Indonesian Medicinal Plants. VI.[1] On the Chemical Constituents of the Bark of *Picrasma javanica* Bl. (Simaroubaceae) from Flores Island. Absolute Stereostructures of Picrajavanins A and B

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Two new quassinoids named picrajavanins A and B were isolated, together with known β-carboline alkaloids and picrasidine G, from the bark of *Picrasma javanica* Bl. (Simaroubaceae), an Indonesian folk medicine, collected on Flores Island. The absolute stereostructures of picrajavanins A (6) and B (7) have been elucidated on the basis of chemical and physicochemical evidence, together with the application of the modified Mosher's method.

Keywords Indonesian medicinal plant; *Picrasma javanica*; Simaroubaceae; picrajavanin; quassinoid; Mosher's method modified

Picrasma javanica Bl. is a medium-sized tree of Simaroubaceae growing in humid forests of New Guinea, Southeast Asia, and India. In Indonesia, the decoction of the bark or leaves has been administered as a folk medicine to cure febris abscess or maturation, and has also been used as a substitute for quinine.[2] In chemical studies on the constituents of the bark of *Picrasma javanica*, a number of quassinoids and alkaloids have been identified,[3,4] and des-4-methylpicrasane type quassinoids have been shown to be characteristic constituents of the bark of *Picrasma javanica* Bl. collected in Java Island, Indonesia.[4]

In search of new biologically active substances from Indonesian medicinal plants,[1] we have been investigating the chemical constituents in the bark of *Picrasma javanica* Bl. (local name "Beo") which was collected on our 1988 expedition to Flores Island, Indonesia.[2b] We have so far isolated two new quassinoids named picrajavanins A (**6**) and B (**7**), together with 4-methoxy-1-vinyl-β-carboline (**1**),[3a] 4-methoxy-1-ethyl-β-carboline (**2**),[3a] 4-methoxy-1-acetyl-β-carboline (**3**),[5] 6-methoxy-7,8-methylenedioxycoumarin (**4**),[6] and picrasidine G (**5**).[7] In this paper, we report the isolation and the absolute stereostructure elucidation of two new quassinoids: picrajavanins A (**6**) and B (**7**).[8]

The methanol extract of the bark was partitioned into a 1-butanol–water mixture. Separation of the 1-butanol-soluble portion by silica gel column chromatography provided picrajavanins A (**6**, 0.0065% from the bark) and B (**7**, 0.0036%) together with **1** (0.011%), **2** (0.002%), **3** (0.001%), **4** (0.001%), and **5** (0.112%) (Chart 1).

Picrajavanin A (6) This quassinoid was obtained as colorless needles of mp 171—172 °C. The molecular formula $C_{36}H_{40}O_{10}$ was determined from the molecular ion (M^+) peak observed in the mass spectrum (MS) and by high-resolution mass spectral (high MS) measurement. The ultraviolet (UV) and infrared (IR) spectra of picrajavanin A (**6**) suggested the presence of a benzoyl group and a 3″,4″-methylenedioxybenzoyl group in its structure. The proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra of **6** showed signals ascribable to two tertiary methyls, two secondary methyls, one methoxyl, two methines each bearing one acyl group, and a δ-lactone moiety, together with the signals of one benzoyl group and one 3″,4″-methylenedioxybenzoyl group.

