Indonesian Medicinal Plants. VIII.[1] Chemical Structures of Three New Triterpenoids, Bruceajavanin A, Dihydrobruceajavanin A, and Bruceajavanin B, and a New Alkaloidal Glycoside, Bruceacanthinoside, from the Stems of *Brucea javanica* (Simaroubaceae)

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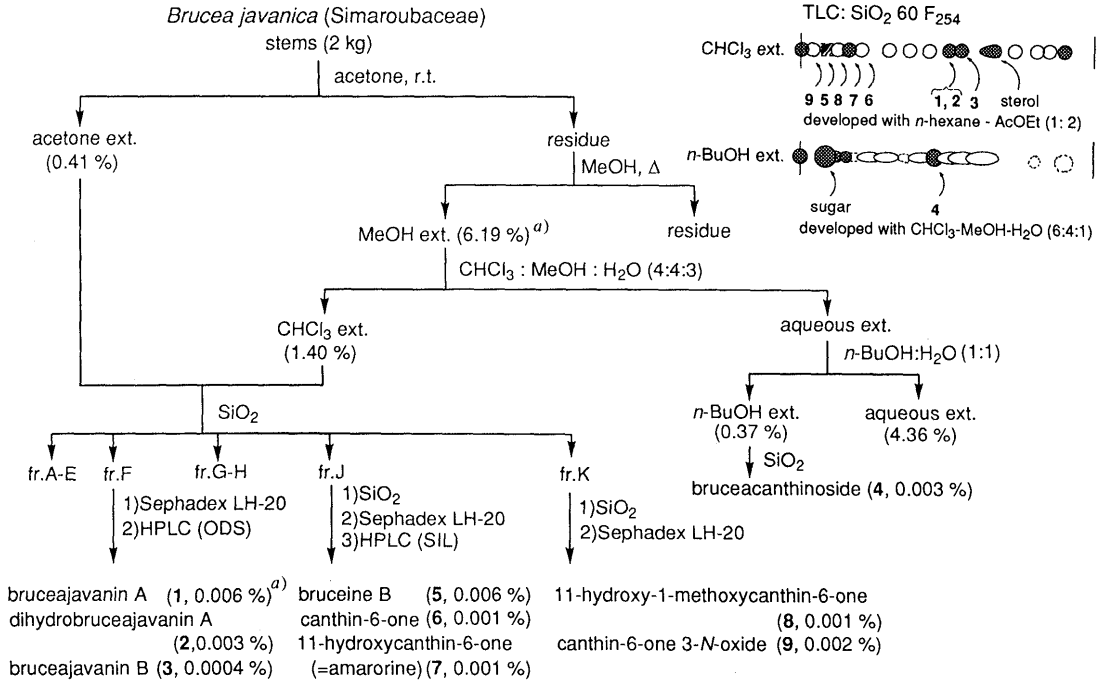
Three new apotirucallane-type triterpenoids named bruceajavanin A (1) dihydrobruceajavanin A (2), and bruceajavanin B (3), and a novel β-carboline alkaloidal glycoside named bruceacanthinoside (4) were isolated from the stems of *Brucea javanica* (Simaroubaceae), a traditional medicine used to treat malaria in the Bengkulu area, Sumatra, Indonesia. Their chemical structures have been elucidated on the bases of their chemical and physicochemical properties. Bruceajavanin A (1), dihydrobruceajavanin A (2) and bruceacanthinoside (4) were shown to inhibit growth of the cultured malarial parasite *Plasmodium falciparum* K1 of a chloroquine-resistant strain.

Keywords Indonesian medicinal plant; *Brucea javanica*; Simaroubaceae; apotirucallane triterpenoid; β-carboline alkaloidal glycoside

Brucea javanica (L.) MERR. is a simaroubaceous tree which is widely distributed throughout Asia, and is traditionally considered as a remedy for malaria, dysentery and cancer.[2] In Indonesia, particularly in Java, the air-dried fruit of *Brucea javanica* is one of the best-known "Jamu" traditional medicines. During our expedition in 1990 searching for Indonesian traditional medicinal plants, we found that people in the Rejang Lebong area of Sumatra use the decoction of not only fruit but also all parts of the plant *Brucea javanica*, called "pegeu buang," for the treatment of malaria.[3] As a part of our chemical characterization studies of Indonesian medicinal plants,[1,4] we have been investigating the chemical constituents of the stems of *Brucea javanica*, which was collected in August 1990 at the above-mentioned place. In this paper, we present a full account of the structure elucidation of four new compounds, three apotirucallane-type triterpenoids and one β-carboline alkaloidal



a) Percent yield from the air-dried stems.

