Indole Alkaloids from the Leaves of *Alstonia villosa* in Sunbawa (*Alstonia* 6)[1)]

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Seventeen alkaloids were isolated from the air-dried leaves of *Alstonia villosa* and their structures characterized. One of the seven new alkaloids was elucidated to be (19*Z*)-5α-methoxyrhazimine, having a 3,4-dihydroquinoline nucleus.

Key words indole alkaloid; 3,4-dihydroquinoline alkaloid; *Alstonia villosa*; Apocynaceae

Genus *Alstonia* is widely distributed in tropical districts of Southeast Asia, and the barks and leaves of some species are utilized locally for the remedy of malaria, diarrhea, and several other diseases. As a part of chemical investigations into the constituents of Apocynaceous plants, we have reported a number of indole alkaloids from *Alstonia scholaris*[2)] and *A. macrophylla*,[3)] collected from several points in these districts, along with those from *Tabernaemontana*,[4)] *Leuconotis*,[5)] and pyrrolizidine alkaloids from *Parsonsia*.[6)] *Alstonia villosa* BIL. is indigenous to northern Australia and Java, Indonesia, and villalstonine, one of the dimer alkaloids, was reported in 1934 from a plant sample collected in Australia.[7)] This paper reports on alkaloids isolated from the leaves of *A. villosa* obtained in Sunbawa Island, Indonesia.

The air-dried leaves were percolated with MeOH and the chloroform-soluble fraction of the MeOH extract was further fractionated by column chromatography and preparative TLC. A total of seventeen alkaloids (**1**—**17**) were isolated and their structures characterized principally by NMR and FAB-MS. Among these, ten were identified as known alkaloids, previously obtained from *A. macrophylla* in the Philippines (**1**, **4**—**10**)[1,3)] and Thailand (**2**, **3**).[3)] These known alkaloids were yohimbine-17-*O*-acetate (**1**), vincamajine (**2**), vincamajine-17-*O*-3′,4′,5′-trimethoxybenzoate (**3**), N_4-oxide of **3** (**4**), 19,20α-epoxy-11-methoxyakuammicine (**5**), quaternine (**6**), norquaternine (**7**), 10-methoxy-N_1-methylburnamine-17-*O*-veratrate (**8**), 10-methoxy-N_1-methylburnamine-17-*O*-benzoate (**9**) and 5α,10,11-trimethoxystrictamine (**10**).

The FAB-MS of **11** showed a $[M+H]^+$ peak at *m/z* 367.1658, which was coincident with that of picralinal (**11a**).[2a,c)] The presence of an aldehyde group was confirmed by the signals at δ_H 8.75 (s) and δ_C 197.5 in the ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2). H-15, 19, 21a and 21b were observed at different chemical shifts (−0.29,