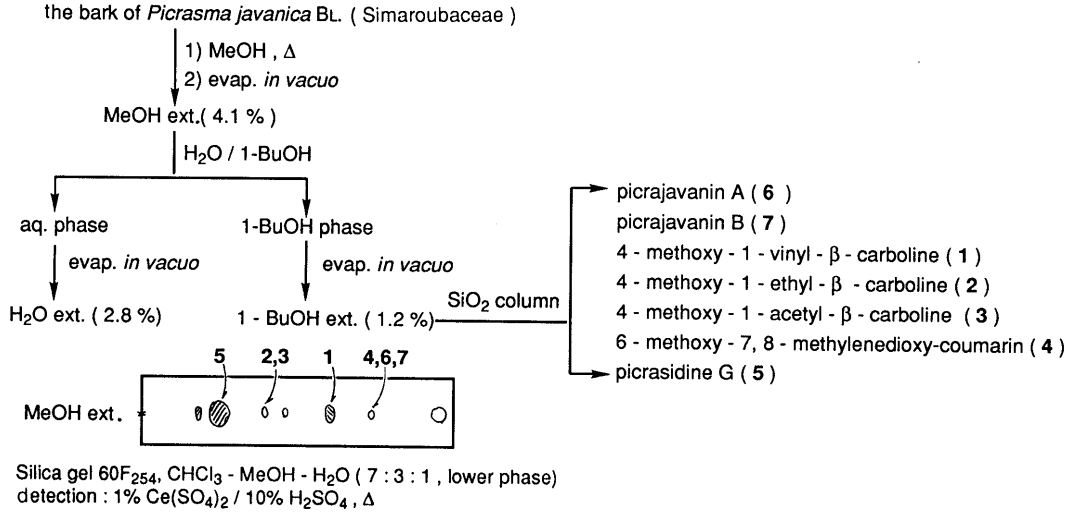

Chart 1

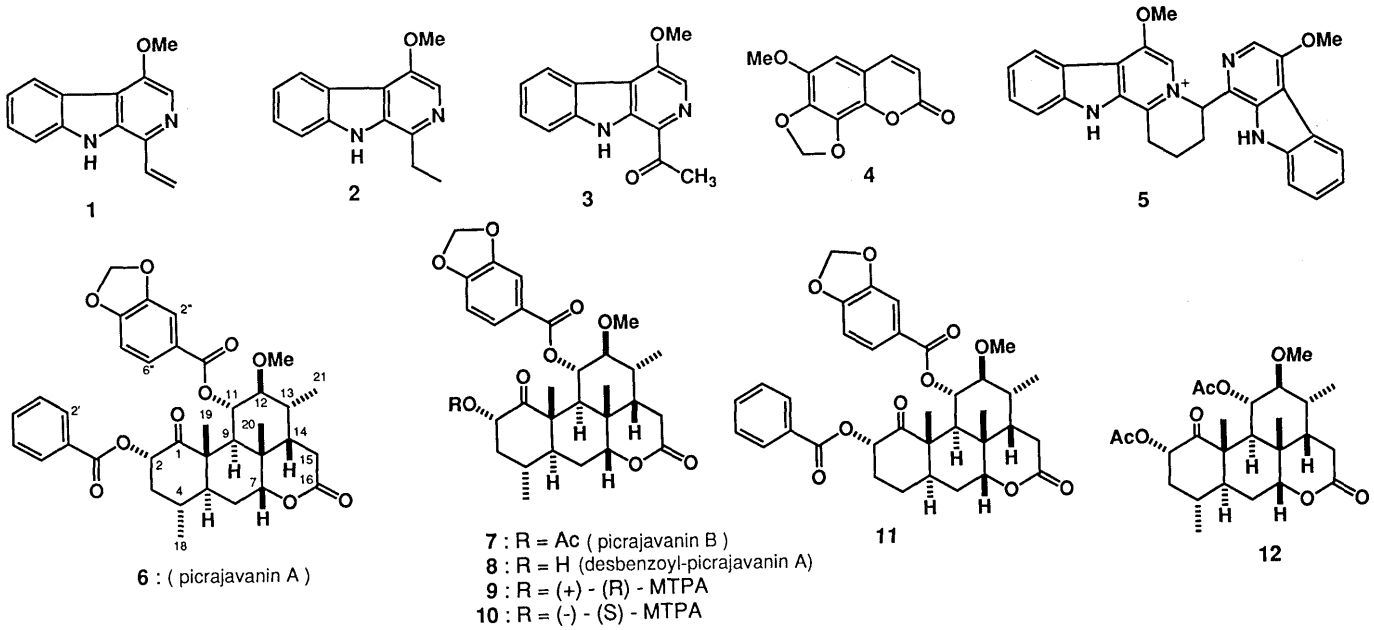

Fig. 1

TABLE I. ^{1}H-NMR Data for Picrajavanin A(**6**), Picrajavanin B(**7**), and Desbenzoyl-picrajavanin A(**8**) (at 270 MHz, δ)[a]

