Monoterpene Alkaloids from *Kopsia pauciflora*

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Six new monoterpene alkaloids, kinabalurines A−F (**1**−**6**), were obtained from an EtOH extract of the leaves of *Kopsia pauciflora*. The structures of the alkaloids were established by spectral analysis and chemical correlations and, in the case of kinabalurines A (**1**) and D (**4**), by X-ray crystallographic analysis.

The genus *Kopsia* (Apocynaceae) comprises some 30 species of shrubs and trees and is distributed mainly in Southeast Asia, although some scattered species are found in India and China.[1,2] About 17 *Kopsia* species occur in Malaysia. The phytochemistry of this genus has received considerable attention, which has resulted in a number of new natural products with intriguing structures as well as useful bioactivities.[3−11] For instance, we recently reported the structure and novel bioactivity of two new indoles, pauciflorines A and B, isolated from the leaves of *Kopsia pauciflora* Hook. f., a species native to North Borneo, which have been found to be potent inhibitors of melanin biosynthesis.[3] We have also reported the presence of the lundurines,[4] members of a new class of indoles having an unusual hexacyclic structure incorporating a cyclopropyl unit, of which one has been found to be a potent antimelanoma substance from *Kopsia tenuis* (Kam, T. S. and Koyano, T.; unpublished data), and we have also recently reported the isolation of the tenuisines, new dimeric indoles of a novel structure type possessing a C_2 axis from the same plant.[7] We now wish to report the structures of several new monoterpene alkaloids obtained from *Kopsia pauciflora*.

Results and Discussion

The monoterpene alkaloids, kinabalurines A−F (**1**−**6**), were obtained from the leaf extract of *Kopsia pauciflora*, which also furnished a number of new indole alkaloids.[3] Kinabalurine A (**1**), was obtained as colorless plates, mp 92−93 °C, $[\alpha]_D$ +26° (*c* 0.35, $CHCl_3$). The mass spectrum showed a molecular ion at *m*/*z* 183 ($C_{11}H_{21}NO$), with other significant fragments due to loss of H (*m*/*z* 182), CH_3 (*m*/*z* 168), and OH (*m*/*z* 166) from the parent ion. The presence of characteristic fragments at *m*/*z* 84, 58, and 44 indicated a skytanthine-type alkaloid.[10] The IR spectrum showed the presence of a hydroxyl group (3355 cm^{-1}), which was supported by the presence of an OH absorption at δ 3.27 in the ^{1}H-NMR spectrum. The ^{13}C-NMR spectrum accounted for all 11 carbon atoms, and the presence of an oxymethine was confirmed by the resonance at δ 80.0. Other significant peaks in the ^{1}H-NMR spectrum included a pair of three-proton doublets at δ 0.97 and 1.06 corresponding to two CH_3CH− groups and an *N*-methyl singlet at δ 2.25. The spectral data thus suggested that kinabalurine A (**1**) is a hydroxyskytanthine derivative.[12] Further support for this was provided by COSY and HETCOR experiments, which indicated that hydroxy substitution is at C-7 and which allowed the full assignments of the NMR spectral data (Tables 1 and 2). COSY experiments also showed the presence of long-range *W* coupling between H-1 and H-3, which is possible only if both hydrogens are α. The stereochemistry of H-9 was deduced to be α from the $J_{1\beta-9}$ value of 10 Hz requiring that H-9 and H-1β be in a *trans*-diaxial arrangement, an arrangement possible only if H-9 is α. The NMR data, however, were insufficient to establish the stereochemistry completely and unequivocally, and as a result, the structure was established by X-ray analysis (Figure 1), which revealed the structure as shown in **1**.[13]

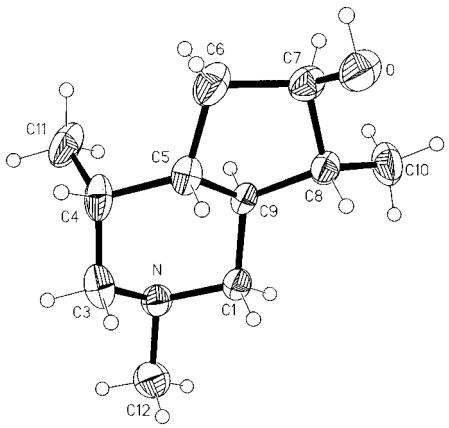

Figure 1. Perspective diagram of kinabalurine A (**1**).