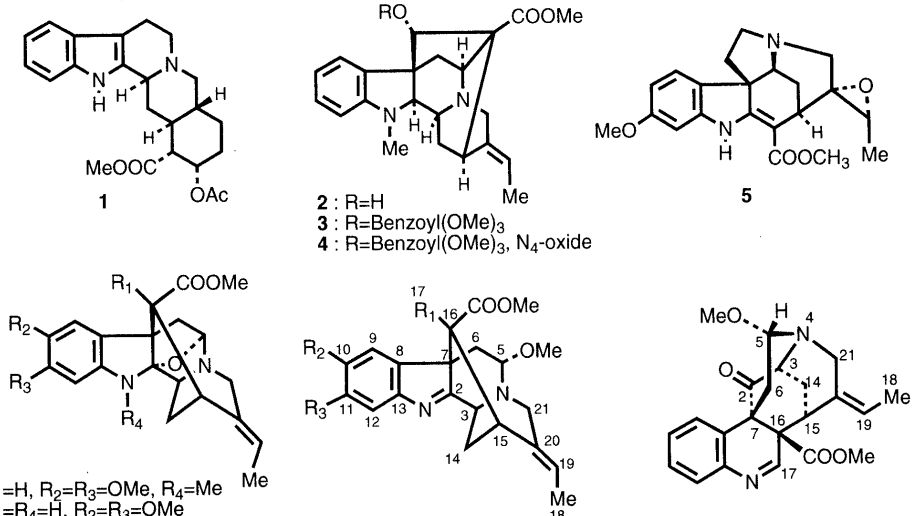

Chart 1

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−0.13, +0.22 and −0.26 ppm, respectively), while the other signals showed similar multiplicity to those of **11a**. Similarly, C-15 and 16 were shifted to lower field (+5.5, and +3.6 ppm, respectively) and C-21 to higher field (−1.9 ppm) in comparison with those of **11a**. Therefore, **11** was considered to be an isomer of **11a** at C-19. Based on cross peaks between H-15/H-19 and H-21a/H-18,H-5 in the two-dimensional (2D) nuclear Overhauser effect (NOE) spectroscopy (NOESY) experiment, **11** was confirmed to be (19*Z*)-picralinal.

Compound **12**, mp 168—173 °C, $C_{31}H_{34}N_2O_8$, showed two geminally coupled proton signals at δ 4.11 and 4.53 (each d, $J=11$ Hz), suggesting the presence of an acylated primary carbinol at C-17. The acyl group was identified as 3,4,5-trimethoxybenzoic acid, based on the singlet signal for two aromatic protons at δ 6.96 (2H, s) and a singlet signal for 9 protons at δ 3.89. Multiplicities in the ^{1}H- and ^{13}C-NMR spectra were similar to those of **11**, except for the chemical shifts of H-15, 17 and C-15, 16, 17, due to the influence of the acid residue at the C-17 hydroxyl group in **12**. Since C-21 and H-21 were observed with almost the same chemical shifts as those of **11**, stereochemistry at C-19 was assigned to be *Z*-type. The structure was thus determined to be (19*Z*)-burnamine-17-*O*-3′,4′,5′-trimethoxybenzoate.

In **13**—**16**, only one olefinic carbon signal was observed in the δ 186—188 region besides indole and ethylidene signals, while the H-3 signal was present at lower field (δ 4.42—4.47), suggesting they were strictamine/akuammiline-type alkaloids with a $N_1=C_2$ linkage. The $[M+H]^+$ peak (*m/z* 381.1817) in FAB-MS suggested **13** had the molecular formula, $C_{22}H_{24}N_2O_4$, 14 mass units larger

Table 1. ^{13}C-NMR Spectral Data for Alkaloids **11**—**17** [δ ppm in $CDCl_3$ (125 MHz)]

	11	**12**	**13**	**14**	**15**	**16**	**17**
2	106.6	107.2	188.6	188.4	185.9	186.0	210.2
3	51.6	51.5	51.0	51.5	51.1	51.2	56.5
5	87.7	87.5	90.7	90.0	90.8	90.9	90.1
6	44.2	44.4	42.5	38.5	42.1	42.2	38.6
7	53.2	52.6	54.9	53.7	55.9	56.0	61.5
8	131.7	133.3	142.3	146.9	145.4	145.6	129.1
9	127.2	127.7	125.5	112.9	114.2	112.9[a]	125.4[a]
10	121.1[a]	121.1	125.7	157.8	157.5	157.7	127.9[a]
11	128.7	127.9	128.8	110.0	111.1	112.4[a]	128.0[a]
12	110.7	111.1	120.9	120.9[a]	120.7	120.9	129.1[a]
13	147.9	148.2	155.9	149.4	149.6	149.6	142.0
14	22.3	21.5	31.6	35.9	31.2	31.2	29.9
15	37.2	40.7	38.8	32.8	37.8	37.8	41.9
16	69.0	58.4	73.0	56.0	60.2	60.7	49.9
17	197.5	67.3	194.9		67.1	66.5	158.6
18	12.9	12.9	13.1	12.9	13.5	13.5	13.1
19	121.6[a]	121.3	121.9	120.8[a]	121.6	121.7	122.1
20	138.0	138.9	138.3	136.8	138.1	138.1	137.9
21	41.7	41.6	44.5	50.4	50.8	50.9	43.9
COOMe	168.4	172.4	168.0	171.6	171.3	171.3	167.6
	52.2	51.2	52.2	51.5	51.7	51.7	51.9
5-OMe			54.7	54.5	54.6	54.7	54.6
10-OMe				55.7	55.1	55.2	
1′		124.3			124.0	129.3	
2′		107.0			106.9	129.5	
3′		152.6			152.7	128.1	
4′		142.3			142.1	132.8	
5′		152.6			152.7	128.1	
6′		107.0			106.9	129.5	
7′		164.6			164.0	164.9	
3′,5′-OMe		56.2			56.2		
4′-OMe		60.9			60.9		

a) Signal assignment may be interchangeable.