	6[b]	6[c]	7[b]	7[c]	7[d]	8[b]
H-2	5.79 dd (12, 7)	5.98 dd (12, 7)	5.56 dd (12, 7)	5.76 dd (12, 7)	5.63 dd (12, 7)	4.51 ddd (12, 7, 7)
H-3	1.60 m	1.37 m	1.38 m	1.29 m	2.10 m	1.02 m
	2.39 ddd (15, 12, 12)	2.20 m	2.26 m	2.01 m	2.26 ddd (15, 11, 10)	2.43 ddd (15, 12, 12)
H-4	2.09 ddd (12, 12, 6)	1.88 m	2.22 m	1.84 m	1.28 m	1.89 m
H-5	1.55 m	1.42 m	1.48 m	1.52 m	1.49 m	1.48 ddd (12, 9, 2)
H-6	1.84 m	1.73 2H, m	1.83 m	1.73 2H, m	1.69 ddd (15, 14, 2)	1.83 m
	2.00 dt (15, 3, 3)		1.98 m		1.93 ddd (14, 3, 3)	1.96 ddd (14, 3, 3)
H-7	4.22 br s	4.23 br s	4.21 br s	4.19 br s	4.33 br s	4.23 br s
H-9	2.92 d (12)	3.21 d (12)	2.87 d (12)	3.35 d (12)	2.81 d (12)	2.94 d (12)
H-11	5.50 dd (12, 9)	5.82 dd (12, 9)	5.49 dd (12, 9)	5.76 dd (12, 9)	5.48 dd (12, 9)	5.50 dd (12, 9)
H-12	3.17 dd (11, 9)	3.43 dd (10, 9)	3.18 dd (10, 9)	3.41 dd (11, 9)	3.30 dd (10, 9)	3.23 dd (11, 9)
H-13	2.24 ddd (11, 6, 6)	2.20 m	2.24 m	2.22 m	2.20 m	2.25 ddd (11, 6, 6)
H-14	1.82 m	1.75 m	1.82 m	1.75 m	1.33 m	1.85 m
H-15	2.57 dd (20, 13)	2.95 dd (19, 13)	2.56 dd (19, 12)	2.70 dd (19, 8)	2.65 2H, d (9)	2.61 dd (19, 7)
	2.67 dd (20, 8)	2.73 dd (19, 7)	2.70 dd (19, 7)	2.87 dd (19, 12)		2.70 dd (19, 12)
18-H_3	0.97 d (7)	0.73 d (7)	0.93 d (6)	0.69 d (6)	0.93 d (7)	0.88 d (6)
19-H_3	1.43 s	1.54 s	1.34 s	1.43 s	1.36 s	1.34 s
20-H_3	1.36 s	1.18 s	1.34 s	1.17 s	1.39 s	1.24 s
21-H_3	1.02 d (7)	0.97 d (7)	1.03 d (6)	0.96 d (7)	1.02 d (6)	1.05 d (7)
12-OMe	3.23 s	3.26 s	3.25 s	3.28 s	3.23 s	3.29 2H, s
H-2′, 6′	7.84 d (7)	8.08 d (8)				
H-3′, 5′	7.40 dd (7, 7)	7.47 dd (8, 8)				
H-4′	7.55 t (7)	7.54 t (8)				
H-2″	7.35 d (2)	7.78 d (2)	7.38 d (2)	7.79 d (2)	7.29 d (2)	7.40 d (1)
H-5″	6.53 d (8)	6.83 d (8)	6.80 d (8)	6.99 d (8)	6.85 d (8)	6.82 d (8)
H-6″	7.55 dd (8, 2)	7.96 dd (8, 2)	7.60 dd (8, 2)	7.95 dd (8, 2)	7.55 dd (8, 2)	7.58 dd (8, 1)
H-8″	5.62 d (1)	5.82 d (1)	6.01 br s	6.01 br s	6.05 br s	6.02 2H, br s
	5.85 d (1)	5.98 d (1)	6.01 br s	6.06 br s	6.09 br s	
2-OH						3.43 d (7)
OAc			1.94 s	1.98 s		

