Structure Determination of a New Bitter Principle, Shinjulactone L, from *Ailanthus altissima*

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(Received May 30, 1985)

Synopsis. A new quassinoid, shinjulactone L, was isolated from *Ailanthus altissima* SWINGLE and the structure was determined to be 12β-acetoxy-2α-hydroxypicrasane-1,11,16-trione by spectral and chemical means.

In previous papers we have reported the isolation and structure elucidation of several quassinoids[1-5] and quassinoid glycosides[6] from *Ailanthus altissima* SWINGLE (Shinju or Niwaurushi in Japanese). Further investigation on bitter principles of the plant led to the isolation of a new quassinoid, shinjulactone L (**1**) from the root bark of this plant.

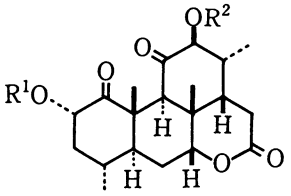
Shinjulactone L (**1**) crystallized from acetone–benzene as colorless prisms, mp 261—262 °C. High-resolution mass spectrum indicated the molecular formula, $C_{22}H_{30}O_7$. The ^1H and ^{13}C NMR spectra showed the presence of two secondary methyl, two tertiary methyl, two isolated carbonyl, one lactone, and one acetoxyl groups. Since six of seven oxygen atoms were thus characterized, the remaining one oxygen atom was ascribed to a hydroxyl group, the presence of which was supported by the IR absorption band at 3450 cm^{-1}.

The ^1H NMR spectrum of shinjulactone L (**1**) was very similar to that of shinjulactone H (**2**)[3] except for the presence of a signal due to an acetoxyl group and a lower field resonance of a doublet (δ 5.12) which is ascribed to a proton attached to an acetoxyl-bearing carbon atom. In the ^1H NMR of **1** a signal due to a proton attached to a hydroxyl-bearing carbon atom was observed at δ 4.70 as double-double doublets, which are very similar to the signal due to $C_{(2)}$–H (δ 4.77 ddd) observed in ^1H NMR of **2** (see Table 1). This fact suggests that the structure of the A ring of shinjulactone L (**1**) is the same as that of shinjulactone H (**2**). The presence of a carbonyl group at C-11 position and the acetoxyl group at C-12β position in the C ring was also clarified by the ^1H NMR spectrum of **1**; $C_{(9)}$–H appeared at δ 2.93 as a singlet signal and a large coupling constant (J=12.5 Hz) of the doublet signal due to $C_{(12)}$–H was observed. As a result of discussions developed above, the structure of shinjulactone L (**1**) was proposed to be 12-*O*-acetylshinjulactone H, which was finally confirmed by chemical conversion as follows. Shinjulactone L (**1**) was acetylated with acetic anhydride and pyridine to give a diacetate (**3**), which was completely identical with the diacetate (**3**) derived from shinjulactone H (**2**). Thus the structure of shinjulactone L (**1**) was determined to be 12β-acetoxy-2α-hydroxypicrasane-1,11,16-trione. This structure had been previously proposed for acetylamarolide by Casinovi *et al.*[7] but the structure of acetylamarolide was later revised to **4**.[8]

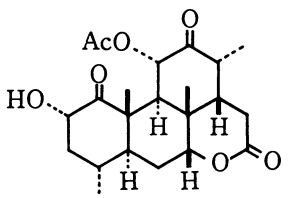
TABLE 1. ^1H NMR SPECTRA OF SHINJULACTONES L AND H (**1** AND **2**)[a]

	1[b]		**2**[c],[3]	
	δ	J	δ	J
2-H	4.70 ddd	11.5, 7, 5	4.77 ddd	12, 7.5, 4.5
7-H	4.29 t	2.5	4.31 dd	3, 2.5
9-H	2.93 s		2.94 s	
12-H	5.12 d	12.5	4.01 dd	11, 3
4-Me	0.94 d	6.5	0.95 d	6.5
8-Me	1.18 s [d]		1.13 s [e]	
10-Me	1.56 s [d]		1.58 s [e]	
13-Me	1.09 d	7.5	1.20 d	7
2-OH	3.84 d	5	3.43 d	4.5
12-OH	—		3.53 d	3
12-OAc	2.20 s		—	

a) δ and J values are expressed in ppm and Hz, respectively. b) Measured at 90 MHz in $CDCl_3$. c) Measured at 400 MHz in $CDCl_3$. d) Signals may be reversed. e) Signals may be reversed.



