Pergamon 0031-9422(95)00058-5 Phytochemistry, Vol. 40, No. 3, pp. 949–952, 1995

0031-9422/95 $9.50 + 0.00

FURANOFLAVONES FROM ROOT BARK OF *MILLETTIA SANAGANA**

J. T. MBAFOR, A. T. ATCHADE, A. E. NKENGFACK, Z. T. FOMUM† and OLOV STERNER‡

Department of Organic Chemistry, Faculty of Science, University of Yaounde 1, P.O. Box 812 Yaounde, Cameroon; ‡Chemical Centre, Organic Chemistry-2, Lund Institute of Technology, University of Lund, P.O. Box 124S-22100 Lund, Sweden

(*Received* 28 *November* 1994)

Key Word Index—*Millettia sanagana*; Leguminosae; root bark; furanoflavones; furanochalcone.

Abstract—A new furanoflavone, named sanaganone, was isolated from the root bark of *Millettia sanagana* in addition to four known compounds, pongamol, lanceolatin B, kanjone and 5-methoxy furano [7,8:4″,5″] flavone. The structure of the new compound was elucidated by spectroscopic analysis, including 2D NMR techniques (DQF COSY, HETCOR, long-range HETCOR and NOESY), as 2‴,2‴-dimethylpyrano [5,6:5‴,6‴] furano [7,8:4″,5″] flavone.

INTRODUCTION

Millettia sanagana is a shrub that grows in the undergrowth of the rain forest of the Central and South provinces of Cameroon [1]. Its use in the treatment of intestinal parasites and cholic in children, coupled with the fact that other members of this genus have been reported to show insecticidal [2, 3], piscicidal [3, 4] and molluscicidal [3, 4] activities, prompted our investigation on this species.

Recent chemical investigations of some *Millettia* species revealed the presence of alkaloids [5–7], flavonoids [8] and diterpenoids [9]. In this paper, we describe the isolation and characterization of a new furanoflavone, sanaganone (**1**), from the root bark of *M. sanagana* along with the known compounds, pongamol (**2**), lanceolatin B (**3**), kanjone (**4**) and its isomer, 5-methoxy furano [7,8:4″,5″] flavone (**5**).

RESULTS AND DISCUSSION

Dried and powdered root bark of *M. sanagana* was extracted with methanol in a Soxhlet apparatus and the extract concentrated to dryness. The residue was then suspended in a mixture of methanol–water (7:3) and successively fractionated into *n*-hexane-, CH_2Cl_2-, acetone-, methanol-soluble fractions and insoluble material. Extensive chromatography over silica gel of the CH_2Cl_2 extract afforded a new furanoflavone, sanaganone (**1**), in addition to four known compounds (**2**)–(**5**).

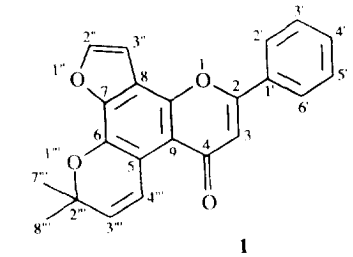
Sanaganone (**1**), mp 168°, was isolated as yellow needles. Its molecular formula, $C_{22}H_{16}O_4$, was determined by HR mass spectrometry and is in accord with ^1H and ^{13}C NMR data summarized in Table 1. The EI mass spectrum showed a stable ion $[M - 15]^+$ peak at *m/z* 329 as the base peak and only two other intense peaks at *m/z* 344 $[M]^+$ and *m/z* 227. A yellow-brown colouration of (**1**) in the Shinoda test and its UV spectrum [λ^{MeOH} nm (log ε): 224 (4.38), 252 (4.15), 306 (4.48)] are characteristic of a furanoflavonoid chromophore [10–12]. The IR spectrum showed an absorption band due to the presence of conjugated carbonyl (1649 cm^{-1}) but no band for hydroxyl groups. Based on ^1H–^1H COSY, ^1H–^{13}C HETCOR, long-range HETCOR and NOESY experiments, structure (**1**) was established for sanaganone.

