Pergamon

PII: S0031–9422(97)00326–9

Phytochemistry, Vol. 46, No. 3, pp. 591–593, 1997
© 1997 Elsevier Science Ltd. All rights reserved
Printed in Great Britain
0031–9422/97 \$17.00+0.00

AN *O*-GERANYLATED ISOFLAVONE FROM *MILLETTIA GRIFFONIANA**

EMMAUEL YANKEP, Z. T. FOMUM† and ERMIAS DAGNE‡

Department of Organic Chemistry, University of Yaounde I, P.O. Box 812, Yaounde, Cameroon; ‡ Department of Chemistry, Addis Ababa University, P.O. Box 30270, Addis Ababa, Ethiopia

(*Received* 14 *February* 1997)

Key Word Index—*Millettia griffoniana*; Leguminosae; Papilionoideae; isoflavones; chalcones; *O*-geranylated isoflavone.

Abstract—A new *O*-geranylated isoflavone, 3′,4′-methylenedioxy-7-*O*-[(*E*)-3,7-dimethyl-2,6-octadienyl] isoflavone, 7-*O*-geranylpseudobaptigenin, was isolated in addition to seven other known compounds from the root bark of *Millettia griffoniana*. The structure of the new compound was elucidated on the basis of spectroscopic data. © 1997 Elsevier Science Ltd

INTRODUCTION

The genus *Millettia* is widespread in Africa [2] with many of its species exhibiting interesting biological properties [3]. *Millettia* species are known to elaborate isoflavonoids [4]. As part of our continuing investigations on *Millettia* species which are indigenous to Cameroon, we have examined the hexane and chloroform extracts of the stem bark of *M. griffoniana*, a species that grows in the central part of Cameroon. We report here the isolation and structural elucidation of one new 3′,4′-methylenedioxy-7-*O*-[(*E*)-3,7-dimethyl-2,6-octadienyl] isoflavone (**1**) and seven other known compounds namely 7-*O*-geranylformononetin (**2**), calapogonium isoflavone B (**3**), 7-2′-dimethoxy-4′,5′-methylenedioxy isoflavone (**4**), jamaicin (**5**), 4′-*O*-geranylisoliquiritigenin (**6**), durmillone (**7**) and odorantin (**8**).

RESULTS AND DISCUSSION

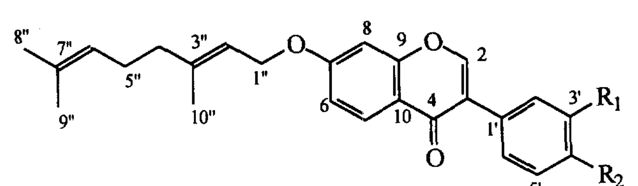
The powdered root bark of *M. griffoniana* was successively extracted with hexane and chloroform at room temperature. On repeated CC over silica gel, with petrol–ethyl acetate gradient elution followed by subsequent PTLC and recrystallization, the hexane extract yielded the compounds: 7-*O*-geranylpseudobaptigenin (**1**), 7-*O*-geranylformononetin (**2**) [5] and calapogonium isoflavone B (**3**) [6], while the chloroform extract after similar treatment gave compounds: 7,2′-dimethoxy-4′,5′-methylenedioxy isoflavone (**4**) [7], jamaicin (**5**) [6], 4′-*O*-geranylisoliquiritigenin (**6**) [5], durmillone (**7**) [6] and odorantin (**8**) [8]. The known compounds were identified by comparison of their spectroscopic data with the literature and by co-TLC with authentic samples.

