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Structure Determination of Bitter Principles of *Ailanthus altissima.* Structures of Shinjulactones B, D, and E[1)]

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Bitter quassinoids, shinjulactones B, D, and E were isolated from *Ailanthus altissima* Swingle. Shinjulactone B is the first example of natural bitter principles with a 1,2-seco-1-nor-6(5→10)*abeo*-picrasane skeleton and shinjulactones D and E are a hexahydro derivative and a 6α-hydroxy derivative of ailanthone, respectively.

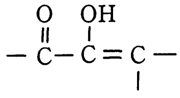
As a continuation of studies on bitter principles of Simaroubaceous plants,[2)] we have examined *Ailanthus altissima* Swingle and reported several new quassinoids.[1,3,4)] This paper describes the structure determination of shinjulactones B (**1**), D (**2**), and E (**3**) in detail.

Shinjulactone B (**1**) was isolated from both stem bark and root bark of the plant. The stem barks were extracted with hot water and the aqueous extract, after concentration, was continuously extracted with dichloromethane. The organic layer was evaporated to give a bitter residue, which was separated by silica-gel column chromatography. Gradient elution with methanol in chloroform gave shinjulactone B (**1**, *ca.* 0.001% yield) together with known quassinoids, amarolide 11-acetate,[5)] amarolide,[5)] shinjudilactone,[3)] and ailanthone (**4**).[4,6,7)] By the same procedure, shinjulactone B (**1**, *ca.* 0.004% yield) and shinjulactone D (**3**, *ca.* 0.001% yield) were isolated from the root bark together with known shinjulactone C,[3)] chaparrolide,[8)] and $\Delta^{13(18)}$-dehydroglaucarubolone,[9)] besides the known quassinoids mentioned above.

Shinjulactone B (**1**), mp 265.5—268 °C, was shown to have a norpicrasane skeleton, $C_{19}H_{22}O_7$, by high-resolution mass spectrum and elementary analysis. The IR spectrum showed the presence of hydroxyl(s) (3420 cm^{-1}), γ-lactone (1770 cm^{-1}), δ-lactone (1750 cm^{-1}), and a conjugated carbonyl (1680 cm^{-1}). The presence of a diosphenol grouping (**A**) was indicated by UV absorption maximum at 279 nm (ε 8100), which shifted to 330 nm on addition of alkali. These spectral data are similar to the observed values, 280 and 328 nm, for bruceantin in an ethanolic solution and an alkaline solution, respectively.[10)] The fact that shinjulactone B (**1**) possesses the diosphenol moiety in a ring other than A ring was inferred from the mass spectrum, in which a peak at *m/z* 151 (**B**) was not observed. This peak is characteristic of 3-hydroxy-2-oxo-3-picrasenes such as bruceantin and its congeners[10)] and 2-hydroxy-1-oxo-2-picrasenes.[10)] Instead of the peak at *m/z* 151, characteristic fragmentation peaks at *m/z* 265 $(M-C_5H_5O_2)^+$ and *m/z* 235 $(M-CH_2O-C_5H_5O_2)^+$ were observed; these peaks were not observed for normal quassinoids. The appearance of these peaks implies the presence of $C_5H_5O_2$ grouping susceptible of fragmentation on electron bombardment.

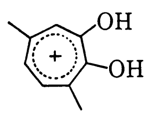
^1H and ^{13}C NMR spectra showed the presence of a tertiary methyl, a secondary methyl, a vinyl methyl, a hydroxymethyl (**C**), an olefinic proton (δ 5.95, dd), and a proton (δ 5.26) assignable to $C_{(7)}$-H on a δ-lactone terminus. On irradiation at δ 5.26, signals (δ 1.99, dd and δ 2.20, dd) due to $C_{(6)}$-H_2 changed into an AB quartet (J_{AB}=16 Hz). This observation indicates that the C-6 atom was connected with a carbon atom bearing no hydrogen atom, leading to a partial structure (**D**).

When the olefinic proton at δ 5.95 was irradiated, a doublet signal due to the vinyl methyl and a doublet



$$-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}}=\underset{|}{C}-$$

A

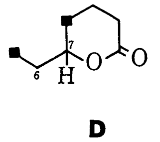


B

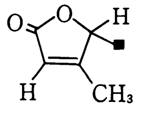
m/z 151

■–CH_2OH

C

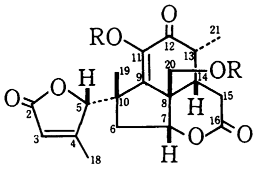


D

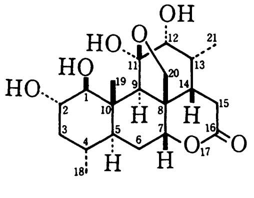


E

■ Carbon atom bearing no hydrogen atom



1 R=H
5 R=Ac



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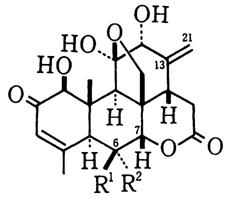


3 R^1=H R^2=OH
4 R^1=R^2= H

signal at δ 6.12 changed into singlets, respectively. On irradiation at the frequency of the vinyl methyl, an allylic coupling with J=2 Hz between the olefinic proton and the proton resonating at δ 6.12 was observed. Thus the partial structure (**E**) was proposed from these NMR measurement together with the IR absorption band due to the γ-lactone and with the $C_5H_5O_2$ moiety deduced from fragmentation of mass spectrum of **1**.