The presence of a *gem*-dimethylchromene moiety in (**1**) was supported by a sharp 6H singlet at δ1.53 and an AB spin system at δ5.72 (J = 10.3 Hz, H-3‴) and δ8.11 (J = 10.3 Hz, H-4‴). The ^1H NMR spectrum of (**1**) also revealed the presence of a sharp one-proton singlet at δ6.74 for H-2, which fell in the normal chemical shift region for flavone [11]. A typical two one-proton doublet at δ7.12 and δ7.70 (J = 1.8 Hz) could be assigned to the H-3″ and H-2″ protons, respectively, of the furan ring. Furthermore, a two-proton multiplet centred at δ7.88 and a three-proton multiplet centred at δ7.50 suggested the presence of aromatic protons in the unsubstituted B ring.

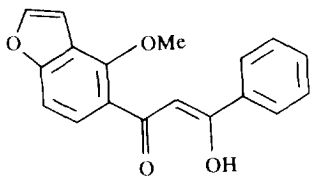
The position of the furan ring on ring A was unambiguously determined on the basis of the NOESY spectrum which showed correlation contours between H-2′/H-6′ and H-3″ (H-2′/H-6′ also gave correlation contours with H-3 and H-3′/H-5′). This finding indicated clearly that the furan ring was fused in an angular form on ring A at positions 7, 8. This led us to conclude that the pyran moiety was also fused in an angular manner on ring A, but at positions 5, 6. The position of the *gem*-

†Author to whom correspondence should be addressed.

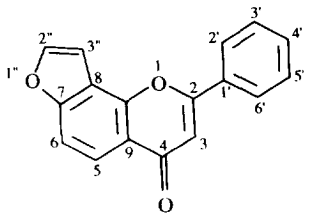
*Part 4 in the series, "The *Millettia* of Cameroon". For Part 3, see ref. [7].



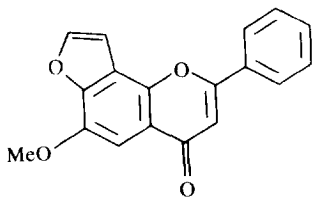
1



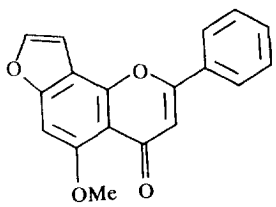
2



3



4

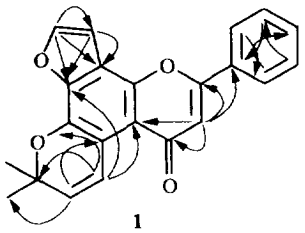


5

Table 1. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectral data for sanaganone (**1**) and lanceolatin B (**3**) in $CDCl_3$[a*]

	(1)		(3)
Compound	^{1}H [δ, multiplicity, I (Hz)]	^{13}C (δ, multiplicity)	^{13}C (δ, multiplicity)
C			
2		160.8 *s*	162.7 *s*
3	6.74 (*s*)	108.9 *d*	108.1 *d*
4		180.4 *s*	178.2 *s*
5		115.3 *s*	121.8 *d*
6		136.8 *s*	110.2 *d*
7		146.9 *s*	158.4 *s*
8		118.4 *s*	117.2 *s*
9		146.2 *s*	150.9 *s*
10		114.9 *s*	119.4 *s*
1′		131.6 *s*	131.8 *s*
2′	7.88 (*m*)	125.9 *d*	126.2 *d*
3′	7.50 (*m*)	129.0 *d*	129.1 *d*
4′	7.50 (*m*)	131.2 *d*	131.5 *d*
5′	7.50 (*m*)	129.0 *d*	129.1 *d*
6′	7.88 (*m*)	125.9 *d*	126.2 *d*
2″	7.70 (*d*, 1.8)	146.0 *d*	145.8 *d*
3″	7.12 (*d*, 1.8)	104.9 *d*	104.2 *d*
2‴		76.5 *s*	—
3‴	5.72 (*d*, 10.3)	129.6 *d*	—
4‴	8.11 (*d*, 10.3)	121.2 *d*	—
7‴	1.53 (*s*)	27.5 *q*	—
8‴	1.53 (*s*)	27.5 *q*	—

*Chemical shifts in ppm relative to solvent signals (7.26 for ^{1}H and 77.0 ppm for ^{13}C NMR).



