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Oxygen-containing sulfur-rich compounds from the bark of the tropical garlic tree *Scorodophloeus zenkeri* Harms

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Abstract

Two sulphoxides (2,3,5-trithiahexane 5-oxide and 2,4,5,7-tetrathiaoctane 2-oxide), three novel sulphones [*S*-(methylthiomethyl)-methanesulfonothioate, methylthio(methylthio-methyl)sulfone, 2,3,5,7-tetrathiaoctane3,3-dioxide] and four known sulphones [methyl-sulphonylmethylthiomethane, methylmethanethiosulfonate, bis-methyl-sulphonylmethane, and bis-(methylthiomethyl)sulfone] were isolated from the bark extracts of *Scorodophloeus zenkeri* Harms. The structures were determined by spectral methods, essentially MS and NMR experiments. © 2002 Published by Elsevier Science Ltd.

Keywords: *Scorodophloeus zenkeri*; Caesalpiniaceae; Sulphoxides; Sulphones

1. 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 (Aubréville and Leroy, 1970). The tree has a garlic-like odor which comes from its sulfur containing compounds (Amvam Zollo et al., 1995). This odor is similar to that of the fungus *Marasmius alliatus* (Hegnauer and Hegnauer, 1996). Another fungus of this genus (*M. alliaceus*) has been found to contain many sulfur compounds (Rapior et al., 1997).

The bark, seeds and wood of *Scorodophloeus zenkeri* are used as spices in some traditional foods such as “Nà-pôô”, “Nkuii” and “Bongo-tjobi” in Cameroon. In Gabon, the bark and the young leaves are used as condiments. The bark delivers the so-called “Bubimbi-bark” drug (Hegnauer and Hegnauer, 1996). Many healing powders in Central Africa contain parts of this plant.

Sulfides and alkylthiosulfides have been isolated from the bark essential oil and extracts of *S. zenkeri* (Kouokam et al., 2001).

Until now, no report has been given on the oxygen-containing sulfur compounds from this plant. In this paper we report on some sulphoxides and sulphones, isolated from the bark extracts of *S. zenkeri.*

2. Results and discussion

We used vacuum liquid chromatography (VLC), size exclusion chromatography (SEC), thin layer chromatography (TLC) and high pressure liquid chromatography (HPLC) to fractionate the dichloromethane and methanol extracts of the bark of *S. zenkeri*. The fractions and the isolated compounds were analysed by GC–MS and NMR spectroscopy. Most of the oxygen-containing sulfur-rich compounds were found in the methanol extract.

Two sulfoxides were found: The EIMS of compound **1** showed the molecular ion peak at *m*/*z* 156. The base peak at *m*/*z* 93 was attributed to a $CH_3SSCH_2^+$ fragment. The mass peak at *m*/*z* 63 represented a CH_3SO^+ fragment. The ^1H and ^{13}C NMR spectra of **1** showed singlets for two methyls (δ_H 2.53, δ_C 24.2, CH_3SS; δ_H 2.68, δ_C 37.5, CH_3SO). The two hydrogens of the methylene group showed a geminal coupling in the ^1H NMR spectrum and appeared as an AB spin system (δ_{HA} 3.89, δ_{HB} 4.01, $J = 13,7$ Hz). The data of **1** led to its identification as 2,3,5-trithiahexane 5-oxide, in good accordance to the literature (Block and O’Connor, 1974; Furukawa et al., 1980).

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Compound **2** showed the molecular ion peak at *m*/*z* 202 in the EIMS, indicative of a compound with an additional methylene group and a sulphur than **1**. The mass peak at *m*/*z* 93 represented a $CH_3SCH_2S^+$ fragment. The mass peak at *m*/*z* 139 was attributed to a $C_3H_7S_3^+$ fragment and the mass peak at *m*/*z* 63 represented a CH_3SO^+ fragment. The ^1H NMR spectrum showed three singlets at δ_H 2.21 (3H, CH_3S); 2.67 (3H, CH_3SO) and 3.95 (2H, $SSCH_2S$). The methylene group attached to the sulphoxide group appeared as an AB spin system (δ_{HA} 3.96, δ_{HB} 4.05, $J = 13.7$ Hz) in the ^1H NMR spectrum as seen for **1**. These data led to the identification of 2,4,5,7-tetrathiaoctane 2-oxide for the structure of **2**, supported by the NMR data from Block et al. (1994). This is the first time that **1** and **2** have been isolated as natural products.