Although seven oxygen atoms of shinjulactone B (**1**) were thus characterized as shown in partial structures (**A**, **C**, **D**, and **E**), the whole structure for **1** with the norpicrasane skeleton could not be unambiguously constructed by connecting these partial structures.

Acetylation of **1** with acetic anhydride in pyridine gave a diacetate (**5**), mp 194—198 °C. Spectral information obtainable from **5** was of no use for the structure elucidation of shinjulactone B (**1**).

Unequivocal structure for shinjulactone B (**1**) was provided by X-ray diffraction analysis. A single crystal in orthorhombic space group $P2_12_12_1$ was obtained from methanol solution and the lattice parameters are a=12.594 (5), b=19.016 (8), and c=7.755 (3) Å. Four molecules of **1** and four water molecules are contained in the unit cell to give D_c=1.36 g cm^{-3}. Intensity data were collected on a Philips PW1100 automatic four-

TABLE 1. ^{1}H-NMR SPECTRA OF **1**, **2**, **3**, **5**, **7**, **8**, AND **11** (δ (J/Hz))

	1	**2**	**3**	**5**	**7**	**8**	**11**
1-H		3.59 d (9)	4.54 s		4.70 d (9.5)	4.70 d (9.5)	5.28 s
2-H		*ca.* 4.05 br m			5.04 ddd (11, 9.5, 5)	*ca.* 5.0 m	
3-H	5.95 dd (2, 1)	*	6.18 m	5.96 m	1.25 m and *ca.* 2.1 m	*	6.10 m
4-H		*			1.63 m	*	
5-H	6.12 d (2)	*	*	5.63 br s	1.36 ddd (13, 11, 2.5)	*	3.53 d (11.5)
6-H	1.99 dd (16, 1)	*	4.62 dd (11.5, 3)	*	*ca.* 2.0 ddd (15, 2.5, 2.5)	*	5.25 dd (11.5, 3)
6-H′	2.20 dd (16, 6)	*		*	1.76 ddd (15, 13, 2.5)	*	
7-H	5.26 dd (6, 1)	4.43 br s	4.87 d (3)	4.98 d (5)	4.46 t (2.5)	4.44 t (2.5)	4.84 d (3)
9-H		2.95 s	*		3.41 s	3.17 s	3.22 s
12-H		3.97 br s	*		3.76 d (2.5)	5.03 d (*ca.* 2)	
13-H	3.30 m	*		*	*ca.* 2.15 m	*	
14-H	3.25 m	*	*	*	2.38 ddd (13, 6.5, 6)	*	*
15-H	2.92 dd (16, 13)	*	*	*	3.85 dd (19, 13)	*	*
15-H′	2.67 dd (16, 5)	*	*	*	2.74 dd (19, 6.5)	*	*
20-H	3.92 d (12)	3.73 d (8)	3.64 d (8)	4.41 d (12)	3.84 d (12.5)	3.86 d (13)	4.20 d (11.5)
20-H′	4.08 d (12)	4.14 d (8)	4.27 d (8)	4.73 d (12)	4.49 d (12.5)	4.51 d (13)	4.69 d (11.5)
4-CH_3	1.95 d (1)	0.83 d (6.5)	2.52 br s	1.93 d (1)	0.91 d (6.5)	0.91 d (6.5)	2.03 br s
10-CH_3	1.60 s	1.65 s	1.70 s	1.49 s	1.46 s	1.44 s	1.43 s
13-CH_3	1.05 d (7)	1.08 d (7)		1.11 d (7)	1.13 d (7)	0.97 d (6.5)	1.82 s
13=CH_2			5.13 br s 5.19 br s				
-OAc				2.13 s 2.31 s	1.94 s 1.98 s 2.07 s	1.82 s 1.96 s 2.08 s 2.20 s	2.07 s 2.14 s 2.17 s 2.22 s
Solv.	C_5D_5N	C_5D_5N	C_5D_5N	C_5D_5N	$CDCl_3$	$CDCl_3$	$CDCl_3$
MHz	400	270	90	100	400	90	400

* Not assigned.

circle diffractometer using monochromated Cu $K\alpha$ radiation. A total of 2096 independent structure factors with $F_o \geq 2.5\sigma(F_o)$ within $2\theta=156°$ were obtained by the $2\theta-\theta$ scanning mode. The structure was solved by the direct method using the MULTAN program. An E-map revealed the positions of all the non-hydrogen atoms, and the hydrogen atoms were located in a difference electron density map. The structure was refined by the block-diagonal least-squares calculations using

