Structure Determination of Bitter Principles of *Ailanthus altissima*. Structures of Shinjulactones F, I, J, and K[1)]

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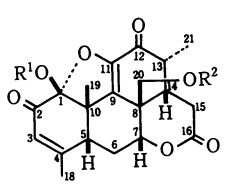
Four new quassinoids, shinjulactones F, I, J, and K were isolated from *Ailanthus altissima* Swingle. The structure of shinjulactone F was established to be 1α,11-epoxy-1β,20-dihydroxy-5β*H*-picrasa-3,9(11)-diene-2,12,16-trione by X-ray diffraction analysis. The structures of shinjulactones I, J, and K were determined to be 11α-acetoxy-2α,12α-dihydroxypicrasane-1,16-dione, 1β,12β-dihydroxypicrasane-2,11,16-trione, and 12α-acetoxy-2α,11α-dihydroxypicrasane-1,16-dione, respectively, by spectral and chemical means.

Bitter principles of Simaroubaceous plants have been extensively investigated from the interest in structure determination and their useful biological activities. In previous papers we have reported the isolation and structure elucidation of several quassinoids from *Ailanthus altissima* Swingle (Japanese name: Shinju or Niwaurushi).[2-5)] Recently quassinoid glycosides have been isolated from seeds of this plant.[6)] This paper describes structure determination of four new bitter principles, shinjulactones F, I, J, and K (**1**, **2**, **3**, and **4**), isolated from the same plant.

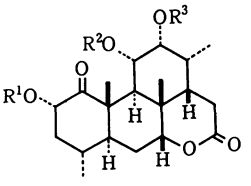
Aqueous extract of the root bark of *A. altissima* was continuously extracted with dichloromethane. The organic layer was subjected to separation by a silica-gel column chromatography and then further purified by a partition column chromatography on silicic acid to afford four minor bitter quassinoids, shinjulactones F (**1**, *ca.* 0.003% yield), I (**2**, *ca.* 0.0002% yield), J (**3**, *ca.* 0.0001% yield), and K (**4**, *ca.* 0.0005% yield) together with other known quassinoids.[2-5)]

Shinjulactone F (**1**), mp 201—203 °C, was shown to have a molecular formula, $C_{20}H_{22}O_7$, by elemental analysis and high-resolution mass spectrum. IR and UV spectra indicated the presence of hydroxyl(s) (ν_{max} 3450 cm^{-1}), δ-lactone (ν_{max} 1735 cm^{-1}), and two α,β-unsaturated carbonyls (ν_{max} 1685 cm^{-1}; λ_{max} 244 nm and 291 nm). Investigation on ^1H and ^{13}C NMR spectra of **1** revealed that shinjulactone F (**1**) possesses a vinyl methyl, a tertiary methyl, a secondary methyl, and a hydroxymethyl group.

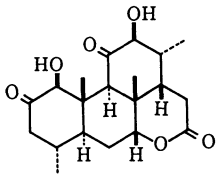
Spectral comparison with known quassinoids such as ailanthone (**5**)[3)] and shinjulactone B (**6**)[5)] suggested the presence of partial structures **A** and **B** for shinjulactone F (**1**). The A ring of shinjulactone F (**1**) was shown to resemble that of ailanthone (**5**) except for the facts described below. ^{13}C NMR of **1** showed a signal assignable to a hemiacetal carbon (δ 120.6 s) instead of a signal (δ 84.4 d) due to C-1 for **5**. In ^1H NMR spectrum of **1** a signal due to a proton attached to C-1 was not observed. Thus the partial structure **A** was proposed for the A ring of shinjulactone F (**1**). In the part of the C ring the presence of the partial structure **B** was inferred from the following evidence. In ^{13}C NMR spectrum of **1** signals ascribable to the partial structure **B** were observed at δ 135.9 s, 149.9 s, and 194.3 s. These signals are similar to those assignable to a diosphenol part (δ 138.5 s; C-9, δ 145.1 s; C-11, and δ 195.9 s; C-12) of shinjulactone B (**6**) in its



1 R^1-R^2-H
7 R^1-R^2-Ac
12 R^1-CH_3, R^2-H
14 R^1-CH_3, R^2-Ac



2 R^1-R^3-H, R^2-Ac
4 R^1-R^2-H, R^3-Ac
18 R^1-R^2-Ac, R^3-H
26 R^1-R^2-R^3-Ac



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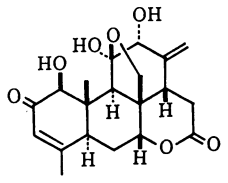

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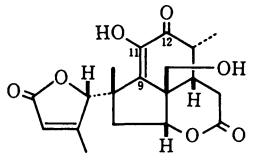
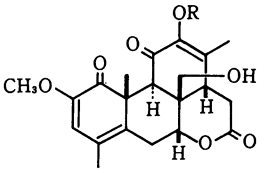
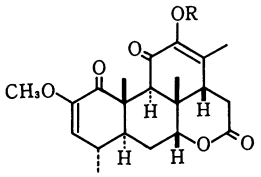


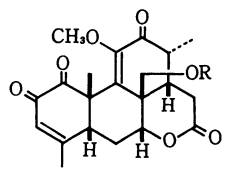
6



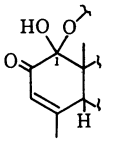
8 R=CH_3
9 R=H



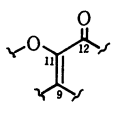
10 R=CH_3
11 R=H



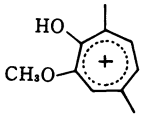
13 R=H
15 R=Ac



A



B



C

^{13}C NMR spectrum.

Acetylation of **1** gave a diacetate (**7**), which did not show the IR absorption band due to hydroxyl groups, indicating the presence of two hydroxyl groups for **1**. Assuming the picrasane skeleton, the presence of a 1,11-epoxide structure would be proposed for **1**, because the nature of all the seven oxygen atoms including the hemiacetal one at C-1 and nine of the ten unsaturation degrees have been clarified. Polonsky *et al.*[7] isolated karinolide from *Simaba multiflora*, for which 1α,11α-epoxypicrasane structure has been proposed. Treatment of **1** with hydrogen chloride in methanol afforded a reaction mixture, from which a dimethoxy derivative (**8**) and a monomethoxy derivative (**9**) were obtained by preparative TLC separation. The presence of a dienone moiety in the A ring of both **8** and **9** was indicated by UV (λ_{max} 325 nm) and MS (*m/z* 165; fragment ion **C**) spectra. In the UV spectra **8** exhibited an absorption maximum at 252 nm, while **9** showed it at 276 nm. These absorption maxima were reminiscent of quassin (**10**; 255 nm) and the diosphenol (**11**; 270 nm), respectively.[8] These observations indicated the presence of an enone moiety in the C ring for **8** and **9**. On methylation with diazomethane shinjulactone F (**1**) afforded 1-*O*-methyl derivative (**12**) and 11-*O*-methyl derivative (**13**), which were acetylated to give the corresponding acetates, **14** and **15**, respectively. Formation of these compounds adequately demonstrates the presence of the hemiacetal functionality at C-1 position for shinjulactone F (**1**).