The following sulphones were identified: The EIMS of compound **3** had some similarities with that of 2,3,5-trithiahexane: the base peak at *m*/*z* 61 and the molecular ion peak at *m*/*z* 140 (Block and O'Connor, 1973; Dubs and Stüssi, 1978; Moir et al., 1980; Baerlocher et al., 1999; Kouokam et al., 2001). A mass peak at *m*/*z* 79 was attributed to a $CH_3SO_2^+$ fragment. The ^1H NMR spectrum showed signals for two methyls (δ_H 2.41, CH_3S; δ_H 3.01, CH_3SO_2) and a methylene group (δ_H 3.79, SCH_2SO_2). The compound was identified as methyl(methylthio)methylsulfone also named methylsulphonylmethylthiomethane or 2,4-dithiapentan 2,2-dioxide, in agreement with the ^1H NMR data reported by Poje and Balenovic (1978), Ogura et al. (1980) and Alphand et al. (1997).

Compound **4**, was assigned the molecular formula $C_2H_6S_2O_2$ (EIMS, *m*/*z* 126). The ^1H and ^{13}C NMR spectra showed signals for two methyls (δ_H 2.69, δ_C 18.5, CH_3S; δ_H 3.29, δ_C 48.7, CH_3SO_2). These data led to the structure of methyl methanethiosulfonate, which were in good accordance with the literature data (Douglass et al., 1967; Boelens et al., 1971; Freeman and Angeletakis, 1983; Freeman and Keindl, 1988). Compound **4**, also named 2,3-dithiabutane 2,2-dioxide, had been isolated from onion (*Allium cepa* L.) and some Cruciferae species (Boelens et al., 1971; Nakamura et al., 1996).

Compound **5** showed a molecular ion peak in the EIMS at *m*/*z* 172. The base peak at *m*/*z* 94 was attributed to a $C_2H_6SO_2^+$ fragment. The ^1H NMR spectrum showed two singlets at δ_H 3.25 (6H, $2{\times}CH_3SO_2$) and δ_H 4.41 (2H, $SO_2CH_2SO_2$). Accordingly **5**, a symmetrical compound was identified as bis-methylsulphonyl methane, supported by the data from Fiecchi et al. (1967) and Grossert et al. (1984). Compound **5** had been isolated from the fungus *Tuber magnatum* Pico by Fiecchi et al. (1967).

The mass spectrum of compound **6** showed the molecular ion peak at *m*/*z* 172 and 6 could be identified as an isomer of **5**. The mass peak at *m*/*z* 79 represented the $CH_3SO_2^+$ fragment. The base peak was at *m*/*z* 93 and was attributed to a $C_2H_5S_2^+$ fragment. The mass peak at *m*/*z* 61 indicated the presence of a $CH_3SCH_2^+$ fragment. The ^1H NMR spectrum revealed an asymmetrical structure for **6** with two methyls (δ_H 2.25, CH_3S and δ_H 3.42, CH_3SO_2) and one methylene group (δ_H 4.28, SCH_2SSO_2). These data led to the identification of **6** as *S*-(methylthio) methyl methanesulfonothioate or 2,3,5-trithiahexane 2,2-dioxide.

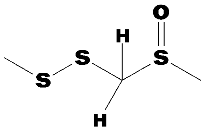
Compound **7**, (EIMS, *m*/*z* 172) was another isomer of **5** and **6**. The base peak at *m*/*z* 61 represented a $CH_3SCH_2^+$ fragment. The ^1H and ^{13}C NMR spectra showed signals for two methyls (δ_H 2.41, δ_C 17.3, CH_3S; δ_H 2,73, δ_C 19.1, CH_3SSO_2) and one methylene group (δ_H 4.16, δ_C 65.0, SCH_2SO_2). The sulfone group of **6** moved from position 2 to 3 for the formation of **7** (2,3,5-trithiahexane 3,3-dioxide), also named methylthio (methylthiomethyl) sulfone.

