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7-*O*-ACETYL LOGANIC ACID FROM *ALANGIUM PLATANIFOLIUM* VAR. *TRILOBUM*

KYOUMI NAKAMOTO, HIDEAKI OTSUKA and KAZUO YAMASAKI*

Institute of Pharmaceutical Sciences, School of Medicine, Hiroshima University, 1-2-3, Kasumi, Minami-ku, Hiroshima, 734 Japan

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Key Word Index—*Alangium platanifolium* var. *trilobum*; Alangiaceae; iridoid glucoside; loganic acid; 7-*O*-acetyl loganic acid.

Abstract—7-*O*-Acetyl loganic acid was isolated for the first time in Nature from the stem bark of *Alangium platanifolium* var. *trilobum*. A compound previously reported to be 7-*O*-acetyl loganic acid, isolated from *Monochasma savatieri*, was not identical with our compound, and the structure should be revised as 7-*O*-acetyl-8-*epi*-loganic acid.

From the methanol extract of *Alangium platanifolium* Harms var. *trilobum* Ohwi, two iridoid glucosides, **1** and **2** were isolated. Compound **1** was identified as loganic acid by spectral evidence [1], and by conversion to loganin pentaacetate for direct comparison with an authentic sample.

Compound **2** showed similar ^{13}C and ^{1}H NMR spectra to those of **1**, with additional signals of an acetyl group. Comparison of the ^{13}C NMR spectra of **1** and **2** in CD_3OD indicated that the carbon signals of C-6, C-7 and C-8 of **2** were significantly shifted by -2.2, $+3.6$ and -1.2 ppm, respectively compared with the corresponding signals of **1**. Since the similar shift trend (-2.2, $+3.9$ and -1.1 ppm) was observed between loganin and periclymenoside, a 7-*O*-acyl derivative of loganin [1], the structure of **2** seemed to be 7-*O*-acetyl loganic acid. Methylation of compound **2** with diazomethane, followed by acetylation, afforded loganin pentaacetate (**4**), which was identified by comparison of its ^{13}C NMR and ^{1}H NMR spectra, TLC properties and mmp with an authentic sample. From this evidence, probable candidates of **2**, such as 7-*O*-acetyl-7-*epi*- and 8-*epi*-loganic acid were definitely excluded.

A compound, here designated as **2'**, was isolated from *Monochasma savatieri* [2] and claimed to be 7-*O*-acetyl loganic acid. However, the reported physical data, including the ^{13}C NMR data (in acetone-d_6), were not identical with those of our compound **2** (Table 1). In the previous report, **2'** was methylated (**3'**), followed by alkaline hydrolysis to afford 'loganin' (**5'**). The ^{13}C NMR spectrum in CD_3OD of **5'** was not in accord with literature data of loganin (**5**) [1], nor with 7-*epi*-loganin (**7**) [3]. To clarify the relationship, a sample of **2'** (donated by the authors of ref. [2]) was analysed by ^{13}C NMR in D_2O. The data was not identical with the reported value of loganin (in D_2O), but was the same as those of 8-*epi*-loganin (**6**) [4] (Table 1).

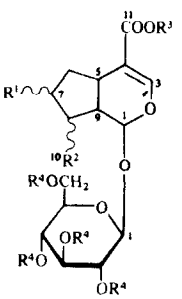
In conclusion, the compound found in *A. platanifolium* is 7-*O*-acetyl loganic acid (**2**) while that isolated from *Monochasma savatieri* (Scrophulariaceae) is 7-*O*-acetyl-8-*epi*-loganic acid. Both these iridoids appear to be new natural compounds.

EXPERIMENTAL

Mp: uncorr. ^{1}H and ^{13}C NMR: 100 and 25 MHz, respectively. EIMS; 75 eV.