The ^1H NMR spectrum of shinjulactone F (**1**) showed a multiplet signal at δ 2.71 due to a methine proton

Table 1. ^1H NMR Spectra of Shinjulactones F, I, J, and K (**1**, **2**, **3**, and **4**)

	δ (*J*/Hz)			
	1[a]	**2**[b]	**3**[b]	**4**[b]
1-H			3.82 br s	
2-H		4.72 ddd (10.5, 7.6, 7)		4.75 ddd (11.6, 7.6, 5.5)
3α-H		*	*	*
	6.26 br s			
3β-H		2.50 ddd (12.8, 7.6, 4.3)	2.58 dd (14.6, 4.8)	2.50 ddd (12.8, 7.6, 3.9)
5-H	2.71 m	1.53 ddd (13, 12.8, 3.6)	*	1.54 ddd (12.8, 12, 3.4)
6α-H	2.65 ddd (16, 3, 2.9)	1.97 ddd (14.5, 3.6, 3.3)	*	2.01 dt (14.6, 3.4)
6β-H	2.52 ddd (16, 5.5, 2.1)	1.79 ddd (14.5, 12.8, 2.1)	*	1.85 ddd (14.6, 12, 2.1)
7-H	5.20 dd (2.9, 2.1)	4.15 dd (3.3, 2.1)	4.39 dd (4.0, 1.8)	4.15 dd (3.4, 2.1)
9-H		3.35 d (11.9)	2.80 s	2.83 d (11.3)
11-H		5.15 dd (11.9, 2.7)		3.88 dd (11.3, 3.1)
12-H		3.97 t (2.7)	3.95 br d (11.0)	5.37 t (3.1)
13-H	3.34 dq (3.7, 7)	2.15 m	*	2.27 m
14-H	3.18 ddd (12.5, 6.4, 3.7)	*	*	1.67 ddd (12.8, 7.0, 5.2)
15α-H	2.10 dd (18, 12.5)	3.55 dd (19.2, 12.2)	2.69 dd (19.2, 12.8)	3.06 dd (19.2, 12.8)
15β-H	2.60 dd (18, 6.4)	2.59 dd (19.2, 6.7)	2.86 dd (19.2, 7.0)	2.56 dd (19.2, 7.0)
20-H	4.22 d (11.9)			
20-H′	4.16 d (11.9)			
4-CH_3	2.08 br s	0.90 d (6.4)	1.05 d (6.4)	0.94 d (6.7)
8-CH_3		1.25 s[c]	1.24 s[c]	1.42 s[c]
10-CH_3	1.69 s	1.21 s[c]	1.10 s[c]	1.22 s[c]
13-CH_3	0.98 d (7)	1.10 d (7.0)	1.17 d (6.7)	0.95 d (7.3)
CH_3CO-		1.93 s		2.24 s
1-OH	*		3.49 br s	
2-OH		3.60 d (7)		3.41 d (5.5)
12-OH		*	3.53 br s	*

a) 400 MHz in C_5D_5N. b) 400 MHz in $CDCl_3$. c) Signals may be reversed.
* not assigned

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). These coupling patterns have never been observed in ^{1}H NMR of any known quassinoids. However this observation could be reasonably explained if an inversion of a chiral center at C-5 occurs so as to form the 1,11-epoxide ring with a less strain. Configurations of the hydroxyl group at C-1 and the hydrogen at C-5 could be determined by NOE measurement of 1-*O*-methyl monoacetate (**14**). 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 X-ray diffraction analysis. The crystal of **1** obtained from benzene–acetone solution belongs 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, and β=105.3(2)°. Two molecules of **1** and two water molecules are contained in the unit cell to give D_c=1.42 g·cm^{-3}. Intensity data were measured on a Philips PW1100 automatic four-circle diffractometer using monochromated Cu $K\alpha$ radiation. A total of 1883 independent structure factors with $F_o \geq 2.5\sigma(F_o)$ within 2θ=156° were obtained by the 2θ–θ scanning mode. The structure was solved by the direct method using MULTAN 80 program. An E-map revealed the positions of all the non-hydrogen atoms, and the hydrogen atoms except those of water molecule were located in a difference electron density map. The structure was refined by the block-diagonal least-squares calculations assuming anisotropic thermal motions for non-hydrogen atoms and isotropic ones for hydrogen atoms. The final R-factor was 0.036. The final atomic coordinates are listed in Table 2 and bond lengths and bond angles are listed in Tables 3 and 4[9]. The hemiacetal structure and the $C_{(5\beta)}$-H configuration were clearly established as shown in Fig. 1. Thus the structure of shinjulactone F (**1**) was established to be 1α,11-epoxy-1β,20-dihydroxy-5βH-picrasa-3,9(11)-diene-2,12,16-trione.

Table 2. Atomic positonal parameters (×10^4) and isotropic temperature factors (×10^2) for non-hydrogen atoms of shinjulactone F (**1**) with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq} [a]
C(1)	3603(3)	2317(0)	7089(3)	208(3)
C(2)	4687(3)	2338(2)	5734(3)	242(3)
C(3)	6335(3)	2700(2)	6342(4)	284(4)
C(4)	6947(3)	3095(2)	7954(3)	263(3)
C(5)	5941(3)	3258(2)	9309(3)	231(3)
C(6)	6137(3)	4222(2)	10102(3)	271(4)
C(7)	5358(3)	4960(2)	8752(3)	254(3)
C(8)	3516(3)	4806(2)	7824(3)	208(3)
C(9)	3170(3)	3829(2)	7489(3)	184(3)
C(10)	4078(3)	3052(2)	8594(3)	196(3)
C(11)	1982(3)	3508(2)	6088(3)	212(3)
C(12)	907(3)	4054(2)	4667(3)	249(3)
C(13)	1131(3)	5061(2)	4957(3)	232(3)
C(14)	2935(3)	5298(2)	5974(3)	220(3)
C(15)	4095(3)	5083(2)	4762(4)	269(4)
C(16)	5903(3)	5097(2)	5698(4)	287(4)
C(18)	8753(3)	3343(3)	8545(5)	428(5)
C(19)	3350(3)	2804(2)	10190(3)	302(4)
C(20)	2545(3)	5150(2)	9190(3)	281(4)
C(21)	484(3)	5582(2)	3182(4)	331(4)
O(1)	3552(2)	1471(1)	7775(2)	272(3)
O(2)	4154(3)	1984(2)	4226(3)	374(3)
O(3)	1937(2)	2584(1)	6009(2)	251(2)
O(4)	−73(3)	3712(2)	3348(3)	445(4)
O(5)	6955(3)	5154(2)	4855(3)	419(4)
O(6)	6427(2)	5022(1)	7497(3)	317(3)
O(7)	2671(3)	6080(2)	9461(3)	394(3)

