

# Alschomine and Isoalschomine, New Alkaloids from the Leaves of *Alstonia scholaris*<sup>1)</sup>

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A new indole alkaloid, named alschomine, was obtained from the leaves of *Alstonia scholaris* planted in Taipei, along with its C-5 isomer, isoalschomine, and the known alkaloids of this plant, picrinine, picralinal and nareline. The structure of alschomine was determined by X-ray analysis, supported by spectral considerations.

**Keywords** *Alstonia scholaris*; Apocynaceae; indole alkaloid; alschomine; 4,5-secopicrinine; X-ray analysis

*Alstonia scholaris* R. BR. is grown widely in South-East Asian and South Asian districts. Many alkaloids have been isolated from the bark, root, leaves and flowers. As for the constituents of the leaves, ten alkaloids are known.<sup>2–5)</sup> As a part of our studies on the constituents of Apocynaceae plants, we examined the alkaloids from the leaves of *Alstonia scholaris* planted in Taipei. This paper deals with the structure elucidation of alschomine and isoalschomine, new secopicrinine-type alkaloids.

When the air-dried leaves of *A. scholaris* were percolated with MeOH and the MeOH percolate was partitioned with benzene and CHCl<sub>3</sub>, the benzene- and CHCl<sub>3</sub>-soluble fractions were found by thin layer chromatography (TLC) to contain several alkaloids. Each fraction was then subjected to column chromatography to isolate five alkaloids as crystals (compounds 1–5), of which three were identified as picrinine (1),<sup>2)</sup> picralinal (2)<sup>3)</sup> and nareline (3),<sup>4)</sup> respectively, on the basis of the physical constants, the proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra, the

carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR) spectra and the mass spectra (MS).

The <sup>1</sup>H-NMR spectrum of 4 showed the signals of four protons of a di-substituted benzene ring, an ethylidene side chain and a carbomethoxyl group as in 1, 2 and 3, along with a singlet peak at  $\delta$  3.00 due to one methoxyl group. Since a singlet peak at  $\delta$  7.49 was assignable to an olefinic proton and a strong absorption maximum was observed at 287 nm in the ultraviolet (UV) spectrum, 4 seemed to retain the 19,21(4)-diene system. In the <sup>1</sup>H–<sup>1</sup>H correlation spectroscopy (COSY) measurement, cross peaks were observed between H-15/H-16, H-15/H-14a,b and H-14a,b/H-3 as observed in that of 1, suggesting the presence of a cyclohexane ring composed of C-2, C-3, C-14, C-15, C-16 and C-7. In the <sup>13</sup>C-NMR spectrum, C-5 of 4 was observed in the acetal carbon region ( $\delta$  104.4) with a large downfield shift in comparison with that of 1. A proton signal at  $\delta$  5.01, showing a coupling to the methylene protons at C-6, was assigned to H-5, based on the cross peak to C-5 in the

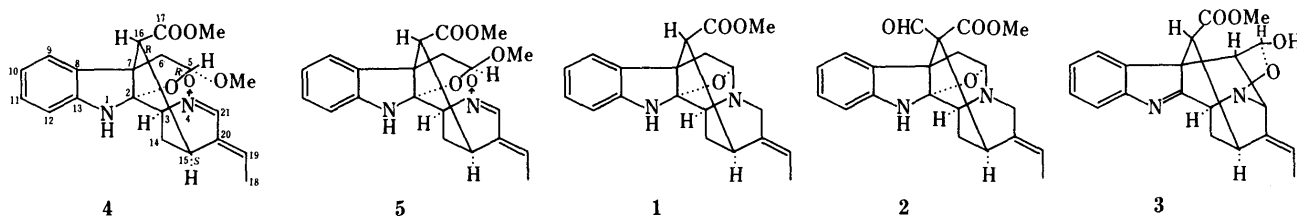


Chart 1

TABLE I. <sup>1</sup>H Chemical Shifts of 1–5 [ $\delta$  (ppm) from TMS in CDCl<sub>3</sub>–CD<sub>3</sub>OD (J/Hz in Parentheses)]