Plant material. Alangium platanifolium Harms var. *trilobum* Ohwi was collected during June in Hiroshima city, Japan. The voucher specimen is deposited at the Herbarium of Department of Pharmacognosy, Hiroshima University, School of Medicine (Voucher no. Al-8406-1).

Isolation of compounds **1** *and* **2**. Dried stem bark (500 g) was crushed and extracted with hexane (8 l) and then with MeOH (8 l) to afford the hexane extract (16 g) and the MeOH extract (29 g). The MeOH extract was chromatographed on highly porous polymer, Diaion HP-20(20, 40, 60, 80 and 100% of MeOH). The 20% MeOH eluent (5.4 g) was chromatographed on silica gel ($CHCl_3$–MeOH–H_2O, 70:30:1) to obtain a fraction rich in **1** (870 mg). A portion (109 mg) of this fraction was chromatographed on Sephadex LH-20 (MeOH) to give compound **1**. The 40–60% MeOH fraction (3.7 g) of the Diaion CC, was chromatographed on silica gel ($CHCl_3$–MeOH) and Sephadex LH-20 (MeOH) to give compound **2** (81 mg).



	R¹	R²	R³	R⁴
1	β-OH	β-Me	H	H
2	β-OAc	β-Me	H	H
2'	β-OAc	α-Me	H	H
3	β-OAc	β-Me	Me	H
3'	β-OAc	α-Me	Me	H
4	β-OAc	β-Me	Me	Ac
5	β-OH	β-Me	Me	H
5' = **6**	β-OH	α-Me	Me	H
7	α-OH	β-Me	Me	H

* Author to whom correspondence should be addressed.

Table 1. ^{13}C NMR data of loganin (**5**) and related compounds in CD_3OD and/or another solvent (in parentheses): 25 MHz*

C	**1** CD_3OD	**2** CD_3OD (d-A)	**2′** (d-A)*	**5** CD_3OD† (D_2O)‡	**5′** CD_3OD* (D_2O)	**6** (D_2O)‡	**7** CD_3OD§
1	97.5	97.6		97.8	96.3		97.8
		(96.9)	(95.2)	(97.5)	(96.5)	(96.5)	
3	152.1	152.6		152.2	152.5		152.5
		(151.8)	(151.8)	(151.7)	(152.2)	(152.2)	
4	114.0	113.1		114.1	114.0		113.3
		(112.7)	(113.1)	(113.9)	(nd‖)	(114.0)	
5	31.9	32.6		32.2	30.9		31.5
		(32.1)	(30.6)	(30.7)	(29.3)	(29.4)	
6	42.5	40.3		42.8	42.9		42.0
		(39.8)	(38.4)	(41.3)	(39.5)	(39.6)	
7	75.0	78.6		74.8	78.0		79.7
		(77.4)	(81.8)	(75.0)	(79.0)	(79.0)	
8	42.0	40.8		42.2	45.0		44.0
		(40.1)	(42.3)	(41.0)	(43.7)	(43.5)	
9	46.4	46.9		46.6	41.9		47.1
		(46.7)	(42.3)	(45.8)	(41.7)	(41.8)	
10	13.5	13.7		13.6	14.4		17.7
		(13.6)	(14.2)	(12.9)	(13.9)	(14.0)	
11	170.9	170.7		169.6	169.6		169.5
		(170.7)	(171.5)	(170.7)	(nd‖)	(170.7)	
1′	99.9	100.1		100.1	99.7		100.4
		(99.9)	(99.2)	(99.5)	(99.1)	(99.1)	
2′	74.6	74.6		75.1	74.2		74.8
		(74.5)	(74.2)	(73.5)	(73.4)	(73.5)	
3′	77.8	77.9		78.0	78.3		78.3
		(77.8)	(77.3)	(76.6)	(76.5)	(76.6)	
4′	71.4	71.5		71.6	71.7		71.7
		(71.5)	(71.1)	(70.5)	(70.4)	(70.5)	
5′	78.1	78.2		78.4	79.3		78.1
		(77.8)	(77.6)	(77.2)	(77.1)	(77.1)	
6′	62.6	62.7		62.8	62.9		62.8
		(62.8)	(62.6)	(61.6)	(61.5)	(61.6)	
OMe				51.9	51.8		51.7
				(52.6)	(52.6)	(52.6)	
MeCO	—	21.0					
		(20.9)	(21.2)				
MeCO		172.6					
		(168.5)	(169.1)				

