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A coumarin derivative from the stem bark of *Jatropha multifida*

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ABSTRACT

A Coumarin derivative, 4-ethoxy-6-((hydroxymethoxy)methyl)-2H-chromen-2-one, was isolated from the stem bark of *Jatropha multifida*, and its structure was elucidated from UV, IR, MS and 2D NMR spectra. The compound has 1-oxygenated structure with a lactone moiety.

Introduction

Jatropha multifida Linn (Euphorbiaceae) is a small tree originating from tropical South America. It is grown as ornamental shrub in north Australia and South east Africa [1,2], likewise in Philippines, Srilanka and Indonesia, expecially in Java, Sulawesi Islands and Nigeria where it is commonly known as Ogege by the Yorubas [3]. Its use in traditional medicine for the treatment of several ailments like coated tongue, infected wounds, as purgative and febrifuge, gonorrhoea and urinary infections were reported [3,4,5]. The leaves are used in scabies: the latex is applied over wounds and ulcer and the oil is used both internally and externally as abortifacient [6]. The bark and leaves are used as medicine for neurodermatitis, itchy skin and skin eczema [7]. The stems were employed as chewing sticks used for dental care in Ekiti State, Nigeria [8].The therapeutic properties of the plant have been established by various researchers. For instance, the latex and root extracts of the plant are known to possess antimicrobial activity [4,9,10,11,12]. Earlier examination of the latex of the plant afforded some cyclic peptides, phenolics, diterpenoids and glycosides [13,14,15,16,17]. The diterpenoid, multidione[18,19] was isolated from the stems of *J. multifida* Linn. The compound possesses a phenolic moiety and a long side chain, structurally similar to the B ring of other lathyrane-diterpenoids in seco-form.

In continuation of our systematic work on the constituents of medicinal plants we examined the stem bark of *Jatropha multifida* and isolated a coumarin compound. Hence, we describe the isolation and structural elucidation of this compound.

Experimental

General: FT-IR spectra were obtained on a Nicolet DX system, and sample was prepared in chloroform solution; UV spectra were measured in EtOH; Specific rotation measurements were recorded with a Rudolf Autopol III Polarimeter; NMR spectra were obtained in DMSO-d_6 on a Bruker AM-400 Spectrometer using a residual solvent signal as internal reference (δ_H 7.27, δc 77.0ppm). Standard Bruker pulse programs were used for DEPT, 2D NMR, COSY, HMBC, HMQC spectra; The silica gel used for TLC was precoated kieselgel 60 F_{254} (0.25mm thick, merek); Mass spectra were taken under electron impact (EI) condition. GC-MS analysis was on Hewlett: Packard 5890 series 11; 24m x 0.2mm 1.d. column coated with DB5 bonded phase (0.3µm film); temperature program: 10^{O}Cmin^{-1}, then held at 280^{O}C;injector temperature: 250^{O}C; detector temperature: 280^{O}C; injector volume, typically 1µL at 70:1 split ratio; flowrate, 0.43mL min^{-1}.

Plant material: The stems of *Jatropha multifida* were collected from the campus of the University of Ibadan, Ibadan, Nigeria in May 2006 and authenticated at the Department of Botany, University of Ibadan.

Extraction and Isolation: The air-dried plant material (1.2Kg) was milled and successively extracted with hot hexane, ethylacetate and methanol. The MeOH extract was concentrated to afford thick brown mass (25g). A portion of the residue (5g) was subjected to vacuum liquid chromatography (VLC) and was eluted with solvents of increasing polarity using hexane, EtOAc and MeOH, separation of the components in the mixture being monitored by TLC. The fraction eluted with hexane-EtOAc (7:3) contained a compound which was purified to yield 4-ethoxyl-6-((hydroxymethoxy)methyl)-2H-chromen-2-one (1.2g). Purification of this fraction eluted with preparative TLC [n-hexane:EtOAc (8:3)] gave compound **1**.

Compound **1**: Pale yellow solid, mp 125-127^{O}C; UV λmax: 202, 208, 226, 238, 245(sh), 258(sh), 286nm; IR (KBr) νmax: 3310, 1697, 1610, 1412, 1250cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 2.50 (3H,t), 3.34 (2H, s), 3.79 (2H, m), 4.04 (2H, s), 6.37 (1H, d, J=7.9Hz), 6.82 (1H, s), 7.92 (1H, d, J=7.9Hz), 9.80 (1H, s,

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J=8.7Hz); 13C NMR (DMSO-d6): δ 39.77, 55.94, 60.49, 62.30, 100.19, 114.39, 114.50, 138.20, 138.47, 140.08, 144.61, 149.67, 160.08.

