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J. Nat. Prod., **1994**, 57 (2), 291-293 • DOI:
10.1021/np50104a015 • Publication Date (Web): 01 July 2004

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TWO POLYMETHOXYLATED FLAVONES FROM *DISTEMONANTHUS BENTHAMIANUS*

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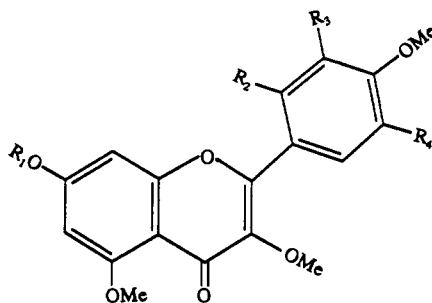
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ABSTRACT.—A new natural flavanoid, 5'-hydroxy-3,5,7,2',4'-pentamethoxyflavone [**1**], was isolated and identified by spectroscopic methods. The known flavanoid, quercetin-3,5,3',4'-tetramethyl ether [**2**], was identified from this plant for the first time.

Distemonanthus benthamianus Baill. (Caesalpinioideae) is a large rainforest tree of the central African region. Its yellow timber is highly appreciated for heavy construction, and it had proven to be a major source of methoxylated flavones (1-4). In this report, two polymethoxylated flavones **1** and **2** were isolated from the CH₂Cl₂ extract of the heartwood, and their structures were established by spectroscopy as 5'-hydroxy-3,5,7,2',4'-pentamethoxyflavone [**1**] and quercetin-3,5,3',4'-tetramethyl ether [**2**].

Compound **1** was obtained as white crystals. Elemental analyses indicated the molecular formula C₂₀H₂₀O₈, confirmed by molecular ion in the eims at *m/z* 388. Its uv spectrum showed maxima at 252, 298, and 330 nm, consistent with the flavone skeleton (5); this was confirmed by a positive Shinoda test (6). Strong absorption in the ir at 3280 cm⁻¹ indicated that the compound had an OH whose acetylation gave a monoacetate [**3**].

The substitution pattern of **1** was determined from its ¹H nmr and ms. The ¹H nmr showed signals of five methoxyl groups at δ 3.96, 3.94, 3.85, 3.76, and 3.60. At δ 6.38 and 6.47, two doublets (*J*=2.4 Hz) of one proton each were assigned to H-6 and H-8, respectively; signals at δ 6.64 and 6.87 could be assigned to H-3' and H-6', respectively, on the basis of signals observed for flavonol-3-methyl ethers with the 2',4',5'-oxygenated system (7-9). In the eims, the [B₂]⁺ peak corresponding to (ring B+CO) was observed at *m/z* 181, showing that the OH and two methoxyl groups were



	R ₁	R ₂	R ₃	R ₄
1	Me	OMe	H	OH
2	H	H	OMe	H
3	Me	OMe	H	OAc

located in ring B. Upon acetylation the signal at δ 6.87 moved downfield to δ 7.12, showing that the OH occupied position 5'. Therefore, **1** was identified as 5'-hydroxy-3,5,7,2',4'-pentamethoxyflavone. This assignment was supported by additional ¹H-nmr data and the nOe effects (Table 1). This is a new natural flavonoid.

Compound **2** showed an [M]⁺ at *m/z* 358 in its eims, which, together with elemental analysis, established the molecular formula as C₁₉H₁₈O₇. Its uv spectrum (see Experimental), consistent with a flavone skeleton (5), exhibited a bathochromic shift in the major absorption band (band II) of 34 nm with NaOAc, relative to its spectrum in EtOH, which indicated the presence of an OH at the 7 position (10). The ¹H-nmr of **2** revealed three singlets at δ 3.87 (3H), 3.87 (3H), and 3.96 (6H), corresponding to four MeO groups. Protons H-6 and H-8 formed an AB pattern at δ 6.35 and 6.64 (*J*=2.2 Hz). At δ 6.98 (d, *J*=8 Hz), 7.73

TABLE 1. $^1\text{H-Nmr}$ Data and nOe Effects of Compound **1**.

Proton	δ	correlated to
H-6	6.38 (d)	5-OMe and 7-OMe
H-8	6.47 (d)	7-OMe
H-3'	6.66 (s)	2'-OMe and 4'-OMe
H-6'	6.87 (s)	—
3-OMe	3.85 (s)	—
5-OMe	3.94 (s)	H-6
7-OMe	3.76 (s)	H-6 and H-8
2'-OMe	3.96 (s)	H-3'
4'-OMe	3.60 (s)	H-3'