	2 <sup>a)</sup>	3	1 <sup>a)</sup>	4	5
H-3	3.57 (brs)	4.57 (t, 3)	3.58 (d, 5)	4.28 (t, 2)	4.24 (brs)
H-5	4.81 (d, 2)	4.18 (s)	4.81 (d, 2)	5.01 (d, 5)	4.83 (dd, 6, 5)
H-6	2.47 (dd, 14, 2), 3.54 (d, 14)	3.74 (d, 3)	2.25 (dd, 14, 2), 3.41 (d, 14)	2.59 (dd, 15, 5), 2.72 (d, 15)	2.29 (dd, 14, 5), 3.04 (dd, 14, 6)
H-9	7.32 (d, 7)	7.77 (d, 7)	7.13 (d, 7)	6.98 (d, 7)	7.05 (d, 7)
H-10	6.88 (t, 7)	7.29 (t, 7)	6.78 (t, 7)	6.76 (t, 7)	6.77 (t, 7)
H-11	7.11 (t, 7)	7.45 (t, 7)	7.07 (t, 7)	7.08 (t, 7)	7.12 (t, 7)
H-12	6.70 (d, 7)	7.66 (d, 7)	6.74 (d, 7)	6.72 (d, 7)	6.72 (d, 7)
H-14	1.98 (ddd, 14, 3, 2), 2.24 (dd, 14, 2)	2.14 (dd, 14, 3), 1.85 (dd, 14, 3), 2.36 (dd, 14, 2)	2.13 (ddd, 14, 5, 3)	2.18 (dt, 14, 4), 2.30 (dt, 14, 2)	2.2–2.3
H-15	3.67 (brs)	3.41 (q, 3)	3.27 (brs)	3.34 (brs)	3.38 (brs)
H-16		2.35 (d, 2)	2.44 (d, 2)	2.66 (d, 3)	2.63 (d, 3)
H-18	1.50 (dd, 7, 2)	1.73 (d, 7)	1.48 (dd, 7, 2)	1.80 (d, 7)	1.80 (d, 8)
H-19	5.40 (q, 7)	5.86 (q, 7)	5.40 (q, 7)	6.12 (q, 7)	6.10 (q, 8)
H-21	3.11 (d, 18), 3.80 (dd, 18, 2)	4.13 (d, 3)	3.08 (br d, 18), 3.74 (dt, 18, 2)	7.49 (s)	7.44 (s)
–COOMe	3.69	3.75	3.65	3.74	3.73
Others	8.57 (–CHO)			3.00 (–OMe)	3.39 (–OMe)

a) Dissolved in CDCl<sub>3</sub>.

TABLE II.  $^{13}\text{C}$  Chemical Shifts of 1–5 ( $\delta$  (ppm) from TMS in  $\text{CDCl}_3$ – $\text{CD}_3\text{OD}$ )

	2 <sup>a)</sup>	3	1 <sup>a)</sup>	4	5
C-2	106.1	184.4	106.3	103.8	102.1
C-3	51.8	62.1	52.0	68.1	67.8
C-5	87.4	99.6	87.4	104.4	106.3
C-6	43.6	55.4	40.6	40.7	39.8
C-7	53.6	55.0	51.2	52.4	53.1
C-8	136.8	138.9	135.3 <sup>b)</sup>	135.6	134.4
C-9	126.1	125.0	125.0	121.9	122.3
C-10	121.5	125.6	120.7	119.4	119.5
C-11	128.7	128.5	127.9	127.7	128.4
C-12	110.7	119.8	110.6	109.8	110.3
C-13	148.6	156.2	147.6	144.3	145.1
C-14	22.6	34.5	26.1	29.2	29.9
C-15	31.7	31.9	31.1	26.8	27.2
C-16	65.4	53.3	51.9	52.9	52.6
C-17	168.2	170.5	172.6	171.2	171.1
C-18	12.8	11.6	12.7	13.9	13.9
C-19	120.6	122.6	120.2	136.1	135.2
C-20	131.9	130.1	136.5 <sup>b)</sup>	129.4	129.6
C-21	43.6	65.1	46.4	140.4	139.7
–COOMe	52.4	51.0	51.3	51.2	51.2
	197.2			53.7	56.3
(–CHO)				(–OMe)	(–OMe)

a) Dissolved in  $\text{CDCl}_3$ . b) Signal assignments marked b) may be reversed.

