (2H, *br t*, J = 7 Hz, H-11′), 3.85 (1H, *dtd*, J = 2.9, 6.5 and 8.3 Hz, H-9), 4.11~4.14 (1H, *m*, H-10), 5.33 (1H, *dt*, J = 1.0 and 9.7 Hz, H-1), 5.30~5.42 (4H, *m*, H-9′~H-10′ and H-12′~H-13′), 5.53 (1H, *dt*, J = 1.0 and 16.6 Hz, H-1), 5.86 (1H, *ddd*, J = 5.7, 9.7 and 16.6 Hz, H-2), 5.92 (1H, *dqui*, J = 1.0 and 5.7 Hz, H-3). ^{13}C NMR(125 MHz, $CDCl_3$): δ14.1(*q* × 2, C-17 and C-18′), 22.6 (*t*, C-16 or C-17′), 22.7 (*t*, C-17′ or C-16), 24.9 (*t*, C-3′), 25.7 (*t*, C-11′), 25.9 (*t*, C-8), 26.7 (*t*, C-12), 27.2 (*t*, C-8′ or C-14′), 27.3 (*t*, C-14′ or C-8′), 29.1 (× 2), 29.2 (× 3), 29.4, 29.7 (each *t*, C-13~C-14, C-4′~C-7′ and C-15′), 31.6 (*t*, C-15 or C-16′), 31.8 (*t*, C-16′ or C-15), 34.3 (*t*, C-2′), 34.9 (*t*, C-11), 64.3 (*d*, C-3), 66.8 (*s*, C-7), 66.9 (*d*, C-10), 71.4, 77.1 (overlapping with solvent), 71.8 (each *s*, C-4~C-6), 72.2 (*d*, C-9), 119.5 (*t*, C-1), 128.0 (*d*, C-12′), 128.2

Table 2. ^{13}C NMR spectral data for 1~5 and 7 (δ in $CDCl_3$, 125 MHz)

C	1	2	3	4[10]	5	7
1	119.3	119.4	119.4	116.9	116.9	116.9
2	132.7	132.4	132.3	136.2	136.2	136.3
3	64.4	64.3	64.2	63.3	63.4	63.3
4	71.0[a]	71.7[a]	71.7[a]	74.5	75.2	75.4
5	71.9[a]	71.4[a]	71.4[a]	71.1	70.7	70.6
6	64.1	66.3	66.3	64.3	66.4	66.5
7	80.4	76.9	76.9	80.0	76.6	76.5
8	17.7	19.5	19.5	17.7	19.5	19.4
9	121.9	54.2	54.2	122.1	54.4	54.4
10	133.2	56.9	56.9	133.0	57.1	57.0
11	27.3[b]	27.5[b]	27.5[b]	27.2	27.5	27.4
12	29.2[c]	26.5	26.3	29.3[a]	26.5	26.3
13	29.1[c]	29.1[c]	28.8[c]	29.3[a]	29.4[a]	28.9[a]
14	29.1[c]	29.0[c]	28.9[c]	29.3[a]	29.2[a]	28.8[a]
15	31.9[d]	31.8[d]	33.6	31.9	31.7	33.6
16	22.7[e]	22.6[e]	138.9	22.7	22.6	138.9
17	14.1[f]	14.1[f]	114.4	14.1	14.1	114.4
linoleoyl [11]						
1′	172.3	172.2	172.3			
2′	34.2	34.2	34.2			
3′	24.9	24.8	24.8			
4′,5′	29.0[c], 29.1[c]	29.1[c], 29.2[c]	29.0[d], 29.1[d] (×2)			
6′,7′	29.2[c], 29.4[c]	29.3[c], 29.4[c]	29.4[d]			
15′	29.6[c]	29.6[c]	29.6[d]			
8′,14′	27.2[b] (×2)	27.2[b] (×2)	27.2[b] (×2)			
9′	130.1	130.1	130.1			
10′	128.1	128.1	128.1			
11′	25.7	25.7	25.7			
12′	128.0	127.9	127.9			
13′	130.3	130.3	130.3			
16′	31.6[d]	31.6[d]	31.5			
17′	22.6[e]	22.5[e]	22.6			
18′	14.0[f]	14.1[f]	14.1			

Signal assignments were based on ^{13}C–^{1}H COSY and DEPT experiments.
[a–f]Assignments may be interchanged in each column.

(*d*, C-10′), 130.1 (*d*, C-9′), 130.3 (*d*, C-13′), 132.4 (*d*, C-2), 172.3 (*s*, C-1′).

Esterification of **5** *with linoleic anhydride.* A mixt. of **5** (70 mg), linoleic anhydride (excess amount), Et_3N(0.2 ml) and 4-dimethylaminopyridine (catalytic amount) in CH_2Cl_2(1.5 ml) was stirred at room temp. for 60 min. To the reaction mixt. was added 10% malonic acid soln and extracted with hexane. The hexane layer was dried over $MgSO_4$ and concd under red. pres. The residue was purified by prep. HPLC, eluted with hexane–C_6H_6(1 : 2) to give **2** (77 mg).