The second new monoterpene in the series is kinabalurine B (**2**), which was obtained in minute amounts as a light yellow oil, $[\alpha]_D$ −100° (*c* 0.025, $CHCl_3$). The mass spectrum showed a molecular ion at *m*/*z* 181 ($C_{11}H_{19}NO$) differing from **1** by the loss of two hydrogens, thereby suggesting it was an oxo-derivative. This was supported by an IR absorption band at 1741 cm^{-1}, which is consistent with a ketonic function in a five-membered ring. Further confirmation was provided by the ^{1}H- and ^{13}C-NMR spectral data, which were generally similar to those of **1** except for the absence of the lowfield oxymethine peak in the ^{1}H-NMR spectrum and the appearance of a ketonic carbonyl absorption instead at δ 219.1 in place of the C-7 oxymethine resonance in ^{13}C-NMR. These observations suggested that **2** is the 7-oxo derivative of **1** which is confirmed when oxidation (PCC) of **1** gave a product similar in all respects to **2**. Kinabalurine C (**3**), $[\alpha]_D$ +25° (*c* 0.09, $CHCl_3$), showed a molecular ion at *m*/*z* 167 ($C_{10}H_{17}NO$), differing from compound **2** by replacement of an *N*-methyl substituent

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Table 1. ^{1}H-NMR Spectral Data for Compounds **1**−**6** ($CDCl_3$)[a]

H	1	2	3[b]	4	5	6[b]
1b	1.62 t (10)	1.73 m	2.45 t (12)	2.86 dd (10.5, 2.5)	2.98 br d (11)	2.89 br dd (10.5, 2.5)
1a	2.96 m	3.09 br d (10)	3.28 dd (12, 4)	1.70 t (10.5)	1.90 t (10.5)	1.85 t (10.5)
3b	2.06 dd (11, 3.5)	2.21 dd (11, 3.5)	2.89 dd (12.5, 3)	2.69 br d (11)	2.82 br d (11)	2.85 dd (11, 2)
3a	2.69 dt (11, 2)	2.80 br d (11)	2.93 dt (12.5, 1)	2.00 m	2.17 m	1.61 t (11)
4	1.92 m	1.68 m	1.97 m	1.94 m	2.08 m	1.54 m
5	1.69 m	1.94 m	1.90 m	1.55 m	2.08 m	1.03 m
6	1.49 m	1.68 m	1.92 m	1.24 td (12, 6)	2.02 m	1.07 td (12, 6)
6	1.74 m	1.86 m	2.20 m	2.12 dt (12, 3.5)	2.02 m	2.38 m
7	3.86 m			3.84 td (6, 2)		3.87 td (6, 2)
8	1.35 m	2.04 m	1.72 dq (12.4)	1.94 m	2.33 m	1.95 m
9	1.30 m	2.19 m	1.56 qd (12, 4)	2.15 m	2.21 m	1.90 m
*N*Me	2.25 s	2.28 s		2.25 s	2.30 s	2.32 s
8-Me	1.06 d (7)	1.05 d (7)	1.03 d (7)	0.84 d (7)	0.98 d (7)	0.85 d (7)
4-Me	0.97 d (7)	1.04 d (7)	1.00 d (7)	1.03 d (7)	1.09 d (7)	0.86 d (7)
7-OH	3.27 br s			*c*		5.41 br s[d]

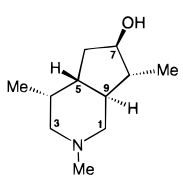
[a] 270 MHz; assignments based on COSY, HMQC, and NOESY. [b] 600 MHz. [c] Not observed. [d] Observed at 233 K.