$^{13}\text{C}$ – $^1\text{H}$  COSY. In the long-range  $^{13}\text{C}$ – $^1\text{H}$  COSY spectrum, a cross peak was observed between C-5 and the methoxyl protons, and the presence of an acetal structure was confirmed. Based on the cross peaks between H-9/H-6 $\alpha$ , H-6 $\alpha$ /5-OCH<sub>3</sub> and 5-OCH<sub>3</sub>/H-5 in the two-dimensional nuclear Overhauser effect (NOESY) spectrum of **4**, the orientation of the methoxyl group at C-5 was assignable as  $\alpha$  (C-5: *R*), and the 19,21(4)-diene system with 19,20-*E* configuration was also confirmed by the cross peaks between H-18/H-15 and H-19/H-21. Since an  $\text{M}^+ + \text{Na}$  peak was observed at  $m/z$  407.158 ( $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_5\text{Na}$ ), one extra oxygen was suggested to form the  $\text{N}_4$ -oxide. The structure of **4** was finally confirmed by X-ray analysis, and **4** was named alschomine.

Compound **5** has the same molecular formula as **4** and showed similar features to **4** in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, except for the H-5 peak which was observed as a doublet of doublets ( $J=6, 5\text{ Hz}$ ), suggesting **5** to be the isomer of **4** at C-5. Compound **5** was named isoalschomine.

Following the isolation of **3**,<sup>4)</sup> **4** and **5** are the second and third examples of 4,5-secopicrinine-type alkaloids from *Alstonia scholaris*.

#### Experimental

Melting points were taken on a hot stage and are uncorrected.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a JEOL GX-400 spectrometer in  $\text{CDCl}_3$ – $\text{CD}_3\text{OD}$  unless otherwise mentioned. Chemical shifts are given in  $\delta$  values referred to internal tetramethylsilane (TMS), and the following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet, dd=doublet of doublets, brd=broad doublet. Electron impact (EI)-MS and fast atom bombardment (FAB)-MS were recorded on a JEOL D-300-FD spectrometer. Optical rotations were measured on a JASCO DIP 360 polarimeter. The UV spectra were taken in MeOH on a Shimadzu 200S double-beam spectrometer. The following solvent systems were employed for silica gel column chromatography and TLC: solvent 1,  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  (bottom layer); solvent 2, AcOEt–MeOH– $\text{H}_2\text{O}$  (top layer for column, or 4:1:0.5 for TLC). TLC plates were heated until the spots appeared after being sprayed with 5% *p*-dimethylaminobenzaldehyde in