Table 2. Atomic positional parameters ($\times 10^4$) and isotropic temperature factors ($\times 10^2$) for non-hydrogen atoms of shinjulactone B (**1**) with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}[a])
O (1)	5917 (1)	8889 (1)	6721 (2)	346 (2)
O (2)	6255 (2)	8185 (1)	8968 (3)	640 (3)
O (3)	4881 (1)	10324 (1)	4402 (3)	370 (3)
O (4)	2743 (2)	10359 (1)	4543 (4)	546 (3)
O (5)	4077 (2)	7395 (1)	7845 (2)	511 (3)
O (6)	4802 (1)	7556 (1)	5335 (2)	445 (2)
O (7)	3164 (1)	7938 (1)	849 (2)	266 (2)
C (2)	6585 (2)	8502 (1)	7724 (3)	338 (3)
C (3)	7648 (2)	8567 (1)	7016 (4)	355 (4)
C (4)	7624 (2)	8955 (1)	5584 (4)	266 (3)
C (5)	6496 (2)	9191 (1)	5287 (3)	278 (3)
C (6)	5989 (2)	8150 (1)	3336 (3)	283 (3)
C (7)	4876 (2)	7864 (1)	3596 (3)	274 (2)
C (8)	4122 (2)	8476 (1)	3245 (3)	240 (2)
C (9)	4772 (2)	9121 (1)	3686 (3)	253 (2)
C (10)	5953 (2)	8964 (1)	3592 (3)	272 (2)
C (11)	4310 (2)	9735 (1)	4079 (3)	308 (3)
C (12)	3140 (2)	9788 (1)	4234 (3)	373 (3)
C (13)	2465 (2)	9135 (1)	3974 (4)	350 (3)
C (14)	3087 (2)	8452 (1)	4276 (3)	266 (3)
C (15)	3346 (2)	8335 (1)	6185 (3)	356 (3)
C (16)	4084 (2)	7733 (1)	6511 (3)	297 (3)
C (18)	8537 (2)	9147 (2)	4465 (5)	447 (4)
C (19)	6443 (2)	9364 (1)	2071 (3)	439 (4)
C (20)	3901 (2)	8479 (1)	1272 (3)	284 (3)
C (21)	1425 (2)	9168 (2)	4964 (6)	602 (5)

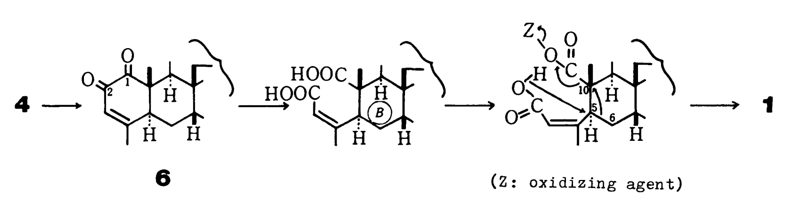
a) $B_{eq}=8\pi^2(u_1{}^2+u_2{}^2+u_3{}^2)/3$.

Table 3. Bond lengths of shinjulactone B (**1**) with estimated standard deviations in parentheses

Bond length		l/Å	Bond length		l/Å
Atom 1	Atom 2		Atom 1	Atom 2	
O (1)	-C (2)	1.361 (3)	C (6)	-C (10)	1.562 (3)
O (1)	-C (5)	1.448 (3)	C (7)	-C (8)	1.527 (3)
O (2)	-C (2)	1.213 (3)	C (8)	-C (9)	1.514 (3)
O (3)	-C (11)	1.355 (3)	C (8)	-C (14)	1.530 (3)
O (4)	-C (12)	1.218 (3)	C (8)	-C (20)	1.555 (3)
O (5)	-C (16)	1.218 (3)	C (9)	-C (10)	1.519 (3)
O (6)	-C (7)	1.473 (3)	C (9)	-C (11)	1.339 (3)
O (6)	-C (16)	1.327 (3)	C (10)	-C (19)	1.534 (3)
O (7)	-C (20)	1.425 (3)	C (11)	-C (12)	1.482 (3)
C (2)	-C (3)	1.452 (4)	C (12)	-C (13)	1.518 (3)
C (3)	-C (4)	1.334 (4)	C (13)	-C (14)	1.535 (3)
C (4)	-C (5)	1.508 (3)	C (13)	-C (21)	1.520 (4)
C (4)	-C (18)	1.486 (4)	C (14)	-C (15)	1.533 (3)
C (5)	-C (10)	1.544 (3)	C (15)	-C (16)	1.496 (3)
C (6)	-C (7)	1.516 (3)			

Table 4. Bond angles of shinjulactone B (**1**) with estimated standard deviations in parentheses

