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## GUAIAZULENOPENTATHIEPIN AND RELATED COMPOUNDS: REACTIONS OF GUAIAZULENE WITH REACTIVE SULFURATION REAGENTS

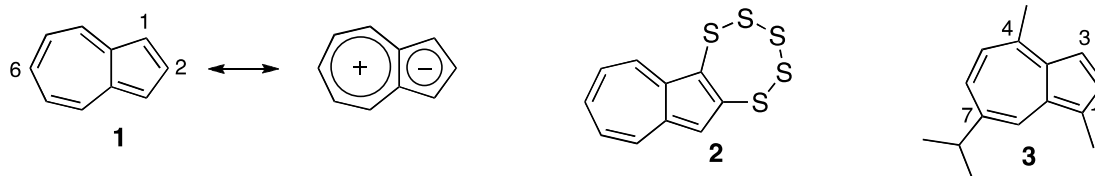
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**Abstract** – Guaiazulene reacted with reactive sulfuration reagents to give guaiazulenopentathiepin together with a 1,2-dithiin compound and a mixture of bis(guaiazulyl)sulfides. The yield of the pentathiepin was improved by the reaction with the reagent prepared from sulfur chloride and imidazole in a molar ratio of one to two. Reduction of the pentathiepin and the successive reaction with *N,N'*-(thio)carbonyldiimidazoles afforded 2-(thio)oxo-1,3-dithioles.

### INTRODUCTION

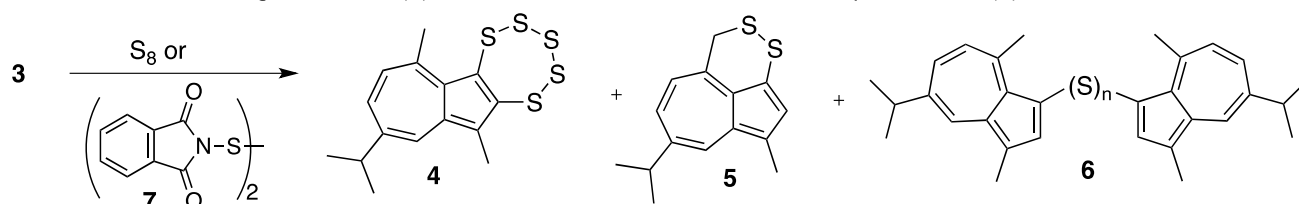
Azulene (**1**) and its derivatives, which have polarized structures, are familiar class in non-benzenoid aromatics, and their chemical, physical and biological properties have attracted much attention.<sup>1</sup> Even among them, azulenes with sulfur groups should be expected to be the key compounds for the construction of azulene-based electron donors, whereas synthetic methods for them have not been much investigated.<sup>2</sup> Recently we have reported the reaction of **1** with S<sub>8</sub>/pyridine<sup>3</sup> to produce azulenopentathiepin (**2**).<sup>4</sup> It is well known the low reactivity at a 2-position of azulenes in electrophilic substitutions.<sup>5</sup> Therefore, the investigation has been the only method for direct introduction of sulfur groups at the 2-position, so far.<sup>6</sup> Pentathiepins<sup>7</sup> are stable seven-membered ring compounds with five sulfur atoms, and the fusion with azulenes is of interest. Thus we next focused on guaiazulene (**3**).<sup>8</sup> It is a low cost azulene derivative, and the alkyl substituents will cause good solubility to organic solvents and restriction of reaction points. In this manuscript, we report the preparation of guaiazulenopentathiepin (**4**) and related compounds by the reactions with reactive sulfuration reagents.



## RESULTS AND DISCUSSION

We first applied the synthetic method for azulenopentathiepin (2)<sup>4</sup> to guaiazulene (3). That is, 3 reacted with elemental sulfur in pyridine under thermal conditions (Table 1, Entry 1). Unfortunately, the product was not guaiazulenopentathiepin (4) but a small amount of bis(guaiazulyl)sulfides (6) and recovery of 3 even though the long reaction time. The results suggested that the reactivity of the 3-position of 3 is very low due to the existence of the 4-methyl group. *N,N'*-Dithiobisphthalimide (7),<sup>9</sup> a more reactive sulfuration reagent than elemental sulfur, reacted in the same solvent at 80 °C to afford 4 and an unexpected dithin compound (5) in low yields, respectively. The reaction in DMF with pyridine as an additive slightly increased the yields of 4 and 5 (Entry 3).