TABLE III. Atomic Parameters ( $\times 10^4$ ) and Equivalent Thermal Parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
O2A	7566 (2)	890 (1)	2599 (3)	3.33 (6)
O4A	6038 (2)	1403 (1)	3397 (4)	4.14 (8)
O5A	7891 (2)	229 (1)	4135 (4)	4.44 (8)
O17A	9681 (3)	1589 (1)	6255 (5)	6.31 (11)
O17'A	9753 (2)	2371 (1)	5625 (4)	4.88 (9)
N1A	8324 (2)	1390 (1)	868 (4)	3.18 (8)
N4A	6691 (2)	1655 (1)	3775 (4)	3.25 (8)
C2A	7934 (2)	1359 (1)	2390 (5)	2.80 (9)
C3A	7278 (3)	1759 (1)	2490 (5)	3.09 (9)
C5A	7681 (3)	715 (1)	4161 (5)	3.35 (10)
C6A	8370 (3)	1018 (2)	4907 (5)	3.58 (11)
C7A	8649 (2)	1375 (1)	3608 (5)	2.92 (9)
C8A	9353 (2)	1188 (1)	2606 (5)	3.18 (10)
C9A	10140 (3)	1050 (2)	3026 (6)	4.05 (12)
C10A	10709 (3)	942 (2)	1861 (8)	5.32 (15)
C11A	10482 (3)	979 (2)	288 (7)	5.22 (14)
C12A	9688 (3)	1106 (2)	–164 (6)	4.62 (13)
C13A	9128 (3)	1212 (1)	1018 (5)	3.45 (10)
C14A	7659 (3)	2262 (1)	2763 (5)	3.12 (10)
C15A	8116 (3)	2249 (1)	4342 (5)	3.17 (10)
C16A	8863 (2)	1903 (1)	4108 (5)	2.95 (9)
C17A	9458 (3)	1925 (2)	5461 (6)	3.81 (11)
C18A	8194 (4)	2530 (2)	7981 (6)	5.23 (14)
C19A	7573 (3)	2218 (2)	7166 (5)	3.98 (11)
C20A	7532 (3)	2099 (1)	5642 (5)	3.31 (10)
C21A	6828 (3)	1810 (2)	5197 (5)	3.73 (11)
C22A	7216 (3)	–83 (2)	3708 (9)	6.16 (18)
C23A	10312 (3)	2449 (2)	6938 (8)	6.80 (18)
O2B	5271 (2)	1667 (1)	7454 (3)	2.94 (6)
O4B	6835 (2)	1228 (1)	8576 (4)	3.83 (7)
O5B	4788 (2)	2296 (1)	8981 (4)	4.30 (8)
O17B	3073 (2)	810 (1)	10635 (4)	4.93 (9)
O17'B	3076 (2)	57 (1)	9669 (4)	4.07 (7)
N1B	4710 (2)	1127 (1)	5562 (4)	3.07 (8)
N4B	6193 (2)	948 (1)	8815 (4)	2.97 (8)
C2B	4995 (2)	1180 (1)	7155 (5)	2.62 (9)
C3B	5710 (2)	818 (1)	7408 (5)	2.88 (9)
C5B	5039 (3)	1826 (1)	9009 (5)	3.47 (10)
C6B	4348 (2)	1486 (1)	9554 (5)	3.02 (9)
C7B	4215 (2)	1125 (1)	8201 (5)	2.61 (9)
C8B	3551 (2)	1279 (1)	7031 (5)	2.99 (9)
C9B	2724 (3)	1375 (1)	7264 (6)	3.94 (11)
C10B	2240 (3)	1457 (2)	5937 (7)	5.11 (14)
C11B	2570 (3)	1437 (2)	4443 (7)	5.33 (14)
C12B	3395 (3)	1344 (2)	4212 (6)	4.41 (12)
C13B	3883 (2)	1261 (1)	5532 (5)	3.12 (10)
C14B	5400 (2)	296 (1)	7610 (5)	3.14 (9)
C15B	4837 (3)	282 (1)	9048 (5)	3.24 (10)
C16B	4056 (2)	579 (1)	8617 (5)	2.67 (9)
C17B	3365 (2)	513 (1)	9760 (5)	3.19 (10)
C18B	4502 (4)	18 (2)	12592 (7)	6.90 (19)
C19B	5147 (3)	354 (2)	11970 (6)	4.35 (12)
C20B	5297 (3)	469 (1)	10457 (5)	3.31 (10)
C21B	5991 (3)	786 (1)	10202 (5)	3.27 (10)
C22B	5464 (3)	2631 (2)	8687 (7)	4.93 (14)
C23B	2406 (3)	–75 (2)	10706 (7)	5.20 (14)

diluted  $\text{H}_2\text{SO}_4$ .

**Extraction and Isolation of Alkaloids** Air-dried leaves of *Alstonia scholaris* R. BR. (550 g) collected in January 1988, at Taipei, R.O.C., were powdered and percolated with MeOH. The MeOH percolate was concentrated *in vacuo* to 0.5 l and  $\text{H}_2\text{O}$  (0.5 l) was added. The mixture was filtered and the filtrate was extracted with benzene and then  $\text{CHCl}_3$ . Each fraction was evaporated *in vacuo* to give the residue (1.4 g and 1.0 g). The insoluble fraction separated by filtration of the MeOH– $\text{H}_2\text{O}$  mixture was stirred with 10% HOAc in MeOH– $\text{H}_2\text{O}$  (1:1) and filtered. The filtrate was alkalinized with  $\text{NH}_4\text{OH}$  and extracted with  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  extract (0.7 g) showed the same pattern as the original  $\text{CHCl}_3$  extract on TLC, and