Table 2. ^{1}H-NMR Spectral Data for Alkaloids **11**—**17** [δ ppm in $CDCl_3$ (500 MHz)]

	11	**12**	**13**	**14**	**15**	**16**	**17**
3	3.58 (br d, 4)	3.63 (br d, 4)	4.47 (d, 5)[a]	4.42 (d, 5)[a]	4.43 (d, 5)[a]	4.43 (d, 5)	3.65 (d, 5)
5	4.80 (d, 3)[a]	4.76 (d, 2)	3.84 (d, 4)[b,c]	3.85 (d, 4)[b]	3.84 (d, 4)[b]	3.83 (d, 4)	4.07 (d, 3)[a]
6	2.52 (dd, 14, 3)	2.48 (dd, 14, 2)	2.36 (d, 15)	2.18 (d, 15)	2.41 (d, 15)[c]	2.41 (d, 15)	3.01 (d, 16)
	3.05 (d, 14)	3.00 (d, 14)	3.40 (dd, 16, 4)	3.70 (dd, 15, 4)[c]	3.50 (dd, 15, 4)	3.56 (dd, 15, 4)	3.22 (dd, 16, 3)
9	7.55 (d, 7)	7.60 (d, 7)	7.73 (br d, 7)	6.97 (d, 2)[c,d]	7.27 (d, 2)[c,d]	7.28 (d, 2)	7.30—7.38
10	6.89 (t, 7)	6.56 (t, 7)	7.18 (br t, 7)				7.30—7.38
11	7.11 (t, 7)	6.85 (t, 7)	7.33 (br t, 7)	6.84 (dd, 9, 2)[e]	6.54 (dd, 8, 2)[e]	6.60 (dd, 8, 2)	7.30—7.38
12	6.71 (d, 7)	6.69 (d, 7)	7.58 (br d, 7)	7.49 (d, 9)	7.41 (d, 8)	7.41 (d, 8)	7.30—7.38
14	2.04 (ddd, 15, 5, 3)	1.99 (br d, 15)	2.15 (dd, 14, 3)	1.73 (dd, 14, 3)[f]	1.94 (dd, 14, 3)	1.94 (m)	2.00 (dd, 15, 3)
	2.19 (br d, 15)	2.08 (ddd, 15, 5, 3)	2.52 (ddd, 14, 5, 2)	2.64 (ddd, 14, 5, 2)	2.49 (ddd, 14, 5, 2)	2.50 (m)	2.47 (ddd, 15, 5, 3)
15	3.38 (br s)[b]	3.13 (br s)	3.47 (br s)	3.42 (br s)[g]	3.53 (br s)[f]	3.56 (br s)	3.50 (br s)[b,c]
16				1.93 (d, 4)[f]			
17	8.75 (s)	4.11 (d, 11)	8.36 (s)		3.65 (d, 11)	3.59 (d, 11)	7.48 (s)[b]
		4.53 (d, 11)			3.80 (d, 11)	3.97 (d, 11)	
18	1.56 (dt, 7, 1)[c]	1.57 (br d, 7)	1.63 (dr d, 6)[d,e]	1.53 (dd, 7, 2)[g]	1.67 (dd, 7, 2)[f]	1.65 (dd, 7, 2)	1.65 (d, 7)[d]
19	5.27 (br q, 7)[b]	5.38 (br q, 7)	5.44 (br q, 6)	5.48 (br q, 7)[h]	5.51 (br q, 7)	5.50 (q, 7)	5.44 (br q, 7)[c]
21a	3.33 (d, 18)[a,c]	3.36 (br d, 18)	3.45 (br d, 17)[d,c]	3.05 (d, 17)[h]	3.11 (d, 17)[b]	3.10 (br d, 17)	3.52 (br d, 16)[a,d]
21b	3.54 (br d, 18)	3.54 (br d, 18)	3.82 (br d, 17)[e]	4.04 (dd, 17, 2)	4.10 (br d, 17)	4.09 (br d, 17)	3.83 (br d, 16)
COOMe	3.73 (s)	3.68 (s)	3.82 (s)	3.69 (s)	3.73 (s)	3.66 (s)	3.58 (s)
5-OMe			3.22 (s)[a,b]	3.20 (s)[a,b]	3.19 (s)[a]	3.19 (s)	3.32 (s)
10-OMe				3.77 (s)[d,e]	3.42 (s)[d,e]	3.55 (s)	
Acyl							
2′,6′		6.96 (s)			6.96 (s)	7.68 (br d, 8)	
4′						7.51 (t, 8)	
3′, 5′						7.35 (br t, 8)	
OMe		3.89 (s, 3′, 4′, 5′)			3.92 (s, 3′, 5′)		
					3.89 (s, 4′)		