a) Coupling constants (J values in Hz) are given in parentheses. b—d) Measured in b) $CDCl_3$, c) pyridine-d_5, or d) CD_3OD.

The proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra (taken in pyridine-d_5) of picrajavanin A (**6**) were very similar to those of javanicin K (**11**), which was initially isolated from the bark of *Picrasma javanica* from Java Island,[4g] except that some signals due to protons and carbons around C-4 of **6**, differed slightly from those of **11**. On the other hand, the signals (in $CDCl_3$) assignable to the protons on the picrasane skeleton of **6** were superimposable on those of the diacetate (**12**) of picrasin C, which was previously isolated from the wood of *Picrasma quassioides* ("nigaki" in Japanese).[9]

Detailed ^{1}H- and ^{13}C-NMR analyses of **6**, including homo- and heteronuclear correlation spectroscopies (COSY), have enabled us to make complete assignments of the proton and carbon signals, as shown in Tables I and II. Furthermore, the relative configuration of **6** has been

TABLE II. ^{13}C-NMR Data for Picrajavanins A(**6**), B(**7**) and Desbenzoylpicrajavanin A(**8**) (at 75 or 68 MHz, δ_C)[a]

	6		**7**			**8**
	b)	c)	b)	c)	d)	b)
1(s)	207.6	208.1	207.6	208.3	211.0	214.7
2(d)	72.2	73.0	71.8	72.4	73.3	69.9
3(t)	43.0	42.9	42.8	43.0	44.3	49.2
4(d)	29.0	28.9	28.8	28.9	29.8	28.7
5(d)	47.3	48.0	47.1	47.9	49.5	45.2
6(t)	26.4	26.6	26.3	26.6	27.3	26.4
7(d)	82.5	82.2	82.4	82.3	83.8	82.5
8(s)	35.6	35.9	35.7	36.0	36.8	35.7
9(d)	35.7	36.0	35.5	36.0	35.9	35.8
10(s)	50.0	50.6	49.9	50.5	51.5	48.9
11(d)	73.1	73.9	73.0	73.8	74.6	73.2
12(d)	85.8	85.9	85.7	85.9	86.9	85.6
13(d)	34.9	35.0	34.9	35.0	36.8	35.2
14(d)	45.3	45.3	45.2	45.3	45.9	47.8
15(t)	28.0	28.3	27.9	28.3	28.6	28.0
16(s)	170.1	170.0	169.2	169.2	170.6	170.2
18(q)	18.6	18.5	18.5	18.4	19.0	22.0
19(q)	13.4	13.3	13.3	13.3	13.6	13.6
20(q)	22.2	21.8	22.1	21.8	22.2	18.4
21(q)	14.4	14.4	14.3	14.4	14.6	14.4
–OMe	61.0	60.3	61.0	60.3	61.0	61.1
1′(s)	133.0	130.3				
2′,6′(d)	129.8	130.1				
3′,5′(d)	128.1	128.6				
4′(d)	129.6	133.4				
7′(s)	164.8	164.9				
1″(s)	124.1	125.4	124.1	125.4	125.4	125.9
2″(d)	110.1	110.6	110.3	110.8	111.0	109.7
3″(s)	147.4	148.1	147.4	148.1	148.9	147.9
4″(s)	151.3	151.8	151.5	151.9	153.1	152.0
5″(d)	107.7	108.1	107.6	108.1	108.6	108.1
6″(d)	126.1	126.5	126.2	126.6	127.2	123.5
7″(s)	165.4	165.6	165.4	165.6	166.9	165.4
8″(t)	101.5	102.2	101.6	102.3	103.2	101.9
$\underline{C}H_3CO$–			20.3	20.3	20.3	
$CH_3\underline{C}O$–			170.1	169.8	173.1	

a) The characterization of each carbon signal was based on a DEPT experiment. *b*—*d*) Measured in *b*) $CDCl_3$, *c*) pyridine-d_5, or *d*) CD_3OD.

