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Structure Determination of Bitter Principles in *Ailanthus altissima*. Structure of Shinjulactone A and Revised Structure of Ailanthone[1)]

Hirokazu Naora, Masami Ishibashi, Tetsuo Furuno, Takahiko Tsuyuki,
Tatsushi Murae, Hiroshi Hirota, Takeyoshi Takahashi,*
Akiko Itai,† and Yoichi Iitaka†

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
†*Department of Pharmaceutical Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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The structure of a new bitter principle, shinjulactone A, isolated from *Ailanthus altissima* Swingle was determined to be 11β,20-epoxy-1β,2α,11α,12α-tetrahydroxypicrasa-3,13(21)-dien-16-one and the configuration of a hydroxyl group at C-12 of ailanthone was revised to α-orientation by X-ray analysis.

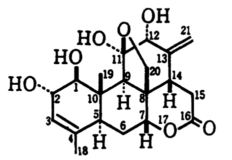
Bitter principles of Simaroubaceous plants have been extensively investigated and a number of quassinoids have been reported.[2)] In connection with our studies on bitter principles of *Picrasma ailanthoides* Planchon,[3)] constituents of *Ailanthus altissima* Swingle (=*A. glandulosa* Desf.; Japanese name: Shinju or Niwaurushi) grown in Japan were examined and some of new picrasane derivatives were reported.[4—7)] This paper deals with structural elucidation of a new bitter principle, shinjulactone A (**1**), isolated from the stem bark of the plant and also describes structural revision of ailanthone (**2**), a main bitter principle of the plant.

Concentrated methanolic extract of the stem bark of *A. altissima* was separated by silica-gel column chromatography to afford ailanthone (**2**)[8,9)] in 0.05% yield and a crude new quassinoid together with other bitter principles. The new quassinoid was subjected to further separation by silicic acid-Celite column chromatography and crystallization to afford a new cytotoxic[10)] bitter principle, shinjulactone A (**1**) in 0.002% yield.

Shinjulactone A (**1**), mp 245—245.5 °C (decomp) was shown to have a molecular formula, $C_{20}H_{26}O_7$ by high-resolution mass spectrum, and the IR and UV spectra showed the presence of hydroxyl(s) and δ-lactone and the absence of an α,β-unsaturated carbonyl group. Comparison of the ^1H and ^{13}C NMR spectra of **1** with those of ailanthone (**2**) could lead to the structure (**1**) for shinjulactone A except for the configuration of hydroxyl groups (see Tables 1 and 2).

The configuration of the hydroxyl groups at C-1 and C-12[11)] could be established for **1** by NOE measurement operated at 270 MHz. On saturation of the signal due to $C_{(1)}$–H, the signals due to $C_{(9\alpha)}$–H and $C_{(5\alpha)}$–H showed increase by 12 and 5%, respectively. When the resonance frequency of $C_{(9\alpha)}$–H was irradiated, increase of signals due to $C_{(1)}$–H and $C_{(5\alpha)}$–H by 9 and 6% was observed, respectively. These observations imply the $C_{(1\alpha)}$–H and $C_{(1\beta)}$–OH orientations. On irradiation at the frequency of $C_{(12)}$–H, counterpart signals resonating in high field of an AB quartet signal due to $C_{(20\beta)}$–hemiacetal bridge methylene resulted in increase by 4%. Thus the orientation of the $C_{(12)}$–H was determined to be in β-orientation. The configuration of the hydroxyl group at C-2 was determined by differential NOE measurement operated at 400 MHz; on saturation of the singlet signal at δ 1.68 due to $C_{(10\beta)}$–CH_3, the multiplet signal at δ 4.62 due to $C_{(2)}$–H caused increase in area, indicating the $C_{(2\beta)}$–H and $C_{(2\alpha)}$–OH orientation. From these observations, the structure (**1**) having 1β-OH, 2α-OH, and 12α-OH configurations, is proposed for shinjulactone A.