a–*h*) NOE was observed between these signals in the difference (DIF)-NOE or 2D-NOESY spectra.

than **11**. Besides similar chemical shifts and coupling patterns to those of **11** in ^{1}H-NMR and ^{1}H–^{1}H correlation spectroscopy (COSY), one methoxy proton signal (δ 3.22) showed a cross peak to the ^{13}C-signal at δ 90.7, which showed further correlation to H-21a (^3J) and H-6a (^2J) by heteronuclear multiple-bond correlation (HMBC) spectroscopy. Therefore, the methoxy group was located at C-5. The ^{1}H-signal at δ 4.80 (d, J=3 Hz) was assignable to H-5β by its small coupling constant, as already observed in **11**. Of the two protons at C-5, only H-5β can be placed in close proximity to H-21a (*pro-S*), one of the methylene protons at C-21. Based on the cross peaks between 5-OMe/H-5, H-5/H-21a, H-21a/H-18 and H-18/COOMe in the NOESY experiment, **13** was determined to be (19*Z*)-16-formyl-5α-methoxystrictamine.

In **14**, one methine proton was observed at δ 1.93 (d, J=4 Hz) which was coupled with H-15 (δ 3.42, br s), and assigned as H-16. Therefore, C-16 was considered to be a secondary carbon bearing a carbomethoxy group. Besides the 5α-methoxy signal at δ 3.20, an additional methoxy group was suggested by the signal at δ 3.77. Since three aromatic protons due to the indole nucleus were observed as ABX type signals, the methoxy group was assigned to C-10 or C-11. The H-9 signal, which has an NOE response to H-6a, was observed in a *m*-coupling pattern (J=2 Hz) and the location of the methoxy group was thus determined to be C-10. The C-19 side chain was assigned as *E*-type based on NOEs between H-18/H-15 and H-19/H-21a. The structure of **14** was thus established to be 5α,10-dimethoxystrictamine.

In the ^{1}H-NMR spectrum of **15**, characteristic proton signals due to 3,4,5-trimethoxybenzoic acid were observed at δ 3.92 (s, 6H), 3.89 (s, 3H) and δ 6.96 (s, 2H), along with a hydroxymethyl group (δ 3.65, 3.80, each d, J=11 Hz), a carbomethoxy (δ 3.73), 5α-methoxy (δ 3.19), 10-methoxy (δ 3.42) and (19*E*)-ethylidene groups, as observed in **14**. The structure of **15**, 17-deacetyl-5α,10-dimethoxyakuammiline-17-*O*-3′,4′,5′-trimethoxybenzoate, was confirmed by the ^3J correlation of the hydroxymethyl protons with the methoxycarbonyl and the acylcarbonyl carbons.

Compound **16** showed quite similar multiplicity to **15** in the ^{1}H- and ^{13}C-NMR spectra, except for the signals due to the trimethoxybenzoyl residue. Five protons due to the benzoyl group were assignable, suggesting that benzoic acid was attached to the 17-hydroxyl, instead of 3,4,5-trimethoxybenzoic acid. The molecular formula of $C_{30}H_{32}N_2O_6$, proposed by FAB-MS also supported the structure.