**Table 1.** The reaction of guaiazulene (3) with elemental sulfur or *N,N'*-dithiobisphthalimide (7)



Entry	$S_8$ or 7 (atoms as S)	Solvent (mol·L <sup>-1</sup> )	Additive (molar eq.)	Temperature	Time	Yield			
						4	5	6	3
1	$S_8$ (14)	Pyridine (6.0 × 10 <sup>-2</sup> )	-	reflux	3 d	-	-	4wt.% <sup>a</sup>	56%
2	7 (5)	Pyridine (1.0 × 10 <sup>-2</sup> )	-	80 °C	3 d	2%	2%	38wt.% <sup>a</sup>	5%
3	7 (5)	DMF (1.0 × 10 <sup>-2</sup> )	Pyridine (3.5)	80 °C	1 d	5%	11%	51wt.% <sup>a</sup>	5%

<sup>a</sup> Percent by weight

Sulfur chloride is a highly reactive sulfuration reagent and has been used to produce pentathiepins fused with pyrroles and thiophenes by the reaction with/without diazabicyclo[2.2.2]octane (DABCO).<sup>10</sup> We next applied these methods to 3 (Table 2, Entries 1 and 2). Sulfur chloride was added to 3 (Addition Method A) to give hardly complicated products within a small amount of 5 and 6 even though the reaction at low temperature (-40 °C). The reaction in the presence of DABCO gave 6 as a main product. In the case with imidazole instead of DABCO, the similar results were shown (Entry 3). Whereas, the reaction in the high diluted concentration (Entry 4, 2.0 × 10<sup>-4</sup> mol·L), which preferred an intramolecular cyclization, improved the yields of 4 (17%) and 5 (14%). The reverse addition (Method B), that is, 3 was added by drop to sulfuration reagents, was carried out as expected the similar effect in Entry 4. A

somewhat effective result was shown not in Entry 5 (**4**: 5%) but in Entry 6 (**4**: 12%). The difference is arising from sulfur chloride to imidazole ratio in sulfuration reagents (Entries 5 and 6, sulfur chloride/imidazole = 1/4 and 1/2). As shown in Scheme 1, the former might form a reagent (**I**) and the latter form a more reactive one (**II**). The reagents reacted with **3** to generate the intermediates (**III**) and the successive sulfuration formed the intermediate (**IV**), which cyclized intramolecularly to produce the pentathiepin (**4**). An increased reagent of **II** improved the yield of **4** (27%, Entry 7). Although the yield of **4** was still not enough, these results suggested that the imidazolium salt moieties of **II** and **IV** are reasonably good leaving groups to react at the 3-position of **3** and at the 2-position of **IV**. The reactions of azulene (**1**) with sulfur chloride/imidazole gave hardly complicated products in any case.

**Table 2.** The reaction of guaiazulene (**3**) with sulfuration reagents derived from sulfur chloride in CH<sub>2</sub>Cl<sub>2</sub>

Entry	S <sub>2</sub> Cl <sub>2</sub> (molar eq.)	Concentration (mol·L <sup>-1</sup> )	Additive (molar eq.)	Temperature / Time	Addition Method	Yield			
						<b>4</b>	<b>5</b>	<b>6</b>	<b>3</b>
1	2.5	1.0 × 10 <sup>-2</sup>	-	-40 °C / 2 h	A <sup>a</sup>	trace	5%	10wt.% <sup>c</sup>	-
2	2.5	1.0 × 10 <sup>-2</sup>	DABCO (5)	-40 °C / 2 h	A <sup>a</sup>	-	-	66wt.% <sup>c</sup>	39%
3	2.5	1.0 × 10 <sup>-2</sup>	Imidazole (10)	-40 °C / 2 h	A <sup>a</sup>	trace	trace	76wt.% <sup>c</sup>	3%
4	2.5	2.0 × 10 <sup>-4</sup>	Imidazole (10)	-78 °C / 1 h	A <sup>a</sup>	17%	14%	14wt.% <sup>c</sup>	trace
5	5	1.0 × 10 <sup>-2</sup>	Imidazole (20)	-40 °C / 6 h	B <sup>b</sup>	5%	1%	81wt.% <sup>c</sup>	3%
6	5	1.0 × 10 <sup>-2</sup>	Imidazole (10)	-40 °C / 6 h	B <sup>b</sup>	12%	5%	27wt.% <sup>c</sup>	trace
7	7.5	1.0 × 10 <sup>-2</sup>	Imidazole (15)	-40 °C / 6 h	B <sup>b</sup>	27%	trace	11wt.% <sup>c</sup>	trace