Fig. 1

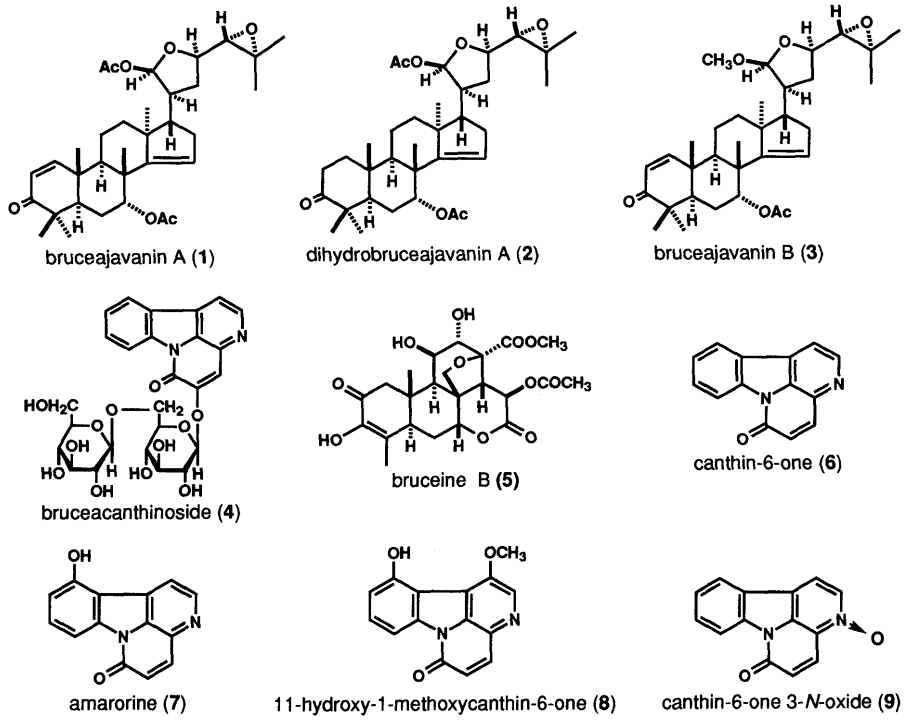


Fig. 2

glycoside, which were isolated from the stems.

The isolation of the chemical constituents from the air-dried stems of *Brucea javanica* was carried out through the procedure shown in Fig. 1. The acetone extract and the chloroform-soluble portion of the methanolic extract were combined and subjected to silica gel and Sephadex LH-20 column chromatography and high-performance liquid chromatography (HPLC) to afford three new apotirucallane-type triterpenoids, named bruceajavanin A (**1**, 0.006% from the stems), dihydrobruceajavanin A (**2**, 0.003%), and bruceajavanin B (**3**, 0.0004%), together with a known quassinoid bruceine B (**5**)[5] and four known β-carboline alkaloids, canthin-6-one (**6**),[6] 11-hydroxycanthin-6-one (=amarorine, **7**),[6] 11-hydroxy-1-methoxycanthin-6-one (**8**),[7-9] and canthin-6-one 3-*N*-oxide (**9**).[10] A new β-carboline alkaloidal glycoside named bruceacanthinoside (**4**, 0.003%) was isolated from the aqueous phase prepared from the methanolic extract.

Bruceajavanin A (1) Bruceajavanin A (**1**) was crystallized from an *n*-hexane–chloroform mixture as colorless prisms of mp 204—206 °C. In its fast atom bombardment (FAB) mass spectrum (MS), **1** gave the *quasi*-molecular ion $(M+Na)^+$ peak at *m/z* 591, the composition of which was defined as $C_{34}H_{48}NaO_7$ from the high-resolution MS analysis. The infrared (IR) spectrum of **1** showed absorption bands assignable to acetate groups (1738, 1232 cm^{-1}) and an enone group (1670 cm^{-1}). The ultraviolet (UV) absorption maximum at 229 nm ($\varepsilon=12900$) suggested the presence of an α,β-unsaturated carbonyl group in **1**.

The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **1** showed the signals characteristic of an apotirucallane-type triterpenoid as compared with reported data[11] (Table I). On the other hand, the proton magnetic resonance (^{1}H-NMR) spectrum (Table II) of **1** showed characteristic signals at δ 6.26 ppm (1H, d, $J=4.0$ Hz, 21-H), 3.92 (1H, m, 23-H), 2.67 (1H, d, $J=7.6$ Hz, 24-H), 1.33 and 1.29 (3H each, both s, 26- and 27-H_3) assignable to the protons in the side chain, comprising a five-membered acetal ring and an epoxide moiety, which was very similar to the side chain of 21-*O*-acetyltoosendantriol, the structure of which had been determined by X-ray analysis by Nakanishi *et al.*[12] The ^{1}H-NMR spectrum also showed signals at δ 7.13 (1H, d, $J=10$ Hz, 1-H) and 5.86 (1H, d, $J=10$ Hz, 2-H), which were assignable to the protons on an α,β-unsaturated carbonyl moiety.[11]