Ginsenoyne A linoleate (**3**). Oil. $[\alpha]_D$ −13.9° ($CHCl_3$; *c* 6.0). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3008, 2260 (C≡C), 1746 (C=O), 1642 (C=C), 994, 976, 938. UV λ_{max}^{EtOH} nm (log ε): 220 (3.01), 232 (3.06), 244 (2.99), 257 (2.72). HR-FABMS *m/z*: 521.3955 (Calcd for $C_{35}H_{53}O_3$ $[M+H]^+$: 521.3988).

Esterification of **7** *with linoleic anhydride.* A mixt. of **7** (43 mg), linoleic anhydride (excess amount), Et_3N(0.2 ml) and 4-dimethylaminopyridine (catalytic amount) in CH_2Cl_2 was worked-up by the above method and purified by prep. HPLC, eluted with hexane–EtOAc (18 : 1) to give **3** (64 mg).

Panaxyne epoxide (**6**). Oil. $[\alpha]_D$ −79.1° ($CHCl_3$; *c* 13.1). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3308, (H–C≡C), 2300 (C≡C), 2228 (C≡C), 1640 (C=C), 1462, 914, 624. (H–C≡C). UV λ_{max}^{EtOH} nm (log ε): 212 (2.68), 224 (2.61), 237 (2.58), 251 (2.40). CIMS (*iso*-butane), 200 eV, *m/z* (rel. int.): 203 $[M+H]^+$(64), 185 $[M+H-H_2O]^+$(41), 157 (46), 143 (94), 105 (100). ^1H NMR (500 MHz, $CDCl_3$): δ1.35~1.45 and 1.45~1.56 (each 4H, *m*, H-8~H-11), 2.01 (1H, *t*, *J* = 1.2 Hz, H-1), 2.06 (2H, *br qt*, *J* = 1.4 and 6.7 Hz, H-12), 2.36 (1H, *ddd*, *J* = 1.2, 7.1 and 17.7 Hz, H-5), 2.67 (1H, *ddd*, *J* = 1.2, 5.5 and 17.7 Hz, H-5), 2.96 (1H, *ddd*, *J* = 4.1, 5.5, 6.8 Hz, H-7), 3.14 (1H, *ddd*, *J* = 4.1, 5.5 and 7.1 Hz, H-6), 4.94 (1H, *ddt*, *J* = 1.5, 2.1 and 10.2 Hz, H-14a), 5.00 (1H, *ddt*, *J* = 1.5, 2.1 and 17.0 Hz, H-14b), 5.81 (1H, *dtt*, *J* = 6.7, 10.2 and 17.0 Hz, H-13). ^{13}C NMR (125 MHz, $CDCl_3$): δ19.3 (*t*, C-5), 26.3 (*t*, C-9), 27.5 (*t*, C-8), 28.8 (*t*, C-

10 or C-11), 28.9 (*t*, C-11 or C-10), 33.6 (*t*, C-12), 54.2 (*d*, C-6), 56.9 (*d*, C-7), 65.5 (*s*, C-2 or C-3), 66.7 (*s*, C-3 or C-2), 68.0 (*d*, C-1), 73.0 (*s*, C-4), 114.4 (*t*, C-14), 138.9 (*d*, C-13).

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REFERENCES

1. Hirakura, K., Morita, M., Nakajima, K., Ikeya, Y. and Mitsuhashi, H. (1992) *Phytochemistry* **31**, 899.
2. Chang, H. M. and But, P. P. H. (1986) in *Pharmacology and Applications of Chinese Materia Medica* Vol. 1, p. 17. World Scientific, Singapore.
3. Takahashi, M. and Yoshikura, M. (1966) *Yakugaku Zasshi* **86**, 1053.
4. Poplawski, J., Wrobel, J. T. and Glinka, T. (1980) *Phytochemistry* **19**, 1539.
5. Kim, S. I., Kang, K. S. and Lee, Y. H. (1989) *Arch. Pharm. Res.* **12**, 48.
6. Fujimoto, Y., Wang, H., Kirisawa, M., Satoh, M. and Takeuchi, N. (1992) *Phytochemistry* **31**, 3499.
7. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) in *Naturally Occurring Acetylenes*, p. 4. Academic Press, London.
8. Kitagawa, I., Taniyama, T., Shibuya, H., Noda, T. and Yoshikawa, M. (1987) *Yakugaku Zasshi* **107**, 495.
9. Hirakura, K., Morita, M., Nakajima, K., Ikeya, Y. and Mitsuhashi, H. (1991) *Phytochemistry* **30**, 3327.
10. Gafner, F., Reynolds, G. W. and Rodriguez, E. (1989) *Phytochemistry* **28**, 1256.
11. Gunstone, F. D., Pollard, M. R., Scrimgeour, C. M. and Vedanayagam, H. S. (1977) *Chem. Phys. Lipids* **18**, 115.