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SHINJULACTONE F, A NEW BITTER PRINCIPLE WITH A 5β*H*-PICRASANE SKELETON FROM *AILANTHUS ALTISSIMA* SWINGLE

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A new quassinoid, shinjulactone F, was isolated from *Ailanthus altissima* SWINGLE and the structure was determined to be 1α,11-epoxy-1β,20-dihydroxy-5β*H*-picrasa-3,9(11)-diene-2,12,16-trione by X-ray analysis.

In previous studies on the bitter principles of Simaroubaceous plants, we have reported isolation and structure elucidation of six quassinoids from *Ailanthus altissima* SWINGLE (Japanese name: Shinju).(1) Further investigation on the constituents of this plant has now led to the isolation of a new bitter quassinoid, shinjulactone F (**1**). This communication deals with the structure determination of **1**.

Aqueous extract of root bark of *A. altissima*(2) was continuously extracted with dichloromethane. The organic layer was subjected to separation by silica-gel column chromatography. A fraction eluted with 13% methanol-chloroform was further purified by a partition column chromatography to afford a new bitter principle, shinjulactone F (**1**; *ca*. 0.003% yield),(3) mp 201-203 °C, $[\alpha]_D^{20}$ -148° (*c* 2.1, pyridine); Found: *m/z* 374.1364. Calcd for $C_{20}H_{22}O_7$: M 374.1366.

Spectral comparison with known quassinoids suggested that shinjulactone F (**1**) possesses a 1,11-epoxypicrasane system(4) with two enone moieties in A and C rings and a hemiacetal group at C-1 position. Shinjulactone F (**1**) showed a multiplet signal at δ 2.71 due to a methine proton at C-5, which is coupled with methylene protons at C-6 with coupling constants, $J_{5,6\alpha}$=3 Hz and $J_{5,6\beta}$=5.5 Hz (see Table 1). However, this coupling pattern had never been observed in ^{1}H NMR of any known quassinoids. This fact suggests an inversion of a chiral center at C-5 position resulting in a formation of the 1,11-epoxy ring with a less strain. Configuration of the hydroxyl group at C-1 and the hydrogen at C-5 could be determined by NOE measurement of 1-*O*-methyl monoacetate (**2**).(5) On saturation of the signal due to $C_{(10)}$-CH_3, the signals due to $C_{(1)}$-OCH_3 and $C_{(5)}$-H showed increase in area by 3% and 9%, respectively. This observation implies the $C_{(1\beta)}$-OCH_3 and $C_{(5\beta)}$-H orientations.

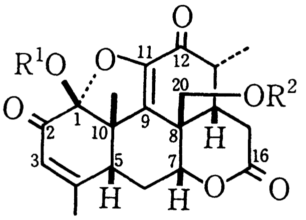
Unambiguous proof for the structure of shinjulactone F (**1**) was provided by single crystal X-ray analysis. Crystals of **1** belong to a monoclinic space group $P2_1$ with the cell parameters of a=8.392(2), b=14.920(4), c=7.581(2) Å, β=105.3(3)°, Z=2, and D_c=1.42 g cm^{-3}. The final R factor was 0.036.(6) Figure 1 shows a computer-generated perspective drawing of the molecule **1**, indicating $C_{(5\beta)}$-H configuration.

Thus the structure of shinjulactone F (1) was established to be 1α,11-epoxy-1β,20-dihydroxy-5β*H*-picrasa-3,9(11)-diene-2,12,16-trione.

Shinjulactone F (1) contains several interesting structural features. It is the first example of 5β*H*-picrasane skeleton with all *cis* configurations at A/B, B/D, and C/D ring junctures, forming an unusual folded-shape molecule.

Table 1. ^{1}H NMR spectrum at 400 MHz of shinjulactone F (1) in C_5D_5N

	δ		J / Hz		δ		J / Hz
3-H	6.26	br s		15α-H	2.10	dd	18, 12.5
5-H	2.71	m		15β-H	2.60	dd	18, 6.5
6α-H	2.65	ddd	16, 3, 3	4-CH_3	2.08	br s	
6β-H	2.52	ddd	16, 5.5, 2	10-CH_3	1.69	s	
7-H	5.20	dd	3, 2	13-CH_3	0.98	d	7
13-H	3.34	dq	4, 7	20-H	4.22	d	12
14-H	3.18	ddd	12.5, 6.5, 4	20-H'	4.16	d	12



1 $R^1=R^2=H$
2 $R^1=CH_3$, $R^2=Ac$

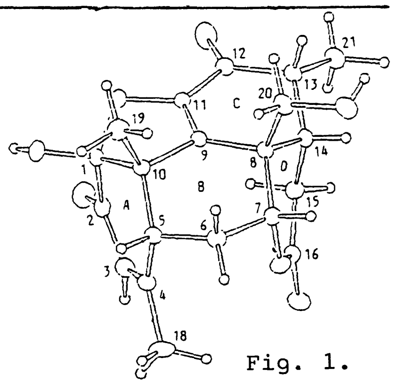


Fig. 1.

References

1) M. Ishibashi, T. Tsuyuki, T. Murae, H. Hirota, T. Takahashi, A. Itai, and Y. Iitaka, Bull. Chem. Soc. Jpn., 56, 3683 (1983); H. Naora, M. Ishibashi, T. Furuno, T. Tsuyuki, T. Takahashi, A. Itai, and Y. Iitaka, *ibid.*, 56, 3694 (1983).

2) The plant, *A. altissima*, was collected at the Botanical Gardens, Faculty of Science, the University of Tokyo in August 1982.

3) 1: IR (KBr) 3450, 1735, 1685, and 1220 cm^{-1}; UV (EtOH) 291 nm (ε 3400) and 244 nm (ε 7400); ^{13}C NMR (C_5D_5N) δ 11.4q, 20.3q, 23.2q, 27.2t, 27.6t, 30.1d, 38.8d, 40.8s, 41.9d, 47.8s, 63.0t, 78.1d, 120.6s, 126.8d, 135.9s, 149.9s, 164.3s, 168.0s, 190.4s, and 194.3s; MS *m/z* (%) 374 (M^+, 1.5), 356 (7), and 282 (100).

4) Two types of 1,11-epoxypicrasanes have been reported. Artificial bisnorquassin and its derivatives: J. A. Findlay, R. F. Langler, and J. S. Tandon, Can. J. Chem., 48, 313 (1970). Karinolide: J. Polonsky, J. Gallas, J. Varenne, T. Prange, C. Pascard, H. Jacquemin, and C. Moretti, Tetrahedron Lett., 23, 869 (1982).

5) Compound 2 was obtained by treatment of 1 with diazomethane followed by acetylation. 2: mp 193-195 °C, IR (KBr) 1740, 1685, and 1220 cm^{-1}; UV (EtOH) 291 nm (ε 4500) and 243 nm (ε 12000); ^{1}H NMR ($CDCl_3$) δ 1.10 (3H, d, *J*=7 Hz), 1.42 (3H, s), 2.08 (3H, br s), 2.15 (3H, s), 3.54 (3H, s), 4.33 (2H, s), 4.61 (1H, t, *J*=3 Hz), and 6.03 (1H, br s); MS *m/z* (%) 430 (M^+, 72), 402 (75), 329 (100), and 301 (80); Found *m/z* 430.1622. Calcd for $C_{23}H_{26}O_8$: M 430.1627.

6) The particulars of the manner of X-ray analysis will be described in the full report of this work.

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