In the correlation spectroscopy *via* long-range coupling (COLOC) NMR experiments, bruceajavanin A (**1**) showed ^{1}H–^{13}C correlations between methyl protons at C-28 and C-29 (δ 1.07, 6H) and carbons at C-3 (δ_C 204.5), C-4 (δ_C 44.1) and C-5 (δ_C 46.1), and also between a methine proton at C-7 (δ 5.26) and carbons at C-5 (δ_C 46.1) and C-9 (δ_C 38.0) and an acetyl carbonyl carbon (δ_C 169.9). Further correlations were observed between an olefinic proton at C-15 (δ 5.30) and carbons at C-13 (δ_C 46.4) and C-17 (δ_C 52.6), between methyl protons at C-18 (δ 1.02) and carbons at C-12 (δ_C 32.7), C-13, C-14 (δ_C 158.9), and C-17, between methylene protons at C-16 (δ 2.10) and a carbon at C-20 (δ_C 44.3), and between several other protons and carbons as shown in Fig. 3. Furthermore, the ^{1}H-NMR nuclear Overhauser and exchange spectroscopy (NOESY) experiment on **1** indicated that methyl protons at C-18 were located in the vicinity of protons at C-9 and C-20 and the acetal proton at C-21, indicating that the five-membered acetal ring in **1** is attached to C-17α. The NOESY experiment also disclosed several other spatial correlations as depicted in Fig. 4.

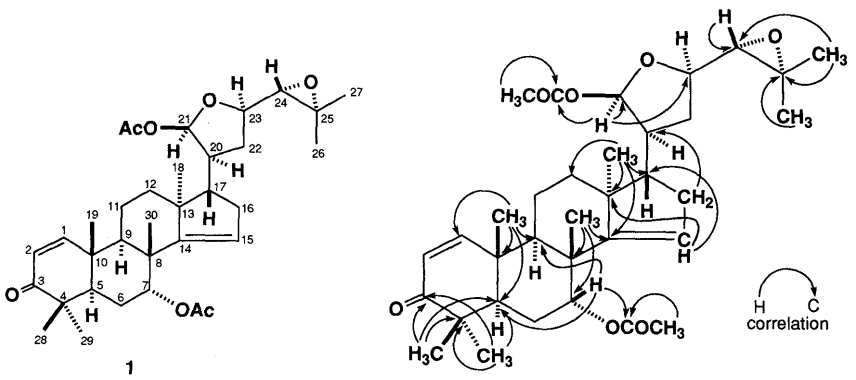


Fig. 3

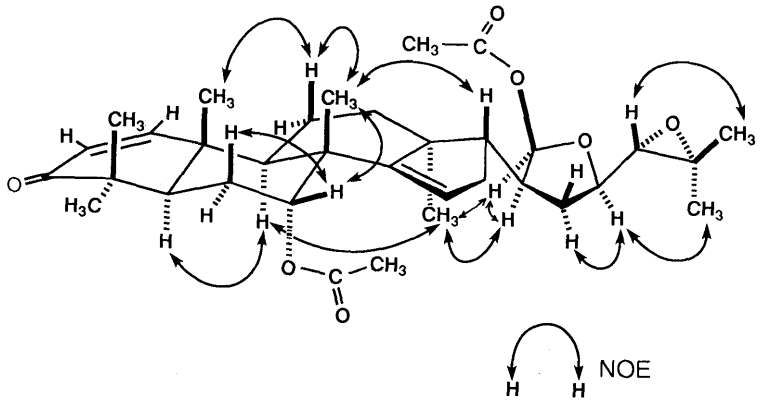


Fig. 4

The above-described physicochemical evidence led us to assign the relative stereostructure as shown and finally, the absolute configuration of **1** was determined on the basis of the circular dichroism (CD) analysis of **1**. Thus, **1** gave a CD curve with a negative maximum at 340 nm and a positive maximum at 232 nm.[13] Consequently, the chemical structure of bruceajavanin A (**1**) has been determined to be as shown in Fig. 3.

Dihydrobruceajavanin A (2) and Bruceajavanin B (3) Dihydrobruceajavanin A (**2**) was obtained as colorless prisms of mp 206—207 °C by crystallization from an *n*-hexane and chloroform mixture. The IR spectrum of **2** showed absorption bands ascribable to acetoxyl groups (1738, 1244 cm^{-1}) and a ketone group (1705 cm^{-1}). The FAB-MS of **2** showed the *quasi*-molecular ion $(M+Na)^+$ peak at *m/z* 593, and the molecular composition of **2** was defined as $C_{34}H_{50}O_7$ by high-resolution MS analysis of the ion. The ^{1}H-NMR spectrum of **2** was very similar to that of bruceajavanin A (**1**) except that the former lacked the signals of two vicinal olefinic protons at C-1 and C-2. These findings have led us to presume that **2** is a dihydro derivative of **1**. Further support for this presumption was obtained from ^{13}C-NMR (Table I) and two-dimension (2D) NMR [^{1}H–^{1}H correlation spectroscopy (COSY), ^{1}H–^{13}C COSY, NOESY] analyses. Finally, the structure of dihydrobruceajavanin A (**2**) was determined to be as shown in Fig. 2, on the basis of selective catalytic hydrogenation of **1** over platinum black[11] to provide **2**.