Compound **17**, mp 260—263 °C, had the same molecular formula as **13**, $C_{22}H_{24}N_2O_4$, based on the $[M+H]^+$ peak at *m/z* 381.1817 in FAB-MS. ^{1}H-NMR, ^{1}H–^{1}H and ^{13}C–^{1}H COSY measurements suggested the presence of four aromatic protons due to the indole moiety (δ 7.30—7.38), one methoxy group at C-5α (δ 3.32), an ethylidene (H-18: δ 1.65, d, J=7 Hz; H-19: δ 5.44, br q, J=7 Hz) and carbomethoxy protons (δ 3.58). ^{1}H–^{1}H Couplings from H-3 to H-15 through H-14 were also observed. In the ^{13}C-NMR spectrum, no signal corresponding to the formyl carbon in **13** (δ 194.9) nor C-2 in **13**—**16** (δ 185—189) was observed, while the presence of one carbonyl carbon and one olefinic carbon was shown by the signals at δ 210.2 and δ 158.6, respectively. Based on ^3J correlation of the carbonyl carbon with H-6a and H-14a in HMBC, the carbonyl group was located to C-2. On the other hand, eight of nine olefinic carbon signals were assignable to the aromatic ring of the indole nucleus and the ethylidene group. The remaining one was considered to be due to the $-N_1=CH-$ linkage, which can be formed by the coupling between the N_1-residue and the formyl group at C-16 in alkaloids such as **11** or **13**. The HMBC correlation of the signal at δ 7.48, assignable for the $-N_1=CH-$ structure, was observed to C-7, 13, 15 (^3J) and to C-16 (^2J). The NOESY measurement showed the proximity of H-21a to H-5β and H-18. Therefore, **17** was considered to be a dihydro-

