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CHROMENOFLAVONES FROM *MACARANGA INDICA*

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Key Word Index—*Macaranga indica*; Euphorbiaceae; macaflavone I: 6,7,2,2-dimethylchromeno-8,γ,γ-dimethylallyl-3,3′,4′-trihydroxyflavone; macaflavone II: 6,7,2,2-dimethylchromeno-8,γ,γ-dimethylallyl-3′,4′-dihydroxy-3-methoxyflavone.

Abstract—Two new chromenoflavones, macaflavones I and II, isolated from the leaves of *Macaranga indica*, have been characterized as 6,7,2,2-dimethylchromeno-8,γ,γ-dimethylallyl-3,3′,4′-trihydroxyflavone and 6,7,2,2-dimethylchromeno-8,γ,γ-dimethylallyl-3′,4′-dihydroxy-3-methoxyflavone, respectively, on the basis of UV, ^{1}H NMR and mass spectral data.

INTRODUCTION

The genus *Macaranga* contains 12 species distributed in the Eastern Himalayas and Sikkim, being abundant in Andmans Island and Ceylon. In a broad programme on the flavonoid constituents of plant species, we undertook the chemical examination of the leaves of *Macaranga indica*. There have been no previous reports on the flavonoids of *M. indica*. We have been able to isolate two new flavonols named macaflavone I and macaflavone II.

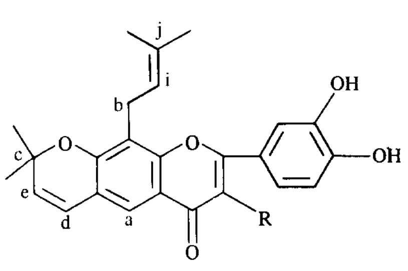
RESULTS AND DISCUSSION

From the acetone extract of the dried leaves of *M. indica* two new flavonoids, macaflavones I (**1**) and II (**2**) were isolated by chromatographic methods. Compound **1** ($C_{25}H_{24}O_6$, mp 165–166°; permethylether, mp 67°) gave a positive Shinoda test for flavonoids and a yellow-green ferric reaction. Its UV spectrum exhibited maxima at 224 and 294 nm. The shift in band I on addition of aluminium chloride and the 20 nm bathochromic shift with NaOAc–H_3BO_3 indicated the presence of a free 3-hydroxyl and an *ortho*-dihydroxy system in ring B [1]. The formation of 3,4-dihydroxybenzoic acid, on alkaline fusion of **1** lead us to conclude that the two hydroxyls in ring B are attached at C-3′ and C-4′.

The ^{1}H NMR spectrum of **1** acetate showed evidence for the presence of a γ,γ-dimethylallyl unit and a 2,2-dimethylchromene ring. The singlet at δ1.42 for six protons and the two doublets at δ5.8 and 6.7 ($J = 11$ Hz) indicated the presence of the dimethylchromene ring. The two three protons singlet at δ1.8 and 1.9, the doublet at δ3.4 ($J = 7$ Hz) for two protons and an olefinic proton multiplet at δ5.2 revealed the presence of a γ,γ-dimethylallyl unit [2–4]. A three protons multiplet centred at δ7.04, analysed as one doublet ($J = 10$ Hz), one *dd* ($J = 10$, 3 Hz), one doublet ($J = 3$ Hz) can be attributed only to the 2′-, 5′- and 6′-protons. The $[M]^+$ m/z 420 (40%) of **1** confirmed the dimethylallyl-dimethylchromeno trihydroxy flavone system. In support of the above observation a fragment ion at m/z 137 (25) for a dihydroxy substituted B-ring was obtained. The peak at m/z 365 could be accounted for by the loss of C_4H_7. A peak at m/z 215 corresponds to an ion arising by R.D.A. from m/z 365, indicating that both the chromene unit and the allyl group are on ring A. Hence the signal at δ7.9 was assigned to H-5. Macaflavone I is therefore assigned the structure as 6,7,2,2-dimethylchromeno-8,γ,γ-dimethylallyl-3,3′,4′-trihydroxyflavone (**1**).