The FAB-MS of bruceajavanin B (**3**) showed the *quasi*-molecular ion $(M+H)^+$ peak at *m/z* 541, which was defined as $C_{33}H_{49}O_6$ by the high-resolution MS analysis. The IR and UV spectra of **3** showed similar absorption patterns to those of bruceajavanin A (**1**). The ^{1}H- and ^{13}C-NMR spectra of **3** suggested the presence of a methoxyl group instead of one of two acetoxyl groups contained in **1** (Tables I and II). The location of the methoxyl group in **3** was deduced to be at C-21 from the finding that the carbon signal of C-21 was observed at δ_C 109.1 with a lower-field chemical shift as compared to that observed in **1**. Furthermore, **3** showed a negative maximum ($[\theta]$ −19400) at 340 nm and a positive one ($[\theta]$ +112000) at 230 nm in the CD spectrum, which were similar to those observed for **1**.[13] Consequently, the absolute stereostructure of bruceajavanin B (**3**) was concluded to be as shown in Fig. 2. Bruceajavanin B (**3**) is a natural compound, since it was detected by thin-layer chromatography (TLC) in the initial acetone extract of the stems.

Bruceacanthinoside (4) Bruceacanthinoside (**4**) was obtained as a white amorphous solid, which colored orange with Dragendorff's reagent. The UV spectrum of **4** showed typical absorption maxima [239 nm (ε=16300), 244 nm (ε=15200), 296 nm (ε=6100), 338 nm (ε=7200), 354 nm (ε=13200), 371 nm (ε=13300)] ascribable to a β-carboline skeleton,[6] while the IR spectrum showed absorption bands due to hydroxyl (3354 cm^{-1}, br) and amide (1668 cm^{-1}) groups. The FAB-MS of **4** showed the

quasi-molecular ion $(M+Na)^+$ peak at *m/z* 583, the composition of which was defined as $C_{26}H_{28}N_2NaO_{12}$ by the high-resolution MS analysis.

The ^{1}H-NMR spectrum of bruceacanthinoside (**4**) exhibited signals characteristic of the protons on a β-carboline moiety and two anomeric proton signals at δ 4.21 (1H, d, $J=7.3$ Hz) and δ 5.22 (1H, d, $J=7.6$ Hz), which were attributable to two β-glycosidic linkages. The ^{13}C-NMR spectrum of **4** showed the presence of a gentiobiosyl[14] moiety: two β-anomeric carbon signals at δ_C 100.2 and 103.6. Finally, enzymatic hydrolysis of **4** with β-glucosidase yielded 5-hydroxycanthin-6-one (**10**)[9] and D-(+)-glucose, which was confirmed by HPLC with an optical rotation detector. Thus, the structure of bruceacanthinoside (**4**) can be expressed as 5-*O*-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl-5-hydroxycanthin-6-one.

In conclusion, we have isolated three new apotirucallane-type triterpenoids named bruceajavanin A (**1**), dihydrobruceajavanin A (**2**), and bruceajavanin B (**3**), and a new β-carboline alkaloidal glycoside, bruceacanthinoside (**4**),[15] together with a quassinoid, bruceine B (**5**), and four known β-carboline alkaloids (**6**—**9**), from the stems of an Indonesian simaroubaceous plant *Brucea javanica*. Among these new compounds, **1** and **2** were found to exhibit moderate *in vitro* inhibitory activities (IC_{50} 1.1 μM, IC_{90} 4.4 μM for **1**; IC_{50} 2.5 μM, IC_{90} 4.3 μM for **2**) against the cultured parasite *Plasmodium falciparum* (a chloroquine-resistant K1 strain in human erythrocytes),[16] while **4** was shown to exhibit weak inhibition (IC_{50} 25 μM, IC_{90} 43 μM) against the same pathogen. Thus, in addition to the quassinoids, which are well known to exhibit anti-malarial activity,[2,5] there are other types of anti-malarial compounds in *Brucea javanica*.