Compound **1**, obtained as fine crystals, analysed for $C_{26}H_{26}O_5$ (HRMS). It was identified as an isoflavone through its IR (γ_{max} 1637 cm^{-1}), UV (λ_{max} 245, 249 and 295 nm), ^1H NMR (δ 7.89 ppm, *s*, H-2) and ^{13}C NMR (δ 152.1 ppm, C-2) spectra [9]. Its ^{13}C NMR (Table 1) along with the DEPT revealed signals for 26 different carbon atoms corresponding to three methyls, four methylenes, nine methines and 10 quaternary carbons including carbonyl carbon. The ABX pattern with doublets at δ 6.84 and 7.07 ppm (1-H each) and doublets of doublets at δ 6.96 ppm (1H) and two proton singlets at δ 5.97 ppm indicated that ring B of an isoflavone moiety is substituted by a methylenedioxy group at the 3′ and 4′ positions. The presence of a geranyl moiety attached to one of the oxygens was evident from the ^1H and ^{13}C NMR [10] spectra and also from the EIMS in which a fragment ion at *m*/*z* 137 was observed. Furthermore, a set of peaks characteristic of another ABX pattern with an *ortho* coupled doublet at δ 8.17 ppm, a doublet of doublets at δ 6.97 ppm and a *meta* coupled doublet at 6.83 ppm suggested that ring A is unsubstituted at C-5, C-6 and C-8 positions, thus indicating presence of an *O*-geranyl group at C-7. Confirmation of the above assignment for **1** was possible from NOESY measurements which showed correlation b/n the two aromatic protons (H-6 and H-8) with the oxymethylene protons at C-1″. Hence **1** is 3′,4′-methylenedioxy-7-*O*-[*E*-3,7-

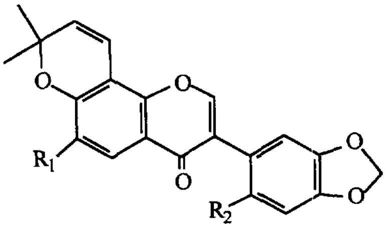
---

* Part 5 in the series 'The *Millettia* of Cameroon'. For part 4 see Ref. [1].

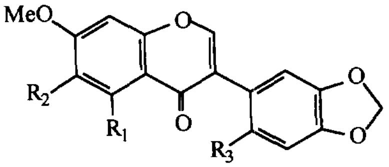
† Author to whom correspondence should be addressed.



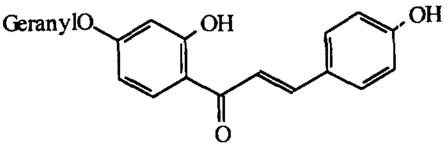
	R_1	R_2
1	OCH_2O	
2	H	OMe



	R_1	R_2
3	H	H
5	H	OMe
7	OMe	H



	R_1	R_2	R_3
4	H	H	OMe
8	OMe	OMe	H



6

Table 1. ^1H and ^{13}C NMR spectral data of isoflavone **1** in $CDCl_3$

1	H	C
2	7.89 *s*	152.1
3	—	125.7
4	—	175.7
5	8.17 *d* (8.9)	127.7
6	6.95 *dd* (8.9, 1.8)	115.1
7	—	163.3
8	6.83 *d* (1.8)	100.8
9	—	157.8
10	—	118.2
1′	—	125.0
2′	7.07 *d* (1.5)	109.8
3′	—	147.6
4′	—	147.6
5′	6.84 *d* (8.6)	108.3
6′	6.97 *dd* (8.6, 2.3)	122.4
1″	4.62 *d* (6.5)	65.5
2″	5.48 *t* (6.4)	118.4
3″	—	142.4
4″	2.10 *m*	39.5
5″	2.10 *m*	26.2
6″	5.07 *m*	123.6
7″	—	131.9
8″	1.75 *s*	16.8
9″	1.59 *s*	17.7
10″	1.65 *s*	25.6
OCH_2O	5.97 *s*	101.1

Coupling constants (*J* in Hz) in parentheses.

dimethyl-2,6-octadienyl]isoflavone for which we suggest the trivial name 7-*O*-geranylpseudobaptigenin.