In regard to the configuration at C-12, however, a



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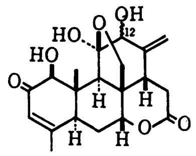
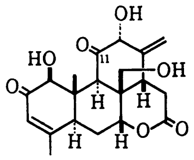


2 12α-OH

3 12β-OH



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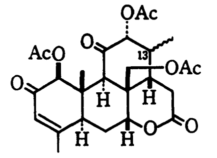
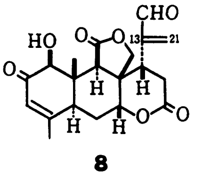


5 13β-CH₃

6 13α-CH₃



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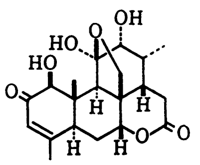

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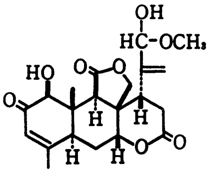

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TABLE 1. ^{1}H NMR SPECTRA OF **1**, **2**, **8**, AND **9**[a)]

Assignment	**1**[b)]	**2**[c)]	**8**[d)]	**9**[e)]
1-H	4.02 d (8)	4.54 s	4.20 s	4.59 s
2-H	4.62 m	—	—	—
3-H	5.79 br s	6.13 br s	6.10 br s	6.09 br s
5-H	2.67 br d (13)	3.07 br d (13)	2.0—3.7[f)]	2.0—3.3[f)]
6α-H	2.07 ddd (15, 2.5, 2.5)	2.22 br d (14)		
6β-H	1.92 ddd (15, 13, 2.5)	2.05 br dd (14, 13)		
7-H	4.57 t (2.5)	4.64 br s	4.61 t (2.5)	3.92 t (2.5)
9-H	3.30 s	3.53 s	2.84 s	3.34 s
12-H	4.59 s	4.46 s	9.55 s[g)]	5.30 br s[h)]
14-H	2.80 dd (13.5, 5.5)	2.83 dd (13, 5)	2.0—3.7[f)]	2.0—3.3[f)]
15α-H	3.57 dd (18, 13.5)	3.69 dd (18, 13)		
15β-H	2.90 dd (18, 5.5)	2.90 dd (18, 5)		
4-CH_3	1.60 br s	1.78 br s	2.20 br s	1.80 br s
10-CH_3	1.68 s	1.52 s	0.92 s	1.04 s
20-CH_2	3.67 d (8)	3.66 d (8)	3.89 d (11)	3.86 d (11)
	4.17 d (8)	4.11 d (8)	4.40 d (11)	4.25 d (11)
21-CH_2	5.20 d (2)	5.19 br s	6.33 br s	5.84 br s
	5.28 d (2)	5.28 br s	6.54 br s	5.95 br s
-OCH_3	—	—	—	3.60 s

a) Chemical shifts are expressed in δ downfield from TMS as an internal standard and coupling constants in Hz in parantheses; s: singlet, d: doublet, t: triplet. b) In pyr-d_5 at 400 MHz. c) pyr-d_5+2% $CDCl_3$ at 400 MHz. d) $CDCl_3$ at 90 MHz. e) pyr-d_5 at 90 MHz. f) Not assignable. g) An aldehyde proton. h) A methine proton of a hemiacetal.

TABLE 2. ^{13}C NMR SPECTRA OF **1**, **2**, **8**, AND **9**[a)]

Assignment No. of C	**1**[b)]	**2**[c)]	**8**[d)]	**9**[e)]
1	83.6	84.4	83.6	84.7
2	72.7	197.3	196.0	196.9
3	127.1	126.2	125.8	126.5
4	134.8	162.1	161.1	160.5
5	49.6	44.8	44.3	51.7
6	26.2	26.2	25.9	25.5
7	79.2	78.5	77.8	66.4
8	45.8	45.7	43.9	48.4
9	48.0	48.0	48.2	55.4
10	44.9	45.5	40.0	44.7
11	110.5	110.3	174.7	178.2
12	80.7	80.6	193.6	95.1
13	148.0	147.4	144.8	146.4
14	41.9	42.5	35.7	40.9
15	35.4	35.3	30.9	31.3
16	169.6	169.4	168.0	172.0
18	21.2	22.5	22.7	22.3
19	10.6	10.3	10.6	10.4
20	72.7	72.3	71.3	69.8
21	118.0	118.2	139.0	112.0
-OCH_3	—	—	—	45.5

a) Chemical shifts are expressed in δ downfield from TMS as an internal standard. b) pyr-d_5 at 22.5 MHz. c) pyr-d_5 at 25 MHz. d) $CDCl_3$ at 22.5 MHz. e) pyr-d_5 at 22.5 MHz.