(dd, $J=8$ Hz and 2.2 Hz), 7.78 (d, $J=2.2$ Hz) was observed an AMX system of three protons, respectively assigned to H-5', H-6', and H-2'. In the eims, peaks at m/z 343 $[\text{M}-15]^+$ and m/z 315 $[\text{M}-43]^+$ were diagnostic of a 3-methoxyflavone (11); fragments at $[\text{A}+\text{H}]^+$ at m/z 167 and $[\text{B}_2]^+$ were indicative of one OH and one MeO in ring A and two MeO in ring B. Therefore, **2** was identified as quercetin-3,5,3',4'-tetramethyl ether. This compound has been previously reported as a synthetic product (12).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were determined on digital mp (OSI) apparatus and are uncorrected; ^1H and ^{13}C nmr were measured at 200 MHz and 25 MHz, respectively, in CDCl_3 using TMS as internal standard; chemical shifts are expressed in δ values. Eims data were recorded on a DPO:W 22632 mass spectrometer with electron impact ionization at 70 eV. The elemental analysis was carried out on Hosli's micro combustion apparatus type CHA. The ir spectra in KBr were recorded on a Perkin Elmer 727 B. Si gel GF₂₅₄ (Merck) and Si gel 60 (70–230 mesh ASTM) were used for tlc and cc, respectively, and the spots were visualized by spraying with H_2SO_4 (50%) and heating at 150°.

PLANT MATERIAL.—The plant material (heartwood of *D. benthamianus*) was collected from ESSE, about 70 km from Yaounde, center province of Cameroon, in October 1988 and identified at the National Herbarium in Yaounde, where a voucher specimen is deposited.

EXTRACTION AND ISOLATION.—The finely powdered, sun-dried, heartwood (3.5 kg) was extracted with MeOH in a Soxhlet extractor. Evaporation of the solvent afforded 232 g of the red

residue. Part of this residue (70 g) was re-extracted successively with hexane and CH_2Cl_2 ; 10 g of the CH_2Cl_2 extract was chromatographed on 250 g of Si gel using hexane/EtOAc mixtures and gave **1** (50 mg) and **2** (25 mg).

5'-Hydroxy-3,5,7,2',4'-pentamethoxyflavone [1].—White crystals: mp 215–216°; uv λ max (EtOH)(ϵ) 298 (13260), 300 (3500), 330 (20100); ir (KBr) ν max 3280 (OH), 1620 (C=O), 1580, 1220; eims m/z (%) $[\text{M}]^+$ 388 (25.7), $[\text{M}-\text{OMe}]^+$ 357 (100), $[\text{B}_2]^+$ 181 (23). Anal. calcd for $\text{C}_{20}\text{H}_{20}\text{O}_8$: C 61.85, H 5.19; found C 61.63, H 5.26. ^1H nmr δ 6.87 (1H, s, H-6'), 6.64 (1H, s, H-3'), 6.47 (d, $J=2.4$ Hz, H-8), 6.38 (1H, d, $J=2.4$ Hz, H-6), 3.96 (3H, s, 2'-OMe), 3.94 (3H, s, 5-OMe), 3.85 (3H, s, 3-OMe), 3.76 (3H, s, 7-OMe), 3.60 (3H, s, 4'-OMe); ^{13}C nmr δ 174.2 (s, C-4), 163.5 (s, C-7), 160.9 (s, C-5), 158 (s, C-2), 153.3 (s, C-2'), 151.5 (s, C-9), 151.0 (s, C-4'), 141.9 (s, C-5'), 139.5 (s, C-3), 116.2 (d, C-6'), 111.9 (s, C-1'), 109.6 (s, C-10), 97.2 (d, C-6), 95.6 (d, C-3'), 92.5 (d, C-8), 60.2 (q, OCH₃), 58.8 (q, OCH₃), 58.1 (q, OCH₃), 56.0 (q, OMe), 55.6 (s, OCH₃), 55.6 (s, OCH₃).

5'-Hydroxy-3,5,7,2',4'-pentamethoxyflavone acetate [3].—A solution of 25 mg of **1** in 0.5 ml of pyridine and 0.5 ml of Ac₂O was allowed to stand overnight at room temperature. Usual workup and tlc gave 22 mg of **3**: mp 114°; ir (KBr) ν max 1725 (C=O), 1620 (C=O), 1580 (C=C), 1250 (C-O-C); ^1H nmr δ 7.12 (1H, s, H-6'), 6.62 (1H, s, H-3'), 6.42 (1H, d, $J=2.3$ Hz, H-8), 6.31 (1H, d, $J=2.3$ Hz, H-6), 3.87 (3H, s, OMe), 3.80 (3H, s, OMe), 3.76 (6H, s, 2 OMe), 3.69 (3H, s, OMe).

Quercetin-3,5,3',4'-tetramethyl ether [2].—Yellow crystals: mp 283–284°; uv λ max (EtOH)(ϵ) 248 (15900), 270 (14700), 341 (16500); λ max (EtOH+NaOAc) 282 (band II), 350 (band I); ^1H nmr δ 7.73 (1H, dd, $J=2.2$ Hz and 8.0 Hz, H-6'), 6.64 (1H, d, $J=2.2$ Hz, H-8), 6.35 (1H, d, $J=2.2$ Hz, H-6), 3.96 (6H, s, 2 OMe), 3.87 (3H, s, OMe), 3.85 (3H, s, OMe); eims m/z (%) $[\text{M}]^+$ 358 (100), 357 (58.3), 343 (52.3), 327 (17), 315 (75.7), 311 (11.9), 285 (15.7), 167 (20), 165 (18.6), 95 (15.3). Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{O}_7$: C 63.68, H 5.06; found C 63.48, H 5.11.

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Received 13 May 1993