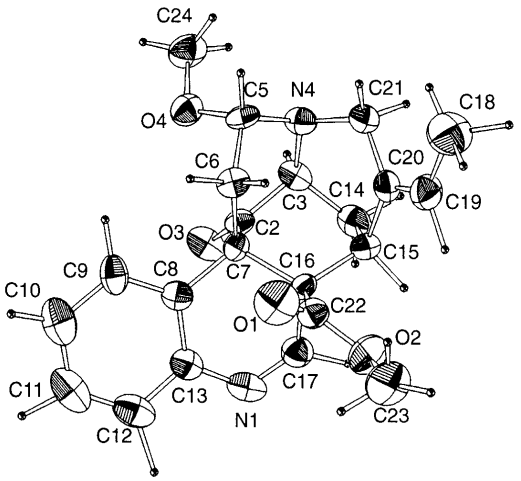

Fig. 1. ORTEP Drawing of **17**

Table 3. Positional Parameters and B_{eq} for **17**

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
O1	1.3634 (6)	0.4538 (4)	0.1092 (3)	5.29 (14)
O2	1.2544 (7)	0.4121 (4)	−0.0047 (3)	4.97 (13)
O3	0.9484 (5)	0.2119 (3)	0.2363 (3)	3.81 (11)
O4	0.9354 (5)	0.4044 (3)	0.3345 (2)	3.47 (10)
N1	1.2252 (7)	0.1911 (3)	0.0947 (3)	4.02 (14)
N4	0.8108 (6)	0.4530 (3)	0.2189 (3)	3.01 (11)
C2	0.9537 (7)	0.2943 (3)	0.2140 (3)	2.53 (12)
C3	0.8004 (7)	0.3509 (4)	0.1927 (4)	3.05 (14)
C5	0.9491 (7)	0.4681 (4)	0.2719 (3)	2.86 (13)
C6	1.1170 (7)	0.4479 (4)	0.2335 (3)	2.88 (13)
C7	1.1172 (7)	0.3468 (4)	0.1938 (3)	2.30 (12)
C8	1.2635 (7)	0.2818 (4)	0.2164 (3)	2.85 (13)
C9	1.3410 (8)	0.2872 (4)	0.2871 (4)	3.56 (15)
C10	1.4699 (8)	0.2224 (5)	0.3071 (5)	4.57 (18)
C11	1.5193 (9)	0.1526 (5)	0.2540 (5)	4.75 (18)
C12	1.4412 (9)	0.1457 (5)	0.1835 (4)	4.42 (18)
C13	1.3107 (8)	0.2074 (4)	0.1646 (3)	3.17 (14)
C14	0.7949 (8)	0.3437 (4)	0.1055 (4)	3.62 (16)
C15	0.9421 (8)	0.4005 (4)	0.0730 (3)	3.06 (14)
C16	1.1091 (7)	0.3577 (4)	0.1034 (3)	2.51 (12)
C17	1.1338 (8)	0.2571 (4)	0.0689 (3)	3.41 (15)
C18	0.9570 (13)	0.6843 (5)	0.0591 (5)	6.09 (25)
C19	0.9754 (9)	0.5776 (4)	0.0458 (4)	3.89 (16)
C20	0.9153 (8)	0.5081 (4)	0.0897 (3)	3.05 (14)
C21	0.8017 (8)	0.5259 (4)	0.1572 (3)	3.22 (15)
C22	1.2580 (8)	0.4158 (4)	0.0722 (3)	3.19 (14)
C23	1.3819 (13)	0.4677 (6)	−0.0441 (5)	6.80 (26)
C24	0.7868 (10)	0.4169 (5)	0.3782 (4)	4.42 (18)

quinoline alkaloid having 5α-methoxyl and 19*Z*-ethylidene groups. The structure was finally confirmed by X-ray analysis as shown in Fig. 1.

Investigation of the indole alkaloids from *A. villosa* collected on Sunbawa Island revealed a similar alkaloid pattern to those from *A. macrophylla* in the Philippines and Thailand. However, villalstonine, the only reported alkaloid from *A. villosa*,[7] was not obtained by the described procedure. It is a characteristic feature that *A. villosa* from Sunbawa contains several 19*Z*-type alkaloids. Among several quinoline-type alkaloids in Apocynaceae,[8] **17** is a (19*Z*)-5α-methoxy-homologue of rhazimine from *Melodinus actiflorus*.[9] The results of anti-malarial activity studies on some of the alkaloids from this plant will be described elsewhere.

Experimental

Melting points were measured on a hot stage and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were measured on JEOL GX-400 and JNM-A500 spectrometers in $CDCl_3$ unless otherwise noted. Chemical shifts are given in δ values, relative to internal tetramethylsilane, and the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. FAB-MS were recorded on a JEOL HX-110 spectrometer. Optical rotations were measured on a JASCO-DIP 360 polarimeter. UV spectra were recorded in MeOH on a Shimadzu 200S double beam spectrometer. The following solvent systems were used for column chromatography and TLC, 1: $CHCl_3$–MeOH–H_2O (8 : 1 : 1.6—2 : 1 : 1.2, bottom layer), 2: hexane–EtOAc (5 : 1—1 : 3), 3: benzene–acetone (2 : 1—1 : 2), 4: EtOAc–MeOH–H_2O (10 : 1 : 1.2—6 : 1 : 1.2, top layer). Spray reagent for TLC: Dragendorff's reagent.

Extraction and Isolation Air-dried leaves of *Alstonia villosa* Bɪʟ. (1.4 kg), collected on Sunbawa Island, Indonesia in August, 1996 (Sample No. 8044LK by H. Shibuya) were percolated with MeOH. The MeOH solution was concentrated to 1 l *in vacuo* and diluted with 1 l of H_2O. After removing the deposit by filtration, the filtrate was partitioned with $CHCl_3$. The $CHCl_3$ soluble extract (20.6 g) was subjected to column chromatography on a silica gel column with solvent 1, and fractions containing alkaloids were monitored by Dragendorff's reagent. The fractions were further purified by chromatography on a silica gel column with solvent systems 2, 3, or 4, to afford 17 alkaloids. Some alkaloids were further purified by preparative TLC; **1** (44 mg), **2** (28 mg), **3** (200 mg), **4** (10 mg), **5** (13 mg), **6** (17 mg), **7** (13 mg), **8** (200 mg), **9** (90 mg), **10** (56 mg), **11** (17 mg), **12** (47 mg), **13** (26 mg), **14** (79 mg), **15** (100 mg), **16** (8 mg), and **17** (12 mg).