discrepancy between shinjulactone A and ailanthone arose. Two different structures (**3** and **4**) have been proposed for ailanthone so far. A hemiacetal structure (**3**), in which the $C_{(12)}$-OH was assigned to be β-equatorial, has been proposed for ailanthone by Polonsky *et al.*;[9)] ailanthone was hydrogenated and followed by acetylation to afford dihydroailanthone triacetate (**5**), whose coupling constant between $C_{(12)}$-H and $C_{(13)}$-H was 8 Hz. A comparison of the coupling constant with that ($J_{12,13}=3$ Hz) observed in chaparrinone triacetate (**6**) led to the conclusion that the orientations of the $C_{(12)}$-OH groups of ailanthone and chaparrinone (**7**) were β-equatorial and α-axial configurations, respectively. On the other hand, Casinovi *et al.*[8b)] proposed a $C_{(11)}$-keto structure (**4**) with 12α(axial)-OH configuration.

The structure of ailanthone was reinvestigated by NOE measurement of ^{1}H NMR spectrum in pyridine-d_5 solution and the $C_{(12)}$-H was suggested to be in β-equatorial disposition; on irradiation at δ 4.46 due to $C_{(12)}$-H, a signal resonating at δ 5.28 due to one of olefinic protons at C-21 showed an increase by 6%, and the irradiation at δ 5.28 resulted in increase in area of the signal due to $C_{(12)}$-H by 10%.

In order to establish the structure of ailanthone unambiguously, a single crystal obtained from chloroform–methanol solution was subjected to X-ray diffraction analysis. The crystal belongs to an orthorhombic space group $P2_12_12_1$, and the lattice parameters are $a=17.067(8)$, $b=16.608(8)$, and $c=6.594(2)$ Å with four ailanthone molecules and four water molecules in a unit cell. Intensity data were measured on a PW1100 four-circle diffractometer using Cu $K\alpha$ radiation monochromated by a graphite plate. A total of 1874 independent structure factors with $F_o \geq 2.5\ \sigma(F_o)$ within $2\theta=156°$

Table 3. ATOMIC POSITIONAL PARAMETERS ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($\times 10^2$) FOR NON-HYDROGEN ATOMS OF AILANTHONE (**2**) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}[a)]
O(1)	-1030(1)	2763(1)	1173(3)	369(3)
O(2)	-2285(1)	2275(2)	-920(3)	469(4)
O(3)	-272(1)	2800(1)	4572(4)	312(3)
O(4)	1209(1)	2914(1)	2700(4)	419(3)
O(5)	1870(1)	17(1)	-1297(4)	402(3)
O(6)	921(1)	-167(1)	836(4)	236(3)
O(7)	104(1)	1660(1)	6213(3)	289(3)
C(1)	-1003(2)	1986(2)	313(4)	304(3)
C(2)	-1788(2)	1766(2)	-598(5)	361(4)
C(3)	-1895(2)	923(2)	-1162(6)	308(4)
C(4)	-1386(2)	353(2)	-619(5)	259(4)
C(5)	-670(2)	549(2)	644(4)	212(3)
C(6)	-385(2)	-152(2)	1982(5)	229(4)
C(7)	447(2)	1(2)	2654(5)	243(4)
C(8)	582(2)	828(2)	3550(4)	214(3)
C(9)	116(1)	1550(1)	2625(4)	227(3)
C(10)	-730(1)	1348(2)	1879(4)	234(3)
C(11)	228(2)	2140(2)	4420(4)	234(3)
C(12)	1081(2)	2443(2)	4493(5)	219(4)
C(13)	1651(2)	1761(2)	4719(5)	231(4)
C(14)	1472(2)	1001(2)	3538(4)	224(3)
C(15)	1781(2)	1001(2)	1355(5)	282(4)
C(16)	1544(2)	264(2)	224(5)	312(4)
C(18)	-1467(2)	-496(2)	-1393(6)	223(5)
C(19)	-1349(2)	1292(2)	3574(5)	330(4)
C(20)	306(2)	845(2)	5770(5)	310(4)
C(21)	2252(2)	1812(2)	5984(6)	278(5)