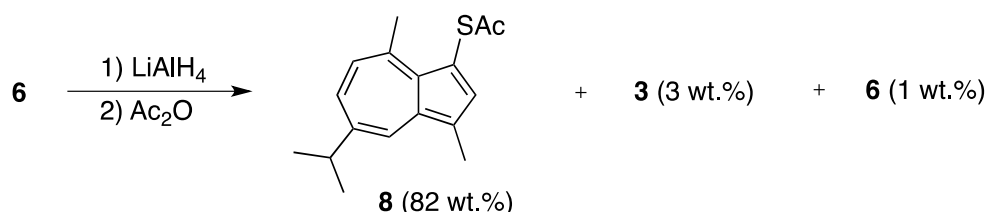
<sup>a</sup> Method A: The sulfuration reagent was added to **3**. <sup>b</sup> Method B: Reverse addition <sup>c</sup> Percent by weight

Guaiazulenopentathiepin (**4**) was bluish green plates (mp 110.5-111 °C). The <sup>1</sup>H NMR spectrum showed seven membered ring's protons at  $\delta$  7.18, 7.47 and 8.14 and alkyl groups' protons at  $\delta$  1.35 (6H), 2.72 (3H), 3.07 (1H) and 3.24 (3H). The <sup>13</sup>C NMR spectrum showed fourteen kinds of carbons arising from an azulene skeleton and alkyl side chains. The longest wave-maximum of UV-VIS spectrum appeared at 615 nm (log  $\epsilon$  2.78) as a characteristic peak of azulene derivatives. The MS spectra (FAB and MALDI-TOF) gave molecular ion and fragment ion peaks [ $m/z$  356 (M<sup>+</sup>), 292 (M<sup>+</sup>-2S)]. Together with the result of elemental analysis, those spectral data supported the proposed structure. Cyclic voltammogram of **4** showed an irreversible wave and the first reduction potential was nearly equal to that of azulenopentathiepin (**2**) [(E<sub>1</sub><sup>red</sup>)<sub>pc</sub>: **4**; -1.43 V, **2**; -1.48 V]. On the other hand, the electron donation ability was slight smaller than that of **2** [(E<sub>1</sub><sup>ox</sup>)<sub>pa</sub>: **4**; +0.88 V, **2**; +0.75 V].

A 1,2-dithin compound (**5**) was green crystals (mp 56.0-57.0 °C), and might be formed by an intramolecular cyclization of the intermediate (**III**, Scheme 1). It is reported that the 4-Me proton of guaiazulene (**3**) is rather acidic.<sup>11</sup> The <sup>1</sup>H NMR spectrum showed seven membered ring's protons at  $\delta$

6.75, 7.36, 7.52 and 8.14 and alkyl groups' protons at  $\delta$  1.35 (6H), 2.61 (3H), and 3.05 (1H). The NOE correlation appeared between the protons at  $\delta$  4.37 (s, 2H, CH<sub>2</sub>S) and  $\delta$  6.75 (d,  $J$  = 10.2 Hz, 1H, H-5). The <sup>13</sup>C NMR spectrum showed thirteen kinds of carbons (two carbons were overlapped at  $\delta$  135.0). The longest wave-maximum of UV-VIS spectrum appeared at 680 nm (log  $\epsilon$  2.34), which was a longer one than that of pentathiepin (**4**). The MS spectrum [MALDI-TOF:  $m/z$  260 ( $M^+$ )] and elemental analysis data also supported the proposed structure.