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

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

Bond length		l/Å
Atom 1	Atom 2	
C(1)	−C(2)	1.542 (4)
C(1)	−C(10)	1.556(3)
C(1)	−O(1)	1.370(2)
C(1)	−O(3)	1.475(3)
C(2)	−C(3)	1.442(4)
C(2)	−O(2)	1.231(3)
C(3)	−C(4)	1.332(4)
C(4)	−C(5)	1.511(4)
C(4)	−C(18)	1.509(4)
C(5)	−C(6)	1.551(4)
C(5)	−C(10)	1.544(3)
C(6)	−C(7)	1.528(4)
C(7)	−C(8)	1.538(3)
C(7)	−O(6)	1.473(4)
C(8)	−C(9)	1.494(3)
C(8)	−C(14)	1.543(3)
C(8)	−C(20)	1.564(4)
C(9)	−C(10)	1.514(3)
C(9)	−C(11)	1.338(3)
C(10)	−C(19)	1.538(4)
C(11)	−C(12)	1.458(3)
C(11)	−O(3)	1.381(3)
C(12)	−C(13)	1.523(4)
C(12)	−O(4)	1.226(3)
C(13)	−C(14)	1.548(3)
C(13)	−C(21)	1.523(4)
C(14)	−C(15)	1.538(4)
C(15)	−C(16)	1.496(3)
C(16)	−O(5)	1.222(4)
C(16)	−O(6)	1.322(3)
C(20)	−O(7)	1.403(4)

Shinjulactone F (**1**) contains several interesting structural features. 1,11-Epoxypicrasanes are rarely found and only two types have been reported; artificial bisnorquassin and its derivatives[10] and karinolide.[7] It is noteworthy that shinjulactone F (**1**) is the first example of 5β-H picrasane skeleton with all-*cis* configurations at A/B, B/D, and C/D ring junctures to form a unique folded-shape molecule.

Shinjulactone I (**2**) crystallized from acetone as colorless prisms, mp 220—223 °C. High-resolution mass spectrum indicated the molecular formula $C_{22}H_{32}O_7$. IR spectrum showed the presence of hydroxyl(s) (3430 cm^{-1}), a δ-lactone (1725 cm^{-1}), and an isolated carbonyl group (1705 cm^{-1}). ^{1}H (Table 1) and ^{13}C NMR spectra revealed that shinjulactone I (**2**) possesses two

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

Bond angle			ϕ/°
Atom 1	Atom 2	Atom 3	
C(2)	−C(1)	−C(10)	113.1(2)
C(2)	−C(1)	−O(1)	110.7(2)
C(2)	−C(1)	−O(3)	105.3(2)
C(10)	−C(1)	−O(1)	113.5(2)
C(10)	−C(1)	−O(3)	103.8(2)
O(1)	−C(1)	−O(3)	109.8(2)
C(3)	−C(2)	−C(1)	118.7(2)
C(3)	−C(2)	−O(2)	122.7(2)
C(1)	−C(2)	−O(2)	118.5(2)
C(4)	−C(3)	−C(2)	124.3(3)
C(5)	−C(4)	−C(3)	123.1(2)
C(5)	−C(4)	−C(18)	117.1(2)
C(3)	−C(4)	−C(18)	119.7(3)
C(6)	−C(5)	−C(4)	113.1(2)
C(6)	−C(5)	−C(10)	108.4(2)
C(4)	−C(5)	−C(10)	115.1(2)
C(7)	−C(6)	−C(5)	115.2(2)
C(8)	−C(7)	−C(6)	113.5(2)
C(8)	−C(7)	−O(6)	115.1(2)
C(6)	−C(7)	−O(6)	104.6(2)
C(9)	−C(8)	−C(7)	110.5(2)
C(9)	−C(8)	−C(14)	108.0(2)
C(9)	−C(8)	−C(20)	108.7(2)
C(7)	−C(8)	−C(14)	112.4(2)
C(7)	−C(8)	−C(20)	106.5(2)
C(14)	−C(8)	−C(20)	110.5(2)
C(10)	−C(9)	−C(8)	127.3(2)
C(10)	−C(9)	−C(11)	109.0(2)
C(8)	−C(9)	−C(11)	123.7(2)
C(19)	−C(10)	−C(1)	109.2(2)
C(19)	−C(10)	−C(5)	110.4(2)
C(19)	−C(10)	−C(9)	111.9(2)
C(1)	−C(10)	−C(5)	115.9(2)
C(1)	−C(10)	−C(9)	98.0(2)
C(5)	−C(10)	−C(9)	110.9(2)
C(12)	−C(11)	−C(9)	124.9(2)
C(12)	−C(11)	−O(3)	121.5(2)
C(9)	−C(11)	−O(3)	113.4(2)
C(13)	−C(12)	−C(11)	114.6(2)
C(13)	−C(12)	−O(4)	124.0(2)
C(11)	−C(12)	−O(4)	121.4(2)
C(14)	−C(13)	−C(12)	111.3(2)
C(14)	−C(13)	−C(21)	113.4(2)
C(12)	−C(13)	−C(21)	112.0(2)
C(15)	−C(14)	−C(8)	110.2(2)
C(15)	−C(14)	−C(13)	110.2(2)
C(8)	−C(14)	−C(13)	112.1(2)
C(16)	−C(15)	−C(14)	115.9(2)
O(6)	−C(16)	−C(15)	120.5(2)
O(6)	−C(16)	−O(5)	117.1(3)
C(15)	−C(16)	−O(5)	122.4(3)
O(7)	−C(20)	−C(8)	112.9(2)
C(1)	−O(3)	−C(11)	103.6(2)
C(7)	−O(6)	−C(16)	125.3(2)

tertiary methyls, two secondary methyls, and an acetoxyl group. Since five oxygen atoms were characterized by a lactone, an isolated carbonyl, and an acetoxyl group, the remaining two oxygen atoms were shown to be those of hydroxyl groups. Spectral comparison with amarolide (**16**)[11] suggests that

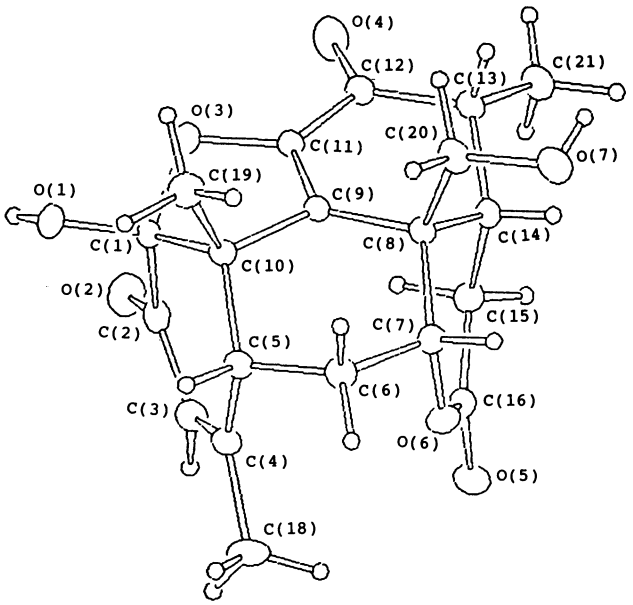
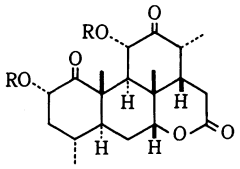


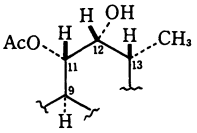
Fig. 1. Perspective view of shinjulactone F (**1**).[a]
a) For clarity hydrogen atoms are represented by spheres of arbitrary radius.