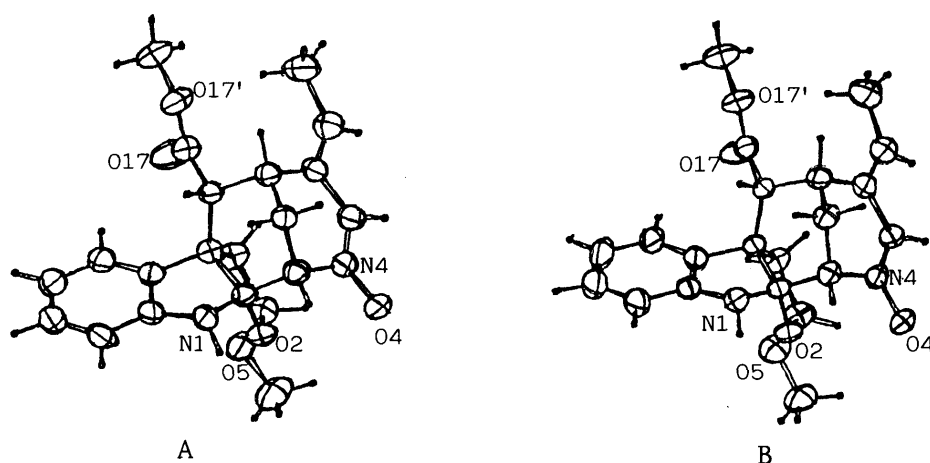


Fig. 1. Perspective View of the Crystal Structure of 4

TABLE IV. Bond Lengths (Å)

O2A-C2A	1.432 (5)	O2A-C5A	1.427 (5)
O4A-N4A	1.309 (4)	O5A-C5A	1.388 (5)
O5A-C22A	1.442 (6)	O17A-C17A	1.198 (6)
O17'A-C17A	1.325 (5)	O17'A-C23A	1.457 (7)
N1A-C2A	1.445 (5)	N1A-C13A	1.407 (5)
N4A-C3A	1.482 (5)	N4A-C21A	1.303 (6)
C2A-C3A	1.537 (6)	C2A-C7A	1.561 (6)
C3A-C14A	1.533 (5)	C5A-C6A	1.536 (6)
C6A-C7A	1.547 (6)	C7A-C8A	1.519 (6)
C7A-C16A	1.553 (5)	C8A-C9A	1.384 (6)
C8A-C13A	1.401 (6)	C9A-C10A	1.390 (8)
C10A-C11A	1.393 (9)	C11A-C12A	1.396 (7)
C12A-C13A	1.389 (7)	C14A-C15A	1.537 (6)
C15A-C16A	1.557 (6)	C15A-C20A	1.516 (6)
C16A-C17A	1.508 (6)	C18A-C19A	1.498 (7)
C19A-C20A	1.339 (6)	C20A-C21A	1.446 (6)
O2B-C2B	1.436 (4)	O2B-C5B	1.443 (5)
O4B-N4B	1.315 (4)	O5B-C5B	1.357 (5)
O5B-C22B	1.458 (6)	O17B-C17B	1.203 (5)
O17'B-C17B	1.342 (5)	O17'B-C23B	1.449 (6)
N1B-C2B	1.440 (5)	N1B-C13B	1.398 (5)
N4B-C3B	1.477 (5)	N4B-C21B	1.304 (6)
C2B-C3B	1.546 (5)	C2B-C7B	1.560 (5)
C3B-C14B	1.532 (5)	C5B-C6B	1.535 (6)
C6B-C7B	1.536 (6)	C7B-C8B	1.531 (6)
C7B-C16B	1.562 (5)	C8B-C9B	1.387 (6)
C8B-C13B	1.387 (6)	C9B-C10B	1.395 (8)
C10B-C11B	1.381 (9)	C11B-C12B	1.384 (7)
C12B-C13B	1.396 (7)	C14B-C15B	1.530 (6)
C15B-C16B	1.557 (6)	C15B-C20B	1.505 (6)
C16B-C17B	1.499 (6)	C18B-C19B	1.497 (8)
C19B-C20B	1.348 (7)	C20B-C21B	1.445 (6)

TABLE V. Bond Angle (°)