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

were obtained by $2\theta-\theta$ scanning mode. The structure was solved by the direct method using MULTAN program and was refined by the block-diagonal least-squares method. All hydrogen atoms, except for those of O(3) hydroxyl and water molecule, were located in a different electron density map. The final R-value was 0.043 using anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for hydrogen atoms. The final atomic coordinates are listed in Table 3 and bond lengths and bond angles are listed in Tables 4 and 5.[12)] The hemiacetal structure and the $C_{(12\alpha)}$–OH configuration were clearly established as shown in Fig. 1. Molecules were strongly linked by the four hydrogen bondings, one is an intermolecular hydrogen bond between O(2) carbonyl and O(4) hydroxyl, and the others are between water and O(1) hydroxyl, O(3) hydroxyl, and O(5) lactone carbonyl in the three different ailanthone molecules. The distances are 2.843(4), 2.709(3), 2.861(3), and 3.007(4) Å, respectively.

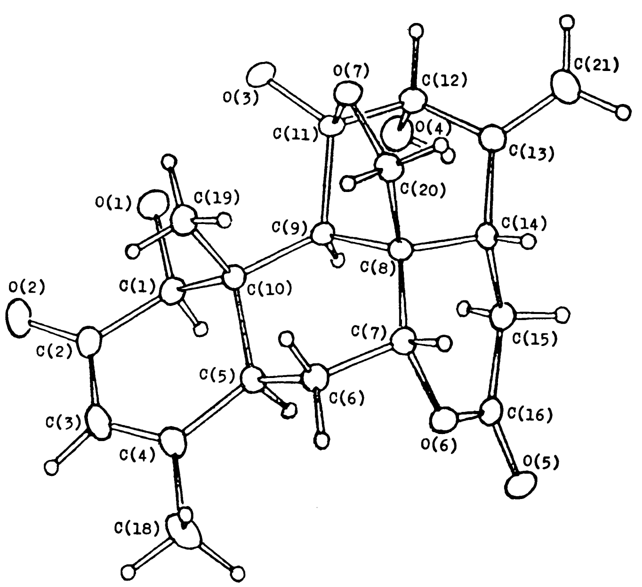


Fig. 1. Perspective view of ailanthone (**2**).[a)]

a) For clarity hydrogen atoms are represented by spheres of arbitrary radius.

The structure of ailanthone was thus shown to be revised to 11β,20-epoxy-1β,11α,<u>12α</u>-trihydroxypicrasa-3,13(21)-dien-2,16-dione (**2**) and the X-ray analysis also proved that the C-ring exists in a chair conformation. Therefore, when the hydrogenation occurs from

Table 4. BOND LENGTHS OF AILANTHONE (**2**) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

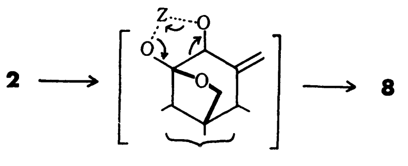
Bond length		l/Å	Bond length		l/Å
Atom 1	Atom 2		Atom 1	Atom 2	
O(1)	-C(1)	1.410(3)	C(5)	-C(10)	1.560(4)
O(2)	-C(2)	1.218(4)	C(6)	-C(7)	1.509(4)
O(3)	-C(11)	1.393(3)	C(7)	-C(8)	1.514(4)
O(4)	-C(12)	1.434(4)	C(8)	-C(9)	1.563(4)
O(5)	-C(16)	1.218(4)	C(8)	-C(14)	1.546(4)
O(6)	-C(7)	1.472(4)	C(8)	-C(20)	1.538(4)
O(6)	-C(16)	1.345(3)	C(9)	-C(10)	1.563(4)
O(7)	-C(11)	1.442(3)	C(9)	-C(11)	1.548(4)
O(7)	-C(20)	1.427(4)	C(10)	-C(19)	1.540(4)
C(1)	-C(2)	1.513(4)	C(11)	-C(12)	1.541(4)
C(1)	-C(10)	1.551(4)	C(12)	-C(13)	1.500(4)
C(2)	-C(3)	1.459(5)	C(13)	-C(14)	1.514(4)
C(3)	-C(4)	1.334(4)	C(13)	-C(21)	1.324(5)
C(4)	-C(5)	1.515(4)	C(14)	-C(15)	1.533(4)
C(4)	-C(18)	1.506(5)	C(15)	-C(16)	1.489(4)
C(5)	-C(6)	1.539(4)			