Bond angle			ϕ/°
Atom 1	Atom 2	Atom 3	
C (2)	-O (1)	-C (5)	109.9 (2)
C (7)	-O (6)	-C (16)	124.9 (2)
C (3)	-C (2)	-O (1)	108.0 (2)
C (3)	-C (2)	-O (2)	131.3 (2)
O (1)	-C (2)	-C (2)	120.7 (2)
C (4)	-C (3)	-C (2)	109.9 (2)
C (5)	-C (4)	-C (3)	108.2 (2)
C (5)	-C (4)	-C (18)	124.6 (2)
C (3)	-C (4)	-C (18)	127.2 (2)
C (10)	-C (5)	-O (1)	108.6 (2)
C (10)	-C (5)	-C (4)	117.7 (2)
O (1)	-C (5)	-C (4)	103.9 (2)
C (7)	-C (6)	-C (10)	108.1 (2)
C (8)	-C (7)	-O (6)	115.3 (2)
C (8)	-C (7)	-C (6)	106.1 (2)
O (6)	-C (7)	-C (6)	108.9 (2)
C (9)	-C (8)	-C (7)	104.0 (2)
C (9)	-C (8)	-C (14)	111.5 (2)
C (9)	-C (8)	-C (20)	108.4 (2)
C (7)	-C (8)	-C (14)	114.4 (2)
C (7)	-C (8)	-C (20)	106.8 (2)
C (14)	-C (8)	-C (20)	111.2 (2)
C (10)	-C (9)	-C (8)	111.0 (2)
C (10)	-C (9)	-C (11)	127.5 (2)
C (8)	-C (9)	-C (11)	121.5 (2)
C (19)	-C (10)	-C (5)	109.7 (2)
C (19)	-C (10)	-C (6)	112.5 (2)
C (19)	-C (10)	-C (9)	109.5 (2)
C (5)	-C (10)	-C (6)	111.9 (2)
C (5)	-C (10)	-C (9)	109.7 (2)
C (6)	-C (10)	-C (9)	103.3 (2)
C (12)	-C (11)	-O (3)	117.2 (2)
C (12)	-C (11)	-C (9)	120.6 (2)
O (3)	-C (11)	-C (9)	122.1 (2)
C (13)	-C (12)	-O (4)	121.7 (2)
C (13)	-C (12)	-C (11)	119.3 (2)
O (4)	-C (12)	-C (11)	119.0 (2)
C (14)	-C (13)	-C (12)	112.8 (2)
C (14)	-C (13)	-C (21)	113.4 (2)
C (12)	-C (13)	-C (21)	112.4 (2)
C (15)	-C (14)	-C (8)	109.1 (2)
C (15)	-C (14)	-C (13)	112.3 (2)
C (8)	-C (14)	-C (13)	109.2 (2)
C (16)	-C (15)	-C (14)	114.0 (2)
O (7)	-C (20)	-C (8)	109.9 (2)
O (5)	-C (16)	-O (6)	117.1 (2)
O (5)	-C (16)	-C (15)	122.8 (2)
O (6)	-C (16)	-C (15)	120.1 (2)



Scheme 1.

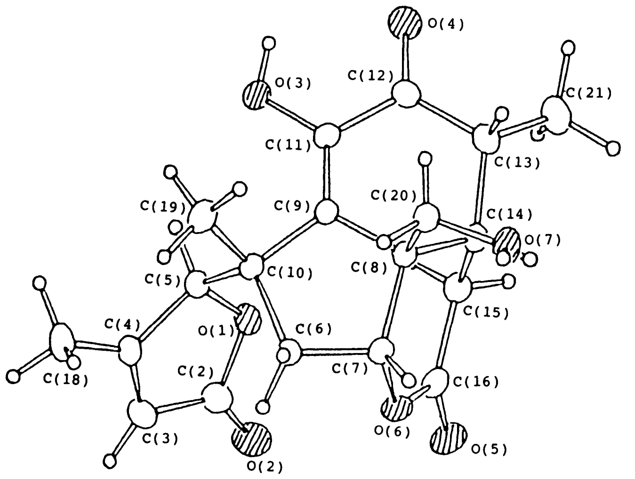


Fig. 1. Perspective view of shinjulactone B (1).[a)]
a) For clarity hydrogen atoms are represented by spheres of arbitrary radius.

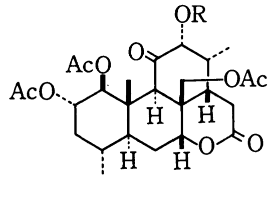
anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms. The final *R* factor was 0.039. The final atomic coordinates are listed in Table 2 and bond lengths and bond angles are listed in Tables 3 and 4.[11)]

Figure 1 is a computer-generated drawing of the molecule of **1**. The structure of shinjulactone B (**1**) is thus established as (5*R*,10*S*)-11,20-dihydroxy-12,16-dioxo-1,2-seco-1-nor-6(5→10)*abeo*-picrasa-3,9(11)-dien-2,5-olide. The novel 1,2-seco-1-nor-6(5→10)*abeo*-picrasane skeleton is likely derived biogenetically from ailanthone (**4**), a major picrasane-type bitter principle in *A. altissima*. Successive oxidation of an intermediate diketone (**6**) through bond-cleavage between $C_{(1)}$ and $C_{(2)}$ and decarboxylation accompanying with a contraction of the B ring and a formation of the α,β-unsaturated γ-lactone would afford shinjulactone B (**1**) (Scheme 1). Conversion of ailanthone (**4**) into shinjulactone B (**1**) is now in progress.