C2A-O2A-C5A	111.4 (3)	C5A-O5A-C22A	113.0 (3)
C17A-O17'A-C23A	116.2 (4)	C2A-N1A-C13A	107.9 (3)
O4A-N4A-C3A	116.5 (3)	O4A-N4A-C21A	122.8 (4)
C3A-N4A-C21A	120.8 (3)	O2A-C2A-N1A	110.5 (3)
O2A-C2A-C3A	110.1 (3)	O2A-C2A-C7A	104.8 (3)
N1A-C2A-C3A	108.2 (3)	N1A-C2A-C7A	105.4 (3)
C3A-C2A-C7A	117.6 (3)	N4A-C3A-C2A	110.6 (3)
N4A-C3A-C14A	108.9 (3)	C2A-C3A-C14A	107.5 (3)
O2A-C5A-O5A	110.2 (4)	O2A-C5A-C6A	107.3 (3)
O5A-C5A-C6A	110.5 (3)	C5A-C6A-C7A	105.3 (3)
C2A-C7A-C6A	103.7 (3)	C2A-C7A-C8A	100.5 (3)
C2A-C7A-C16A	112.1 (3)	C6A-C7A-C8A	114.1 (3)
C6A-C7A-C16A	117.6 (3)	C8A-C7A-C16A	107.5 (3)
C7A-C8A-C9A	130.3 (4)	C7A-C8A-C13A	109.2 (4)
C9A-C8A-C13A	120.3 (4)	C8A-C9A-C10A	119.5 (5)
C9A-C10A-C11A	119.6 (5)	C10A-C11A-C12A	122.0 (5)
C11A-C12A-C13A	117.5 (5)	N1A-C13A-C8A	110.4 (4)
N1A-C13A-C12A	128.3 (4)	C8A-C13A-C12A	121.1 (4)
C3A-C14A-C15A	107.9 (3)	C14A-C15A-C16A	106.3 (3)
C14A-C15A-C20A	109.9 (3)	C16A-C15A-C20A	114.7 (3)
C7A-C16A-C15A	115.5 (3)	C7A-C16A-C17A	113.0 (3)
C15A-C16A-C17A	112.5 (3)	O17A-C17A-O17'A	122.9 (4)
O17A-C17A-C16A	126.5 (4)	O17'A-C17A-C16A	110.5 (4)
C18A-C19A-C20A	128.5 (4)	C15A-C20A-C19A	127.5 (4)
C15A-C20A-C21A	117.2 (4)	C19A-C20A-C21A	115.2 (4)
N4A-C21A-C20A	124.0 (4)	C2B-O2B-C5B	111.3 (3)
C5B-O5B-C22B	112.0 (3)	C17B-O17'B-C23B	117.6 (4)
C2B-N1B-C13B	107.6 (3)	O4B-N4B-C3B	116.1 (3)
O4B-N4B-C21B	122.8 (3)	C3B-N4B-C21B	121.1 (3)
O2B-C2B-N1B	111.2 (3)	O2B-C2B-C3B	109.8 (3)
O2B-C2B-C7B	104.1 (3)	N1B-C2B-C3B	108.1 (3)
N1B-C2B-C7B	105.3 (3)	C3B-C2B-C7B	118.2 (3)
N4B-C3B-C2B	111.1 (3)	N4B-C3B-C14B	108.1 (3)
C2B-C3B-C14B	111.6 (3)	O2B-C5B-O5B	110.5 (3)
O2B-C5B-C6B	106.6 (3)	O5B-C5B-C6B	111.2 (3)
C5B-C6B-C7B	105.7 (3)	C2B-C7B-C6B	104.5 (3)
C2B-C7B-C8B	100.3 (3)	C2B-C7B-C16B	111.0 (3)
C6B-C7B-C8B	114.1 (3)	C6B-C7B-C16B	118.3 (3)
C8B-C7B-C16B	107.2 (3)	C7B-C8B-C9B	130.3 (4)
C7B-C8B-C13B	108.2 (3)	C9B-C8B-C13B	121.2 (4)
C8B-C9B-C10B	117.7 (5)	C9B-C10B-C11B	121.2 (5)
C10B-C11B-C12B	121.1 (5)	C11B-C12B-C13B	118.1 (5)
N1B-C13B-C8B	111.7 (4)	N1B-C13B-C12B	127.4 (4)
C8B-C13B-C12B	120.8 (4)	C3B-C14B-C15B	108.2 (3)
C14B-C15B-C16B	106.8 (3)	C14B-C15B-C20B	109.2 (3)
C16B-C15B-C20B	114.6 (3)	C7B-C16B-C15B	114.9 (3)
C7B-C16B-C17B	112.8 (3)	C15B-C16B-C17B	113.4 (3)
O17B-C17B-O17'B	122.0 (4)	O17B-C17B-C16B	128.1 (4)
O17'B-C17B-C16B	109.9 (3)	C18B-C19B-C20B	127.6 (5)
C15B-C20B-C19B	126.2 (4)	C15B-C20B-C21B	118.5 (4)
C19B-C20B-C21B	115.3 (4)	N4B-C21B-C20B	122.7 (4)

they were combined.