Table 5. Bond angles of ailanthone (**2**) with estimated standard deviations in parentheses

Bond angle			ϕ/°	Bond angle			ϕ/°
Atom 1	Atom 2	Atom 3		Atom 1	Atom 2	Atom 3	
C(7)	-O(6)	-C(16)	125.4(2)	C(8)	-C(9)	-C(11)	97.2(2)
C(11)	-O(7)	-C(20)	108.7(2)	C(19)	-C(10)	-C(1)	108.6(2)
C(2)	-C(1)	-O(1)	110.6(2)	C(19)	-C(10)	-C(5)	111.9(2)
C(2)	-C(1)	-C(10)	111.3(2)	C(19)	-C(10)	-C(9)	114.7(2)
O(1)	-C(1)	-C(10)	111.5(2)	C(1)	-C(10)	-C(5)	104.7(2)
C(3)	-C(2)	-O(2)	122.3(3)	C(1)	-C(10)	-C(9)	109.9(2)
C(3)	-C(2)	-C(1)	116.4(3)	C(5)	-C(10)	-C(9)	106.6(2)
O(2)	-C(2)	-C(1)	121.2(3)	C(12)	-C(11)	-O(3)	108.7(2)
C(4)	-C(3)	-C(2)	122.1(3)	C(12)	-C(11)	-O(7)	107.1(2)
C(5)	-C(4)	-C(3)	121.3(3)	C(12)	-C(11)	-C(9)	110.3(2)
C(5)	-C(4)	-C(18)	117.5(3)	O(3)	-C(11)	-O(7)	106.6(2)
C(3)	-C(4)	-C(18)	120.9(3)	O(3)	-C(11)	-C(9)	118.5(2)
C(6)	-C(5)	-C(4)	114.0(2)	O(7)	-C(11)	-C(9)	105.0(2)
C(6)	-C(5)	-C(10)	111.4(2)	C(13)	-C(12)	-O(4)	113.3(2)
C(4)	-C(5)	-C(10)	114.6(2)	C(13)	-C(12)	-C(11)	111.7(2)
C(7)	-C(6)	-C(5)	109.8(2)	O(4)	-C(12)	-C(11)	107.2(2)
C(8)	-C(7)	-O(6)	113.9(2)	C(14)	-C(13)	-C(12)	116.5(2)
C(8)	-C(7)	-C(6)	114.2(2)	C(14)	-C(13)	-C(21)	122.3(3)
O(6)	-C(7)	-C(6)	104.2(2)	C(12)	-C(13)	-C(21)	121.1(3)
C(9)	-C(8)	-C(7)	117.8(2)	C(15)	-C(14)	-C(8)	110.1(2)
C(9)	-C(8)	-C(14)	110.8(2)	C(15)	-C(14)	-C(13)	114.4(2)
C(9)	-C(8)	-C(20)	101.6(2)	C(8)	-C(14)	-C(13)	110.6(2)
C(7)	-C(8)	-C(14)	108.5(2)	C(16)	-C(15)	-C(14)	112.2(2)
C(7)	-C(8)	-C(20)	109.9(2)	O(5)	-C(16)	-O(6)	115.4(3)
C(14)	-C(8)	-C(20)	107.6(2)	O(5)	-C(16)	-C(15)	124.4(3)
C(10)	-C(9)	-C(8)	115.4(2)	O(6)	-C(16)	-C(15)	120.1(2)
C(10)	-C(9)	-C(11)	119.4(2)	O(7)	-C(20)	-C(8)	106.6(2)