TABLE I. ^{13}C-NMR Data for Bruceajavanin A (**1**), Azadirachtol,[11] 21-*O*-Acetyltoosendantriol,[12] Dihydrobruceajavanin A (**2**), and Bruceajavanin B (**3**) (at 67.5 MHz in $CDCl_3$, δ_C)

Carbon	1	Azadirachtol[11]	21-*O*-Acetyl-toosendantriol[12]	2	3
C-1	157.9	158.1		38.6	158.1
C-2	125.5	125.6		33.9	125.5
C-3	204.5	204.5	76.1	216.6	204.6
C-4	44.1	43.8		46.8	44.1
C-5	46.1	39.9		48.2	46.1
C-6	23.7	23.4		24.2	23.8
C-7	74.3	73.8	72.3	74.8	74.4
C-8	42.6	44.2		41.9	42.7
C-9	38.0	46.3		42.4	38.3
C-10	39.9	39.4		37.1	39.9
C-11	16.4	72.5		16.4	16.5
C-12	32.7	42.9		32.7	34.3
C-13	46.4	46.6		46.4	46.8
C-14	158.9	158.8	162.3	161.5	159.3
C-15	118.6	119.5	119.2	119.6	118.5
C-16	35.1	35.0		35.1	34.8
C-17	52.6	52.1		52.5	57.8
C-18	20.0			19.8	20.1
C-19	18.9			15.0	18.9
C-20	44.3	157.6	44.3	44.3	46.7
C-21	96.6	96.1	96.7	96.6	109.1
C-22	31.3	119.8	31.4	31.3	33.4
C-23	79.7	67.6	79.7	79.7	77.2
C-24	66.6	43.9	66.7	66.7	65.2
C-25	57.1	29.7	57.1	57.1	57.1
C-26	19.3			19.3	19.3
C-27	24.9			24.9	24.9
C-28	21.3			21.0	21.3
C-29	26.9			25.8	27.0
C-30	27.4			27.0	27.3
7-OAc	169.9	170.0		170.0	170.1
	21.1	21.1		21.1	21.1
21-OAc	170.1		169.9	170.2	
	21.5		21.5	21.4	
21-OCH_3					55.4

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are recorded as read. The UV spectra were obtained with a Hitachi 330 spectrophotometer, and the IR spectra were taken with a JASCO FT/IR-5300 spectrometer (by a diffusion-reflection method on KBr powder). The electron impact-mass spectra (EI-MS) were taken

TABLE II. ^{1}H-NMR Data for Bruceajavanin A (**1**), 21-*O*-Acetyltoosendantriol,[12] Dihydrobruceajavanin A (**2**), and Bruceajavanin B (**3**) (at 270 MHz in $CDCl_3$, *J* Values in Hz, δ)

Proton(s)	1	21-*O*-Acetyl-toosendantriol[12]	2	3
1-H	7.13 (d, $J=10$)			7.16 (d, $J=10$)
2-H	5.86 (d, $J=10$)			5.85 (d, $J=10$)
7β-H	5.26 (m)		5.23 (m)	5.23 (m)
15-H	5.30 (m)	5.47 (m)	5.28 (m)	5.27 (m)
20α-H	2.31 (m)		2.33 (m)	2.35 (m)
21α-H	6.26 (d, $J=4$)	6.24 (d, $J=4$)	6.24 (d, $J=4$)	4.86 (d, $J=3$)
23α-H	3.92 (m)	3.92 (m)	3.91 (m)	3.78 (m)
24β-H	2.67 (d, $J=7.5$)	2.67 (d, $J=7.5$)	2.66 (d, $J=8$)	2.69 (d, $J=7.5$)
7-OAc	1.94 (s)		1.94 (s)	1.94 (s)
21-OAc	2.07 (s)	2.06 (s)	2.05 (s)	
OCH_3				3.38 (s)
Methyls	1.02, 1.18, 1.29, 1.33, 1.07, 1.07, 1.18 (all s)	1.03, 1.05, 1.29, 1.33, 0.94, 0.89, 0.84 (all s)	1.00, 1.02, 1.28, 1.32, 1.02, 1.00, 1.13 (all s)	1.04, 1.17, 1.29, 1.32, 1.07, 1.07, 1.17 (all s)

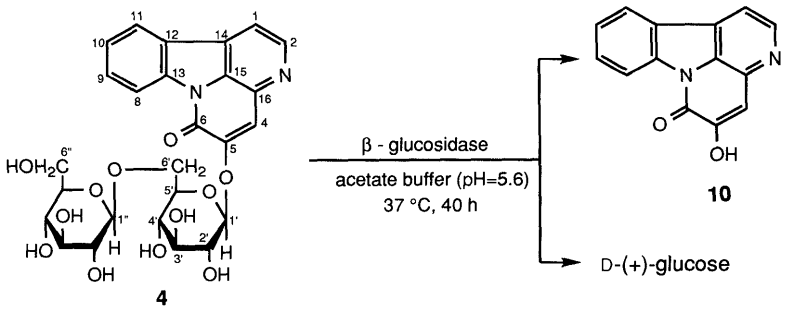


Fig. 5

TABLE III. ^{13}C-NMR Data for Bruceacanthinoside (**4**) (at 67.5 MHz in DMSO-d_6, δ_C)

