

## SHORT COMMUNICATION

### SCORODOPHLONE A, A NOVEL ALKYL SULFONE FROM THE SEEDS OF *SCORODOPHLOEUS ZENKERI*. HARMS

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**ABSTRACT.** A novel alkylsulfone, scorodophlone A **1**, from the seeds of *Scorodophloeus zenkeri* Harms, has been assigned the structure 6-(methylsulfonyl)-1,2,3-dithiazinan-4-one on the basis of its spectroscopic properties. The known compounds  $\alpha$ -sophoradiol (12-oleanene-3 $\beta$ ,22 $\alpha$ -diol), lupeol and sitosterol were also obtained.

**KEY WORDS:** *Scorodophloeus zenkeri*, Caesalpiniaceae, Scorodophlone A, Pentacyclic triterpene, Phytosterol

## INTRODUCTION

*Scorodophloeus zenkeri* Harms (Caesalpiniaceae) is a tropical tree of Central Africa. It is of restricted height with a trunk diameter rarely exceeding 80 cm [1]. The tree has a garlic – like odour which comes from its sulphur containing compounds [2]. The bark, seeds and wood of *Scorodophloeus zenkeri* are used as spices in some traditional dishes such as “bongo-tjobi”, “nkuii” and “na-pôô” in Cameroon, and also in folk medicine for the treatment of several diseases. Previous work on *S. zenkeri* Harms concerned only the bark essential oil and extract of this plant from which sulfides, alkylthiosulfides, sulfoxides and sulphones have been isolated [2-5].

Until now, no report has been given on the nitrogen-containing sulfur compounds from this plant. We now report the isolation and structural elucidation of a novel alkylsulfone **1** from the seeds of this plant

## RESULTS AND DISCUSSION

The methanol extract of the finely powdered seeds of *S. zenkeri* Harms, on chromatographic separation, afforded a novel alkylsulfone named scorodophlone A **1**, together with sitosterol [6], lupeol [7] and  $\alpha$ -sophoradiol (12-oleanene-3- $\beta$ ,22- $\alpha$ -diol) [8]. The known compounds were identified by direct comparison of their physical and spectral data with the published values.

Soluble in D<sub>2</sub>O, compound **1**, was obtained as white powder, m.p.: 206-208 °C,  $[\alpha]_D^{19} - 90^\circ$  (c 0.6, H<sub>2</sub>O). Its molecular formula C<sub>4</sub>H<sub>7</sub>NO<sub>3</sub>S<sub>3</sub> was deduced from the high resolution TOF mass spectrum (HRTOFMS), which shows the pseudomolecular ion peak (M+H)<sup>+</sup> at  $m/z = 214.3010$

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(calcd. for  $C_4H_7NO_3S_3$ , 213.3013). This formula indicated two degrees of unsaturation. The IR spectrum of **1** showed characteristics bands for N-H ( $3552.5\text{ cm}^{-1}$ ), carbonyl ( $1630.7\text{ cm}^{-1}$ ), sulfone ( $1301.6$  and  $1104.2\text{ cm}^{-1}$ ) and S-S ( $487.5$  and  $454.5\text{ cm}^{-1}$ ) moieties [9-11]. The broad band decoupled  $^{13}\text{C}$  NMR spectrum showed four signals, an amide carbonyl ( $174.7\text{ ppm}$ ) [12], a methine ( $56.5\text{ ppm}$ ), a methylene ( $36.1\text{ ppm}$ ) and a methyl group ( $40.9\text{ ppm}$ ). The  $^1\text{H}$  NMR spectrum of **1** showed a typical AMX spin system at  $\delta$  4.10 ppm (1H, dd,  $J = 3.3\text{ Hz}$  and  $4.6\text{ Hz}$ ),  $\delta$ : 3.42 ppm (1H, dd,  $J = 3.3\text{ Hz}$  and  $11.0\text{ Hz}$ ),  $\delta$  3.38 ppm (1H, dd,  $J = 4.6\text{ Hz}$  and  $11.0\text{ Hz}$ ). A singlet of three protons at  $\delta$  3.18 ppm is characteristic of a group  $\text{CH}_3\text{SO}_2$  [5]. The HMBC spectrum showed connectivity from the methine proton at  $\delta$  4.10 and the methylene protons at 3.42 and 3.38 ppm to the carbonyl group at  $\delta$  174.7 ppm. The methylsulfonyl group was located at position 6 according to the chemical shifts of methylene and methine protons and carbons. Further confirmation came from the HMBC spectrum which presented significant correlation between the methyl protons at  $\delta$  3.18 ppm and the carbon C-6 ( $56.5\text{ ppm}$ ). The HMBC spectrum showed correlations from the methine and methylene protons to the carbonyl group at  $\delta$  174.7 ppm and the expected correlations from the methylene protons to the methine carbon and from the methine proton to the methylene carbon. A critical correlation was observed from the sulfone methyl protons to the methine carbon C-6 (Figure 1). These data led to structure **1** for scorodophlone A. The alternative structure, 5-(methylsulfonyl)-1,2,3-dithiazinan-4-one, was excluded on chemical shift arguments.