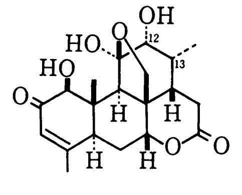
Shinjulactone D (**2**), mp 267—269 °C, was obtained together with shinjulactone B (**1**) and other known quassinoids from the aqueous extract of root bark of *A. altissima*. The molecular formula, $C_{20}H_{30}O_7$, was determined by high-resolution mass spectrum. The ^{1}H NMR spectrum was similar to that of ailanthone (**4**) except for a difference due to the absence of double bond, indicating the presence of hydroxyl(s), a δ-lactone, a tertiary methyl, two secondary methyls, and a hemiacetal group. In the mass spectrum of shinjulactone D (**2**), a fragment ion (**F**) was observed at *m/z* 268 ($C_{14}H_{20}O_5^{+\cdot}$) as a base peak. In comparison with the corresponding fragment ion at *m/z* 264 observed for ailanthone (**4**), the substitution pattern of the A ring was revealed. The UV spectrum showed no characteristic absorption maximum due to any ketone grouping. Therefore the presence of four hydroxyl groups containing a hemiacetal one was deduced. This is supported by acetylation of shinjulactone D (**2**) giving a triacetate (**7**) and tetraacetate (**8**).

The planer structure (**G**) is therefore proposed for shinjulactone D. The configuration of the hydroxyl groups at C-1, C-2, and C-12 of **2** was determined by measurement of ^{1}H and ^{13}C NMR spectra of **2**, **7**, and **8** and by proton magnetic double resonance (NMDR) measurement for **2**. In the ^{1}H NMR spectrum of **2**, signals due to three protons attached to hydroxyl-bearing carbons were observed at δ 3.59 (d, J=9 Hz), δ *ca.* 4.05 (br m), and δ 3.97 (br s), respectively. The doublet signal at δ 3.59 was assignable to H-1 and the NMDR measurement revealed the doublet signal coupled with the signal at δ 4.05 with a coupling constant, J=9 Hz, indicating a *trans*-diaxial-relationship for these protons. Thus the configurations of the vicinal hydroxyl groups were determined to be 1β-equatorial and 2α-equatorial, respectively.

The configuration of 12-H was established as follows. The doublet signals due to 12-H were observed at δ 3.76 for a triacetate (**7**) and δ 5.03 for a tetraacetate (**8**),



7 R=H
8 R=Ac



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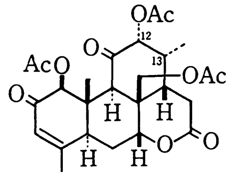

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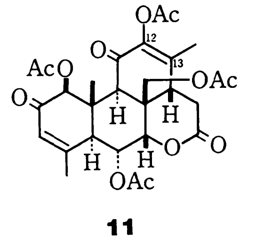

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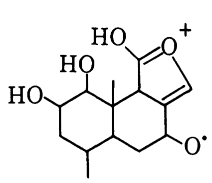
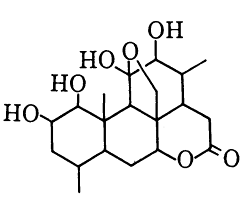


F



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and their coupling constants were J=2.5 Hz and J=*ca.* 2 Hz, respectively. These values were almost the same as the coupling constant, J=3 Hz, observed for chaparrinone triacetate (**10**)[12] derived from chaparrinone (**9**). The observation implies that the configrations at C-12 and C-13 of shinjulactone D (**2**) are identical with those for chaparrinone (**9**) with 12β(equatorial)-H and 13β(axial)-H.

In conclusion, the structure of shinjulactone D (**2**) was established to be 11β,20-epoxy-1β,2α,11α,12α-tetrahydroxypicrasan-16-one and this compound corresponds to a perhydroailanthone derivative.

Shinjulactone E (**3**) was isolated from the stem bark of *A. altissima* collected in Hyogo Prefecture. Methanol extract was partitioned between carbon tetrachloride and water, and the aqueous layer was extracted with dichloromethane. From the organic layer, a fraction containing ailanthone as a main component was collected by silica-gel column chromatography. Minor components in the fraction were found to be chaparrinone (**9**), sitosteryl glucoside, and a new quassinoid. The new quassinoid, named shinjulactone E (**3**) was obtained by preparative TLC as amorphous solid in *ca.* 0.0001% yield. The molecular formula, $C_{20}H_{24}O_8$, was determined by high-resolution mass spectrum, indicating the presence of one more oxygen atom than that of ailanthone (**4**). The ^{1}H and ^{13}C NMR spectra showed the presence of a tertiary methyl, a vinyl methyl, an *exo*-methylene, an α,β-unsaturated carbonyl, and a lactone grouping; these observations suggest that shinjulactone E (**3**) would be a hydroxy derivative of ailanthone (**4**).

In the ^{1}H NMR spectrum of **3**, a lactone-terminus proton appeared at δ 4.87 as a doublet and a signal due to H-6 was observed at δ 4.61 as a double-doublet, resonating in lower field than that of ailanthone (**4**). Therefore the hydroxyl group was determined to be located at C-6.