Table 2. ^{13}C-NMR Spectral Data for Compounds **1**−**6** (67.5 MHz, $CDCl_3$)[a]

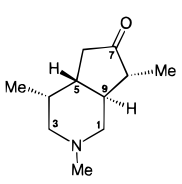
C	1	2	3	4	5	6
1	60.9	60.9	52.9	58.7	57.8	57.2
3	62.9	63.0	51.2	63.3	62.7	63.6
4	30.1	29.8	29.8	30.5	29.7	36.6
5	44.6	42.7	43.2	42.3	40.2	46.5
6	36.7	40.2	40.4	38.1	41.3	39.5
7	80.0	219.1	218.6	81.1	220.3	80.7
8	47.3	48.6	48.3	43.7	44.4	44.1
9	43.8	42.6	43.0	39.8	37.6	44.6
N-Me	46.6	46.7		47.1	46.7	46.1
8-Me	16.4	12.0	11.8	14.7	10.8	14.4
4-Me	12.6	12.5	11.1	13.0	12.3	17.4

[a] Assignments based on HMQC.

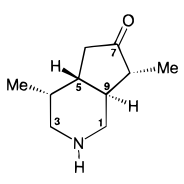
with H. This was supported by the IR spectrum, which showed bands due to NH (3330 cm^{-1}) and ketone (1741 cm^{-1}) functions. Comparison of the NMR spectrum with that of **2** showed that the ketonic carbonyl was still present (δ 218.6), but peaks due to the *N*-methyl group were now absent in both ^{1}H- and ^{13}C-NMR. The ^{13}C-NMR resonances of **3** were, in general, quite similar to those of **2** except for C-1 and C-3, which are α to the nitrogen. The ^{1}H-NMR spectral data could be assigned by the application of COSY, HMQC, and NOE difference experiments, which also confirmed the structure as shown in **3**. The key piece of evidence permitting the establishment of the stereochemistry at positions C-5, C-8, and C-9 was the resonance due to H-9, which was observed as a quartet of doublets (J = 12, 4 Hz). This requires H-9 to be *trans*-diaxial with H-5, H-8, and H-1, which is only possible in a *trans*-ring junction in which H-9 and the 8-methyl group are both α. The stereochemistry of the 4-methyl group was deduced to be α since irradiation of H-9α resulted in NOE enhancement of the 4-methyl signal (in addition to the 8-methyl, H-1α, and H-6α resonances).



1 Kinabalurine A



2 Kinabalurine B



3 Kinabalurine C

Kinabalurine D (**4**) was obtained as a light yellow oil, $[\alpha]_D$ −13° (*c* 0.29, $CHCl_3$). The mass spectrum was similar to that of kinabalurine A (**1**), and the IR spectrum showed the presence of a hydroxyl group (3355 cm^{-1}). The ^{13}C-NMR spectrum was somewhat similar to that of compound **1**, although some slight changes in the chemical shifts were noted. However, in contrast, the ^{1}H-NMR spectrum of **4**, although showing the presence of the same groups, was significantly different from that of **1** with respect to the chemical shifts and multiplicities of the signals. The spectrum could be assigned with the standard 2D techniques but proved insufficient to establish the complete stereochemistry. Repeated attempts at obtaining suitable crystals were unsuccessful. Eventually kinabalurine D (**4**) was converted to its methyl iodide salt (**4a**), which furnished suitable crystals for X-ray analysis. The crystals of **4a** are orthorhombic belonging to the space group $P2_12_12_1$. The structure was solved by the direct method SHELX86[14] and refined by the full-matrix least-squares method. The results are shown in Figure 2, which also represents the absolute configuration.[15] It can be seen that kinabalurine D (**4**) differs from kinabalurine A (**1**) in having a *trans*-ring junction in which the stereochemistry of H-5 and H-9 are now reversed and in which the 4-methyl group is now β.

