Bull. Chem. Soc. Ethiop. **2003**, 17(1), 113-115. ISSN 1011-3924
Printed in Ethiopia

A NEW ISOFLAVONE FROM STEM BARK OF *MILLETTIA DURA*

Solomon Derese[1], Abiy Yenesew[1*], Jacob O. Midiwo[1], Matthias Heydenreich[2] and Martin G. Peter[2]

[1]Department of Chemistry, University of Nairobi, P.O. Box 30197, Nairobi, Kenya
[2]Institut für Chemie, Universität Potsdam, P.O. Box 60 15 53, D-14415 Potsdam, Germany

(Received September 19, 2002; revised March 26, 2003)

ABSTRACT. A new isoflavone (7,3'-dimethoxy-4',5'-methylenedioxyisoflavone) and three known isoflavones [isoerythrinin A 4'-(3-methylbut-2-enyl) ether, isojamaicin and nordurlettone] were isolated from the stem bark of *Millettia dura* (Leguminosae). The structures were determined by spectroscopic methods.

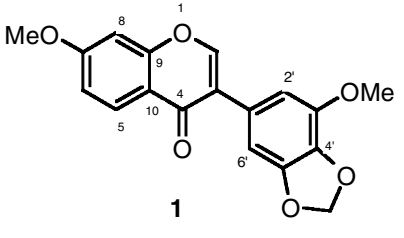
KEY WORDS: *Millettia dura*, Leguminosae, Isoflavone, 7,3'-Dimethoxy-4',5'-methylenedioxyisoflavone, Isoerythrinin A 4'-(3-methylbut-2-enyl) ether, Isojamaicin, Nordurlettone

INTRODUCTION

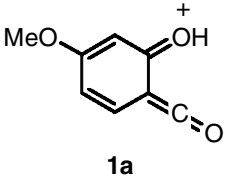
Some 100 *Millettia* species are known worldwide, and in Kenya this genus is represented by six species, namely, *M. dura, M. lasiantha, M. leucantha, M. oblata, M. tanaensis* and *M. usaramensis* [1]. Of these *M. dura* Dunn is cultivated as a timber tree [1] and also as a shade and ornamental tree [2]. Rotenoids and isoflavones have been isolated from the seeds, seed pods, stem bark and root bark of this plant [3-6]. We have now isolated a new isoflavone along with three known compounds from the stem bark of this plant, and the isolation and structure elucidation of the new compound is presented.

RESULTS AND DISCUSSION

The new compound (**1**) was isolated as colourless crystals, m.p. 194-196 °C. EIMS analysis showed a molecular ion peak at *m/z* 326 ($C_{18}H_{14}O_6$). The UV (λ_{max} 232, 256, 312 nm), ^{1}H (δ 8.28, *s*, for H-2) and ^{13}C (δ 154.8 for C-2, 125.8 for C-3 and 176.1 for C-4) NMR spectra are consistent with an isoflavone skeleton for this compound. In addition the NMR spectra (Table 1) showed the presence of two methoxyl and a methylenedioxy substituents on the isoflavone skeleton. In the EIMS the fragment at *m/z* 151 (**1a**) resulting from retro-Diels-Alder cleavage of C-ring is consistent with the placement of one methoxyl on ring-A and hence the second methoxyl and the methylenedioxy on ring-B. From biogenetic considerations, the methoxyl group in ring-A should be placed at C-7.



1



1a

*Corresponding author. E-mail: ayenesew@uonbi.ac.ke

In support of this, the ^{1}H NMR displayed three aromatic protons with an AXY spin system for A-ring protons (Table-1). In the B-ring the chemical shift values of the oxygenated carbon atoms are in agreement with the placement of the methoxyl at C-3' and the methylenedioxy group at C-4'/5' [5, 7]. Two *meta*-coupled (J = 1.5 Hz) protons at δ 6.86 and 6.93 could then be assigned to H-2' and H-6'. On this basis this new compound was characterized as 7,3'-dimethoxy-4',5'-methylenedioxyisoflavone. The identity of this compound was confirmed through HMQC and HMBC (Table-1) experiments.

Three known isoflavones were also isolated from the stem bark of this plant and were identified as isoerythrinin A 4'-(3-methylbut-2-enyl) ether [5], isojamaicin [7] and nordurlettone [8]. Isoerythrinin A 4'-(3-methylbut-2-enyl) ether has earlier been reported from the seeds of this plant [5], while isojamaicin and nordurlettone are reported here for the first time from this plant.

Table 1. ^{1}H (300 MHz, acetone-d_6) and ^{13}C (75 MHz, acetone-d_6) NMR chemical shift data together with HMBC correlations for **1**.