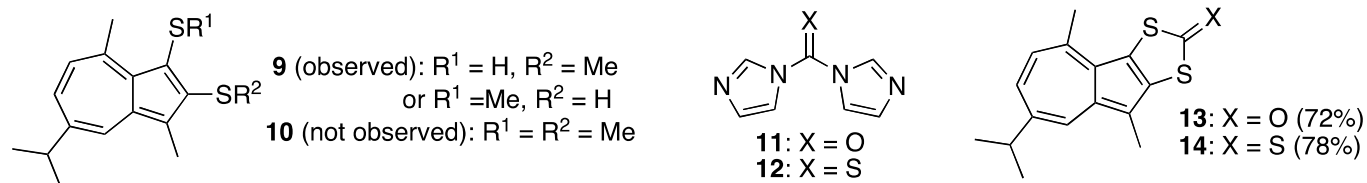
Bis(guaiazulyl)sulfides (**6**), an inseparable mixture of sulfides, would be produced by the condensation of guaiazulene (**3**) with intermediates (**III**, **IV** and the other ones with different numbers of sulfur atoms, Scheme 1). As part of the structure determination of **6**, reductive acetylation was carried out (Scheme 2). Treatment of **6** with LiAlH<sub>4</sub> in THF generated the corresponding thiolate, which was acetylated by acetic anhydride to afford acetylthioguaiazulene (**8**, purple needles, mp 69.5-70.5 °C, 82wt.%). A small amount of **3** was also obtained, therefore, not only cleavage of S-S bonds of **6** but also C-S ones would be occurred in this reaction conditions. Physical data of **8** were consistent with the proposed structure. These results suggested that the structure of **6** could be accepted as described above.



**Scheme 2**

It is expected that guaiazulenopentathiepin (**4**) is a useful precursor for the conversion into 1,2-*S*-substituted guaiazulenes as with azulenopentathiepin (**2**). Reduction of **4** with NaBH<sub>4</sub> in benzene/EtOH generated a bis(thiolate), which was methylated by iodomethane to give not bis(methylthio)guaiazulene (**10**) but methylthioguaiazulenethiol (**9**, blue viscous oil). The result was different from the case of **2**, forming a bis(methylthio) derivative.<sup>4</sup> The <sup>1</sup>H NMR spectrum of **9** showed three kinds of methyl groups ( $\delta$  2.51, 2.68 and 2.80 as two methyl and one methylthio moieties) and a thiol proton ( $\delta$  7.01). The MS spectrum showed a molecular ion peak [FAB:  $m/z$  276 ( $M^+$ )]. Further instrumental data could not be measured due to rather instability of **9**. Although the position of a methylthio group is undecided as far, the 2-substitute (**9**: R<sup>1</sup> = H, R<sup>2</sup> = Me) is plausible considering the steric hindrance at the 4-methyl group.

A bis(thiolate), generated from **4** with LiAlH<sub>4</sub> in THF, was treated with *N,N'*-carbonyldiimidazole (**11**) or *N,N'*-thiocarbonyldiimidazole (**12**) to afford a 2-oxo-1,3-dithiole (**13**, green solid, mp 125-126 °C, 72%) or a 2-thioxo-1,3-dithiole (**14**, dark green needles, mp 186-187 °C, 78%), respectively. Corresponding physical data of **13** and **14** were consistent with their proposed structures.



In conclusion, we have carried out the reactions of guaiazulene (**3**) with reactive sulfuration reagents such as sulfur chloride/imidazole to produce guaiazulenopentathiepin (**4**), which is a precursor for the conversion into 1,2-*S*-substituted guaiazulenes, together with a 1,2-dithiin (**5**) and bis(guaiazulyl)sulfides (**6**). Further work, aimed at the construction of novel azulene-based electron donors derived from **4** and its azulene derivative (**2**), is now under investigation and will appear elsewhere.

## EXPERIMENTAL

Mps were determined with a Laboratory Devices MEL-TEMP apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra (SiMe<sub>4</sub> as the internal standard) were obtained with Bruker AV500, AM400, AV300, AC300 and/or AC200 spectrometers. IR spectra were obtained with a Perkin Elmer System 2000 FT instrument and electronic spectra (UV-VIS) with a JASCO V-560 spectrophotometer. MS spectra were obtained with a JEOL JMS700AM and/or a Bruker AutoflexIII spectrometers. CV was obtained with an ALS-600 electrochemical measuring apparatus. Unless otherwise stated the spectra were taken in the following solvents/media: IR, KBr; UV-VIS, CH<sub>2</sub>Cl<sub>2</sub>; <sup>1</sup>H and <sup>13</sup>C NMR, CDCl<sub>3</sub>; MS spectra were taken at fast atom bombardment (FAB) and/or MALDI-TOF method; CV, V vs. Ag/Ag<sup>+</sup>, GC, Pt wire, 0.1 M TBAP in DMF. The progress of reactions was followed by TLC method using Merck Silica gel 60F<sub>254</sub>.