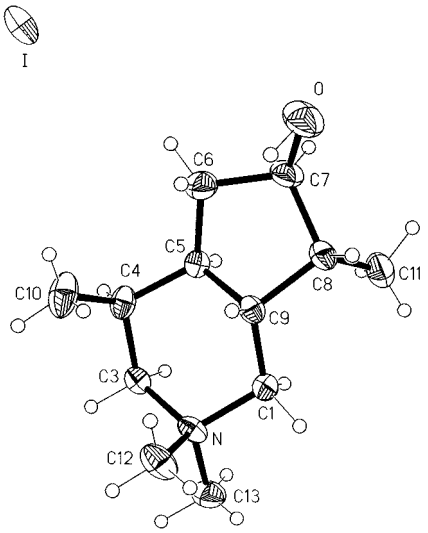
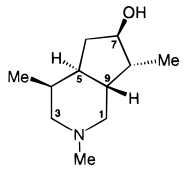


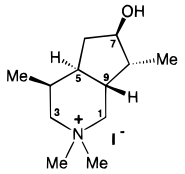
Figure 2. Perspective diagram of compound **4a**.

As in the case of compound **2** versus compound **1**, kinabalurine E (**5**), $[\alpha]_D$ +134° (*c* 0.06, $CHCl_3$), was deduced to be the 7-oxo derivative of **4** by comparison of its spectral data with that of **4** (M^+ *m*/*z* 181; IR 1742 cm^{-1}; general similarity of the NMR data except for the absence of the H-7/C-7 oxymethine signals and the appearance of carbonyl signal at δ_C 220.3) as well as by

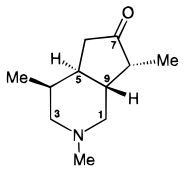
chemical correlation with **4** [oxidation (PCC) of compound **4** gave **5**].



4 Kinabalurine D

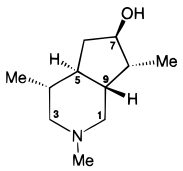


4a

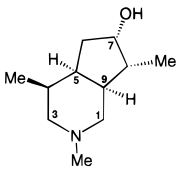


5 Kinabalurine E

Kinabalurine F (**6**) was obtained in trace amounts, $[\alpha]_D$ +56° (*c* 0.025, $CHCl_3$). The mass spectrum gave a M^+ at *m/z* 183. The IR spectrum showed an absorption at 3355 cm^{-1}, and the NMR spectral data showed **6** to be a diastereomer of **1** and **4**. The assignment of the structure of **6** relied on analysis of the NMR data and by comparison with compounds **1** and **4**. It can be seen that in **1** and **4** where the 7-hydroxy group is β, the characteristic C-7 shift is about 80 ppm, whereas in the related compound incarvilline (**7**) (whose structure was also determined by X-ray analysis) and where the 7-hydroxy is α, the C-7 shift is about 73 ppm.[12] Since **6** showed a C-7 shift value of 80.7 ppm, it can be inferred that the 7-hydroxy group is β as in **1** and **4**. The observed NOE interaction from H-7α to 8-methyl and H-6α implies that the 8-methyl also has α stereochemistry. Likewise, the NOE interaction between H-6α and H-5 facilitated the assignment of H-5α. Unfortunately, H-5 and H-9 appeared as multiplets even at 600 MHz, and consequently assignment of the ring junction stereochemistry had to proceed via a more circuitous route. The NOE interaction observed between H-8β with H-1β allowed the assignment of H-1α, which appeared as a triplet with J = 10.5 Hz. This requires H-9 and H-1α to be *trans*-diaxial, an arrangement possible only if H-9 is β. This left the stereochemistry at position 4 to be decided. Unfortunately, H-4 also appeared as a multiplet, and the observed NOEs proved inconclusive in this instance. One of the H-3 resonances was a triplet with J = 11 Hz, while the other appeared as a doublet of doublets with J = 11, 2 Hz. Examination of models showed that this coupling pattern is only consistent with H-4β, resulting in H-4β and H-3α being *trans*-diaxial to each other and thus giving rise to the following J values ($J_{3\alpha-3\beta} = J_{3\alpha-4\beta}$ = 11 Hz; $J_{3\beta-4\beta}$ = 2 Hz). The 4-methyl group of **6** therefore has α stereochemistry.