The EIMS of compound **8** showed the molecular ion peak at *m*/*z* 218. The base peak at *m*/*z* 61 was attributed to a $CH_3SCH_2^+$ fragment. The mass peak at *m*/*z* 93 represented a $CH_3SCH_2S^+$ fragment and the mass peak at *m*/*z* 107 indicated the presence of a $CH_3SCH_2SCH_2^+$ fragment. The ^1H NMR spectrum showed signals for two methyls (δ_H 2.22, CH_3S; δ_H 2.72, CH_3SSO_2) and two methylene groups (δ_H 3.88, SCH_2S, δ_H 4.00, SCH_2SO_2). This led to the identification of 2,3,5,7-tetrathiaoctane 3,3-dioxide as the structure of **8**.

Compound **9** showed the molecular ion peak at *m*/*z* 186 in the EIMS. The base peak at *m*/*z* 61 indicated the presence of a $CH_3SCH_2^+$ fragment. The ^1H NMR spectrum revealed a symmetrical structure for **9** with two singlets at δ_H 2.39 (6H, $2{\times}CH_3S$) and δ_H 4.04 (4H, $2{\times}SCH_2SO_2$). These data implied that the sulphone group (SO_2) is in the center of the molecule and is surrounded by two $CH_3SCH_2^+$ fragments. Compound **9** was therefore identified as 2,4,6-trithiaheptane 4,4 dioxide or bis-methylthiomethylsulfone, in good accordance with the literature data (Ahern et al., 1997).

This is the first report for the sulphones 2,3,5-trithiahexane 2,2-dioxide (**6**), 2,3,5-trithiahexane 3,3-dioxide (**7**) and 2,3,5,7-tetrathiaoctane 3,3-dioxide (**8**). Methylsulphonyl-methylthiomethane (**3**) and bis-methylthiomethylsulfone (**9**) are presented here for the first time as natural products.

Sulfides have been oxidized with H_2O_2 to yield sulphoxides which can further be converted into sulphones using $KMnO_4$ (Ahern et al., 1997). We thus postulate that the oxygen- containing sulfur-rich compounds could be generated biologically from sulfides. In this case, **1**, **6** and **7** would be oxidation products of 2,3,5-trithiahexane which has been previously isolated from *S. zenkeri* Harms (Kouokam et al., 2001). 2,4-Dithiapentane, the probable oxidation substrate of **3** and **5**, was isolated from the fungus *Tuber magnatum*



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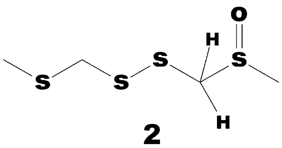

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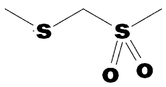

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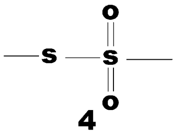

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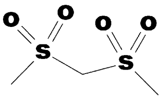

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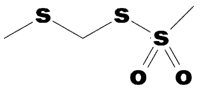

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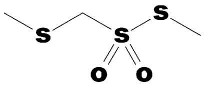

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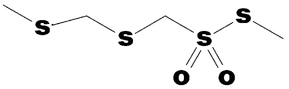

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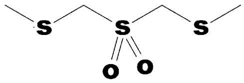

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Pico by Fiecchi et al. (1967). Compounds **2** and **8** may come respectively from the 2,4,5,7-tetrathiaoctane and 2,3,5,7-tetrathiaoctane which were both found in the bark essential oil of *S. zenkeri* (Amvam Zollo et al., 1995; Kouokam et al., 2001). Compound **4** should be a product of the oxidation reaction of dimethyldisulfide which has been isolated from many plant aromas including pineapple (*Ananas comosus*) and cacao (*Theobroma cacao*) (Flament et al., 1967; Näf-Müller and Willhalm, 1971) while compound **9** might be the oxidation product of 2,4,6-trithiaheptane which has not yet been described as a natural product.

3. Experimental

3.1. Plant material

The bark was purchased from the central local market in Yaounde, Cameroon, in March 1999. It was kept at −20 °C until the experiments were carried out. A voucher specimen is retained in the collection of the "Fachrichtung Pharmakognosie und Analytische Phytochemie", Universität des Saarlandes, D-66041 Saarbrücken.