clarified by a nuclear Overhauser enhancement spectroscopy (NOESY) experiment as illustrated in Fig. 2, as well as by detailed comparison of the coupling constants (*J* values) with those reported for the related quassinoids.[4] Thus, picrajavanin A (**6**) was concluded to be the 4-methyl analog of javanicin K (**11**).

In order to confirm the locations of the benzoyl group and the 3″,4″-methylenedioxybenzoyl group in picrajavanin A (**6**), the ^{1}H detected heteronuclear multiple bond correlation (HMBC) spectrum of **6** was examined. As shown in Fig. 2, the benzoyl carbonyl carbon (observed at δ_C

TABLE III. ^{1}H-NMR Data for the (+)-(*R*)-MTPA Ester (**9**) and the (−)-(*S*)-MTPA Ester (**10**) (at 270 MHz, in $CDCl_3$, δ)[a]

	9	**10**
H-2	5.64 dd (12, 7)	5.64 dd (12, 7)
H-3	1.52 m	1.45 m
	2.35 m	2.23 m
H-4	2.10 m	2.04 m
H-5	1.55 m	1.55 m
H-6	1.84 m	1.84 m
	2.00 m	1.97 m
H-7	4.20 br s	4.22 br s
H-9	2.88 d (12)	2.88 d (12)
H-11	5.52 dd (12, 9)	5.51 dd (12, 9)
H-12	3.24 dd (9, 9)	3.24 dd (9, 9)
H-13	2.22 m	2.21 m
H-14	1.83 m	1.83 m
H-15	2.56 dd (19, 8)	2.58 dd (17, 6)
	2.71 dd (19, 5)	2.73 dd (17, 3)
18-H_3	0.94 d (7)	0.92 d (7)
19-H_3	1.44 s	1.44 s
20-H_3	1.36 s	1.36 s
21-H_3	1.03 d (7)	1.04 d (7)
12-OMe	3.26 s	3.24 s
2″-H	7.40 d (2)	7.40 d (2)
5″-H	6.63 d (8)	6.42 d (8)
6″-H	7.61 dd (8, 2)	7.53 dd (8, 2)
8″-H	5.71 d (1)	5.80 d (1)
	5.89 d (1)	5.89 d (1)

a) Coupling constants (*J* values in Hz) are given in parentheses.

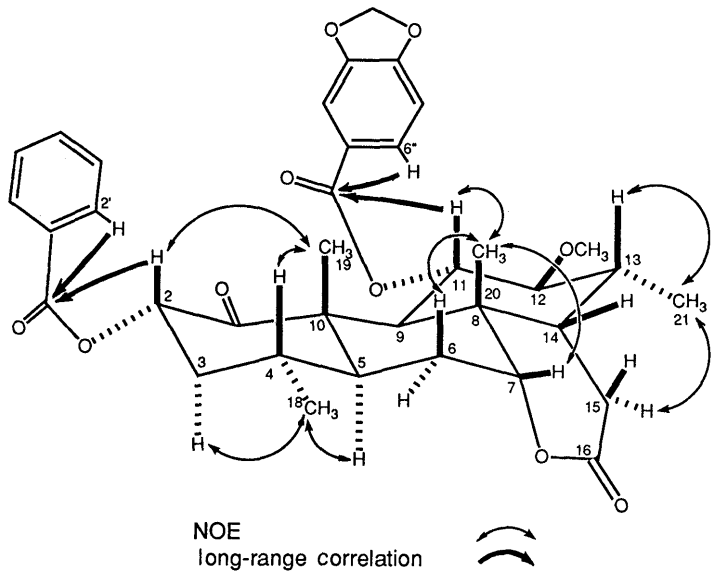

Fig. 2. NOEs and Long-Range Correlations Observed in the NOESY and HMBC Spectra of Picrajavanin A (**6**)