1

Scheme 1. Significant ^1H–^{13}C long-range correlations observed for sanaganone (1).

dimethylchromene on ring A was confirmed by long-range HETCOR experiments shown in Scheme 1 and by the magnitude of the ^{13}C NMR chemical shifts of C-5, C-6, C-7 and C-10 as compared with, e.g. 3 (Table 1). On the basis of the above spectroscopic studies, sanaganone (1) was thus identified as 2‴,2‴-dimethylpyrano [5,6:5‴,6‴] furano [7,8:4″,5″] flavone.

Pongamol (2), mp 127°, obtained as brown prisms, has previously been isolated from seeds and flowers of *Pongamia glabra* [12, 13], as well as from *Tephrosia purpurea* and its structure has been determined by X-ray analysis [14]. The NMR data published [12, 14] for pongamol (2) matched very well with those obtained in the present investigation.

Compound (3), mp 138°, obtained as needles had an empirical formula of $C_{17}H_{10}O_3$. NMR analysis (^1H, ^{13}C, HETCOR) showed that the structure of (3) was identical to that of lanceolatin B previously isolated from the flowers of *P. glabra* [13] and recently reported as constituent of the root bark of *P. pinnata* [15].

Compounds (4), and its isomer (5), were identified as kanjone and 5-methoxyfurano [7,8:4″,5″] flavone, respectively, from spectral data and physical constants which matched with literature values [13, 16].

EXPERIMENTAL

All mps are uncorr. ^1H and ^{13}C NMR spectra were recorded with TMS as int. ref. and chemical shifts are given in δ values. ^1H–^1H COSY, HETCOR, long-range HETCOR and NOESY expts were performed with the usual pulse-sequence and data processing was obtained with standard software.

Plant material. Root bark of *M. sanagana* was collected near Obala in the Central province of Cameroon, in January 1994. A voucher specimen documenting the collection was identified at the National Herbarium, Yaounde, Cameroon and is on deposit there.

Extraction and isolation. Air-dried powdered root bark (11 kg) was extracted with MeOH and evapd to dryness. The MeOH concentrate (590 g) was then dissolved in MeOH–H_2O (7:3) and fractionated into *n*-hexane-, (70 g), CH_2Cl_2- (80 g), Me_2CO- (45 g), MeOH-soluble frs (315 g) and insoluble material (50 g).

The CH_2Cl_2 fr. (80 g) was subjected to coarse sepn by CC over silica gel (0.2–0.5 mm), elution being carried out with *n*-hexane, *n*-hexane–CH_2Cl_2, CH_2Cl_2 and CH_2Cl_2–MeOH mixts. A total of 420 frs of 400 ml each, were collected and combined on the basis of TLC composition. Frs 14–17 (hexane–CH_2Cl_2, 3:1) gave 0.8 g of sanaganone (1), recrystallized from hexane–CH_2Cl_2. Frs 21–24, eluted with hexane–CH_2Cl_2 (2:1), gave 2 g of 2, which was recrystallized from *n*-hexane–CH_2Cl_2. Frs 62–69 (hexane–CH_2Cl_2, 1:2) gave 1.2 g of a pale yellow compound (3), recrystallized from hexane–CH_2Cl_2. Frs 86–88 (hexane–CH_2Cl_2, 1:4) yielded 3.4 g of a mixt. of 3 compounds. Further sepn by CC over silica gel eluting with *n*-hexane–CH_2Cl_2, afforded 4, which was recrystallized from CH_2Cl_2. Frs 97–99 (hexane–CH_2Cl_2, 1:9) gave 0.25 g of 5 which was recrystallized from MeOH–CH_2Cl_2.

