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A FLAVONOID AND INDOLE ALKALOID FROM FLOWERS OF *MURRAYA PANICULATA*

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Key Word Index—*Murraya paniculata*; Rutaceae; flowers; flavonoid; alkaloid; murrayaculatine.

Abstract—A new naturally occurring flavonoid, 3,5,7,3′,4′,5′-hexamethoxyflavone, and a new indole alkaloid, murrayaculatine, were isolated and characterized from the fresh flower of *Murraya paniculata*.

INTRODUCTION

In previous papers [1, 2], we reported the isolation and structural identification of coumarins, flavonoids, aryl acids, alkaloids and an unidentified compound **a** from the chloroform fraction of fresh flowers of *Murraya paniculata*. Further examination of the butanol fraction of this species led to the isolation of a new alkaloid, murrayaculatine (**3**). The present paper deals with the structural elucidation of the previously unidentified compound **a**(**1**) and murrayaculatine (**3**).

RESULTS AND DISCUSSION

Compound **a**(**1**) showed a $[M]^+$ at *m/z* 402.1314, indicating a molecular formula of $C_{21}H_{22}O_8$. The presence of a flavonoid nucleus was suggested by its UV and IR spectra. In the ^1H NMR spectrum of **1**, four aromatic protons appeared at δ6.35, 6.50 (each 1H, *d*, $J = 2.2$ Hz, H-6 and H-8) and δ7.36 (2H, *s*, H-2′ and H-6′) and six methoxy groups at δ3.88 (3H, *s*), 3.91 (3H, *s*), 3.93 (3H, *s*), 3.94 (6H, *s*) and 3.97 (3H, *s*). Methylation of myricetin (**2**) with excess MeI in the presence of dry K_2CO_3 afforded a crystalline compound whose spectral data and mp were identical with those of compound **a**(**1**). Based on these results, the structure of **1** was assigned as 3,5,7,3′,4′,5′-hexamethoxyflavone. This is the first report of the occurrence of **1** in nature, although Rao *et al.* synthesized it in 1979 [3].

Murrayaculatine (**3**) was obtained as optically active needles. The molecular formula $C_{10}H_9NO_3$ was established by HR-mass spectrometry. The presence of an indoline nucleus was suggested by UV absorption maxima at 208.6, 255.0, 266.4(sh) and 289 nm [4], coupled with IR bands at 3375(NH), 1620 and 1475 (aromatic C =C) cm^{-1}. This assumption was substantiated by the ^1H NMR spectrum of **3**, in which the following characteristic signals were observed: (i) four mutually coupling aromatic protons at δ7.30 (1H, *br d*, $J = 7.6$ Hz, H-4), 7.19 (1H, *td*, $J = 7.6$, 1.0 Hz, H-5), 6.93 (1H, *td*, $J = 7.6$, 1.0 Hz, H-6) and 6.86 (1H, *dd*, $J = 7.6$, 1.0 Hz, H-7); (ii) a NH proton at δ9.24 (1H, *br s*, exchangeable with D_2O). The presence of a hydroxy group at C-2 and an epoxy group between C-2 and C-3 was inferred by a hydroxy proton at δ5.0 (1H, *s*, exchangeable with D_2O) in the ^1H NMR spectrum, together with two oxygenated carbons at δ116.1 (*s*, C-2) and 74.8 (*s*, C-3) in the ^{13}C NMR spectrum. On the other hand, an AB-type quartet signal at δ3.08 and 3.31 (each 1H, *d*, $J = 16.6$ Hz, H_2-1′) in the ^1H NMR spectrum, IR bands at 3375, 1730 and 1710 cm^{-1}, together with a methylene carbon at δ51.1 and a carbonyl carbon at δ181.1 in the ^{13}C NMR spectrum and the mass fragment ion peak at *m/z* 207 $[M]^+$, 163 $[M - CO_2H]^+$ and 148 $[M - CH_2CO_2H]^+$ indicated the presence of an ethanolic acid side-chain in the molecule. Furthermore, a ^1H–^1H NOESY experiment was conducted (Fig. 1). The results showed that H-1′ correlated with H-4 (δ7.30), indicating that the ethanolic acid group is located at C-3. The ^1H detected heteronuclear multiple bond connectivity (HMBC) spectrum of **3** (Fig. 2) showed the presence of significant correlations between C-3 (δ_C74.8) and H-1′ (δ_H3.08 and 3.31), and C-2′ (δ_C181.1) and H-1′ (δ_H3.31), respectively. On the basis of the above results, we assigned the structure **3** for murrayaculatine; the stereochemistry remains to be determined. This is the first report of the occurrence of an epoxy group in an indole alkaloid from a natural source.