From the above spectroscopic evidence, the structure of scorodophlone A **1** was established as 6-(methylsulfonyl)-1,2,3-dithiazinan-4-one.

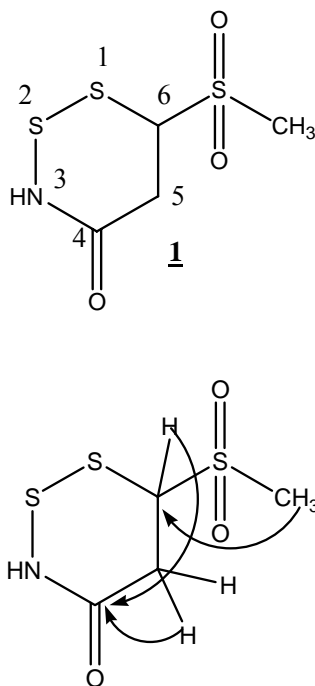


Figure 1. Significant HMBC correlations of **1**.

Table 1.  $^1\text{H}$  (300.135 MHz) and  $^{13}\text{C}$  (75.469 MHz) assignments for compound **1** in  $\text{D}_2\text{O}$ .

Attribution	$^{13}\text{C}$	Multiplicity	$^1\text{H}$ (m, J (Hz))	HMBC
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	174.7	s	-	5,6
5	36.1	t	3.38 (dd, J = 4.6, 11 Hz) 3.42 (dd, J = 3.3, 11 Hz)	6
6	56.5	d	4.10 (dd, J = 3.3, 4.6 Hz)	5
$\text{CH}_3$	40.9	q	3.18 (s)	6

### EXPERIMENTAL

*General experimental procedures.* Melting points were determined on a Buchi apparatus and are uncorrected. NMR spectra were run on a Bruker instrument equipped with a 5 mm  $^1\text{H}$  and  $^{13}\text{C}$  probe operating at 300.135 and 75.469 MHz respectively with TMS as internal standard.  $^1\text{H}$  assignments were made using 2D-COSY and NOESY (mixing time 800 ms) experiments while  $^{13}\text{C}$  assignments were made using 2D-HSQC and HMBC experiments. Silica gel 70-230 mesh (Merck) was used for column chromatography, while precoated aluminium sheets silica gel 60  $\text{F}_{254}$  (Merck) were used for TLC with a mixture of hexane-ethyl acetate and ethyl acetate-methanol as eluents. Spot were visualised by UV (254 nm) and (365 nm) or by iodine vapour, vanillin- $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ - $\text{H}_2\text{SO}_4$  reagents.

*Plant material.* Seeds of *S. zenkeri* Harms were collected in September 2003 in the forest of Yokadouma in south Cameroon. A voucher specimen documenting the collection was identified at the Botanic Department of University of Douala by Dr Ndongo Din and was deposited there.

*Extraction and isolation.* The air dried powdered seeds of *S. zenkeri* Harms (2.8 kg) were extracted with methanol at room temperature and the extract concentrated to dryness to obtain a viscous residue (185 g). The methanol extract was subjected to column chromatography over silica gel 70 – 230 mesh, eluting with n-hexane, n-hexane-ethyl acetate mixture and ethyl acetate-methanol mixture with increasing polarity. A total of 144 fractions of ca. 400 mL each were collected and mixed on the basis of TLC. Fractions 1-15 (series A) contained essentially oil. Fractions 17-24 (series B) were concentrated to dryness and the residue (1.8 g), subjected to column chromatography over silica gel with a gradient of increasing polarity with n-hexane-EtOAc to yield 80 fractions of ca. 100 mL. Fractions 34-37 eluted with n-hexane-ethyl acetate (19:1) gave sitosterol. The combined fractions 47-50 eluted with n-hexane-ethyl acetate (9:1) yielded lupeol. The combined fractions 52-56 eluted with n-hexane-ethyl acetate (17:3) crystallized at room temperature and gave  $\alpha$ -sophoradiol. Fractions 109-111 eluted with ethyl acetate-MeOH (9:1) crystallized at room temperature to afford compound **1** after further purifications.

*6-(Methylsulfonyl)-1,2,3-dithiazinan-4-one.* White powder, m.p.: 206-208 °C.  $[\alpha]_{\text{D}}^{19} - 90^\circ$  (c 0.6,  $\text{H}_2\text{O}$ ). IR  $\nu_{\text{max}}$  (KBr)  $\text{cm}^{-1}$ : 3552.5; 2933.8; 1630.7; 1301.6; 1104.2; 487.5 and 454.5. HRTOFMS:  $m/z = 214.3010$  ( $\text{M}+\text{H}^+$ ) (calcd. for  $\text{C}_4\text{H}_7\text{NO}_3\text{S}_3$ , 213.3013). TOF MSMS NEG:  $m/z$ : 125 (15); 79 (65); 64 (100).  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ )  $\delta$  (ppm): 174.7; 56.5; 40.9; 36.1.  $^1\text{H}$ -NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  (ppm): 4.10; 3.42; 3.38; 3.18 (Table 1).

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