The benzene and  $\text{CHCl}_3$  extracts were separately chromatographed on silica gel columns with solvent 1 (7:1:2—7:2:1) and the corresponding alkaloids (1—5) from the two extracts were combined. Compounds 1—5 were further chromatographed on a silica gel column with solvent 2 (20:1:10—10:1:10), and crystallized from MeOH or EtOAc-hexane.

**Picrinine (1)** Prisms from MeOH (85 mg), mp 221—227 °C (dec.).  $[\alpha]_D^{27} -74.3^\circ$  ( $c=0.27$ , MeOH). UV  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 234 (3.86), 286 (3.49). EI-MS  $m/z$ : 338.164 ( $\text{M}^+$ , Calcd for  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_3$  338.163). (Lit. mp 223—225 °C (dec.),  $[\alpha]_D -42^\circ$  ( $\text{CHCl}_3$ )<sup>21</sup>).

**Picralinal (2)** Prisms from EtOAc-hexane (20 mg), mp 150—155 °C (dec.).  $[\alpha]_D^{25} -169^\circ$  ( $c=0.35$ , MeOH). UV  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 234 (3.86), 286 (3.49). FAB-MS  $m/z$ : 367.167 ( $\text{M}^+ + 1$ , Calcd for  $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_4$  367.166). (Lit. mp 179—180 °C,  $[\alpha]_D -179.7^\circ$  ( $\text{CHCl}_3$ ),<sup>31</sup> mp 154—155 °C<sup>41</sup>).

**Nareline (3)** Prisms from MeOH (19 mg), mp 260—270 °C (dec.).  $[\alpha]_D^{26} -96.3^\circ$  ( $c=0.22$ , pyridine). UV  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 256 (3.57). EI-MS  $m/z$ : 352.142 ( $\text{M}^+$ , Calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4$  352.142). (Lit. mp 275 °C,  $[\alpha]_D -88^\circ$  (pyridine)<sup>41</sup>).

**Alscomine (4)** Prisms from MeOH (37 mg), mp 233–240 °C (dec.).  $[\alpha]_D^{27} +116.1^\circ$  ( $c=0.25$ , MeOH). UV  $\lambda_{\max}$  nm (log  $\epsilon$ ): 237 (3.81), 287 (4.16). FAB-MS  $m/z$ : 407.158 ( $M^+ + Na$ , Calcd for  $C_{21}H_{24}N_2O_5Na$  407.158).

**Isoalscomine (5)** Prisms from MeOH, mp 220–230 °C (dec.).  $[\alpha]_D^{27} +112.3^\circ$  ( $c=0.14$ , MeOH). UV  $\lambda_{\max}$  nm (log  $\epsilon$ ): 236 (3.67), 286 (4.12). EI-MS  $m/z$ : 384.168 ( $M^+$ , Calcd for  $C_{21}H_{24}N_2O_5$  384.169).

**Crystal Data for 4**  $C_{21}H_{24}N_2O_5$ ,  $M_r=384.4$ , orthorhombic, space group  $P2_12_12_1$ ,  $a=16.305(3)$ ,  $b=27.483(5)$ ,  $c=8.510(1)\text{\AA}$ ,  $V=3813.4\text{\AA}^3$ ,  $Z=8$ ,  $D_c=1.339\text{ g/cm}^3$ ,  $F(000)=1632$ ,  $\mu$  for  $CuK\alpha=0.751\text{ mm}^{-1}$ . Intensities were collected on the Enraf-Nonius CAD4F-11 diffractometer using the  $\omega$ - $2\theta$  scan mode with graphite-monochromated  $CuK\alpha$  radiation up to  $\theta=60^\circ$ ; 2920 unique reflections with  $I>2.33\sigma(I)$  were used for refinement. 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 matrix least-squares method. The final  $R$  value was 0.043. Two crystallographically independent molecules (A and B) were observed in the unit cell and showed the same configuration and conformation as each other.

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