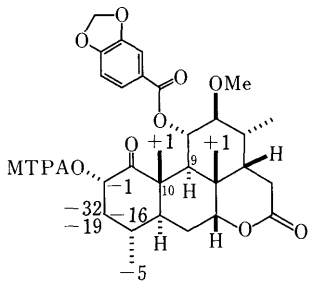

Fig. 3. ^{1}H Chemical Shift Changes Observed in the MTPA Esters (**9** and **10**)

Values [$\Delta\delta = \delta(S) - \delta(R)$] are given in Hz.

164.8) was found to have long-range correlations with the 2-methine proton at δ 5.79 and the 2′-protons at δ 7.84, while the 3″,4″-methylenedioxybenzoyl carbonyl carbon (at δ_C 165.4) was found to have long-range correlations with the 11-methine proton at δ 5.50 and the 6″-proton at δ 7.55. Thus, it has been clarified that the benzoyl and 3″,4″-methylenedioxybenzoyl groups of **6** are connected to the 2- and the 11-hydroxyls, respectively.

On the other hand, alkaline hydrolysis of picrajavanin A (**6**) with 3% sodium methoxide in methanol selectively afforded the desbenzoyl derivative (**8**). The ^{1}H- and ^{13}C-NMR data of **8** have been assigned as shown in Tables I and II on the basis of ^{1}H–^{1}H and ^{1}H–^{13}C COSY experiments. Detailed comparisons of the ^{1}H- and ^{13}C-NMR data for **8** with those for **6** have led us to confirm the structure of **8**, having the 3″,4″-methylenedioxybenzoyl group connected at the 11-hydroxyl.

Finally, the absolute configuration of **6** has been determined by ^{1}H-NMR analysis of the (+)-(*R*)- and (−)-(*S*)-α-methoxy-α-trifluoromethylphenyl acetates (MTPA esters) of **8** (namely by the modified Mosher's method[10]). As given in Table III, the signals due to protons attached to the carbons at 3, 4 and 18 of the (+)-(*R*)-MTPA ester (**9**) were observed at lower fields than those of the (−)-(*S*)-MTPA ester (**10**), while the signals due to the protons on the carbons at 19 and 20 of **9** appeared at slightly higher fields as compared to those of **10** (Fig. 3). Consequently, the absolute configuration at the C-2 of **8** has been elucidated as *S*.

Based on the accumulated evidence presented above, the absolute stereostructure of picrajavanin A (**6**) has been determined to be as shown.

Picrajavanin B (7) The second quassinoid was obtained as a white powder. The high MS measurement of picrajavanin B (**7**) revealed the molecular formula to be $C_{31}H_{38}O_{10}$. The UV and IR spectra of **7** showed the presence of a 3″,4″-methylenedioxybenzoyl group. The ^{1}H-NMR spectrum (in pyridine-d_5) of **7** showed signals assignable to an acetyl group at δ 1.98 together with many other signals which were very similar to those of picrajavanin A (**6**) and desbenzoylpicrajavanin A (**8**). The carbon signals assignable to the picrasane skeleton in the ^{13}C-NMR spectrum of **7** were superimposable on those of **6** and **8** (Table II). So, **7** was presumed to be an acetyl derivative of **8**. In order to verify this presumption, **8** was subjected to ordinary acetylation with acetic anhydride in pyridine to afford picrajavanin B (**7**), which was shown to be identical with authentic **7** obtained from the bark of *Picrasma javanica*. Based on the above evidence, the absolute stereostructure of picrajavanin B (**7**) has been determined to be as shown.