shinjulactone I (**2**) possesses the same structure as **16** in respect of A ring. In the part of C ring the presence of a partial structure **D** was proposed by ^{1}H NMR double resonance experiment for **2** at 90 MHz. Irradiation on a double doublet signal at δ 5.15 (11-H) caused a collapse of a triplet at δ 3.97 (12-H) into a doublet and changed a doublet at δ 3.35 (9-H) into a singlet. Irradiation on a multiplet at δ 2.15 (13-H) changed a doublet methyl-signal at δ 1.10 (13-CH_3) into a singlet and the triplet at δ 3.97 (12-H) into a doublet. The configurations of the four adjacent protons were, therefore, deduced to be 9α-axial, 11β-axial, 12β-equatorial, and 13β-axial orientations from the coupling constants, $J_{9,11}$=11.9, $J_{11,12}$=2.7, and $J_{12,13}$=2.7 Hz, respectively. A low magnetic field resonance due to $C_{(11)}$-H implies that the acetoxyl group is attached to C-11 position. From these observations the structure **2** might be formulated for shinjulactone I. The structure of shinjulactone I (**2**) was firmly established by a conversion into known amarolide diacetate (**17**).[11] Acetylation of shinjulactone I (**2**) at 0°C for 6h afforded its monoacetate (**18**). A signal at δ 4.72 due to $C_{(2)}$-H in ^{1}H NMR spectrum of **2** was shifted to a lower magnetic field at δ 5.56 in that of **18**. Protons at C-12 of **2** and **18** resonated at nearly the same magnetic fields (δ 3.97 and δ 3.90, respectively). This fact shows that the hydroxyl group at C-12 position remained intact. Jones oxidation of the monoacetylated derivative (**18**) afforded amarolide diacetate (**17**), which was completely identical with an authentic sample. Thus the structure of shinjulactone I (**2**) was determined to be 11α-acetoxy-2α,12α-dihydroxypicrasane-1,16-dione.

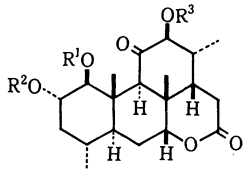
The molecular formula, $C_{20}H_{28}O_6$, of shinjulactone J (**3**), mp 127—130°C, was determined by high-resolution mass spectrum. IR spectrum revealed characteristic absorptions for hydroxyl(s) (3510 cm^{-1}),



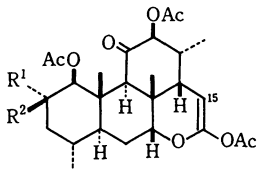
16 R=H
17 R=Ac



D



19 R^1=R^2=R^3=H
20 R^1=R^3=H, R^2=$SiMe_2{}^tBu$
21 R^1=H, R^2=R^3=$SiMe_2{}^tBu$
22 R^1=H, R^2=$SiMe_2{}^tBu$, R^3=Ac



23 R^1=$OSiMe_2{}^tBu$, R^2=H
24 R^1=OH, R^2=H
25 R^1,R^2=O

isolated carbonyl(s) (1715 cm^{-1}), and a δ-lactone (1725 cm^{-1}). ^1H (Table 1) and ^{13}C NMR spectra showed the presence of two secondary methyls, two tertiary methyls, two isolated carbonyls, and a lactone grouping. Four of six oxygen atoms were thus explained and the presence of two hydroxyl groups was indicated by two broad singlet signals at δ 3.49 and δ 3.53 due to hydroxyl protons, which disappeared on addition of D_2O. Signals due to protons attached to carbons with hydroxyl groups were observed as a singlet at δ 3.82 and a doublet at δ 3.95, respectively, the both signals being coupled with hydroxyl protons with small coupling constants. A signal assignable to $C_{(9)}$-H was observed at δ 2.80 as a singlet. These findings suggest that hydroxyl groups exist at C-1 and C-12 positions and isolated carbonyl groups are located at C-2 and C-11 positons. This is also supported by comparison with other quassinoids. Most of quassinoids with six oxygen atoms possess oxygenated functionalities at C-1, C-2, C-11, and C-12 positions other than a δ-lactone moiety. Configurations of hydroxyl groups of shinjulactone J (**3**) was determined by NOE experiment at 400 MHz. On saturation of the proton singlet due to $C_{(9)}$-H, the signals due to $C_{(1)}$-H and $C_{(12)}$-H showed increase in area by 14 and 7%, respectively. This observation indicates the $C_{(1\beta)}$-OH and $C_{(12\beta)}$-OH orientations. From these results the structure **3** was proposed for shinjulactone J.

In order to confirm the proposed structure **3**, a preparation of shinjulactone J (**3**) from known chaparrolide (**19**)[12] was carried out as follows. Treatment of chaparrolide (**19**) with *t*-butyldimethylsilyl chloride in the presence of imidazole in *N*,*N*-dimethylformamide afforded a monosilyl derivative (**20**; yield 40%) and a disilyl derivative (**21**; yield 17%). The monosilyl derivative (**20**) was acetylated at room temperature for 4 d to give 2-siloxy monoacetate (**22**; yield 96%), which was further acetylated at 110°C for 40 h to afford 2-siloxy triacetate (**23**; yield 51%). The ^1H NMR spectrum of **23** showed a signal due to an olefinic proton (δ 5.51 br s; 15-H) and three singlet methyl-signals due to acetyl groups (δ 2.14, 2.16, and 2.30). The ^{13}C NMR of **23** showed a signal at δ 202.9 assignable to a carbonyl carbon atom at C-11 position and a signal at δ 110.6 due to sp^2 carbon atom at C-15. The IR spectrum of **23** revealed no absorption band due to hydroxyl groups, while an absorption at 1670 cm^{-1} with a middle intensity ascribable to $\Delta^{15(16)}$-double bond with two oxygen functions was observed. Since the dihedral angle between $C_{(14)}$-H and $C_{(15)}$-H was estimated to be *ca.* 90° from the Drieding model, the fact that the olefinic proton at C-15 appeared as a singlet signal was well explained. From these observations the structure of 2-siloxy triacetate (**23**) was firmly established. Treatment of **23** with AcOH–H_2O–THF afforded 2-hydroxy triacetate (**24**; yield 64% based on consumed **23**), which was subjected to Jones oxidation to give 2-keto triacetate (**25**; yield *ca.* 80%). Finally this compound (**25**) was hydrolyzed under acidic conditions to afford shinjulactone J (**3**; yield *ca.* 50%), whose spectral data showed good agreements with those of a natural specimen. The structure of shinjulactone J (**3**) was, therefore, concluded to be 1β,12β-dihydoxypicrasane-2,11,16-trione.

Shinjulactone K (**4**), mp 135—139°C, crystallized from chloroform–hexane as colorless prisms. The molecular formula, $C_{22}H_{32}O_7$, was determined by high-resolution mass spectrum. ^1H (Table 1) and ^{13}C NMR spectra showed that shinjulactone K (**4**) possesses two secondary methyls, two tertiary methyls, an isolated carbonyl, a lactone, and an acetoxyl group. The IR absorption band at 3430 cm^{-1} suggested that the remaining two oxygen atoms are ascribed to hydroxyl groups. These spectral features were very similar to those of shinjulactone I (**2**). The ^1H NMR spectral comparison between shinjulactones I (**2**) and K (**4**) is indicative of a difference in the relative position of hydroxyl and acetoxyl groups in C ring. Shinjulactone K (**4**) showed a double doublet at δ 3.88 and a triplet at δ 5.37, which were assignable to protons attached to carbons with hydroxyl and acetoxyl groups, respectively. The shapes of these signals were quite parallel to those of the signals due to $C_{(11)}$-H and $C_{(12)}$-H of shinjulactone I (**2**), respectively, and their chemical shifts seemed to be just reversed. Double resonance experiment on shinjulactone K (**4**) was carried out in the same way as developed in the case of shinjulactone I (**2**). Irradiation on the double doublet at δ 3.88 (11-H) changed the triplet at δ 5.37 (12-H) into a doublet and a doublet at δ 2.83 (9-H) into a singlet. Irradiation on a multiplet at δ 2.27 (13-H) changed a doublet methyl-signal at δ 0.95 (13-CH_3) into a singlet and the triplet at δ 5.37 (12-H) into a doublet. These observations could propose the structure **4** for shinjulactone K.