	^{1}H (J)	^{13}C	^2J	^3J
2	8.28 *s*	154.8	C-3	C-1', C-9, C-4
3		125.8		
4		176.1		
5	8.11 *d* (9.3 Hz)	128.8		C-4, C-9
6	7.07 *dd* (1.5, 9.3 Hz)	116.2		C-8, C-10
7		165.8		
8	7.06 *d* (1.5 Hz)	101.8	C-7, C-9	C-10
9		159.4		
10		119.8		
1'		128.1		
2'	6.93 *d* (1.5 Hz)	110.7	C-1', C-3'	C-3, C-4', C-6'
3'		145.1		
4'		136.7		
5'		150.3		
6'	6.86 *d* (1.5 Hz)	104.7	C-5'	C-3, C-2', C-4'
OCH_2O	6.02 *s*	103.0		C-4', C-5'
OMe-3'	3.92 *s*	57.6		C-3'
OMe-7	3.97 *s*	57.2		C-7

EXPERIMENTAL

General. M.p.: uncorr. Analytical TLC: Merck pre-coated silica gel 60 F_{254}; compounds were detected under UV light (254 nm). CC: silica gel 60 (70-230 mesh) and Sephadex LH-20. EIMS: direct inlet 70 eV. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on ARX 300 Bruker spectrometer using TMS as internal standard. HMQC and HMBC spectra were acquired using standard Bruker software.

Plant material. The stem bark of *Millettia dura* was collected in January 2000 in Nairobi. The plant was identified by Mr. S.G. Mathenge of the University Herbarium, Botany Department, University of Nairobi, where a voucher specimen is deposited.

Extraction and isolation. Dried and ground stem bark (2.3 kg) of *M. dura* was extracted with CH_2Cl_2 by cold percolation. Removal of the solvent under vacuum afforded 143 g of the crude extract. A portion of the extract (100 g) was subjected to CC on silica gel (500 g) eluting with hexane containing increasing percentage of EtOAc. The fraction eluted with 8% EtOAc

contained three compounds which were separated by CC on Sephadex-LH 20 (CH_2Cl_2/MeOH, 1:1) to give isojamaicin (240 mg), isoerythrinin A 4'-(3-methylbut-2-enyl) ether (137 mg) and nordurlettone (23 mg). PTLC (silica gel, CH_2Cl_2) purification of the fraction eluted with 10% EtOAc afforded compound **1** (40 mg).

7,3'-Dimethoxy-4',5'-methylenedioxyisoflavone (**1**). White crystals (MeOH), m.p. 194-196 °C. UV λ_{max} (MeOH) (log $\in$) nm: 232 (4.3), 256 (4.1), 312 (4.2). ^{1}H and ^{13}C NMR (Table 1). EIMS (prob) 70 eV, *m/z* (rel. int.): 326 $[M]^+$ (100), 295 (51), 151 (15).

ACKNOWLEDGEMENTS

We acknowledge support by the Deutsche Forschungsgemeinschaft, Germany, Grant No. Pe 264/14-2 and by the Bundesministerium fuer Zusammenarbeit, Grant No. Pe264/14-3. S.D. is grateful to the Natural Products Research Network for Eastern and Central Africa (NAPRECA) and the German Academic Exchange Service (DAAD) for a scholarship.

REFERENCES

1. Beentje, H. *Kenya Trees, Shrubs and Lianas*, National Museums of Kenya: Nairobi; **1994**; p 278.
2. Gillet, J.B.; Polhill, R.M.; Verdcourt, B. *Flora of Tropical East Africa, Leguminosae*, Whitefriars Press: London; **1971**; p 123.
3. Dagne, E.; Mammo, W.; Bekele, A.; Odyek, O.; Byaruhanga, M.A. *Bull. Chem. Soc. Ethiop.* **1991**, 5, 81.
4. Ollis, W.D.; Rhodes, C.A.; Sutherland, I.O. *Tetrahedron* **1967**, 23, 4741.
5. Yenesew, A.; Midiwo, J.O.; Waterman, P.G. *Phytochemistry* **1996**, 41, 951.
6. Yenesew, A.; Midiwo, J.O.; Waterman, P.G. *J. Nat. Prod.* **1997**, 60, 806.
7. Dagne, E.; Bekele, A.; Waterman, P.G. *Phytochemistry* **1989**, 28, 1897.
8. Dagne, E.; Bekele, A.; Noguchi, H.; Shibuyi, M.; Sankawa, U. *Phytochemistry* **1990,** 29, 2671.