On acetylation, shinjulactone E (**3**) gave a tetraacetate (**11**), mp 112—116 °C. In the ^{1}H NMR spectrum, two singlet signals due to vinyl methyls were observed at δ 1.82 and δ 2.03 together with signals due to a tertiary methyl and four acetyl groups. Seven methyl signals were observed in the ^{13}C NMR spectrum of **11**. The disappearance of the *exo*-methylene and the appearance of an additional vinyl methyl imply the occurrence of isomerization of the $C_{(13)}$–$C_{(21)}$ *exo*-double bond into an *endo*-double bond between $C_{(12)}$ and $C_{(13)}$ in the acetylation reaction to give an enol acetate.

On irradiation at δ 4.84 due to H-7, a double-doublet signal (J=11.5 and 3 Hz) at δ 5.25 due to H-6 of the tetraacetate (**11**) collapsed into a doublet, which was coupled with an α(axial)-H on C-5 with a coupling constant, $J_{5,6}$=11.5 Hz. On saturation at the frequency of H-6, the doublet signal due to H-7 changed into a singlet. Since the large coupling constant, $J_{5,6}$, suggests a *trans*-relationship between H-6 and H-5, the H-6 could be determined to be β(axial)-configuration. Therefore it is concluded that shinjulactone E (**3**) is formulated as 11β,20-epoxy-1β,6α,11α,12α-tetrahydroxypicrasa-3,13(21)-diene-2,16-dione (=6α-hydroxyailanthone) and the structure of the tetraacetate (**11**) is 1β,6α,12,20-tetraacetoxypicrasa-3,12-diene-2,11,16-trione.

Experimental[13]

Extraction and Isolation of Shinjulactones B (1) and D (2). The stem bark (11.2 kg), collected at the Botanical Gardens of Faculty of Science, the University of Tokyo in July 1979, was chipped and extracted with hot water (90 °C, 20 L) overnight. The extraction was repeated twice under the same conditions and the aqueous extracts were combined. Evaporation *in vacuo* gave a concentrated extract (*ca.* 13 L), which was divided into 8 portions and the each portion was continuously extracted with dichloromethane (1 L×2) overnight. All the extracts were combined and evaporated to give a residue (*ca.* 22 g). A part (14 g) of the residue, adsorbed on silica gel (35 g), was placed on a top of a silica-gel (700 g) column, and eluted with the following solvents in succession; $CHCl_3$ (1.4 L), 1%-MeOH in $CHCl_3$ (4.2 L), 2%-, 3%-, and 4%- (each 2.8 L), 5%- (4.2 L), 7%- (2.8 L), 10%-, and 30%-MeOH in $CHCl_3$ (each 1.4 L), and 85 fractions (each 280 mL) were collected. Elution with the 2%-MeOH in $CHCl_3$ gave amarolide 11-acetate (40 mg) and amarolide (650 mg), and elution with the 3%-MeOH in $CHCl_3$ shinjudilactone (50 mg) and ailanthone (1.3 g). Fractions 47—52 eluted with the 4%-MeOH in $CHCl_3$ gave crystals on standing, which were recrystallized from $CHCl_3$–MeOH to afford shinjulactone B (**1**; 110 mg).

The root bark (6.2 kg) was collected at the same botanical garden in August 1982. Extract with hot water was evaporated and continuously extracted with dichloromethane to give a residue (40 g), which was subjected to chromatographic separation of silica gel (2.6 kg). Amarolide 11-acetate (200 mg), amarolide (540 mg), shinjudilactone (1 g), and ailanthone (2.8 g) were eluted with 7—10%-MeOH in $CHCl_3$. Elution with 12%-MeOH in $CHCl_3$ afforded shinjulactone B (**1**; 240 mg) and 13%-MeOH in $CHCl_3$ gave shinjulactone C (130 mg) and chaparrolide (120 mg). Shinjulactone D (**2**; 50 mg) was obtained by elution with 14%-MeOH in $CHCl_3$ together with $\Delta^{13(18)}$-dehydroglaucarubolone (10 mg).

Extraction and Isolation of Shinjulactone E (3). The stem bark collected in Nishinomiya, Hyogo Prefecture, was extracted with hot methanol. The methanol extracts were concentrated and partitioned between carbon tetrachloride and water. The aqueous layer was separated and extracted with dichloromethane continuously. Organic layer was evaporated to give a residue, from which crude ailanthone was isolated by silica-gel chromatography. The crude ailanthone (10 g) was subjected to rechromatography on silica gel (300 g) eluting with 8%-MeOH in $CHCl_3$ and 30 fractions (each 75 mL) were collected. Chaparrinone (60 mg, from fr. 5), pure ailanthone (5 g, from frs. 7—10), and sitosteryl glucoside (1.5 g, from frs. 15—27) were obtained. Fractions 12—14 (82 mg) were combined and further separated by preparative TLC developed with 10%-MeOH in $CHCl_3$ and a fraction containing shinjulactone E (**3**) was obtained. Contaminated triterpenes in the fraction were separated off by crystallization from $CHCl_3$–MeOH to afford shinjulactone E (**3**; 23 mg) as amorphous solid.