* Lit [2], d-A = $(CD_3)_2CO$, †lit. [1], ‡lit. [4], §lit. [3].
‖ Signals were not observed, after 170000 accumulations for 1 mg of the sample. Note that: $2 \neq 2'$, $5' \neq 5$, $5' \neq 7$ and $5' = 6$.

Loganic acid (**1**). Amorphous powder; $[\alpha]_D^{24}$ −73.5° (MeOH; *c* 0.72). (Found: C, 48.9; H, 6.7. Calc. for $C_{16}H_{24}O_{10}\cdot H_2O$: C, 48.7; H, 6.6%). IR ν_{max}^{KBr} cm^{-1}: 3275, 1690, 1070; UV λ_{max}^{EtOH} nm (log ε): 234 (4.03); ^1H NMR (CD_3OD): δ1.10 (3H, *d*, *J* = 6 Hz, H-10), 4.05 (1H, *m*, H-7), 4.67 (1H, *d*, *J* = 8 Hz, anomeric H), 5.27 (1H, *d*, *J* = 4 Hz, H-1), 7.40 (1H, *s*, H-3); ^{13}C NMR: see Table 1.

Conversion of compound **1** *to loganin pentaacetate* (**4**). Methylation of **1** (24 mg) with CH_2N_2, followed by acetylation with Ac_2O in pyridine, afforded **4**, as colourless needles from EtOH, mp 132–136°, $[\alpha]_D^{20}$ −69.2° ($CHCl_3$; *c* 0.64); IR ν_{max}^{KBr} cm^{-1}: 2950, 1755, 1645, 1370, 1230, 1050, 910; UV λ_{max}^{EtOH} nm (log ε): 230 (4.08); ^1H NMR ($CDCl_3$): δ1.02 (3H, *d*, *J* = 6 Hz, H-10), 1.91, 2.00, 2.03 (× 2), 2.09 (each 3H, *s*, five AC), 3.69 (3H, *s*, CO_2Me), 7.28 (1H, *s*, H-3); ^{13}C NMR ($CDCl_3$): δ12.4 C-10), 20.2, 20.6 (× 2), 20.7; 21.1 (five acetyl − Me), 29.8 (C-5), 38.8 (× 2, C-6, 8), 45.5 (C-9), 51.2 (OMe), 61.8 (C-6′), 68.3 (C-4′), 70.7 (C-2′), 72.3 (C-3′), 72.5 (C-5′), 77.1 (C-7), 94.7 (C-1), 95.9 (C-1′), 113.7 (C-4), 149.1 (C-3), 167.1 (C-11), 169.1, 169.4, 170.1, 170.5 (× 2) (five CO of acetyl); identified with an authentic sample from Dr Inouye.

7-O-*Acetyl loganic acid* (**2**). Amorphous powder; $[\alpha]_D^{20}$ −60.2° (MeOH; *c* 0.86). (Found: C, 50.1; H, 6.3. $C_{18}H_{26}O_{11}\cdot H_2O$ requires: C, 50.6; H, 6.5%). IR ν_{max}^{KBr} cm^{-1}: 3400, 2925, 1700, 1650, 1375, 1065. UV λ_{max}^{EtOH} nm (log ε): 231 (4.16); ^1H NMR (CD_3OD): δ1.06 (3H, *d*, *J* = 5 Hz, H-10), 2.08 (3H, *s*, $MeCO_2$), 4.68 (1H, *d*, *J* = 7 Hz, anomeric H), 5.26 (1H, *d*, *J* = 4 Hz, H-1), 7.42 (1H, *d*, *J* = 1 Hz, H-3). ^1H NMR (CD_3COCD_3): δ1.03 (3H, *d*, *J* = 7 Hz,

H-10), 2.02 (3H, *s*, $MeCO_2$), 4.71 (*d*, $J=7$ Hz, anomeric H), 5.28 (1H, *d*, $J=4$ Hz, H-1), 7.41 (1H, *d*, $J=1$ Hz, H-3).