3.2. Extraction

Powdered bark (2.5 kg) was extracted with dichloromethane (4 l) followed by methanol (1 l×4) to yield 58.6 g and 128.0 g respectively of dichloromethane and methanol extracts. The methanol extract was suspended in 800 ml water and subjected to liquid–liquid extraction using ethyl acetate (800 ml×4) to separate the most non-polar compounds. The ethyl acetate fraction obtained was dried to yield 14.2 g of extract.

3.3. Fractionation and isolation

A sub-sample of the dichloromethane extract (14.3 g) was submitted to VLC on silica gel using a gradient of ethyl acetate in *n*-hexane. Similar fractions were pooled together to yield a total of 11 fractions (A–K) according to TLC on silica gel with 50% ethyl acetate in *n*-hexane as mobile phase. The TLC plates were sprayed with anisaldehyde/sulfuric acid reagent and heated. The sulfur-rich compounds appeared in fractions H and K as yellow spots which faded rapidly. Fraction H (566 mg) was further submitted to SEC (size exclusion chromatography) on Sephadex LH-20 using dichloromethane–methanol 1:1 as mobile phase to yield nine fractions (HA-HI). Compound **3** (<1 mg), was isolated from fraction HI (16 mg) by HPLC using a silica gel column (Lichrospher Si 100, 4 mm×250 mm, 5 μm, Merck, Darmstadt) with 30% ethyl acetate in *n*-hexane as mobile phase; a differential refractometer for the detection (RI-8110, Bischoff, Leonberg) and an HPLC pump (Knauer 64, Berlin) with a flow rate of 1.5 ml/min. The retention time (RT) of compound **3** was 9.8 min. Fraction K (941 mg) was submitted to SEC using the same conditions as for fraction K, and seven fractions (KA-KG) were collected. The fraction KD (214 mg) was purified by HPLC using a diol column (Lichrospher Diol 100, 4 mm×250 mm, 5 μm, Merck, Darmstadt) with 80% ethyl acetate in *n*-hexane to afford compound **2** (13 mg, RT = 4.5 min).

The ethyl acetate extract (14.2 g) was submitted to SEC on Sephadex LH-20 with 25% dichloromethane in methanol as eluting solvent and yielded 12 fractions (A–L). A VLC of fraction G (1.7 g) on silica gel with a gradient of ethyl acetate in *n*-hexane afforded nine fractions (GA-GI). Fraction GD (62 mg) was purified by HPLC on silica gel with 10% ethyl acetate in *n*-hexane as mobile phase and yielded compound **9** (2 mg) as a minor component (RT = 10.9 min). Fraction GH (467 mg) was submitted once more to SEC in the same condition as for the ethyl acetate extract to yield five fractions (GHA–GHE). Fraction GHC (198 mg) was separated by HPLC on a diol column with 45% ethyl acetate in *n*-hexane and afforded compounds **8** (< 1 mg, RT = 11.8 min) and **1** (1 mg, RT = 12.9 min) as minor components. Fraction H (2.6 g) was submitted to VLC using the same conditions as for fraction G to yield 10 fractions (HA–HJ). HPLC of fraction HB (568 mg) on silica gel (10% ethyl acetate in *n*-hexane) yielded compound **7** (11 mg, RT = 10.7 min) and **6** (2 mg, RT = 12.7 min). Fraction HC (160 mg) was submitted to HPLC on diol (*n*-hexane–ethyl acetate 3:1) and 7 mg of compound **4** were isolated at a RT of 4.1 min. Compound **5** (< 1 mg) was obtained by HPLC on diol after 5.1 min elution with 35% ethyl acetate in *n*-hexane. All the isolated compounds were oil-like and had an intensive garlic-like odor.

3.4. Identification

GC–MS: Isolated compounds were analysed using an HP G1800A gas chromatograph (Hewlett Packard, Palo Alto), coupled to an electron ionization detector (at 280 °C) with an HP-5 capillary column (0.25 mm × 15 m, 0.25 μm film thickness). The oven temperature was programmed from 50 °C to 325 °C for a total time of 33.3 min. The vector gas was Helium at a rate of 1.0 ml/min and the injection mode was either split or splitless at 250 °C.

The HR-EI-MS of compound **7** was taken on a MAT 90 mass spectrometer (Finnigan, Bremen).

NMR: The one-dimensional NMR-spectra were recorded with an AM 400 NMR-spectrometer [Bruker, Karlsruhe at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR)]. Two dimensional NMR spectra were recorded with a DRX500 NMR spectrometer (Bruker, Karlsruhe).