EXPERIMENTAL

Mps: uncorr. ^1H NMR (200 and 400 MHz) were recorded in $CDCl_3$ except where noted. Chemical shifts are given in δ with TMS as int. standard. MS were recorded

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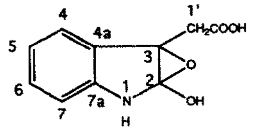
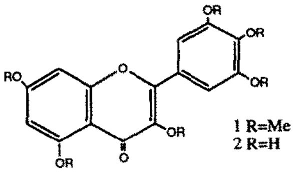


3



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2 R=H

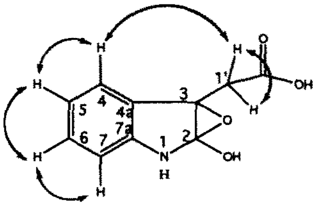

Fig. 1. NOESY spectrum of murrayaculatine (3).

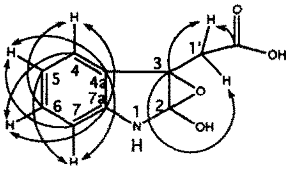

Fig. 2. HMBC spectrum (8 Hz) of murrayaculatine (3).

using a direct inlet system. UV were determined in MeOH, IR in KBr discs.

Extraction and separation. Procedures for extraction and separation of **a**(**1**) from fresh flowers of *M. paniculata* are described in ref. [2]. The BuOH extract was concd and the ppt. collected and identified as scopolin. The filtrate was evapd to afford a brown viscous residue. This was chromatographed on a silica gel column using a gradient of $CHCl_3$-MeOH as eluent to give 46 frs. Frs 10–11 were combined and recrystallized from Me_2CO to afford scopoletin (0.2 g). Frs 13–15 were combined and rechromatographed on a silica gel column and eluted with $CHCl_3$–MeOH (9:1) to obtain **3** (2.7 mg).

3,5,7,3′,4′,5′-Hexamethoxyflavone (**1**). Needles, mp 148–150° (MeOH). HRMS: calcd. for $C_{21}H_{22}O_8$ $[M]^+$ 402.1314; found: 402.1314. UV λ_{max} nm: 238.8, 262, 302.4 and 334.8. IR ν_{max} cm^{-1}: 1622, 1600, 1574, 1506. EI-MS *m/z* (rel. int.): 402 ($[M]^+$, 100), 401 (47), 387 (91), 383 (12), 371 (30), 369 (14), 359 (15), 187 (24).

Methylation of myricetin (**2**). Myricetin (**2**, 5 mg) was dissolved in dried Me_2CO (15 ml) and refluxed with MeI (2 ml) in the presence of dry K_2CO_3 (3 g) for 14 hr. The reaction mixt. was worked-up in the usual way to give needles identical to **1** by comparison of spectral data and mmp.

Murrayaculatine (**3**). Needles, mp 168–170° (Me_2CO). $[\alpha]_D$ +17.2° (MeOH; *c* 0.027). HR-MS: calcd. for $C_{10}H_9O_4N$ $[M]^+$ 207.0532; found: 207.0532. UV λ_{max} nm: 208.6, 255.0, 266.4 (sh), 289.0. IR ν_{max} cm^{-1}: 3375, 1730, 1710, 1620, 1475. EI-MS *m/z* (rel. int.): 207 ($[M]^+$, 20), 163 (47), 162 (66), 148 (100), 120 (77), 119 (22), 92 (30). ^{13}C NMR (CD_3OD, 100 MHz): δ51.1 (*t*, C-1′), 74.8 (*s*, C-3), 111.2 (*d*, C-7), 116.1 (*s*, C-2), 123.4 (*d*, C-5), 124.8 (*d*, C-4), 130.7 (*d*, C-4), 132.3 (*s*, C-4a), 143.6 (*s*, C-7a), 181.1 (*s*, C-2′).

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