Compound **2** ($C_{26}H_{26}O_6$, mp 96°) showed a brown colour in UV and a yellow-green colour with methanolic ferric chloride. Its UV spectrum exhibited maxima at 225 and 295 nm. A bathochromic shift of 58 nm in band I on addition of sodium methoxide without decrease in intensity suggested the presence of a free 4′-hydroxyl. The lack of degeneration in the spectrum ruled out the possibility of a free 3-hydroxyl (also supported by the absence of a shift with aluminium chloride in band I) [5]. The shift in band I on the addition of NaOAc–H_3BO_3 indicated the presence of an *ortho*-dihydroxy system in ring B. Permethylation with dimethyl sulphate yielded a trimethoxy flavone identical with macaflavone I trimethyl ether.

Comparison of the ^{1}H NMR spectra of the acetates of **1** and **2** (Table 1), showed that compound **2** is macaflavone I 3-methyl ether. The mass spectrum of **2** showed a parent



1 R = OH
2 R = OMe

Table 1. NMR spectra of the acetates of macaflavone I and II (δ)

	Macaflavone I	Macaflavone II
Chromene methyls (c)	1.42 (*s*, 6H)	1.45 (*s*, 6H)
Methyl groups on	1.8 (*s*, 3H)	1.8 (*s*, 3H)
double bond (j)	1.9 (*s*, 3H)	1.7 (*s*, 3H)
Benzylic methylene (b)	3.4 (*d*, J = 7 Hz)	3.4 (*d*, J = 7 Hz)
Acetoxyls	2.3 (*s*, 6H)	2.15 (*s*, 3H)
Acetoxyl	2.5 (*s*, 3H)	2.4 (*s*, 3H)
Olefinic proton (i)	5.2 (*m*, 1H)	5.2 (*m*, 1H)
Chromene proton (d)	5.8 (*d*, J = 11 Hz)	5.8 (*d*, J = 11 Hz)
Chromene proton (e)	6.7 (*d*, J = 11 Hz)	6.65 (*d*, J = 11 Hz)
Aromatic protons	7.4 (*m*, 2H)	6.8 (*m*, 3H)
	6.8 (*d*, J = 10 Hz)	—
5H (a)	7.9 (*s*, 1H)	7.8 (*s*, 1H)
OMe	—	3.8 (*s*, 3H)

peak at m/z 434 (30). The peaks at m/z 379, 215 etc. gave the same pattern of fragmentation as those found in **1**.

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR were recorded at 80 MHz in $CDCl_3$ and DMSO-d_6 (TMS int. standard). TLC was performed on silica gel G (Merck).

Material. M. indica (Rich) was collected from Andmans Island. Voucher specimens are deposited in the Herbarium of the Botany Department, Aligarh Muslim University, Aligarh.

Extraction and isolation. Powdered and dried leaves were successively extracted with *n*-hexane and Me_2CO. The concd Me_2CO extract was chromatographed over silica gel eluting with C_6H_6 and C_6H_6–EtOAc mixtures. TLC examination of C_6H_6–EtOAc (1:7) eluates on silica gel G developed in C_6H_6–pyridine–HCO_2H (36:9:5) [6] revealed the presence of two bands. These were separated by repeated CC (silica gel) followed by prep. TLC on silica gel (C_6H_6–pyridine–HCO_2H, 36:9:5) and crystallization from MeOH. They were designated as macaflavone I and macaflavone II.

Macaflavone I (**1**). Yellow needles, mp 165°; UV λ_{max}^{MeOH} nm: 224, 294; NaOAc–H_3BO_3: 225, 314; $AlCl_3$: 228, 354. MS m/z (rel. int.): $[M]^+$ 420 (40%), 405 (100), 377 (15), 365 (5), 349 (5), 215 (8), 202 (12). **1** was acetylated with Ac_2O in pyridine and the acetate crystallized from $CHCl_3$–*n*-hexane to give white needles, mp 120–121°. Methylation of **1** (Me_2SO_4, Me_2CO, K_2CO_3) yielded 6,7,2,2-dimethylchromeno-8,γ,γ-dimethylallyl-3,3′,4′-trimethoxyflavone, mp 67°.

Macaflavone II (**2**). Light yellow needles, mp 96°; UV λ_{max}^{MeOH} nm: 225, 295; $AlCl_3$: 226, 295; NaOAc–H_3BO_3: 228, 315, MS m/z: 434 (64%), 419 (100), 392 (8), 379 (19), 215 (42). Acetylation of **2** yielded a diacetoxy derivative, mp 89–90°.

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