Finally shinjulactones I (**2**) and K (**4**) were chemically correlated to each other. Acetylation of shinjulactone I (**2**) with acetic anhydride in pyridine in the presence of 4-dimethylaminopyridine at room temperature for 6 d gave its diacetate (**26**) together with the monoacetylated product (**18**). Shinjulactone K (**4**) was also acetylated under similar conditions to afford a diacetyl derivative

(**26**), which was completely identical with the diacetyl derivative (**26**) derived from shinjulactone I (**2**). Thus the structure of shinjulactone K (**4**) was established to be 12α-acetoxy-2α,11α-dihydroxypicrasane-1,16-dione.

Experimental

General Procedure. All melting points were measured on a Mel-temp capillary melting apparatus (Laboratory devices) and uncorrected. Optical rotations were determined on a JASCO polarimeter DIP-181. Ultraviolet absorption (UV) spectra and infrared (IR) spectra were measured on a Hitachi 340 and a Hitachi 260-30 spectrometer, respectively. Mass (MS) spectra were run on a JEOL JMS D-300 mass spectrometer operating at 70 eV. Proton nuclear magnetic resonance (^{1}H NMR) spectra (90 MHz) were taken using a Varian EM 390 or a JEOL FX 90Q and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra (22.5 MHz) were measured on a JEOL FX 90Q unless otherwise stated. Measurement of ^{1}H NMR spectra at 400 MHz and ^{13}C NMR at 100 MHz was carried out on a JEOL JMN GX 400 spectrometer. Chemical shifts were expressed in ppm downfield from tetramethylsilane as an internal standard (δ value) and coupling constants in Hz. Thin-layer chromatography (TLC) was carried out on Kieselgel 60 GF_{254} coated in 0.25 mm- or 0.5 mm-thickness. Wakogel C-200 (Wako) or Silicic acid AR (Mallinckrodt) was used for column chromatography.

Plant Material. Roots of *Ailanthus altissima* Swingle were collected at the Botanical Gardens, Faculty of Science, the University of Tokyo in August 1982. Bark was stripped off from the root, air-dried, and chipped to afford 6.2 kg of materials.

Extraction and Separation. The root bark (6.2 kg) was extracted with hot water overnight. The aqueous layer was concentrated and continuously extracted with dichloromethane. The organic layer was evaporated to give a residue (40 g), which was separated by a silica-gel column chromatography. Gradient elution with 7 and 13% methanol-chloroform gave fractions A and B, respectively.

Fraction A was subjected to a partition column chromatography of silicic acid (250 g) on which water (150 ml) was adsorbed. Gradient elution with 1—2 and 4—8% 1-butanol-benzene afforded fractions C and D, respectively. Fraction C was further purified by a silica-gel column chromatography eluted with benzene-acetone (3:1) to afford shinjulactone K (**4**; *ca.* 20 mg). Fraction D was also purified by a silica-gel column chromatography eluted with benzene-acetone (3:1) to give shinjulactone I (**2**; *ca.* 10 mg) and shinjulactone J (**3**; *ca.* 6 mg) together with shinjulactone H.[4]

Fraction B was separated by a partition column chromatography eluted with 0—16% ethanol-chloroform. The fraction eluted with 8% ethanol-chloroform was further purified by a silica-gel column chromatography eluted with 3% methanol-ethyl acetate to give shinjulactone F (**1**; *ca.* 170 mg) together with shinjulactone G.[4]

Shinjulactone F (1). Colorless prisms cryltallized from ethanol-chloroform or benzene-acetone, mp 201—203 °C, $[\alpha]_D^{20}$ −148° (*c* 2.1, pyridine); IR (KBr) 3450, 1735, 1685, 1220, and 1040 cm^{-1}; UV(ethanol) 244 nm (ε 7400) and 291 nm (ε 3400); ^{1}H NMR (Table 1); ^{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), 340 (5), 282 (100), 266 (25), 253 (35), 236 (50), 189 (50), and 177 (45); Found: *m/z* 374.1364. Calcd for $C_{20}H_{22}O_7$: M 374.1366. Found: C, 62.03; H, 5.93%. Calcd for $C_{20}H_{22}O_7 \cdot 2/3H_2O$: C, 62.17; H, 6.09%.

1,20-Di-O-acetylshinjulactone F (7). Shnjulactone F (**1**; 12 mg) was acetylated with acetic anhydride (0.5 ml) in pyridine (2 ml) at room temperature for 40 h. Addition of methanol and the usual work-up afforded a reaction mixture, which was purified by preparative TLC developed with *ca.* 2% methanol-ethyl acetate to give 1,20-di-*O*-acetylshinjulactone F (**7**; 4 mg), mp 128—132 °C (acetone); IR (Nujol) 1740, 1685, 1675, and 1220 cm^{-1}; UV (ethanol) 245 nm (ε 8000) and 285 nm (ε 2900); ^{1}H NMR ($CDCl_3$) δ=1.11 (3H, d, *J*= 7 Hz), 1.40 (3H, s), 2.19 (9H, br s), 4.36 (2H, s), 4.63 (1H, t, *J*= 2.5 Hz), and 6.21 (1H, br s); MS *m/z* (%) 458 (M^+; 30), 416 (100), 398 (45), 356 (50), 193 (55), and 151 (75); Found *m/z* 458.1554. Calcd for $C_{24}H_{26}O_9$: M 458.1576.

Reaction of 1 with Hydrogen Chloride. To a solution of shinjulactone F (**1**; 31 mg) in dry methanol (6 ml), acetyl chloride (0.3 ml) was added and the mixture was stirred at room temperature for 3 h to give a complex mixture, from which a dimethoxy derivative (**8**; *ca.* 1.5 mg) and a monomethoxy derivative (**9**; *ca.* 1.5 mg) were obtained by preparative TLC developed with 2% methanol-ethyl acetate. **8**: Mp 166—169 °C (acetone); UV(ethanol) 252 nm and 325 nm; ^{1}H NMR ($CDCl_3$) δ=1.45 (3H, s), 1.81 (3H, s), 1.93 (3H, br s), 3.64 (3H, s), 3.75 (3H, s), 4.63 (1H, m), and 5.96 (1H, br s); MS *m/z* (%) 402 (M^+; 75), 388 (20), 370 (18), and 165 (100); Found: *m/z* 402.1682. Calcd for $C_{22}H_{26}O_7$: M 402.1677. **9**: Mp 157—160 °C (acetone); UV(ethanol) 276 nm and 325 m; ^{1}H NMR ($CDCl_3$) δ=1.45 (3H, s), 1.80 (3H, s), 1.93 (3H, br s), 3.34 (1H, s), 3.73 (3H, s), 3.78 (2H, br s), 4.81 (1H, m), and 5.94 (2H, br s); MS *m/z* (%) 388 (M^+; 100), 370 (10), 356 (18), 280 (45), and 165 (80); Found: *m/z* 388.1515. Calcd for $C_{21}H_{24}O_7$: M 388.1520.