6 Kinabalurine F



7 Incarvilline

The present study has thus provided definitive structure elucidation for this group of monoterpene alkaloids that are related to skytanthine. Besides the kinabalurines (**1**−**6**), the only previous hydroxyskytanthine derivative reported is incarvilline (**7**) from the Chinese plant *Incarvillea sinensis*.[12] The kinabalurines, together with incarvilline, provide a useful array of stereoisomers in this series with various combinations of ring junction, 7-hydroxy and 4- and 8-methyl group stereochemistry.

Experimental Section

General Experimental Procedures. All melting points were uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Optical rotations were determined on a JASCO DIP-370 digital polarimeter. Mass spectra were obtained on a VG ProSpec spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ using TMS as internal standard on a JEOL JNM-GSX 270 spectrometer at 270 and 67.5 MHz, respectively, and in some cases on a JEOL Lambda-600 spectrometer at 600 MHz.

Plant Material. The plant material was collected in February 1994, at Lahad Datu, Sabah, Malaysia. Herbarium voucher specimens (San 138327) are deposited at the Herbarium of the Sabah Forest Department, Sandakan, Sabah, Malaysia.

Extraction and Isolation. Extraction of the ground leaves was carried out in the usual manner by partitioning the concentrated EtOH extract with dilute acid, as has been described in detail elsewhere.[16,17] The alkaloids were isolated by initial column chromatography on Si gel using $CHCl_3$ with increasing proportions of MeOH followed by rechromatography of appropriate partially resolved fractions using centrifugal TLC. Solvent systems used for centrifugal TLC were $CHCl_3$−MeOH (8:1) and $CHCl_3$−MeOH (7:1). The yields (g kg^{-1}) of alkaloids **1**−**6** were as follows: **1** (0.16), **2** (0.0016), **3** (0.0078), **4** (0.0068), **5** (0.0016), and **6** (0.0009).

Kinabalurine A (**1**): mp 92−93 °C; $[\alpha]_D$ +26° (*c* 0.35, $CHCl_3$); IR (dry film) υ_{max} 3355 cm^{-1} (OH); ^{1}H and ^{13}C NMR, see Tables 1 and 2; EIMS (70 eV) *m/z* [M^+] 183 ($C_{11}H_{21}NO$, 100), 182 (55), 168 (35), 166 (25), 125 (15), 98 (15), 84 (10), 58 (85), 44 (57).

Kinabalurine B (**2**): light yellow oil; $[\alpha]_D$ −100° (*c* 0.025, $CHCl_3$); IR (dry film) υ_{max} 1741 cm^{-1} (C=O); ^{1}H and ^{13}C NMR, see Tables 1 and 2; EIMS (70 eV) *m/z* [M^+] 181 ($C_{11}H_{19}NO$, 100), 180 (65), 166 (15), 153 (8), 125 (8), 110 (15), 98 (70), 84 (15), 58 (75), 44 (90).

Kinabalurine C (**3**): light yellow oil; $[\alpha]_D$ +25° (*c* 0.09, $CHCl_3$); IR (dry film) υ_{max} 3330 (NH) and 1741 (C=O) cm^{-1}; ^{1}H and ^{13}C NMR, see Tables 1 and 2; EIMS (70 eV) *m/z* [M^+] 167 ($C_{10}H_{17}NO$, 100), 152 (17), 139 (10), 124 (11), 110 (15), 96 (25), 84 (45), 70 (15), 55 (75), 44 (95), 30 (65).

Kinabalurine D (**4**): light yellow oil; $[\alpha]_D$ −13° (*c* 0.29, $CHCl_3$); IR (dry film) υ_{max} 3355 cm^{-1} (OH); ^{1}H and ^{13}C NMR, see Tables 1 and 2; EIMS (70 eV) *m/z* [M^+] 183 ($C_{11}H_{21}NO$, 50), 182 (65), 168 (20), 166 (40), 125 (10), 98 (15), 84 (14), 58 (100), 44 (75).