(19*Z*)-Picralinal (**11**): Solid, $[\alpha]_D^{28}$ −144.3° (*c* = 0.85, MeOH), UV λ_{max} nm (log ε): 208 (4.67), 230 (4.40), 290 (4.10). FAB-MS *m/z*: 367.1657 ($[M+H]^+$, Calcd for $C_{21}H_{23}N_2O_4$: 367.1658).

(19*Z*)-Burnamine-17-*O*-3′,4′,5′-trimethoxybenzoate (**12**): Prisms, mp 168—173 °C, $[\alpha]_D^{28}$ −199.2° (*c* = 1.12, MeOH), UV λ_{max} nm (log ε): 213 (4.59), 265 (4.04), 293 (3.83). FAB-MS *m/z*: 563.2390 ($[M+H]^+$, Calcd for $C_{31}H_{35}N_2O_8$: 563.2394).

(19*Z*)-16-Formyl-5α-methoxystrictamine (**13**): Solid, $[\alpha]_D^{25}$ −18.4° (*c* = 0.065, MeOH), UV λ_{max} nm (log ε): 217 (4.18), 230 (sh, 4.09), 297 (3.65). FAB-MS *m/z*: 381.1817 ($[M+H]^+$, Calcd for $C_{22}H_{25}N_2O_4$: 381.1815).

5α,10-Dimethoxystrictamine (**14**): Solid, $[\alpha]_D^{29}$ −71.8° (*c* = 1.23, MeOH), UV λ_{max} nm (log ε): 207 (4.31), 220 (sh, 4.24), 285 (3.87). FAB-MS *m/z*: 383.1974 ($[M+H]^+$, Calcd for $C_{22}H_{27}N_2O_4$: 383.1970).

17-Deacetyl-5α,10-dimethoxyakuammiline-17-*O*-3′,4′,5′-trimethoxybenzoate (**15**): Prisms, mp 190—192 °C, $[\alpha]_D^{25}$ −213.0° (*c* = 0.82, $CHCl_3$), UV λ_{max} nm (log ε): 218 (4.71), 279 (4.22), 300 (sh, 4.13). FAB-MS *m/z*: 607.2656 ($[M+H]^+$, Calcd for $C_{33}H_{39}N_2O_9$: 607.2656).

17-Deacetyl-5α,10-dimethoxyakuammiline-17-*O*-benzoate (**16**): Solid, $[\alpha]_D^{20}$ −169.7° (*c* = 0.38, MeOH), FAB-MS *m/z*: 517.2341 ($[M+H]^+$, Calcd for $C_{30}H_{33}N_2O_6$: 517.2338).

(19*Z*)-5α-Methoxyrhazimine (**17**): Prisms, mp 260—263 °C, $[\alpha]_D^{29}$ +366.6° (*c* = 0.06, $CHCl_3$), UV λ_{max} nm (log ε): 224 (4.24), 270 (3.79), 290 (sh, 3.72), FAB-MS *m/z*: 381.1817 ($[M+H]^+$, Calcd for $C_{22}H_{25}N_2O_4$: 381.1815).

X-Ray Crystallographic Analysis of 17 Crystal data of **17** were $C_{22}H_{24}N_2O_4$, M = 380.44, orthorhombic, $P2_12_12_1$, a = 8.018(1) Å, b = 13.848(2) Å, c = 17.345(2) Å, V = 1925.8(5) Å^3, Z = 4, D_{calc} = 1.31 g/cm^3. The reflection data were collected on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Cu$K\alpha$ radiation (λ = 1.5418 Å) with the ω–2θ scan technique to a maximum θ of 60°. A total of 1672 reflections were collected. The structure was solved by the direct method using MULTAN 11/82. All atomic parameters, with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms, were refined by a block-diagonal least-squares method using 1556 reflections with $F > 3.0\sigma(F)$. The final R value was 0.061.

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