Loganin pentaacetate (**4**) *from compound* **2**. Compound **2** (35 mg) was methylated and acetylated as in the case of **1**, to afford **4**, colourless needles from EtOH mp 135–138°; $[\alpha]_D^{19}$ −76.2° ($CHCl_3$; *c* 0.78); EIMS *m/z* (rel. int.): 600 $[M]^+$ (3), 569 (3), 541 (4), 331 (90), 253 (34), 193 (77), 169 (100), 109 (90); IR ν_{max}^{KBr} cm^{-1}: 2950, 1755, 1645, 1370, 1230, 1050, 910; UV λ_{max}^{EtOH} nm (log ε): 232 (4.18); ^1H NMR ($CDCl_3$): δ 1.03 (3H, *d*, $J=6$ Hz, H-10), 1.92, 2.01, 2.04 (×2), 2.10 (each 3H, *s*, $MeCO_2$), 3.70 (3H, *s*) 7.28 (1H, *s*, H-3). Identical with an authentic sample as well as **4** derived from **1**.

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ESSENTIAL OIL OF *CONYZA CANADENSIS*

BJORN F. HRUTFIORD, WILLIAM H. HATHEWAY and DANIEL B. SMITH

College of Forest Resources, University of Washington, Seattle WA 98195, U.S.A.

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Key Word Index—*Conyza canadensis*; Asteraceae; horseweed; phytochemistry; sesquiterpenes; acetylenes; matricaria esters; bergamotene.

Abstract—GC/MS of the essential oil from horseweed (*Conyza canadensis*) was used to identify three matricaria ester isomers, lachnophylum ester, and two related lactones plus a new ethyl ester of matricaria acid. In addition, eight mono- and 10 sesquiterpenes were resolved and identified. The composition of the sesquiterpene fraction shows seasonal variation indicating a flow of material from β-*trans*-farnesene via several intermediates to the final main product bergamotene in agreement with current biosynthetic pathways.

INTRODUCTION

This study was done to improve the characterization of the essential oil of horseweed (*Conyza canadensis*). The essential oil of numerous members of the Asteraceae have been characterized. However, a thorough and comprehensive analysis of horseweed essential oil has not been carried out using current technology.

In 1952, Guenther [1] reported horseweed, on steam distillation, yielded a colourless or slightly yellow oil which contained *d*-limonene and matricaria methyl ester. Later, Ogg *et al.* [2] confirmed the presence of *d*-limonene and matricaria ester and identified 11 other compounds, including several sesquiterpenes, by GC/MS. Matricaria ester was obtained crystalline in *ca* 20% yield from the oil. Improved analytical techniques have led to the discovery of geometric isomers of matricaria ester and related acetylenic compounds in horseweed. In 1979, Bohlmann and Jakupovic [3] reported the presence of a total of six of these acetylenic compounds. Most reports of horseweed essential oil are concerned only with the matricaria ester and related compounds. In particular, a detailed examination of the sesquiterpene content of horseweed oil using current techniques has not been reported.

RESULTS AND DISCUSSION

Oil yields ranged from 1.35% (O.D.) for juvenile plants to 1.55% (O.D.) for mature plants. Chromatograms of the raw horseweed oil indicated about 25 compounds were present at a concentration above 0.1%. The identities of these compounds are listed in Table 1, in which approximate concentrations in the mature oil are also given. GC/MS of the oil gave very good results, and