	Carbon	4		Carbon	4
5-Hydroxycanthin-6-one moiety	C-1	115.0	5-*O*-β-D-Gluco-pyranosyl moiety	C-1′	100.2
	C-2	145.8		C-2′	73.0[a]
	C-4	114.7		C-3′	76.6[b]
	C-5	151.5		C-4′	69.6[c]
	C-6	154.5		C-5′	76.9[b]
	C-8	116.4		C-6′	68.7
	C-9	130.6	6′-*O*-β-D-Gluco-pyranosyl moiety	C-1″	103.6
	C-10	125.8		C-2″	73.5[a]
	C-11	123.6		C-3″	75.7[b]
	C-12	124.8		C-4″	70.0[c]
	C-13	136.2		C-5″	76.9[b]
	C-14	128.6		C-6″	61.0
	C-15	127.4			
	C-16	138.5			

a—*c*) The assignments may be interchangeable.

on a JEOL JMS-D300 spectrometer, while the FAB-MS were taken on a JEOL SX-102 double-focused high-resolution mass spectrometer with a JMA DA-6000 data system by a direct inlet method. The ^{1}H-NMR and ^{13}C-NMR spectra were measured with a JEOL JNM EX-270 spectrometer. Optical rotations were measured in a 0.5 dm length cell with a JASCO DIP-370 digital polarimeter. The CD spectra were obtained with a JASCO J-500A spectropolarimeter equipped with a 501N data processor. For HPLC, a Shimadzu LC-6A pump module was used with a Hitachi L-4200 UV/VIS detector, a JASCO 830-RI detector, or a Shodex OR-1 optical rotation detector. Column chromatography was carried out using Kieselgel 60 (70—230 mesh, Merck) or Sephadex LH-20. TLC was conducted on precoated Kieselgel 60 F_{254} plates (0.2 mm, Merck) and detection of the spots was carried out by spraying 1% $Ce(SO_4)_2$/10% H_2SO_4 on the TLC plates followed by heating or by spraying Dragendorff's reagent.

Isolation of Bruceajavanin A (1), Dihydrobruceajavanin A (2), Bruceajavanin B (3), Bruceacanthinoside (4), Bruceine B (5), and Four Known β-Carboline Alkaloids The air-dried stems (2 kg) of *Brucea javanica* (Simaroubaceae), collected in the Rejang Lebong area, Bengkulu province, Sumatra Island, Indonesia in 1990, were macerated with acetone for 24 h, and the residue left after removal of the acetone extract by filtration was extracted with MeOH under reflux. The solvents were evaporated off under reduced pressure to yield the acetone extract (8.2 g, 0.41% from the stems) and the MeOH extract (123.9 g, 6.19%), respectively. The MeOH extract was partitioned into a $CHCl_3$–MeOH–H_2O (4:4:3) mixture. The $CHCl_3$ phase (the lower layer) was taken and concentrated under reduced pressure to yield the $CHCl_3$ extract (27.8 g, 1.4%), while the water phase was partitioned with *n*-BuOH. The solvents were evaporated off under reduced pressure to yield the *n*-BuOH extract (7.54 g, 0.37%) and the water extract (87.3 g, 4.36%), respectively. Since the acetone extract and the $CHCl_3$ extract showed a similar TLC pattern, these extracts were combined and a part (29 g) was subjected to silica gel column chromatography (SiO_2 150 g, successive elution with *n*-hexane : AcOEt = 5 : 1—1 : 3, AcOEt, and MeOH) to provide fr. A (0.9 g), fr. B (0.6 g), fr. C (1.7 g), fr. D (0.7 g), fr. E (1.2 g), fr. F (1.8 g), fr. G (1.3 g), fr. H (1.2 g), fr. J (3.3 g), and fr. K (16.2 g). The fr. F (1.75 g) was then subjected to column chromatography on Sephadex LH-20 (elution with $CHCl_3$: MeOH = 1 : 2) to give fr. F1 (40 mg), fr. F2 (260 mg), fr. F3 (720 mg), and frs. F4-F10 (770 mg). The fr. F2 (250 mg) was further purified by HPLC [YMC-Pack octadecyl silica (ODS), AM-323, CH_3CN : H_2O = 7 : 3] to afford bruceajavanin A (**1**, 100 mg, 0.006% from the stems), dihydrobruceajavanin A (**2**, 50 mg, 0.003 %), and bruceajavanin B (**3**, 6 mg, 0.0004%). The fr. J (3.0 g) was separated by silica gel column chromatography (SiO_2 200 g, *n*-hexane : AcOEt = 1 : 2—1 : 4, AcOEt, and MeOH) to give fr. J1 (40 mg), fr. J2 (155 mg), fr. J3 (475 mg), fr. J4 (760 mg), fr. J5 (410 mg), fr. J6 (290 mg), and fr. J7 (810 mg). The fr. J4 was then purified by column chromatography on Sephadex LH-20 ($CHCl_3$: MeOH = 1 : 2) and subsequently by HPLC [Zorbax SIL, *n*-hexane : CH_2Cl_2 : EtOH = 12 : 4 : 1] to give bruceine B[5] (**5**, 90 mg, 0.006%) and canthin-6-one[6] (**6**, 20 mg, 0.001%). The fr. J5 was also purified by silica gel column chromatography (SiO_2 40 g, $CHCl_3$: MeOH = 10 : 1 and MeOH) to give fr. J5-1 (80 mg), fr. J5-2 (70 mg), fr. J5-3 (105 mg), fr. J5-4 (45 mg), and fr. J5-5 (90 mg). Crystallization of fr. J5-3 from MeOH afforded 11-hydroxycanthin-6-one[6] (=amarorine, **7**, 20 mg, 0.001%). On the other hand, fr. K was repeatedly chromatographed over silica gel and Sephadex LH-20 columns to afford 11-hydroxy-1-methoxycanthin-6-one[7—9] (**8**, 15 mg, 0.001%) and canthin-6-one 3-*N*-oxide[9] (**9**, 30 mg, 0.002%). The *n*-BuOH extract (6 g) was also subjected to silica gel column chromatography (SiO_2 200 g, $CHCl_3$: MeOH : H_2O = 10 : 3 : 1—6 : 4 : 1 and MeOH) to afford bruceacanthinoside (**4**, 50 mg, 0.003%).