α-side, the *exo*-methylene group would produce a β-axial methyl group at C-13. Since the β-axial methyl group at C-13 would bring about an unstable diaxial relationship with the 12α-axial hydroxyl group, it seems most likely that an inversion of the C-ring occurs to adopt a stable boat conformation. The ring-inversion resulted in a large dihedral angle between 12-H and 13-H, which could reasonably explain the large coupling constant ($J_{12,13}$=8 Hz) for dihydroailanthone triacetate (**5**) stated above.[9]

The structure, 11β,20-epoxy-1β,2α,11α,12α-tetrahydroxypicrasa-3,13(21)-dien-16-one (**1**) proposed for shinjulactone A, was further confirmed by chemical conversion of **1** into **2**. Shinjulactone A (**1**) was oxidized with manganese dioxide in dichloromethane at room temperature to give two products, one of which was found to be identical with ailanthone (**2**). The other was identical with an oxidation product of ailanthone (**2**) with lead tetraacetate. The molecular formula, $C_{20}H_{22}O_7$, was determined by high resolution mass spectrum, and the UV and IR spectra suggest the presence of an α-substituted α,β-unsaturated aldehyde group (λ_{max} 221 nm and ν_{max} 2850 and 1685 cm^{-1}), an α,β-unsaturated ketone (λ_{max} 238 nm and ν_{max} 1685 cm^{-1}), and δ- and γ-lactone groupings (ν_{max} 1730 and 1775 cm^{-1}, respectively). Examination of ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) and mass spectrum (see Experimental) and mechanistic consideration (Fig. 2) lead to the formulation of an 11,12-seco structure (**8**) for the oxidation product. On treatment with methanol, the compound (**8**) easily afforded a hemiacetal (**9**). The spectral data of **9** were compatible with the suggested structure.



Z: oxidizing agent

Fig. 2.

Experimental

General Procedure. All melting points were measured on a Mel-temp capillary melting point apparatus (Laboratory Devices) and uncorrected. Optical rotations and circular dichroism (CD) were determined on a JASCO polarimeter DIP-181 and a JASCO Model J-15 spectrometer, respectively. Ultraviolet absorption (UV) and infrared (IR) spectra were measured on a Hitachi 340 and a Hitachi 260-30 spectrometer, respectively. Mass (MS) spectra were run on a Hitachi RMU-6 Tokugata mass spectrometer and high-resolution mass spectra on a JEOL JMS-D300 mass spectrometer operating at 70 eV. Proton nuclear magnetic resonance (^{1}H NMR) spectra were taken using a Varian EM390 (90 MHz), JEOL FX90Q (90 MHz), Brucker WH 270 (270 MHz), and JEOL FX400 (400 MHz). Carbon-13 nuclear magnetic resonance

(^{13}C NMR) spectra were taken on a JEOL FX90Q (22.5 MHz) and a JEOL FX100 (25 MHz). Chemical shifts were expressed in δ (ppm) downfield from tetramethylsilane as an internal standard 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), Silicic acid AR (Mallinckrodt) or Celite No. 545 (Wako) was used for column chromatography. Analytical high performance liquid chromatography (HPLC) was carried out on a Waters Chromatograph ALC/GPS 202/401 at room temperature (column: μBondapack C$_{18}$; solvent system: MeOH–H$_2$O, 1 : 1; flow rate: 1.1 ml/min).

Plant Material. Stem bark of *Ailanthus altissima* was collected at the Botanical Gardens, Faculty of Science, The University of Tokyo in July 1979. The bark was air-dried and chipped to afford 9.3 kg of the materials.