**General procedure for the reaction of guaiazulene (**3**) with elemental sulfur or *N,N'*-dithiobisphthalimide (**7**).** To a solution of **3** in the solvent with/without an additive, elemental sulfur or *N,N'*-dithiobisphthalimide (**7**) was added and stirred for the time at the temperature under Ar. After removal of the solvent *in vacuo*, the residue was dissolved in hexane. The soluble component was purified by SiO<sub>2</sub> column chromatography to give guaiazulenopentathiepin (**4**), a 1,2-dithiin compound (**5**) and/or bis(guaiazulyl)sulfides (**6**, an inseparable mixture of sulfides). Atoms as S of sulfuration reagents, solvents, concentrations, (an additive), temperatures, times and yields were indicated in Table 1.

**Guaiazulenopentathiepin (**4**):** bluish green plates; mp 110.5-111 °C; <sup>1</sup>H NMR δ 1.35 (d, *J* = 6.9 Hz, 6H), 2.72 (s, 3H), 3.07 (sep, *J* = 6.9 Hz, 1H), 3.24 (s, 3H), 7.18 (d, *J* = 10.5 Hz, 1H), 7.47 (dd, *J* = 10.5, 1.8 Hz, 1H), 8.14 (d, *J* = 1.8 Hz, 1H); <sup>13</sup>C NMR δ 12.6 (2C), 24.5, 29.6, 37.8, 124.1, 130.8, 132.5, 137.4, 137.7, 138.5, 139.7, 145.7, 149.5, 151.8; UV-VIS (log ε) λ<sub>max</sub> 615 (2.78), 302 (4.28), 280 (4.28); CV (V vs. Ag/Ag<sup>+</sup>) (E<sup>red</sup>)<sub>pc</sub> -1.92, -1.43, (E<sup>ox</sup>)<sub>pa</sub> +0.88; MS (FAB, NBA) *m/z* 356 (M<sup>+</sup>), 292 (M<sup>+</sup>-2S); MS (MALDI,

Dithranol)  $m/z$  356 ( $M^+$ ), 292 ( $M^+-2S$ ). Anal. Calcd for  $C_{15}H_{16}S_5$ : C, 50.52; H, 4.52. Found: C, 50.52; H, 4.44.

**1,2-Dithiin (5):** green crystals; mp 56.0-57.0 °C;  $^1H$  NMR  $\delta$  1.35 (d,  $J = 6.9$  Hz, 6H), 2.61 (s, 3H), 3.05 (sep,  $J = 6.9$  Hz, 1H), 4.37 (s, 2H), 6.75 (d,  $J = 10.2$  Hz, 1H), 7.36 (dd,  $J = 10.2, 1.8$  Hz, 1H), 7.52 (s, 1H), 8.14 (d,  $J = 1.8$  Hz, 1H);  $^{13}C$  NMR  $\delta$  12.6 (2C), 24.5, 38.2, 42.0, 114.8, 122.8, 124.0, 128.9, 133.7, 135.0 (2C), 139.8, 140.8, 141.7; UV-VIS (log  $\epsilon$ )  $\lambda_{max}$  680 (2.34), 410 (3.67), 294 (4.30), 251 (4.35), 233 (4.26), 225 (4.27); MS (MALDI, Dithranol)  $m/z$  260 ( $M^+$ ). Anal. Calcd for  $C_{15}H_{16}S_2$ : C, 69.18; H, 6.19. Found: C, 69.17; H, 6.16.

**Bis(guaiazulyl)sulfides (6, an inseparable mixture):** green viscous oil; Selected  $^1H$  NMR of the mixture (as a major component 1)  $\delta$  1.33 (d,  $J = 6.8$  Hz, 6H), 2.48 (s, 3H), 3.06 (sep,  $J = 6.8$  Hz, 1H), 3.19 (s, 3H), 6.81 (d,  $J = 10.7$  Hz, 1H), 7.19 (s, 1H), 7.25 (dd,  $J = 10.7, 2.2$  Hz, 1H), 7.98 (d,  $J = 2.2$  Hz, 1H); Selected  $^1H$  NMR of the mixture (as a major component 2)  $\delta$  1.33 (d,  $J = 6.8$  Hz, 6H), 2.37 (s, 3H), 3.06 (sep,  $J = 6.8$  Hz, 1H), 3.22 (s, 3H), 6.94 (d,  $J = 10.7$  Hz, 1H), 7.32 (dd,  $J = 10.7, 2.2$  Hz, 1H), 7.54 (s, 1H), 8.11 (d,  $J = 2.2$  Hz, 1H); Selected MS (FAB, NBA) of the mixture  $m/z$  459 [ $MH^+$  ( $n = 2$ )], 458 [ $M^+$  ( $n = 2$ )], 427 [ $MH^+$  ( $n = 1$ )], 426 [ $M^+$  ( $n = 1$ )].