Sanaganone (1). Yellow needles, mp 168°. Positive reaction (yellow-brown colouration) to Mg–HCl test. HREIMS: 344.1061 (calcd 344.1048 for $C_{22}H_{16}O_4$). EIMS *m/z* (rel. int.): 344 $[M]^+$ (38), 329 (100), 303 (6), 227 (22). UV λ^{MeOH} nm (log ε): 224 (4.38), 252 (4.15), 306 (4.48). IR ν^{KBr} cm^{-1}: 2975, 1649 (conj. C=O), 1605, 1443, 1417, 1368, 1336, 1148, 1070, 800 and 762. ^1H NMR (500 MHz, $CDCl_3$): Table 1. ^{13}C NMR (125 MHz, $CDCl_3$): Table 1.

Pongamol (2). Brown prisms from hexane–CH_2Cl_2. Mp 127° (lit. [13] 127–128°). IR, UV, ^1H and ^{13}C NMR matched well with lit. [14].

Lanceolatin B (3). Needles, mp 138° (lit. [13, 16], mp 137°). Yellow colouration with Mg–HCl. HREIMS: 262.0624 (calcd 262.0629 for $C_{17}H_{10}O_3$). IR, UV and ^1H NMR identical to lit. values [15]. For ^{13}C NMR spectral data: Table 1.

Kanjone (4). Needles, mp 189° (lit. [13, 16] mp 187–188°). Orange colouration with Mg–HCl. Spectroscopic data (IR, UV, ^1H and ^{13}C NMR) identical to lit. [13, 16].

5-Methoxy furano [7,8:4″,5″] *flavone* (5). Needles, mp 178° (lit. [16] mp 176°). Spectroscopic data matched well with lit. [16].

Acknowledgements—We are grateful for financial support (in part) to the International Foundation for Science (I. F. S.) research grant (F/2192-1) and the University of Yaounde I, Cameroon, for laboratory facilities.

REFERENCES

1. Mbenkum, T. F. (1986) Ph.D. thesis, University of Reading.
2. Chiu, S. F., Spin, L. and Chiu, Y. S. (1942) *J. Econ. Entomol.* **35**, 80.
3. Dewick, P. M. (1993) in *The Flavonoids: Advances in Research since* 1986 (Harborne, J. B., ed.), p. 117. Chapman and Hall, New York.
4. Singhal, A. K., Sharma, R. P., Baruah, J. N., Govinda, S. V. and Herz, W. (1982) *Phytochemistry* **21**, 949.
5. Ngamga, D., Fanso Free, S. N. Y., Fomum, Z. T., Chiaroni, A., Riche, C., Martin, M. T. and Bodo, B. (1993) *J. Nat. Prod.* **56**, 2126.
6. Kamnaing, P., Fanso free, S. N. Y., Fomum, Z. T., Martin, M. T. and Bodo, B. (1994) *Phytochemistry* MS 635 (in press).

7. Ngamga, D., Fanso Free, S. N. Y., Fomum, Z. T., Martin, M. T. and Bodo, B. (1994) *J. Nat. Prod.* **57**, 1022.
8. Ahmed, V. U., Parveen, S., Bano, S., Shaikh, W. and Shameed, M. (1990) *Phytochemistry* **31**, 1015.
9. Dagne, E., Bakele, A., Noguchi, H., Shibuya, M. and Sankawa, U. (1990) *Phytochemistry* **29**, 2671.
10. Mahey, S., Sharma, P. and Seshadri, T. R. (1972) *Ind. J. Chem.* **10**, 585.
11. Malik, S. B., Sharma, P. and Seshadri, T. R. (1977) *Ind. J. Chem.* **15B**, 536.
12. Sharma, P. and Parthasarathy, M. R. (1977) *Ind. J. Chem.* **15B**, 866.
13. Talapatra, S. K., Malik, A. K. and Talapatra, B. (1980) *Phytochemistry* **19**, 1199.
14. Parmar, V. S., Rathore, J. S., Jain, R., Henderson, D. A. and Malone, J. F. (1989) *Phytochemistry* **28**, 591.
15. Tanaka, T., Iinuma, M., Yuki, K., Fujii, Y. and Mizuno, M. (1992) *Phytochemistry* **31**, 993.
16. Talapatra, S. K., Malik, A. K. and Talapatra, B. (1982) *Ind. J. Chem.* **59**, 534.