Biological activities of the chemical constituents so far isolated were investigated. It is interesting that, among the constituents isolated here from the bark of *Picrasma javanica*, picrasidine G (**5**), the principal component in this folk medicine, has been found to exhibit various biological activities such as anti-ulcer, antimicrobial, and relaxant effects on the isolated guinea pig ileum, and 4-methoxy-1-vinyl-β-carboline (**1**), the second major principle of the bark, has been found to show a potent anti-ulcer effect.[11]

Experimental

The following instruments were used to obtain physical data: melting points, Yanagimoto micro-melting point apparatus (values are uncorrected); specific rotations, Horiba SEPA-200 digital polarimeter (l=5 cm); UV spectra, Shimadzu UV-1200 spectrometer; IR spectra, Shimadzu FTIR-8100 spectrometer; MS and high MS, Hitachi M-80 mass spectrometer; ^{1}H-NMR spectra, JEOL JNM GX-500 (500 MHz), Varian XL-300 (300 MHz), or JEOL GX-270 (270 MHz) spectrometer; ^{13}C-NMR spectra, JEOL JNM GX-500 (125 MHz), Varian XL-300 (75 MHz) or JEOL JNM GX-270 (68 MHz) spectrometer with tetramethylsilane as an internal standard (multiplicities of the ^{13}C-NMR signals were determined on the basis of the distortionless enhancement by polarization transfer (DEPT) experiments).

The following experimental conditions were used for chromatography: column chromatography, Silica gel 60 (Merck, 60—230 mesh); TLC, pre-coated TLC plates with Silica gel 60F_{254} (Merck, 0.25 mm). Detection was done by spraying 1% Ce$(SO_4)_2$–10% aqueous H_2SO_4, followed by heating.

Isolation of Picrajavanins A (6) and B (7), Together with Known Alkaloids (1, 2, 3, 5) and 6-Methoxy-7,8-methylenedioxycoumarin (4) The air-dried bark (8 kg) of*Picrasma javanica*, which was collected in the Bajawa area of Flores Island, Indonesia in 1988, was extracted with MeOH under reflux and the solvent was evaporated under reduced pressure from the extract to give the MeOH extract (331 g, 4.1% from the bark). The MeOH extract was partitioned into 1-BuOH–H_2O (1:1). The 1-BuOH-soluble portion and the water-soluble portion were separated and both were concentrated under reduced pressure to give the 1-BuOH extract (83 g, 1.2%) and the H_2O extract (191 g, 2.8%), respectively. The 1-BuOH extract (53 g) was subjected to column chromatography (SiO_2 1 kg, eluted with $CHCl_3$– MeOH (20:1→10:1) and then with $CHCl_3$–MeOH–H_2O (7:3:1, lower phase) to give fractions I (0.4 g), II (4.9 g), III (13.2 g), IV (10.7 g), V (4.0 g), VI (4.5 g), VII (4.9 g), and VIII (9.6 g).

Fraction III (13.2 g) was further purified by column chromatography [SiO_2 350 g, eluted with benzene–AcOEt (10:1→1:1)] to afford 4-methoxy-1-vinyl-β-carboline (**1**, 475 mg),[3a] 6-methoxy-7,8-methylenedioxycoumarin (**4**, 43 mg),[6] and picrajavanins A (**6**, 279 mg), and B (**7**, 154 mg). Fraction IV (10.7 g) was also purified by column chromatography [SiO_2 100 g, eluted with benzene–AcOEt (1:1)→AcOEt] to give 4-methoxy-1-ethyl-β-carboline (**2**, 86 mg), and 4-methoxy-1-acetyl-β-carboline (**3**, 42 mg).[5] Fraction VIII (9.6 g) was crystallized from MeOH–1% aqueous HCl to give picrasidine G[7] (**5**, 4.8 g).