Kinabalurine E (**5**): light yellow oil; $[\alpha]_D$ +134° (*c* 0.06, $CHCl_3$); IR (dry film) υ_{max} 1742 cm^{-1} (C=O); ^{1}H and ^{13}C NMR, see Tables 1 and 2; EIMS (70 eV) *m/z* [M^+] 181 ($C_{11}H_{21}NO$, 100), 180 (65), 166 (35), 153 (10), 124 (8), 98 (60), 84 (15), 58 (55), 44 (85).

Kinabalurine F (**6**): light yellow oil; $[\alpha]_D$ +56° (*c* 0.025, $CHCl_3$); IR (dry film) υ_{max} 3355 cm^{-1} (OH); ^{1}H and ^{13}C NMR, see Tables 1 and 2; EIMS (70 eV) *m/z* [M^+] 183 ($C_{11}H_{21}NO$, 40), 182 (25), 168 (15), 166 (20), 125 (10), 98 (5), 84 (100), 58 (45), 44 (17).

Oxidation of Compounds 1 and 4. Compound **1** (0.044 mmol, 8 mg) was added with stirring to a solution of PCC (0.045 mmol, 9.7 mg) in anhydrous CH_2Cl_2 (5 mL). The resulting mixture was allowed to stand for 1 h at 4 °C, after which the mixture was filtered through

a pad of Si gel. After evaporation of the solvent, the crude product was purified by centrifugal chromatography over Si gel ($CHCl_3$−MeOH, 8:1) to furnish **2** (4 mg, 51%). Oxidation of **4** by the same procedure gave **5** (46%).

Conversion of Kinabalurine D (4) to Its Methyl Iodide Salt (4a). Kinabalurine D (**4**) (0.11 mmol, 20 mg) was added to iodomethane (3.28 mmol, 465 mg) and allowed to stand for 10 min at room temperature. The solvent was then removed under reduced pressure furnishing a residue that on recrystallization from MeOH, gave **4a** (30 mg, 85%), mp 241−242 °C.

X-ray Diffraction Analysis of 1 and 4a. The crystals of kinabalurine A (**1**) are orthorhombic belonging to the space group $P2_12_12_1$, with $a = 6.6193$ (9) Å, $b = 12.904$ (1) Å, $c = 13.364$ (2) Å, $\alpha = \beta = \gamma = 90°$, $V = 1141.4$ (3) Å^3; $D_x = 1.067$ Mg m^{-3} and $Z = 4$. The final R factor was 0.0843. A total of 2367 reflections were collected up to θ_{max} of 24.97° on a CAD4 diffractometer at 27 °C using Mo Kα ($\lambda = 0.710\ 73$ Å). The data were collected by the $\omega - 2\theta$ method, 2005 observed reflections with $I > 2\sigma(I)$, and were corrected for Lorentz-polarization effect but not for absorption. The structure was solved by using the direct method SHELXS86.[15] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares refinement on an IBM 486 PC to $R = 0.0843$, wR = 0.1463 for the observed reflections, $w = [\sigma^2(F_o^2) + (0.0269P)^2 + 0.7900P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were generated geometrically and were allowed to ride on their respective parent atoms. The analysis of **4a** was carried out by the same general procedure. A total of 1432 reflections were collected up to θ_{max} of 24.96°. The data were also collected by the ω−2θ method with 1432 observed reflections with $I > 2\sigma(I)$. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares refinement on an IBM 486 PC to $R = 0.0268$, wR = 0.0618 for the observed reflections, $w = [\sigma^2(F_o^2) + (0.0404P)^2 + 0.0183P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. The atomic coordinates for the non-hydrogen atoms and their equivalent isotropic displacement parameters, calculated coordinates for the hydrogen atoms, anisotropic displacement parameters for the non-hydrogen atoms, a full list of bond distances and angles and the structure factor table are deposited as supplementary material at the Cambridge Crystallographic Data Centre.[18]

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(18) Atomic coordinates, bond distances and angles, and torsional angles have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from Dr. Olga Kennard, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

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