Pergamon

Phytochemistry, Vol. 49, No. 5, pp. 1425–1426, 1998
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Printed in Great Britain
0031–9422/98/$—see front matter

PII: S0031–9422(97)00799–1

7,3′-DIHYDROXY-4′-METHOXYFLAVONE FROM SEEDS OF *ACACIA FARNESIANA*

Niranjan P. Sahu,* Basudeb Achari and Sukdeb Banerjee

Indian Institute of Chemical Biology, 4 Raja S.C. Mullick Road, Jadavpur, Calcutta 700 032, India

(*Received* 15 *July* 1997)

Key Word Index—*Acacia farnesiana*; leguminosae; seeds; 7,3′-Dihydroxy-4′-methoxyflavone; farnisin; diosmetin; flavones.

Abstract—Besides the known flavone diosmetin and sitosterol glucoside, a new flavone farnisin has been isolated from the seeds of *Acacia farnesiana*. Its structure was established as 7,3′-dihydroxy-4′-methoxyflavone from spectroscopic studies and chemical transformation. © 1998 Elsevier Science Ltd. All rights reserved

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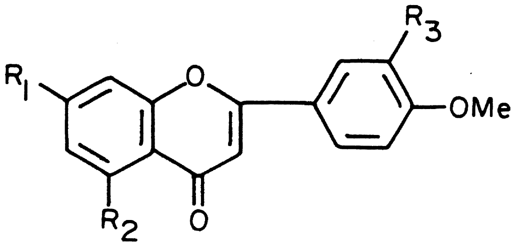
INTRODUCTION

Acacia farnesiana Willd. is a thorny bush or small tree, native to tropical America but extensively cultivated in France for production of the much valued Cassie perfume. It is naturalized in India where it now has a widespread distribution. Different parts of the plant have been used for the treatment of various ailments [1]. Previous chemical investigation on the flowers and pods of the plant have revealed the presence of four homoterpene lactones, flavone glycosides and several polyphenolic compounds [2, 3]. The present paper describes the isolation and structural elucidation of a new flavone, farnisin (**2**), a major constituent of the seeds, together with diosmetin and sitosterol glucoside.



1. $R_1 = R_2 = R_3 = OH$
2. $R_1 = R_3 = OH, R_2 = H$
3. $R_1 = R_3 = OAc, R_2 = H$

RESULTS AND DISCUSSION

The *n*-BuOH soluble fraction of the methanol extract of the defatted seeds of *Acacia farnesiana* on chromatographic purification over a silica gel column furnished two compounds **1** and **2** besides sitosterol glucoside. Both **1** and **2** were found to be flavones from their UV spectra and usual colour reactions. Compound **1**, obtained as an amorphous powder, was identified as diosmetin from its ^{1}H NMR spectrum and comparison of its ^{13}C NMR spectrum with that reported in the literature [4]. Compound **2** proved to be the new flavone, farnisin. The EIMS spectrum of **2** showed the molecular ion peak at *m*/*z* 284. In combination with its ^{13}C NMR spectrum, this suggested the molecular formula to be $C_{16}H_{12}O_5$. The ^{1}H NMR spectrum of **2** showed two low field D_2O exchangeable signals at δ 10.78 and 9.42 assignable to two phenolic hydroxyl groups located at C-7 and C-3′, respectively. In addition, singlets at δ 6.68 (1H) and 3.84 (3H) were attributed to H-3 and 4′-OMe resonances. The remaining aromatic proton signals were suggestive of two 1,2,4-trisubstituted aromatic rings; of these, the double doublet at δ 7.52 (1H, $J = 8, 2$ Hz) and doublets at δ 7.44 (1H, $J = 2$ Hz) and 7.10 (1H, $J = 8$ Hz) could be assigned to H-6′, H-2′ and H-5′, respectively. The most downfield signal (δ 7.90, 1H, *d*, $J = 8.5$ Hz) originated most likely from H-5 which is *peri* to a carbonyl, while signals for H-6 and H-8 partially overlapped to appear as a multiplet centered at δ 6.95.

The absence of hydroxyl groups at C-3 and C-4′ was deduced from the UV spectrum as the position of Bands I and II (found at 235 nm and 338 nm) did not shift on addition of $AlCl_3/HCl$ whereas the presence of a hydroxyl group at C-7 was evident from the bathochromic shift (13 nm) of Band II on addition of

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* Author to whom correspondence should be addressed.

NaOAc to the methanolic solution [5]. Moreover, the ^{1}H NMR spectrum of the derived acetate showed comparatively large deshielding of H-2′, 6′, 8 and 6 signals compared to the rest, confirming that the hydroxyl groups were located at C-7 and C-3′. The ^{13}C NMR spectrum (see Experimental) could also be satisfactorily interpreted on the basis of the assigned structure. The spectrum contained signals due to three oxygenated aromatic carbons (δ 162.1, 150.5 and 146.7) in a flavone skeleton (δ C=O at 176.0). The chemical shift of the carbonyl carbon was suggestive of the absence of a 5-hydroxyl group. Besides, the resonance positions of the A-ring carbons are in good agreement with the values predicted on the basis of a substitution effect of the 7-hydroxyl group in the unsubstituted ring [4]. Similarly, the B-ring carbon resonances are almost identical with those expected for a 3′-hydroxy-4′-methoxy substitution pattern. Thus, from the foregoing evidences the structure of farnisin (**2**) was established unambiguously as 7,3′-dihydroxy-4′-methoxyflavone. It belongs to the rare class of flavones lacking a 5-oxy substituent.