Shinjulactone B (1). Prisms crystallized from $CHCl_3$–MeOH, mp 265.5—268 °C, $[\alpha]_D^{25}$ +167° (*c* 0.65, MeOH); IR (KBr) 3570, 3420, 1770, 1750, 1695, 1680, 1660, and 1635 cm^{-1}; UV (EtOH) 279 nm (ε 8100), which shifted to 330 nm on addition of alkali (pH *ca.* 11); ^{1}H NMR (Table 1); ^{13}C NMR (25.0 MHz, C_5D_5N) δ=12.3q, 16.3q, 23.8q, 28.3t, 37.4d, 39.7d, 40.4t, 48.8s, 51.6s, 64.3t, 85.2d, 87.1d, 120.4d, 138.5s, 145.1s, 167.7s, 168.8s, 171.5s, and 195.9s; MS *m/z* (%) 362 (M^+; 0.4), 344 (0.4), 332 (2.3), 265 (8.4), 235 (34), and 191 (100); Found: *m/z* 362.1395. Calcd for $C_{19}H_{22}O_7$: M 362.1365. Found: C, 60.81; H, 6.38%. Calcd for $C_{19}H_{22}O_7\cdot1/2H_2O$: C, 60.96; H, 6.19%.

11,20-Di-O-acetylshinjulactone B (5). A solution of shinjulactone B (**1**; 9.3 mg) in acetic anhydride (2 mL) and pyridine (2 mL) was allowed to stand at room temperature for 2 d. The usual work-up gave a crude product, which was purified by preparative TLC developed with 8%-MeOH in $CHCl_3$ to afford diacetate (**5**; 9 mg), mp 194—198 °C (from acetone–hexane); IR (Nujol) 1770, 1750, 1720, 1685, 1660, 1640, and 1200 cm^{-1}; UV (EtOH) 240 nm (ε 8200); ^1H NMR (Table 1); ^{13}C NMR (25.0 MHz, C_5D_5N) δ=12.2q, 16.0q, 20.3q, 20.6q, 24.4q, 28.3t, 38.1d, 40.5d, 40.5t, 49.1s, 50.9s, 64.8t, 83.7d, 87.6d, 120.9d, 142.6s, 153.0s, 166.8s, 167.4s, 168.5s, 170.4s, 170.8s, and 192.0s; MS *m/z* (%) 446 (M^+; 8), 404 (40), 386 (30), 344 (45), 307 (70), 247 (90), and 177 (100); Found: *m/z* 446.1566. Calcd for $C_{23}H_{26}O_9$: M 446.1576.

*Shinjulactone D (**2**).* Mp 267—269°C (from acetone); $[\alpha]_D^{22}$ −44° (*c* 0.17, C_5H_5N); IR (KBr) 3400, 1730, 1215, and 1050 cm^{-1}; ^1H NMR (Table 1); ^{13}C NMR (67.80 MHz, C_5D_5N) δ=11.6q, 13.3q, 20.1q, 26.8t, 29.1d, 30.6t, 31.7d, 41.6s, 42.7s, 42.9d, 43.3t, 44.2d, 46.5d, 70.1d, 71.8t, 79.2d, 79.7d, 85.3d, 110.9s, and 169.9s; MS *m/z* (%) 382 (M^+; 8), 364 (3), 268 (100), and 250 (60); Found: *m/z* 382.1969. Calcd for $C_{20}H_{30}O_7$: M 382.1990.

1,2,20-Tri-O-acetylshinjulactone D (7). Shinjulactone D (**2**; 13.3 mg, crude) was acetylated with acetic anhydride (1 mL) in pyridine (2 mL) at room temperature for 20 h. The reaction product, after usual work-up, was purified by preparative TLC developed with 20%-acetone in benzene and crystallized from acetone–hexane to give a triacetate (**7**; 3.6 mg), mp 135—138 °C (sintered at 118—121 °C); IR (KBr) 3530, 2940, 1745, 1725 (sh), 1375, 1240, and 1040 cm^{-1}; ^1H NMR (Table 1); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=12.3, 13.5, 19.1, 20.7, 20.9, 21.5, 25.8, 27.2, 28.3, 35.4, 35.9, 39.0, 41.7, 43.0, 44.8, 48.2, 61.8, 70.8, 77.8, 82.3, 82.6, 170.2, 170.2, 170.4, 174.2, and 212.1; MS *m/z* (%) 508 (M^+; 13), 488 (25), 466 (8), 406 (25), 376 (42), 316 (50), and 55 (100); Found: *m/z* 508.2341. Calcd for $C_{26}H_{36}O_{10}$: M 508.2309.