3.5. Spectroscopic data

3.5.1. 2,3,5-Trithiahexane 5-oxide (*1*)

MS: *m*/*z* (rel. int.) = 156 (0.5) M$^+$, 95 (10), 93 (100), 78 (8), 63 (7), 47 (12), 46 (13). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.53 (*s*, 3H), 2.68 (*s*, 3H), 3.89 and 4.01 (AB spin system, J = 13.7 Hz, 2H). ^{13}C NMR projection from HSQC ($CDCl_3$): δ (ppm) 24.2, 37.5, 62.1.

3.5.2. 2,4,5,7-Tetrathiaoctane 2-oxide (*2*)

MS: *m*/*z* (rel. int.) = 202 (0.4) M$^+$, 186 (2), 139 (48), 111 (15), 93 (55), 61 (100), 46 (15). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.21 (*s*, 3H), 2.67 (*s*, 3H), 3.95 (*s*, 2H), 3.96 and 4.05 (AB spin system, J = 13,7 Hz, 2H). ^{13}C NMR projection from HSQC ($CDCl_3$): δ (ppm) 15.2, 37.5, 45.7, 62.0.

3.5.3. Methyl (methylthio) methylsulfone or 2,4-dithia pentan 2,2-dioxide (*3*)

MS: *m*/*z* (rel. int.) = 140 (6) M$^+$, 79 (2), 63 (8), 61 (100), 46 (7). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.41 (*s*, 3H), 3.01 (*s*, 3H), 3.79 (*s*, 2H).

3.5.4. Methyl methanethiosulfonate or 2,3-dithiabutane 2,2-dioxide (*4*)

MS: *m*/*z* (rel. int.) = 128 (9) M$^+$ + 2, 126 (67) M$^+$, 81 (100), 79 (55), 63 (71), 47 (73), 46 (28). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.69 (*s*, 3H), 3.29 (*s*, 3H). ^{13}C NMR projection from HSQC ($CDCl_3$): δ (ppm) 18.5, 48.7.

3.5.5. Bis-methylsulphonyl methane (*5*)

MS: *m*/*z* (rel. int.) = 172 (10) M$^+$, 94 (100), 79 (63), 78 (31), 63 (73), 48 (8). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.25 (*s*, 6H), 4.41 (*s*, 2H). ^{13}C NMR projection from HSQC ($CDCl_3$): δ (ppm) 41.8, 71.7.

3.5.6. S-(Methylthio) methyl methanesulfonothioate or 2,3,5-trithiahexane 2,2-dioxide (*6*)

MS: *m*/*z* (rel. int.) = 172 (1) M$^+$, 125 (1), 93 (100), 79 (6), 61 (26), 46 (11). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.25 (*s*, 3H), 3.42 (*s*, 3H), 4.28 (*s*, 2H).

3.5.7. 2,3,5-Trithiahexane 3,3-dioxide or methylthio (methylthiomethyl) sulfone (*7*)

MS: *m*/*z* (rel. int.) = 172 (0.2) M$^+$, 125 (0.3), 108 (14), 61 (100), 46 (8). HR-EI-MS: Found:171.9696; Calcd for $C_3H_8O_2S_3$ (M$^+$): 171.9686. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.41 (*s*, 3H), 2.73 (*s*, 3H), 4.16 (*s*, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 17.3, 19.1, 65.0.

3.5.8. 2,3,5,7-Tetrathiaoctane 3,3-dioxide (*8*)

MS: *m*/*z* (rel. int.) = 218 (1) M$^+$, 154 (10), 139 (49), 107 (3), 93 (29), 61 (100), 46 (10). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.22 (*s*, 3H), 2.72 (*s*, 3H), 3.88 (*s*, 2H), 4.00 (*s*, 2H). ^{13}C NMR projection from HSQC ($CDCl_3$): δ (ppm) 15.2, 37.7, 44.3, 56.3.

3.5.9. 2,4,6-Trithiaheptane 4,4 dioxide or bis-methyl thiomethylsulfone (*9*)

MS: *m*/*z* (rel. int.) = 186 (2) M$^+$, 75 (19), 74 (12), 61 (100), 46 (6). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.39 (*s*, 6H), 4.04 (*s*, 4H).

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