**General procedure for the reaction of guaiazulene (3) with sulfuration reagents prepared from sulfur chloride with/without an additive (method A).** To a  $CH_2Cl_2$  solution of **3**, a mixture of sulfur chloride with/without an additive in  $CH_2Cl_2$  was added and stirred for the time at the temperature under Ar. The reaction mixture was quenched with water and the aqueous layer was extracted with  $CH_2Cl_2$ . The organic layer was dried over  $MgSO_4$  and the solvent was removed under reduced pressure. The residue was purified by  $SiO_2$  column chromatography to give guaiazulenopentathiepin (**4**), a 1,2-dithiin compound (**5**) and/or bis(guaiazulyl)sulfides (**6**, a mixture of sulfides). Molar *eq.* of sulfur chloride, concentrations, additives, temperatures, times, and yields were indicated in Table 2.

**General procedure for the reaction of guaiazulene (3) with sulfuration reagents prepared from sulfur chloride with imidazole (method B).** To a  $CH_2Cl_2$  solution of a sulfuration reagent prepared from sulfur chloride with imidazole, a solution of **3** in  $CH_2Cl_2$  was added by drop for 30 min and stirred for 6 h at -40 °C under Ar (concentration:  $1.0 \times 10^{-2}$  mol·L $^{-1}$ ). The reaction mixture was quenched with water and the aqueous layer was extracted with  $CH_2Cl_2$ . The organic layer was dried over  $MgSO_4$  and the solvent was removed under reduced pressure. The residue was purified by  $SiO_2$  column chromatography to give guaiazulenopentathiepin (**4**), a 1,2-dithiin compound (**5**) and bis(guaiazulyl)sulfides (**6**, a mixture of sulfides). Molar *eq.* of sulfur chloride, molar *eq.* of imidazole and yields were indicated in Table 2.

**Reductive acetylation of bis(guaiazulyl)sulfides (6):** To a solution of **6** (202 mg, a mixture of sulfides) in dry THF (10 mL), 105wt.% of LiAlH<sub>4</sub> (5.60 mmol) was added at 0 °C under Ar. The solution was stirred for 30 min at rt and then acetic anhydride (30.1 mmol) was added and stirred for 2 h. The reaction mixture was diluted with Et<sub>2</sub>O and washed with sat. *aq.* NaHCO<sub>3</sub> and water. The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified by SiO<sub>2</sub> column chromatography to give acetylthioguaiazulene (**8**, 165 mg, 82wt.%), guaiazulene (**3**, 6.1 mg, 3wt.%) and **6** (2.3 mg, 1wt.%).

**Acetylthioguaiazulene (8):** purple needles; mp 69.5-70.5 °C; <sup>1</sup>H NMR δ 1.33 (d, *J* = 6.9 Hz, 6H), 2.36 (s, 3H), 2.60 (s, 3H), 3.05 (sep, *J* = 6.9 Hz, 1H), 3.05 (s, 3H), 7.03 (d, *J* = 10.8 Hz, 1H), 7.39 (dd, *J* = 10.8, 2.1 Hz, 1H), 7.54 (s, 1H), 8.17 (d, *J* = 2.1 Hz, 1H); <sup>13</sup>C NMR δ 13.0 (2C), 24.7, 27.1, 29.6, 38.0, 107.0, 125.5, 129.7, 134.5, 136.0, 137.2, 140.1, 142.3, 144.8, 146.7, 197.5; IR ν 1682; MS (MALDI, Dithranol) *m/z* 273 (MH<sup>+</sup>). Anal. Calcd for C<sub>17</sub>H<sub>20</sub>OS: C, 74.96; H, 7.40. Found: C, 74.78; H, 7.46.