1 R^1=H, R^2=Ac
2 R^1=R^2=H
3 R^1=R^2=Ac



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Experimental[9]

Materials and Isolation of Shinjulactone L (1). Root bark of *A. altissima* was collected at the Botanical Gardens, Faculty of Science, The University of Tokyo in August 1982. The isolation procedures are the same as described in the preceding paper.[5] The fraction containing amarolide 11-acetate (**4**)[7,8] mainly was further separated by silica-gel column chromatography eluted with ethyl acetate–chloroform (1:2) to afford shinjulactone L (**1**; *ca.* 0.0005% yield).

Shinjulactone L (1). Colorless prisms from acetone–benzene, mp 261—262 °C; $[\alpha]_D^{26}$ −41° (*c* 0.65, $CHCl_3$); IR (KBr) 3450, 1745, 1730, and 1230 cm^{-1}; ^1H NMR (Table 1); ^{13}C NMR ($CDCl_3$) δ=15.0q, 15.1q, 18.3q, 20.5q, 23.6q, 26.6t, 27.4t, 27.8d, 35.6d, 38.6s, 45.3d, 46.5t, 46.9d, 47.3d, 48.8s, 69.9d, 77.6d, 81.8d, 168.9s, 169.8s, 201.5s, and 212.4s; MS *m/z* (%) 406 (M^+; 19), 378 (13), 364 (18), 362 (19), 346 (100),

303 (36), and 206 (57); Found: *m/z* 406.1979. Calcd for $C_{22}H_{30}O_7$: M, 406.1990.

Acetylation of Shinjulactone L (1). Shinjulactone L (**1**; *ca.* 10 mg) was acetylated with acetic anhydride (2 ml) in pyridine (2 ml) at room temperature for 18 h. After addition of methanol and evaporation, the reaction mixture was purified by silica-gel column chromatography eluted with 15% acetone–benzene to afford 2-*O*-acetylshinjulactone L (**3**; 10 mg), which was identified with 2,12-di-*O*-acetylshinjulactone H (**3**) by TLC, ^{1}H NMR, IR, and mass spectra.

The authors wish to express their thanks to Mr. Eiichi Ishii of the Botanical Gardens for collection of the roots of *A. altissima.*

References

1) M. Ishibashi, T. Tsuyuki, T. Murae, H. Hirota, T. Takahashi, A. Itai, and Y. Iitaka, *Bull. Chem. Soc. Jpn.*, **56**, 3683 (1983).

2) H. Naora, M. Ishibashi, T. Furuno, T. Tsuyuki, T. Murae, H. Hirota, T. Takahashi, A. Itai, and Y. Iitaka, *Bull. Chem. Soc. Jpn.*, **56**, 3694 (1983).

3) M. Ishibashi, S. Yoshimura, T. Tsuyuki, T. Takahashi, and K. Matsushita, *Bull. Chem. Soc. Jpn.*, **57**, 2013 (1984).

4) T. Furuno, M. Ishibashi, H. Naora, T. Murae, H. Hirota, T. Tsuyuki, T. Takahashi, A. Itai, and Y. Iitaka, *Bull. Chem. Soc. Jpn.*, **57**, 2484 (1984).

5) M. Ishibashi, S. Yoshimura, T. Tsuyuki, T. Takahashi, A. Itai, and Y. Iitaka, *Bull. Chem. Soc. Jpn.*, **57**, 2885 (1984).

6) S. Yoshimura, M. Ishibashi, T. Tsuyuki, T. Takahashi, and K. Matsushita, *Bull. Chem. Soc. Jpn.*, **57**, 2496 (1984).

7) C. G. Casinovi, V. Bellavita, G. Grandolini, and P. Ceccherelli, *Tetrahedron Lett.*, **1965**, 2273.

8) W. Stöcklin, M. Stefanović, T. A. Geissman, and C. G. Casinovi, *Tetrahedron Lett.*, **1970**, 2399.

9) General procedures are the same as described in the preceding paper.[5]