Results And Discussion

The dried stem bark of *Jatropha multifida* was dried, weighed and extracted with hexane, ethylacetate and methanol successively. The methanolic extract was evaporated and fractionated using a combination of vacuum liquid chromatography and preparative TLC to give a methoxylcoumarin. Coumarin was isolated as a pale yellow crystal. The molecular formula was established as $C_{13}H_{14}O_5$ by high-resolution (HR)-MS. The UV [λ_{max}: 202, 208, 226, 238, 245(sh), 258(sh), 286nm], and IR spectra [3310 and 1697cm^{-1}] indicated the presence of a hydroxyl and lactone carbon groups. The ^{1}H-NMR spectrum revealed a pair of doublets at δ 6.37 (1H, H-7) and δ 7.63 (1H, H-8) with the same coupling constant (J=7.9Hz) corresponding to aromatic proton signals. The presence of aromatic proton signal at δ_H7.8 (J=8.7Hz, s, H-3) was due to the deshielding effect of the neighbouring carbonyl group closer to C-3. The signal δ 6.82 (1H, s, H-5) was also attributed to aromatic proton signal. Further, the ^{1}H-NMR spectrum showed signals assignable to a vinyl methyl group δ 2.5, (3H, t, H-12), one methylene group δ 3.34 (2H, s, H-13) and two terminal methylene groups δ 4.04 (2H, s, H-14) and δ 3.79 (2H, m, H-11) each on a carbon bearing an oxygen atom, while the signal δ 4.42 (1H, t, H-14) was assigned to proton of hydroxyl group.

Table 1.NMR Spectral Data of Compound 1

Position	1H – NMR	Multiplicity (J in Hz)	13C – NMR
1	_	_	_
2	_	_	160.08
3	7.80	s	149.67
4	_	_	140.08
5	6.82	s	114.50
6	_	_	100.19
7	6.37	d	114.39
8	7.63	d	138.20
9	_	_	144.61
10	_	_	138.47
11	3.79	m	55.94
12	2.50	s	39.77
13	3.34	s	60.49
14	4.04	s	62.30
14	4.42	t	_

^{13}C-NMR spectrum showed the following carbon signals: δ 39.77 was attributed to methyl carbon, δ 55.94 and δ 60.49 for carbons bearing oxygen atom, δ 62.30 indicates the presence of methylene carbon deshielded by two oxygen atoms bonded to it (O-CH_2-O), δ 100.19 δ 114.39, δ 114.50 and δ 138.20 are aromatic carbons. δ 138.47, δ 140.08 and δ 144.61 were assigned to quaternary vinyl carbons, and δ 149.67 for a vinyl carbon α to carbonyl group. The presence of δ 160.08 indicates a ketone R-C=O moiety. These signal assignments were confirmed by HMBC, NOESY, HSQC and DEPT experiments. In 1H-detected heteronuclear multiple bond connectivity (HMBC) spectroscopy, C-H five-bond correlations were detected between the carbon signal at δc 140.08 (C-4) and proton of terminal methyl group at δ_H2.5 (H-12, m), between the carbon signal at δc 138.47 (C-10) and protons at δ_H 7.80 (H-3), 7.63 (H-8); carbon signal at δc 144.61 (C-9) and protons at δ_H7.80 (H-3), δ 6.82 (H-5), δ 6.37 (H-7) and δ 3.34 (H-13). The presence of a lactone carbonyl group at C-2 was suggested by a significant C-H bonds correlation between a carbonyl carbon at δc 160.08 (C=O) and a lone singlet at δ_H7.80 (H-3) and an aromatic proton at δ_H 7.63 (H-8). Again, NOE experiment confirmed the enhancement between the H-3 (δ 7.80) and H-11 (δ 3.79), H-12 (δ 2.5), and H-5 (δ 6.82). Space correlation between the H-5 and H-13 (δ 3.34), H-14 (4.04) signals were observed.

On the basis of these spectra data, it was seen that the structure **1** was a derivative of coumarin.

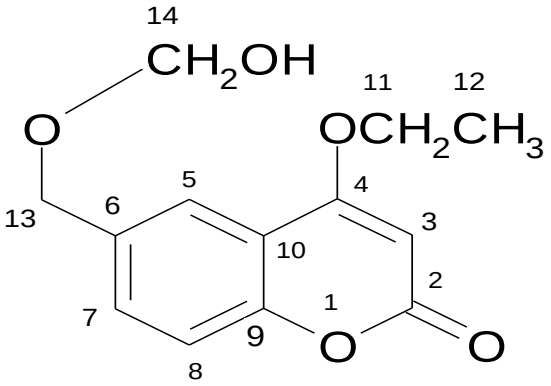

FIG 1: 4 – ethoxy – 6 – ((hydroxylmethoxy) methyl) –2H – chromen – 2 – one

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