Extraction and Separation. The stem bark (9.3 kg) was extracted three times with hot methanol (18 l×3) for 8 h. The combined extracts (*ca.* 50 l) were evaporated under reduced pressure and the residue was treated three times with hot petroleum ether (1.5 l×3) to give a bitter residue (737 g). A part (220 g) of the residue, dissolved in a solution of chloroform (180 ml) and methanol (1.3 l), was adsorbed on silica gel (300 g) and then solvents were removed *in vacuo*. The silica gel was placed on the top of a column of silica gel (2 kg), and the following solvents were passed through the column; chloroform (4 l), 1, 2, 4, 8, 16, 32, 64, and 80% methanol in chloroform (each 4 l), and finally methanol (2 l). The fractions 17 and 18 (each fraction; 1 l) were combined and subjected to fractional crystallization from methanol to give ailanthone (**2**; *ca.* 1.1 g).

The fraction 21 was evaporated and the residue was dissolved in hot methanol. After cooling, the precipitates (mainly sitosteryl glycoside) were filtered off and the filtrate was evaporated, dissolved in chloroform, and subjected to separation by a column of silicic acid and Celite, eluting with 1, 2, 5, 10, 20, and 50% methanol in chloroform. Fractions eluted with 20% and 50% methanol in chloroform were combined and crystallized from chloroform–methanol to give shinjulactone A (**1**; 40 mg). Separation of the fraction 22 under the same conditions afforded additional 17 mg of **1**.

Ailanthone (2). Mp 234—235 °C (lit,[9] mp 234—238 °C), $[\alpha]_D^{20}$ +9.2° (EtOH) (lit,[9] $[\alpha]_D$ +12.5° (EtOH)); CD $[\theta]_{310}$ +977 and $[\theta]_{260}$ +1379.

Shinjulactone A (1). Mp 245—245.5 °C (decomp, from MeOH and CHCl$_3$); $[\alpha]_D^{20}$ +2° (*c* 0.97, C$_5$H$_5$N); IR (Nujol) 3500, 3400, and 1740 cm^{-1}; ^{1}H NMR and ^{13}C NMR (Tables 1 and 2); MS *m/e* (%) 378 (M$^+$; 52), 363 (64), 360 (100), 345 (66), 342 (13), and 316 (100); Found: *m/e* 378.1634. Calcd for C$_{20}$H$_{26}$O$_7$: M 378.1679.

Oxidation of 1 with Manganese Dioxide. A solution of shinjulactone A (**1**; 14 mg) in dichloromethane (10 ml) was treated with manganese dioxide (200 mg, prepared by Attenburrow's procedure[13]) for 21 h at room temperature. After the usual work-up, the reaction mixture was separated by preparative TLC developed with methanol–chloroform (1 : 19). Ailanthone (**2**; 3.6 mg) was identified by HPLC (R_t= 6.4 min), MS, and FT-^{1}H NMR. The aldehyde (**8**; 0.7 mg) was identical with the oxidation product of **2** with lead tetraacetate (*vide infra*). Treatment with methanol in the presence of silica gel, the aldehyde (**8**) was converted into a hemiacetal (**9**), mp 203—205 °C (from acetone); IR (KBr) 3450, 1770 (sh), 1740, 1680, and 1035 cm^{-1}; UV (EtOH) 238 nm (ε 10000); ^{1}H and ^{13}C NMR (Tables 1 and 2); MS *m/e* 406 (M$^+$; 7), 388 (3), 374 (15), 356 (6), 151 (32), and 91 (100); Found: *m/e* 406.1632. Calcd for C$_{21}$H$_{26}$O$_8$: M 406.1627.

Oxidation of 2 with Lead Tetraacetate. Ailanthone (**2**; 26 mg) was treated with lead tetraacetate (36 mg) in 90% aqueous acetic acid (3 ml) at room temperature for 1 h. The reaction product was worked up as usual to afford the aldehyde (**8**) in a quantitative yield, mp 211—214 °C (from acetone); IR (KBr) 3450, 1775, 1730, 1685, and 1240 cm^{-1}; UV (EtOH) 238 nm (sh, ε 9700) and 221 nm (ε 12000); ^{1}H and ^{13}C NMR (Tables 1 and 2); MS *m/e* (%) 374 (M$^+$; 55), 356 (25), 346 (90), 246 (35), and 151 (100); Found: *m/e* 374.1362. Calcd for C$_{20}$H$_{22}$O$_7$: M 374.1366.

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