Bruceajavanin A (**1**): Colorless prisms, mp 204—206 °C (*n*-hexane–$CHCl_3$), $[\alpha]_D$ +25.7° (c = 0.6, $CHCl_3$, 21 °C). IR ν_{max}^{KBr} cm^{-1}: 2930, 1738, 1670, 1458, 1377, 1232, 1118. UV λ_{max}^{MeOH} nm (ε): 229 (12900). ^{1}H-NMR: as given in Table II. ^{13}C-NMR: as given in Table I. High-resolution FAB-MS *m/z*: Calcd for $C_{34}H_{48}NaO_7$ [$(M+Na)^+$]: 591.3270. Found: 591.3284. CD ($c = 6.6 \times 10^{-3}$, MeOH): $[\theta]_{340}$ −21500 (neg. max.), $[\theta]_{276}$ 0, $[\theta]_{232}$ +120000 (pos. max.).

Dihydrobruceajavanin A (**2**): Colorless prisms, mp 206—207 °C (*n*-hexane–$CHCl_3$), $[\alpha]_D$ −3.3° (c = 1.0, $CHCl_3$, 21 °C). IR ν_{max}^{KBr} cm^{-1}: 2934, 1738, 1705, 1456, 1377, 1244, 1118. ^{1}H-NMR: as given in Table II. ^{13}C-NMR: as given in Table I. High-resolution FAB-MS *m/z*: Calcd for $C_{34}H_{50}NaO_7$ [$(M+Na)^+$]: 593.3471. Found: 593.3463.

Bruceajavanin B (**3**): A white amorphous solid, $[\alpha]_D$ −32.6° (c = 0.4, $CHCl_3$, 21 °C). IR ν_{max}^{KBr} cm^{-1}: 2928, 1736, 1670, 1458, 1379, 1248, 1103. UV λ_{max}^{MeOH} nm (ε): 228 (12000). ^{1}H-NMR: as given in Table II. ^{13}C-NMR: as given in Table I. High-resolution FAB-MS *m/z*: Calcd for $C_{33}H_{49}O_6$ [$(M+H)^+$]: 541.3515. Found: 541.3522. CD ($c = 1.0 \times 10^{-2}$, MeOH): $[\theta]_{340}$ −19400 (neg. max.), $[\theta]_{275}$ 0, $[\theta]_{230}$ +112000 (pos. max.).