Picrajavanin A (**6**), colorless needles from 80% aqueous MeOH, mp 171—172 °C, $[\alpha]_D^{20}$ −41.5° (c=0.61, MeOH). High MS: Calcd for $C_{36}H_{40}O_{10}$ (M^+) 632.264. Found 632.262. UV λ_{max}^{EtOH} nm (log ε): 301 (3.4), 263 (3.4), 221 (4.1). IR (KBr): 2900, 1723, 1605, 1505, 1489, 1445, 1315, 1232, 1157, 1037, 716 cm^{-1}. ^{1}H-NMR: as given in Table I. ^{13}C-NMR: as given in Table II. MS (m/z, %): 632 (M^+, 46), 344 (81), 149 (72), 105 (100).

Picrajavanin B (**7**), white powder, $[\alpha]_D^{20}$ −35.1° (c=1.01, $CHCl_3$). High MS: Calcd for $C_{31}H_{38}O_{10}$ (M^+) 570.246. Found 570.247. UV λ_{max}^{EtOH} nm (log ε): 299 (3.5), 265 (3.6), 220 (4.1). IR (KBr): 2971, 1730, 1626, 1600, 1442, 1279, 1257, 1109, 1039, 760 cm^{-1}. ^{1}H-NMR: as given in Table I. ^{13}C-NMR: as given in Table II. MS (m/z, %): 570 (M^+, 30), 344 (64), 261 (35), 166 (25), 149 (100).

Alkaline Hydrolysis of Picrajavanin A (6) A solution of **6** (20 mg) in 3% NaOMe–MeOH (5 ml) was stirred at room temperature (20 °C) under an N_2 atmosphere for 90 min and then the reaction mixture was neutralized with Dowex 50W × 8 (H^+ form). After removal of the resin by filtration, the solvent was evaporated from the filtrate under reduced pressure to yield a product, which was purified by column chromatography [SiO_2 1 g,

eluted with benzene–AcOEt (5 : 1)] to furnish **8** (16 mg).

8: A white powder, $[\alpha]_D^{20}$ −5.3° (c = 1.17, $CHCl_3$). High MS: Calcd for $C_{29}H_{36}O_9$ (M^+) 528.235. Found 528.234. UV λ_{max}^{EtOH} nm (log ε): 299 (3.8), 266 (3.8), 221 (4.3). IR (KBr): 3517, 2932, 1717, 1716, 1445, 1370, 1260, 1157, 1042, 790 cm^{-1}. ^{1}H-NMR: as given in Table I. ^{13}C-NMR: as given in Table II. MS (m/z, %): 528 (M^+, 28), 362 (81), 301 (44), 166 (48), 149 (100).

Preparation of the 2-(+)-(*R*)-MTPA Ester (9) and 2-(−)-(*S*)-MTPA Ester (10) A solution of **8** (5.0 mg) in CH_2Cl_2 (0.35 ml) was treated at room temperature (20 °C) with (+)-(*R*)-α-methoxy-α-trifluoromethylphenylacetic acid (14.3 mg), dicyclohexylcarbodiimide (DCC) (14.6 mg), and dimethylaminopyridine (4.7 mg) for 10 min. The reaction mixture was poured into water and the whole mixture was extracted with CH_2Cl_2. The extract was washed successively with 5% HCl, aqueous saturated $NaHCO_3$, and brine, then dried over $MgSO_4$. Removal of the solvent from the extract gave a residue, which was purified by column chromatography [SiO_2 1 g, eluted with *n*-hexane–AcOEt (1 : 2)] to furnish **9** (6.1 mg). In a similar manner, the 2-(−)-(*S*)-MTPA ester (**10**, 5.8 mg) was prepared from **8** (5.0 mg).

Acetylation of 8 Giving Picrajavanin B (7) A solution of **8** (16 mg) in pyridine (0.5 ml) was treated with Ac_2O (0.5 ml) and the reaction mixture was stirred at room temperature (20 °C) under an N_2 atmosphere for 2 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt. The AcOEt extract was washed successively with 5% aqueous HCl, saturated aqueous $NaHCO_3$ and brine, and then dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure to yield picrajavanin B (**7**, 17 mg), which was shown to be identical with authentic **7** isolated from the bark of *Picrasma javanica* by TLC, IR, UV, ^{1}H- and ^{13}C-NMR comparisons.

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