EXPERIMENTAL

Mps are uncorr. TLC was performed on silica gel G (SRL) using the solvent system $CHCl_3$: MeOH : H_2O (80 : 18 : 1). ^{1}H and ^{13}C NMR spectra were determined in DMSO-d_6 with TMS as internal standard at 99.9 MHz for ^{1}H NMR and 25.05 MHz for ^{13}C NMR, respectively. EIMS (70 eV) were recorded using direct inlet.

Plant material

Seeds of *A. farnesiana* Willd. were collected from Muzaffarpur district, Bihar, India, and a voucher specimen of the plant was deposited at the Herbarium of the Institute.

Extraction and isolation

The air-dried powdered seeds of *A. farnesiana* (1 kg) were successively extracted with light petrol (60–80°), $CHCl_3$ and MeOH in a soxhlet extractor. The concd MeOH extract was partitioned between *n*-BuOH and H_2O. The *n*-BuOH extract was washed with H_2O and evaporated under reduced pressure to give a dark brown powder (5.8 g). This solid was taken up in MeOH (150 ml) and filtered. The concd filtrate was kept in the refrigerator for 48 h when crystals separated out, and were identified as D-glucose by PC and specific rotation. The mother liquor was dried to give a dark brown mass (4.6 g), which was chromatographed over a column of silica gel (60 g), elutions being carried out with $CHCl_3$ and $CHCl_3$-MeOH mixtures (19 : 1, 9 : 1, 17 : 3 and 4 : 1) to give 22 fractions.

Diosmetin (*Luteolin* 4′-*methyl ether*) (**1**). The $CHCl_3$-MeOH (19 : 1) fraction was purified further by rechromatography to furnish an amorphous solid (40 mg); ^{1}H NMR: δ 12.94 (1H, *s*, 5-OH), 10.80 (1H, *s*, 7-OH), 9.44 (1H, *s*, 3′-OH), 7.52 (1H, *dd*, $J = 9$, 2 Hz, H-6′), 7.42 (1H, *d*, $J = 2$ Hz, H-2′), 7.08 (1H, *d*, $J = 9$ Hz, H-5′), 6.72 (1H, *s*, 3-H), 6.48 (1H, *d*, $J = 2$ Hz, H-8), 6.22 (1H, *d*, $J = 2$ Hz, H-6) and 3.88 (3H, *s*, 4′-OCH_3). ^{13}C NMR data were identical with the reported literature data [4].

Farnisin (7,3′-*dihydroxy*-4′-*methoxyflavone*) (**2**). The fractions eluted with $CHCl_3$-MeOH (9 : 1) on further purification over silica gel and subsequent crystallization from MeOH furnished pale yellow needles of farnisin (1.2 g), mp 264–265°, UV $\lambda_{\max}^{\mathrm{MeOH}}$ 338, 235; $AlCl_3$ 334, 235; $AlCl_3 + HCl$ 338, 233; NaOMe 375 (reduced intensity), 261; NaOAc 344, 248 nm. EIMS *m/z* (%) 284 (M^+, 48), 253 ($M^+ - OMe$, 12), 238 (24), 226 (10), 212 (18), 176 (100) and 145 (30). ^{1}H NMR as in the text. ^{13}C NMR: δ 176.0 (*s*, C-4), 162.4 (*s*, C-2), 162.1 (*s*, C-7), 157.2 (*s*, C-9), 150.5 (*s*, C-4′), 146.7 (*s*, C-3′),. 126.2 (*d*, C-5), 123.7 (*s*, C-1′), 118.0 (*d*, C-6′), 116.0 (*s*, C-10), 114.6 (*d*, C-6), 112.8 (*d*,C-2′), 112.2 (*d*, C-5′), 105.0 (*d*, C-3), 102.2 (*d*, C-8) and 55.6 (*q*, -OCH_3).

Farnisin diacetate. The diacetate produced by standard procedure crystallized from MeOH as light pink needles, mp 193–194°, ^{1}H NMR: δ 8.10 (1H, *d*, $J = 9$ Hz, 5-H), 8.18 (1H, *dd*, $J = 8$, 2 Hz; H-6′), 7.96 (1H, *d*, $J = 2$ Hz, H-2′), 7.72 (1H, *d*, $J = 2$ Hz, H-8), 7.36 (1H, *d*, $J = 8$ Hz, H-5′), 7.32 (1H, *dd*, $J = 9$, 2 Hz, H-6), 7.00 (1H, *s*, H-3), 3.92 (3H, *s*, 4′-OCH_3), 2.36 (3H, *s*, -$OCOCH_3$) and 2.32 (3H, *s*, -$OCOCH_3$).

Acknowledgements—The authors thank Shri Rajendra Mahato, helper of this department, for collection of the plant material and for some technical assistance.

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