Bruceacanthinoside (**4**): A white amorphous solid, $[\alpha]_D$ −64.6° (c = 0.45, DMSO, 25 °C). IR ν_{max}^{KBr} cm^{-1}: 3354 (br), 1668, 1444, 1288, 1072. UV λ_{max}^{MeOH} nm (ε): 239 (16300), 244 (15200), 260 sh, 296 (6100), 307 sh, 325 sh, 338 (7200), 354 (13200), 371 (13300). ^{1}H-NMR (270 MHz, DMSO-d_6) δ: 3.01—3.20 (3H, m, 3′-H, 2″-H, 3″-H), 3.26 (1H, m, 4′-H), 3.42 (1H, m, 2′-H), 3.48, 3.67 (each 1H, both m, 6″-H_2), 3.70—3.82 (2H, m, 5′-H, 4″-H), 4.01—4.09 (2H, m, 6′-H, 5″-H), 4.21 (1H, d, J = 7.3 Hz, 1″-H), 4.53 (1H, t, J = 5.6, 5.9 Hz, 6″-OH), 4.86 (1H, d, J = 4.3 Hz, 3″-OH), 4.91 (1H, d, J = 3.6 Hz, 3′-OH), 5.02 (1H, d, J = 4.9 Hz, 2″-OH), 5.20 (1H, d, J = 5.3 Hz, 4′-OH), 5.22 (1H, d, J = 7.6 Hz, 1′-H), 5.24 (1H, d, J = 4.3 Hz, 4″-OH), 7.61 (1H, dd , J = 8.0, 8.0 Hz, 10-H), 7.76 (1H, s, 4-H), 7.77 (1H, m, 9-H), 8.19 (1H, d, J = 5.3 Hz, 1-H), 8.39 (1H, d, J = 8.0 Hz, 11-H), 8.53 (1H, d, J = 8.0 Hz, 8-H), 8.77 (1H, d, J = 5.3 Hz, 2-H). ^{13}C-NMR: as given in Table III. High-resolution FAB-MS *m/z*: Calcd for $C_{26}H_{28}N_2NaO_{12}$ [$(M+Na)^+$]; 583.1496. Found: 583.1518.

Catalytic Hydrogenation of Bruceajavanin A (1) Giving Dihydrobruceajavanin A (2) A solution of **1** (3 mg) in EtOH (1 ml) was added to a suspension of Pt black (*ca.* 50 mg) in EtOH (1 ml) and the whole mixture was stirred under an H_2 atmosphere at room temperature for 2 h. After addition of EtOH (2 ml) to the reaction mixture, the whole was filtered to remove the catalyst. The filtrate was concentrated under reduced pressure to afford **2** (2.7 mg, 90%) (identified by ^{1}H-NMR, IR, and $[\alpha]_D$ comparisons).

Enzymatic Hydrolysis of Bruceacanthinoside (4) A solution of **4** (7 mg) in an acetate buffer (pH = 5.6, 1 ml) was treated with β-glucosidase (Sigma, No. G-0395, from almonds, *ca.* 50 mg) at 37 °C for 40 h. The reaction mixture was extracted with AcOEt, and the AcOEt-soluble portion was evaporated under reduced pressure to afford 5-hydroxycanthin-6-one, which was identified from the ^{1}H-NMR spectrum and by comparison of the physical properties (MS, IR, UV) with those reported.[9] The aqueous phase, separated after the AcOEt extraction, was subjected to HPLC [YMC-Pack Polyamine II, 4.6 mm (i.d.) × 20 cm, CH_3CN : H_2O = 75 : 25, 1 ml/min] to afford D-(+)-glucose, which was found to be identical with an authentic sample (t_R = 17 min 0 s) by using refractive index (RI) detection (JASCO 830-RI) and chiral detection (Shodex OR-1, measured at 780 nm).

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7) 11-Hydroxy-1-methoxycanthin-6-one (**8**) has been reported only by Viala,[8] as cited by Lassak *et al.*[9] Since the report by Viala[8] was unavailable to us, we present here the physical data for **8** isolated by us: pale yellow needles (MeOH), which did not melt below 300 °C. IR ν_{max}^{KBr} cm^{-1}: 3391 (br), 3045, 1682, 1429, 1352, 1257. UV λ_{max}^{MeOH} nm (ε): 235 (10900), 252 sh, 265 (10400), 275 (9500), 346 (17600), 367 sh, 384 sh. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 4.34 (3H, s, 1-OC$\underline{H}_3$), 6.86 (1H, d, J=10 Hz, 5-H), 7.00 (1H, d, J=8 Hz, 10-H), 7.57 (1H, dd, J=8, 8 Hz, 9-H), 7.94 (1H, d, J=10 Hz, 4-H), 8.17 (1H, d, J=8 Hz, 8-H), 8.25 (1H, s, 2-H). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ_C: 57.7 (O$\underline{C}$H$_3$), 108.8 (C-8), 110.9 (C-12), 112.5 (C-10), 116.8 (C-14), 126.4 (C-5), 129.7 (C-2), 131.5 (C-16), 132.3 (C-15), 132.6 (C-9), 138.7 (C-4), 139.5 (C-13), 148.3 (C-1), 152.4 (C-11), 159.8 (C-6). High-resolution FAB-MS *m/z*: Calcd for $C_{15}H_{11}O_3N_2$ [$(M+H)^+$]: 267.0752. Found : 267.0761.
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