**Reductive methylation of guaiazulenopentathiepin (4):** To a solution of **4** in dry benzene and *abs.* EtOH (1 : 1), 10 molar *eq.* of NaBH<sub>4</sub> was added at rt under Ar. The solution was stirred for 15 min at rt and then 100 molar *eq.* of iodomethane was added and stirred for 30 min. The reaction mixture was quenched with sat. *aq.* NH<sub>4</sub>Cl and the aqueous layer was extracted with hexane. The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The main product in the residue was rather unstable methylthioguaiazulenethiol (**9**), and further purification could not be carried out.

**Methylthioguaiazulenethiol (9, an unstable material):** blue viscous oil; <sup>1</sup>H NMR δ 1.35 (d, *J* = 6.9 Hz, 6H), 2.51 (s, 3H), 2.68 (s, 3H), 2.80 (s, 3H), 3.07 (sep, *J* = 6.9 Hz, 1H), 7.01 (s, 1H, SH), 7.04 (d, *J* = 10.6 Hz, 1H), 7.30 (dd, *J* = 10.6, 1.8 Hz, 1H), 8.01 (d, *J* = 1.8 Hz, 1H); MS (FAB, NBA) *m/z* 276 (M<sup>+</sup>).

**Preparation of 2-oxo-1,3-dithiole (13) or 2-thioxo-1,3-dithiole (14).** To a solution of **4** in dry THF (concentration: 2.8 x 10<sup>-2</sup> or 4.3 x 10<sup>-2</sup> M), 10 or 5.0 molar *eq.* of LiAlH<sub>4</sub> was added at 0 °C under Ar. The solution was stirred for 30 min at rt and then 20 or 10 molar *eq.* of *N,N'*-carbonyldiimidazole (**11**) or *N,N'*-thiocarbonyldiimidazole (**12**) was added and stirred for 15 min or 1 h at rt. The reaction mixture was quenched with 2 N HCl and the aqueous layer was extracted with Et<sub>2</sub>O. The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The resulting residue was purified by SiO<sub>2</sub> column chromatography to give **13** (72%) or **14** (78%), respectively.

**2-Oxo-1,3-dithiole (13):** green solid; mp 125-126 °C; <sup>1</sup>H NMR δ 1.36 (d, *J* = 6.9 Hz, 6H), 2.61 (s, 3H), 2.83 (s, 3H), 3.06 (sep, *J* = 6.9 Hz, 1H), 7.01 (d, *J* = 10.8 Hz, 1H), 7.38 (dd, *J* = 10.8, 1.8 Hz, 1H), 8.05 (d, *J* = 1.8 Hz, 1H); <sup>13</sup>C NMR δ 12.8 (2C), 24.7, 26.7, 38.3, 111.8, 117.6, 127.1, 130.5, 132.2, 135.9, 136.8, 139.6, 141.6, 142.6, 195.2; UV-VIS (log ε) λ<sub>max</sub> 607 (2.75), 377 (3.94), 360 (3.90), 315 (4.76), 256 (4.30),

217 (4.22); IR  $\nu$  1651; MS (MALDI, Dithranol)  $m/z$  288 ( $M^+$ ). Anal. Calcd for  $C_{16}H_{16}OS_2$ : C, 66.63; H, 5.59. Found: C, 66.50; H, 5.44.

**2-Thioxo-1,3-dithiole (14):** dark green needles; mp 186-187 °C;  $^1H$  NMR  $\delta$  1.37 (d,  $J = 6.9$  Hz, 6H), 2.61 (s, 3H), 2.85 (s, 3H), 3.09 (sep,  $J = 6.9$  Hz, 1H), 7.11 (d,  $J = 10.8$  Hz, 1H), 7.47 (dd,  $J = 10.8, 1.8$  Hz, 1H), 8.11 (d,  $J = 1.8$  Hz, 1H);  $^{13}C$  NMR  $\delta$  12.3 (2C), 24.6, 26.5, 38.3, 115.8, 122.2, 127.8, 128.7, 133.3, 136.7, 138.3, 142.3, 143.4, 149.0, 216.4; IR  $\nu$  1047; MS (MALDI, Dithranol)  $m/z$  304 ( $M^+$ ). Anal. Calcd for  $C_{16}H_{16}S_3$ : C, 63.11; H, 5.30. Found: C, 62.94; H, 5.00.

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