Methylation of 1 with Diazomethane. Shinjulactone F (**1**; 38 mg) in THF (10 ml) was treated with diazomethane in ether and the reaction mixture was allowed to stand at room temperature for 12 h. Usual work-up and separation by preparative TLC (7% methanol-chloroform) afforded 1-*O*-methyl derivative (**12**; 9.5 mg) and 11-*O*-methyl derivative (**13**; 11 mg). **12**: Mp 200—201 °C (chloroform); IR(KBr) 3450, 1720, 1710, 1680, and 1225 cm^{-1}; UV(ethanol) 245 nm (ε 8200) and 295 nm (ε 3000); ^{1}H NMR ($CDCl_3$) δ=1.09 (3H, d, *J*=7 Hz), 1.40 (3H, s), 2.10 (3H, br s), 3.53 (3H, s), 3.90 (2H, br s), 4.84 (1H, m), and 6.02 (1H, br s); MS *m/z* (%) 388 (M^+; 20), 358 (100), 343 (15), 329 (20), and 314 (45); Found: *m/z* 388.1472. Calcd for $C_{21}H_{24}O_7$: M 388.1520. **13**: Mp 118—122 °C (ethanol-ethyl acetate); IR (KBr) 3450, 1720, 1680, 1275, and 1040 cm^{-1}; UV (ethanol) 256 nm (ε 7200); ^{1}H NMR ($CDCl_3$) δ=1.11 (3H, d, *J*=7 Hz), 1.55 (3H, s), 2.19 (3H, br s), 3.65 (3H, s), 3.77 and 3.98 (each 1H, d, *J*=10 Hz), 4.85 (1H, m), and 6.08 (1H, br s); ^{13}C NMR ($CDCl_3$) δ=12.2, 21.2, 23.6, 27.6, 29.3, 36.9, 40.5, 42.1, 48.3, 51.8, 60.1, 66.3, 77.5, 128.9, 135.8, 151.4, 166.7, 167.9, 188.9, 193.9, and 198.8; MS *m/z* (%) 388 (M^+; 70), 358 (100), 329 (75), and 283 (50); Found: *m/z* 388.1540. Calcd for $C_{21}H_{24}O_7$: M 388.1520.

Acetylation of 12 and 13. A crude mixture (*ca.* 60 mg) of 1-*O*-methyl derivative (**12**) and 11-*O*-methyl derivative (**13**) was acetylated with acetic anhydride (2 ml) in pyridine (5 ml) at room temperature for 16 h. Addition of methanol and the usual work-up afforded a reaction mixture, which was separated by preparative TLC developed with chloroform-ethyl acetate (9:1) to afford 1-*O*-methyl monoacetate (**14**; 15 mg) and 11-*O*-methyl monoacetate (**15**; *ca.* 6 mg). **14**: Mp 193—195 °C (acetone-ether); IR(KBr) 1740, 1685, 1380, and 1220 cm^{-1}; UV(ethanol) 243 nm (ε 12000) and 291 nm (ε 4500); ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.12 (3H, d, *J*= 7 Hz; 13-CH_3), 1.42 (3H, s; 10-CH_3), 1.85 (1H, dd, *J*=18, 12.5 Hz; 15α-H), 2.09 (3H, br s; 4-CH_3), 2.15 (3H, s; CH_3CO-), 2.34 (1H, ddd, *J*=16, 6, 2.5 Hz; 6β-H), 2.52 (1H, dd, *J*=18, 6 Hz; 15β-H), 2.59 (1H, m; 5-H), 2.66 (1H, ddd, *J*=16, 3.5, 2.5 Hz; 6α-H), 2.69 (1H, ddd, *J*=12.5, 6, 3.5 Hz; 14-H), 3.06 (1H, dq, *J*=3.5, 7 Hz; 13-H), 3.53 (3H, s; CH_3O-), 4.32 and 4.36 (each 1H, d, *J*=12 Hz; 20-H), 4.62 (1H, t, *J*=2.5 Hz; 7-H), and 6.05 (1H, br s; 3-H); ^{13}C NMR ($CDCl_3$) δ=11.3q, 20.1q,

20.7q, 22.9q, 26.7t, 26.9t, 38.4s, 39.2d, 41.0d, 41.8d, 47.5s, 54.7q, 62.7t, 76.6d, 108.2s, 126.6d, 133.1s, 148.5s, 162.4s, 167.0s, 170.1s, 188.5s, and 191.0s; MS *m/z* (%) 430 (M^+; 72), 402 (75), 361 (70), 329 (100), and 301 (80); Found: *m/z* 430.1622. Calcd for $C_{23}H_{26}O_8$: M 430.1627. **15**: amorphous solid from ether, mp *ca.* 80—85 °C; IR(film) 1740, 1680, and 1220 cm^{-1}; UV (ethanol) 258 nm (ε 9200); ^1H NMR ($CDCl_3$) δ=1.16 (3H, d, *J*=7 Hz), 1.58 (3H, s), 2.13 (6H, s), 3.70 (3H, s), 4.13 and 4.51 (each 1H, d, *J*=12 Hz), 4.63 (1H, m), and 6.13 (1H, br s); MS *m/z* (%) 430 (M^+; 60), 402 (100), 387 (45), 371 (40), and 329 (93); Found: *m/z* 430.1611. Calcd for $C_{23}H_{26}O_8$: M 430.1627.

Shinjulactone I (2). Colorless prisms crystallized from acetone, mp 220—223 °C; $[\alpha]_D^{16}$+33° (*c* 0.67, $CHCl_3$); IR(KBr) 3430, 1725, 1705, and 1245 cm^{-1}; ^1H NMR (Table 1); ^{13}C NMR ($CDCl_3$) δ=13.4q, 13.9q, 18.3q, 21.1q, 21.7q, 26.4t, 28.8d, 29.4t, 30.5d, 32.1d, 35.9s, 44.8d, 48.0d, 48.6s, 49.0t, 70.1d, 72.8d, 73.4d, 82.3d, 170.0s, 171.1s, and 214.3s; MS *m/z* (%) 408 (M^+; 1.3), 390 (4.5), 380 (7), 352 (8), 348 (12), 330 (10), 320 (15), 302 (29), 258 (76), 242 (62), and 171(100); Found: *m/z* 408.2162. Calcd for $C_{22}H_{32}O_7$: M 408.2146.

2-O-Acetylshinjulactone I (18). Shinjulactone I (**2**; 6 mg) was treated with acetic anhydride (1 ml) in pyridine (2 ml) at 0 °C for 6 h. After addition of methanol and the usual work-up, the reaction mixture was separated by silica-gel column chromatography eluted with benzene–acetone (9:1) to afford the starting shinjulactone I (**2**; 1 mg) and 2-*O*-acetylshinjulactone I (**18**; 4.5 mg), mp 285—288 °C (benzene–acetone); IR (film) 3480, 1720, and 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (3H, d, *J*=5.5 Hz), 1.07 (3H, d, *J*=7 Hz), 1.24 (3H, s), 1.28 (3H, s), 2.04 (3H, s), 2.14 (3H, s), 3.26 (1H, d, *J*=12 Hz), 3.90 (1H, m), 4.10 (1H, t, *J*=2.5 Hz), 5.14 (1H, dd, *J*=12, 3 Hz), and 5.56 (1H, dd, *J*=12, 7 Hz); MS *m/z* (%) 450 (M^+; 11), 406 (10), 390 (65), 330 (100), and 274 (54); Found: *m/z* 450.2228. Calcd for $C_{24}H_{34}O_8$: M 450.2253.