EXPERIMENTAL

General. Mps: uncorr.; UV: MeOH; IR: KBr discs; NMR experiments were run on a Bruker AXR 300 instrument: ^1H NMR (300 MHZ) and ^{13}C NMR (75 MHZ) in $CDCl_3$ with TMS as int. standard. Ms: 70 eV; Prep. TLC: silica gel $60F_{254+366}$ (Merck) TLC: silica gel $60F_{254}$ (Merck); TLC and PTLC solvent system I: C_6H_6–petrol–EtOAc (3:9:1); II; C_6H_6–petrol–EtOAc (3:6:1).

Plant material. The root bark of *M. griffoniana* was collected from Onguesse, in the central province of Cameroon, in July 1994 and vouchers are deposited at the National Herbarium, Yaounde, Cameroon.

Extraction and isolation Air-dried and powdered root bark of *M. griffoniana* (20 kg) was successively extracted with *n*-hexane (24 hr; 3 × 20 l) and chloroform (24 hr; 3 × 20 l) at room temp. yielding 710 and 550 g, respectively. The concd hexane extract (20 g) was initially subjected to VLC over silica gel eluting with petrol–EtOAc gradients. The 10% EtOAc fr. was further purified by repeated CC and PTLC using solvent system I resulting in the isolation of **1** (20 mg), **2** (30 mg) and **3** (11 mg). The concd. $CHCl_3$ extract (50 g) was applied to VLC over silica gel eluting with petrol–EtOAc gradients. Elution with 10% EtOAc followed by PTLC (solvent system II) afforded **4** (15 mg), **5** (20 mg) and **6** (35 mg) while elution with 40 and 50% EtOAc gave **7** (3.5 g) and **8** (2.7 g), respectively.

3′,4′-Methylenedioxy-7-O-[(E)-3,7-*dimethyl*-2,6-*octa-dienyl*]*isoflavone* (**1**). Fine crystals from MeOH, mp 98–100°. HRMS *m/z*: 418.1778 (calcd for $C_{26}H_{26}O_5$, 418.1780). UV λ_{max} nm: 245, 249, 295 IR ν_{max} cm^{-1}: 1637, 1503, 1441, 1382, 1253, 1196, 1048, 937, 853, 818. ^{1}H NMR (Table 1) and ^{13}C NMR (Table 1). EIMS *m/z* (rel. int.): 418 $[M]^+$ (55), 282 (100), 146 (6), 137 (4), 81 (20), 69 (48).

Acknowledgement—We thank Professor Steglich and Ms Veronika Hellwig of University of Munich (Germany) for NMR and EIMS measurements.

REFERENCES

1. Mbafor, J. T., Atchade, A. T., Nkengfack, A. E., Fomum, Z. T. and Sterner, O., *Phytochemistry*, 1995, **40**, 949.
2. Thulin, M., *Operational Botany*, 1983, **68**, 71.
3. Sudarsanam, G., Reddy, M. B. and Nagaraju. N., *International Journal of Pharmacology*, 1995, **33**, 52.
4. Dewick, P., in *The Flavonoids*; *Advances in Research since* 1986, ed. J. B. Harborne. Chapman and Hall, New York, 1994, p. 117.
5. Dagne, E., Bekele, A., Noguchi, H., Shibuya, M. and Sankawa, U., *Phytochemistry*, 1990, **29**, 2671.
6. Dagne, E., Bekele, A. and Waterman, G., *Phytochemistry*, 1989, **28**, 1897.
7. Galina, E. and Gottlieb, O. R., *Phytochemistry*, 1974, **13**, 2593.
8. Nakano, T., Alango, J., Grillet, R. and Martin, A., *Journal of the Chemical Society, Perkin Transactions I*, 1979, 2107.
9. Mabry, T. J., Markham, K. R. and Thomas, M. B., *The Systematic Identification of Flavonoids*. Springer, New York, 1970.
10. Kozawa, M., Morita, N., Baba, K. and Hata, K., *Chemical and Pharmaceutical Bulletin*, 1977, **25**, 515.