1,2,12,20-Tetra-O-acetylshinjulactone D (8). Triacetate (**7**) was acetylated under the same conditions as above for 50 h to afford a tetraacetate (**8**) in almost quantitative yield, mp 129—132 °C (from acetone–hexane); IR (KBr) 1745, 1720 (sh), 1370, 1240, and 1040 cm^{-1}; ^1H NMR (Table 1); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=12.3, 13.0, 19.2, 20.7, 20.7, 20.9, 21.1, 25.6, 27.5, 27.8, 34.2, 35.9, 38.9, 41.7, 43.0, 44.3, 49.5, 61.8, 70.9, 78.1, 80.5, 80.6, 169.5, 169.6, 170.0, 170.2, 171.3, and 204.3; MS *m/z* (%) 550 (M^+; 6), 508 (20), 490 (18), 466 (25), 448 (100), 388 (65), and 328 (80); Found: *m/z* 550.2410. Calcd for $C_{28}H_{38}O_{11}$: M 550.2412.

Shinjulactone E (3). White amorphous solid, ^1H NMR (Table 1); ^{13}C NMR(22.5 MHz, C_5D_5N) δ=11.5, 26.8, 35.2, 43.7, 46.7, 48.2, 48.2, 48.5, 65.9, 71.7, 80.8, 82.0, 84.5, 110.6, 117.8, 128.1, 147.3, 165.3, 169.3, and 197.2; MS *m/z* (%) 392 (M^+; 10), 374 (50), 364 (45), 356 (20), and 314 (100); Found: *m/z* 392.1462. Calcd for $C_{20}H_{24}O_8$: M 392.1469.

1,6,12,20-Tetra-O-acetylshinjulactone E (11). Shinjulactone E (**3**; 22.6 mg, crude) was treated with acetic anhydride (0.5 mL) and pyridine (0.5 mL) in the presence of a catalytic amount of 4-(dimethylamino)pyridine at room temperature for 2.5 d. After usual work-up, purification by preparative TLC (developed with 1%-MeOH in $CHCl_3$) yielded a tetraacetate (**11**; 6.2 mg), mp 112—116 °C (from chloroform); IR (KBr) 1745, 1680, 1620, and 1235 cm^{-1}; UV (EtOH) 243 nm (ε 12000); ^1H NMR (Table 1); ^{13}C NMR (50 MHz, $CDCl_3$) δ=13.5q, 15.5q, 20.0q, 20.6q, 20.7q, 21.3q, 24.0q, 29.7t, 39.1d, 42.6s, 44.6d, 46.9s, 48.5d, 61.1t, 66.7d, 77.4d, 83.8d, 127.7s, 129.1d, 159.5s, 167.0s, 169.9s, 170.1s, 171.3s, 174.5s, 179.2s, 190.9s, and 191.7s; MS *m/z* (%) 560 (M^+; 10), 518 (65), 476 (80), 458 (50), 416 (85), 315 (90), 297 (80), and 43 (100); Found: *m/z* 560.1909. Calcd for $C_{28}H_{32}O_{12}$: M 560.1894.

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References

1) Preliminary accounts of this report: T. Furuno, H. Naora, T. Murae, H. Hirota, T. Tsuyuki, T. Takahashi, A. Itai, Y. Iitaka, and K. Matsushita, *Chem. Lett.*, **1981**, 1797; M. Ishibashi, T. Furuno, T. Tsuyuki, T. Takahashi, and K. Matsushita, *Chem. Pharm. Bull.*, **31**, 2179 (1983).

2) T. Murae, A. Sugie, T. Tsuyuki, and T. Takahashi, *Chem. Pharm. Bull.*, **23**, 2188 (1975) and references cited therein.

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

4) 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).

5) C. G. Casinovi, V. Bellavita, G. Grandolini, and P. Ceccherelli, *Tetrahedron Lett.*, **1965**, 2273; W Stöcklin, M. Stefanović, T. A. Geissman, and C. G. Casinovi, *ibid.*, **1970**, 2399.

6) J. Polonsky and J.-L. Fourrey, *Tetrahedron Lett.*, **1964**, 3983; A. Gaudemer, J.-L. Fourrey, and J. Polonsky, *Bull. Soc. Chim. Fr.*, **1967**, 1676.

7) C. G. Casinovi, P. Ceccherelli, G. Grandolini, and V. Bellavita, *Tetrahedron Lett.*, **1964**, 3991.

8) R. E. Mitchell, W. Stöcklin, M. Stefanović, and T. A. Geissman, *Phytochemistry*, **10**, 411 (1971).

9) J. Moron, J. Rondest, and J. Polonsky, *Experientia*, **22**, 511 (1966); S. M. Kupchan and J. A. Lacadie, *J. Org. Chem.*, **40**, 654 (1975).

10) S. M. Kupchan, R. W. Britton, J. A. Lacadie, M. F. Ziegler and C. W. Sigel, *J. Org. Chem.*, **40**, 648 (1975).

11) The complete F_o-F_c data, anisotropic thermal parameters for non-hydrogen atoms, atomic positional parameters and isotropic thermal parameters for hydrogen atoms, and bond lengths and bond angles containing hydrogen atoms are deposited as Document No. 8434 at the Office of the Editor of Bull. Chem. Soc. Jpn.

12) J. Polonsky and N. Bourguignon-Zylber, *Bull. Soc. Chim. Fr.*, **1965**, 2793.

13) General Procedures are the same described in the preceding papers.[3,4]