Oxidation of 18 with Jones Reagent. 2-*O*-Acetylshinjulactone I (**18**; 3 mg) was treated with Jones reagent (in excess) in acetone (5 ml) at 0 °C for 1 h. After addition of 2-propanol (*ca.* 3 ml) and sodium hydrogencarbonate (*ca.* 1 g), the reaction mixture was filtered through Florisil (Wako, 100—200 mesh; *ca.* 5 g). After evaporation, brine and dichloromethane were added. Extraction with dichloromethane, evaporation, and purification by silica-gel column chromatography eluted with benzene–acetone (4:1) afforded amarolide diacetate (**17**), which was identified with an authentic sample by TLC, ^1H NMR, IR and mass spectra.

Shinjulactone J (3). White powder from benzene, mp 127—130 °C; $[\alpha]_D^{13}$−41° (*c* 0.4, $CHCl_3$); IR (film) 3510, 1725 (shoulder), 1715, and 1120 cm^{-1}; ^1H NMR (Table 1); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=11.0q, 15.0q, 19.7q, 22.2q, 25.9t, 27.8t, 31.4d, 40.7s, 41.5d, 42.1d, 44.5d, 45.0s, 46.9t, 51.3d, 77.0d, 82.3d, 85.5d, 169.6s, 208.2s, and 208.7s; MS *m/z* (%) 364 (M^+; 23), 346 (19), 320 (66), 292 (17), and 206 (100); Found: *m/z* 364.1859. Calcd for $C_{20}H_{28}O_6$: M 364.1884.

t-Butyldimethylsilylation of Chaparrolide (19). Chaparrolide (**19**; 71 mg) was treated with *t*-butyldimethylsilyl chloride (53 mg; 1.8 equiv) in the presence of imidazole (63 mg; 4.7 equiv) in DMF (3 ml) at room temperature for 17 h. After addition of water (2 ml), evaporation under reduced pressure, dichloromethane and 2 M (1 M=1 mol dm^{-3}) hydrochloric acid were added. After extraction with dichloromethane, the organic layer was washed with a saturated solution of sodium hydrogencarbonate, dried over magnesium sulfate, and subjected to separation by a silica-gel column chromatography eluted with benzene–acetone (3:1) to give a monosilyl derivative (**20**; 37 mg) and a disilyl derivative (**21**; 20 mg). 2-*O*-(*t*-Butyldimethylsilyl)chaparrolide (**20**): Mp 178—179 °C (acetone–hexane); IR(KBr) 3460, 1720, 1250, and 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.06 (6H, s), 0.87 (9H, s), 0.90 (3H, d, *J*=*ca.* 6 Hz), 1.09 (3H, s), 1.14 (3H, d, *J*=6 Hz), 1.34 (3H, s), 2.46 (1H, br s), 2.53 (1H, s), 2.92 (1H, br d, *J*=9 Hz), 3.52 (1H, d, *J*=5 Hz), 3.65 (1H, m), 3.88 (1H, dd, *J*=10.5, 5 Hz), and 4.31 (1H, t, *J*=3 Hz); MS *m/z* (%) 465 (M^+−CH_3; 0.8), 423 (63), 331 (100), 313 (70), and 75 (66); Found: *m/z* 465.2695. Calcd for $C_{25}H_{41}O_6Si$ ($M-CH_3$): 465.2672. 2,12-Bis(*O-t*-butyldimethylsilyl)chaparrolide (**21**): Mp 247 °C (chloroform–hexane); IR(film) 3550, 1730, and 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.01 (3H, s), 0.05 (6H, s), 0.12 (3H, s), 0.86 (9H, s), 0.90 (9H, s), 1.05 (3H, d, *J*=7 Hz), 1.10 (3H, s), 1.33 (3H, s), 2.35 (1H, d, *J*=2.5 Hz), 2.38 (1H, s), 2.89 (1H, dd, *J*=9, 2.5 Hz), 3.65 (1H, m). 3.91 (1H, d, *J*=11 Hz), and 4.26 (1H, t, *J*=2.5 Hz); MS *m/z* (%) 579 (M^+−CH_3; 2), 561 (1) 537 (90), 519 (30), and 75 (100); Found: *m/z* 579.3548. Calcd for $C_{31}H_{55}O_6Si_2$ ($M-CH_3$): 579.3537.

Acetylation of 2-O-(t-Butyldimethylsilyl)chaparrolide (20). 2-*O*-(*t*-Butyldimethylsilyl)chaparrolide (**20**; 49 mg) was acetylated with acetic anhydride (1 ml) in pyridine (2 ml) in the presence of a catalytic amount of 4-dimethylaminopyridine at room temperature for 4 d. After the usual work-up, purification by a silica-gel column chromatography eluted with benzene–acetone (9:1) afforded 2-*O*-(*t*-butyldimethylsilyl)-12-*O*-acetylchaparrolide (**22**; 51 mg) as an amorphous solid, IR (film) 3580, 1730, and 1235 cm^{-1}, ^1H NMR ($CDCl_3$) δ=0.05 (6H, s), 0.87 (9H, s), 0.87 (3H, d, *J*=*ca.* 7 Hz), 1.02 (3H, d, *J*=7 Hz), 1.13 (3H, s), 1.31 (3H, s), 2.15 (3H, s), 2.96 (1H, d, *J*=9 Hz), 3.63 (1H, m), 4.30 (1H, t, *J*=3 Hz), and 4.90 (1H, d, *J*=12 Hz); MS *m/z* (%) 507 (M^+-CH_3; 1.2), 465 (32), 373 (42), 331 (13), 313 (66), and 75 (100); Found: *m/z* 507.2742. Calcd for $C_{27}H_{43}O_7Si$ ($M-CH_3$): 507.2777. 2-*O*-(*t*-Butyldimethylsilyl)-12-*O*-acetylchaparrolide (**22**; 51 mg) was further acetylated with acetic anhydride (2 ml) in pyridine (2 ml) in the presence of a catalytic amount of 4-dimethylaminopyridine at 110 °C for 40 h. After the same work-up as above, the reaction mixture was purified by a silica-gel column chromatography eluted with chloroform–ethyl acetate (4:1) to give 2-siloxy triacetate (**23**; 30 mg) as an amorphous solid, IR (film) 1735, 1670, and 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.04 (6H, s), 0.84 (9H, s), 0.93 (3H, d, *J*=6 Hz), 0.98 (3H, d, *J*=6 Hz), 1.14 (3H, s), 1.42 (3H, s), 2.14 (3H, s), 2.16 (3H, s), 2.30 (3H, s), 3.75 (1H, m), 4.30 (1H, t, *J*=3 Hz), 4.60 (1H, d, *J*=9 Hz), 5.11 (1H, d, *J*=12 Hz), and 5.51 (1H, br s); ^{13}C NMR ($CDCl_3$) δ=−4.8, −4.3, 12.0, 14.7, 17.8, 18.1, 19.5, 20.3, 21.0, 23.2, 25.6, 25.6, 25.6, 27.6, 27.7, 37.1, 39.9, 41.8, 43.0, 43.5, 45.1, 52.9, 68.9, *ca.* 77.0(overlapped with the signal of $CDCl_3$), 82.6, 84.2, 110.6, 164.1, 166.0, 167.6, 169.1, and 202.9; MS *m/z* (%) 591 (M^+-CH_3; 12), 549 (3), 507 (10), 465 (17), 447 (14), 405 (6), 387 (21), 373 (30), 313 (50), 159 (100), and 75 (44); Found: *m/z* 591.3031. Calcd for $C_{31}H_{47}O_9Si$ ($M-CH_3$): 591.2989.

Desilylation of 2-Siloxy Triacetate (23). 2-Siloxy triacetate (**23**; 17 mg) was treated with AcOH (4 ml), H_2O (2 ml), and THF (2 ml) at room temperature for 6 d. The reaction mixture was evaporated and separated by a silica-gel column chromatography to afford the starting 2-siloxy triacetate (**23**; 4.5 mg) and 2-hydroxy triacetate (**24**; 6.5 mg), mp 94—98 °C (chloroform–hexane); IR(film) 3460, 1750, 1735, 1670, and 1235 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (3H, d, *J*=7 Hz), 0.96 (3H, d, *J*=6.5 Hz), 1.12 (3H, s), 1.39 (3H, s), 2.13 (3H, s), 2.15 (3H, s), 2.33 (3H, s), 3.80 (1H, m), 4.26 (1H, br s), 4.50 (1H, d, *J*=10 Hz), 5.01 (1H, d, *J*=12 Hz), and 5.54 (1H, s); MS *m/z* (%) 492 (M^+; 1.1), 451 (1.7), 433 (4), 390 (32), 373 (46), 330 (74), 313 (78), and 55 (100); Found: *m/z* 492.2353. Calcd for $C_{26}H_{36}O_9$: M 492.2358.

Oxidation of 24 with Jones Reagent. 2-Hydroxy triacetate (**24**; 6 mg) was treated with Jones reagent (in excess) in acetone (3 ml) at 0 °C for 30 min. The usual work-up afforded 2-keto triacetate (**25**; 5 mg), mp 131—135 °C, IR (film) 1730, 1670, and 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (3H, d, *J*=7 Hz), 1.03 (3H, d, *J*=5.5 Hz), 1.13 (3H, s), 1.34 (3H, s), 2.13 (3H, s), 2.15 (3H, s), 2.33 (3H, s), 4.35 (1H, br s), 4.80

(1H, d, J=12.5 Hz), 4.95 (1H, s), and 5.60 (1H, s); MS m/z (%) 490 (M^+; 72), 406 (82), 362 (74), 206 (64), and 85 (100); Found: m/z 490.2214. Calcd for $C_{26}H_{34}O_9$: M 490.2203.

Acidic Hydrolysis of **25**. A solution of 2-keto triacetate (**25**; 2 mg) in 1.5 M sulfuric acid–THF (each 1.5 ml) was refluxed for 5.5 h. After evaporation and addition of dichloromethane and brine, the mixture was extracted with dichloromethane. The organic layer was dried over magnesium sulfate, and evaporated to give a residue. Purification by silica-gel column chromatography eluted with benzene–acetone (7:3) afforded shinjulactone J (**3**; *ca.* 1 mg), which was identified with a natural specimen by TLC, ^{1}H NMR, IR, and mass spectra.

Shinjulactone K (**4**). Colorless prisms from chloroform–hexane, mp 135—139 °C, $[\alpha]_D^{24}$+33° (c 1.0, $CHCl_3$); IR (KBr) 3430, 1730, and 1230 cm^{-1}; ^{1}H NMR (Table 1); ^{13}C NMR ($CDCl_3$) δ=13.4q, 13.9q, 18.5q, 21.0q, 21.8q, 26.4t, 28.7d, 28.9t, 31.9d, 33.8d, 35.9s, 44.9d, 47.2d, 47.9t, 49.7s, 69.1d, 70.6d, 77.1d, 82.5d, 170.3s, 170.7s, and 221.9s; MS m/z (%) 408 (M^+; 1.1), 390 (12), 380 (8), 362 (7), 348 (20), 302 (15), 258 (32), 222 (58), and 198 (100); Found: m/z 408.2139. Calcd for $C_{22}H_{32}O_7$: M 408.2146.

*2,12-Di-*O*-acetylshinjulactone I* (**26**). Shinjulactone I (**2**; 2 mg) was treated with acetic anhydride (1 ml) in pyridine (2 ml) in the presence of a catalytic amount of 4-dimethylaminopyridine at room temperature for 6 d. After addition of methanol and evaporation under a reduced pressure, the reaction mixture was separated by a silica-gel column chromatography to give 2-*O*-acetylshinjulactone I (**18**; *ca.* 1 mg) and 2,12-di-*O*-acetylshinjulactone I (**26**; *ca.* 1 mg), mp 258—260 °C (chloroform–hexane); IR (film) 1735 and 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.97 (6H, d, J=7 Hz), 1.30 (6H, s), 1.90 (3H, s), 2.15 (3H, s), 2.24 (3H, s), 3.18 (1H, d, J=12 Hz), 4.14 (1H, t, J=3 Hz), 5.18 (1H, dd, J=12, 3 Hz), 5.29 (1H, t, J=3 Hz), and 5.57 (1H, dd, J=12, 7 Hz); MS m/z (%) 492 (M^+; 18), 450 (5), 432 (29), 407 (32), 390 (100), 330 (68), and 258 (69); Found: m/z 492.2378. Calcd for $C_{26}H_{36}O_9$: M 492.2358.

*2,11-Di-*O*-acetylshinjulactone K* (**26**). Shinjulactone K (**4**; 10 mg) was acetylated with acetic anhydride (1 ml) in pyridine (2 ml) in the presence of a catalytic amount of 4-dimethylaminopyridine at room temperature for a week. The usual work-up and purification by a silica-gel column chromatography eluted with 0—10% acetone–benzene afforded 2,11-di-*O*-acetylshinjulactone K (**26**; 7 mg), which was identified with 2,12-di-*O*-acetylshinjulactone I (**26**) by TLC, ^{1}H NMR, IR, and mass spectra.

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References

1) A part of this work was reported in a preliminary form: M. Ishibashi, S. Yoshimura, T. Tsuyuki, T. Takahashi, A. Itai, Y. Iitaka, and K. Matsushita, *Chem. Lett.*, **1984**, 555.

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

3) 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).

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

5) 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).

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

7) J. Polonsky, J. Gallas, J. Varenne, T. Prangé, C. Pascard, H. Jacquemin, and C. Moretti, *Tetrahedron Lett.*, **23**, 869 (1982).

8) T. Murae, T. Tsuyuki, T. Ikeda, T. Nishihama, S. Masuda, and T. Takahashi, *Tetrahedron*, **27**, 1545 (1971).

9) 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. 8448 at the Office of the Editor of *Bull. Chem. Soc. Jpn.*

10) J. A. Findlay, R. F. Langler, and J. S. Tandon, *Can. J. Chem.*, **48**, 313 (1970).

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

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