Isolation of *S*-*n*-Butylcysteine Sulfoxide and Six *n*-Butyl-Containing Thiosulfinates from *Allium siculum*

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Isolation and identification of (S_SR_C)-*S*-*n*-butylcysteine sulfoxide (**1**) from the bulbs of *Allium siculum* is reported. This compound was found in all parts of the plant (bulbs, stem, leaves, and flowers) along with known compounds (S_SR_C)-*S*-methyl- and (R_SR_C)-(*E*)-*S*-(1-propenyl)cysteine sulfoxides (**2** and **3**, respectively). In addition, six *n*-butyl-containing thiosulfinates (**4**−**9**) have been found in a CH_2Cl_2 extract of the bulbs. Structures were determined by a combination of spectral methods (primarily NMR and MS) and by comparison with authentic compounds obtained by synthesis. Antimicrobial activities of **4**−**7** and **9** are reported.

Nectaroscordum (Lindl.) Gren. & Godr. (Alliaceae) is a small subgenus of the genus *Allium* consisting of only two species, *Allium siculum* (Ucria) Lindl. and *Allium tripedale* (Trautv.) Grossh. Both are rare ornamental bulbous plants used in gardening. The former is native to Asia Minor, southern France, and Sicily (hence the trivial name Sicilian honey garlic), where it grows in damp shady woods. It is still sometimes referred to by the synonymous names *Allium nectaroscordum*, *Nectaroscordum siculum* Ucria, *A. dioscorides* auct., or *A. meliophilum* Juz. The second member of the subgenus, *A. tripedale* (syn. *N. tripedale* Trautv. or *N. persicum* (Bornm.) Bornm.), is indigenous to Armenia, Iran, and Iraq.

Both members of the *Nectaroscordum* subgenus, *A. siculum* and *A. tripedale*, are very closely related to other plants of the genus *Allium* L. Due to their close morphological similarities, the relationship between these two groups has long been embroiled in taxonomic controversy. At present, classification of *Nectaroscordum* as a subgenus in the *Allium* genus is generally accepted. The chromosome basic number of $x = 9$, special and unique characteristics of most flower parts, and other morphological peculiarities of *Nectaroscordum* species were the main arguments in support of separating this oligotypic group at a generic level.[1−3]

A. siculum attracted our attention because of its odor, which is notably different from that of common alliaceous plants. This paper describes our investigation of the amino acid odor precursors present in this plant and their primary breakdown products.

Results and Discussion

An amino acid-containing fraction from the bulbs of *A. siculum* was isolated by ion-exchange chromatography. A preliminary GC−MS screening[4] of a methyl chloroformate-derivatized sample revealed the presence of *S*-methyl-, *S*-(1-propenyl)-, *S*-*n*-butyl-, *S*-*n*-propyl-, and *S*-(methylthiomethyl)cysteine derivatives in the extract, with the latter two occurring only in trace amounts (<10 μg g^{-1} fresh weight). Of these five amino acids, only the *S*-*n*-butylcysteine derivative had not been isolated from a natural source, although Hörhammer et al. reported TLC detection of a butylcysteine derivative in garlic.[5] Therefore, we focused our attention primarily on isolation and structural elucidation of this amino acid.

Since the GC method used does not permit distinction between *S*-substituted cysteines and their sulfoxides, the oxidation state and absolute configuration of the derivative remained to be determined by means of spectroscopic methods. Thus, another extract from the bulbs was prepared and subjected to preparative C-18 HPLC. The component having a retention time and UV spectrum identical to that of an authentic sample of *S*-*n*-butylcysteine sulfoxide was collected, affording 23 mg of a white crystalline compound.

The ^{1}H and ^{13}C NMR spectroscopic data together with a very strong IR absorption band at 1020 cm^{-1} (S═O) and MALDI-HRMS [MH^+] of 194.0846 (calcd for $C_7H_{16}NO_3S$ 194.0845) confirmed the structure of the amino acid as *S*-*n*-butylcysteine sulfoxide. CD and ^{1}H NMR spectroscopy were employed to determine the absolute configuration at the two chiral centers of the compound (at the sulfur and the α-carbon). The CD spectrum contained a positive maximum at 212 nm ($\Delta\epsilon$ +4.98), indicating that the absolute configuration of the sulfoxide group was R_S.[6] The ^{1}H NMR spectrum contained a typical splitting pattern of the S(O)-CH_2CH(NH_2) methylene protons. They appeared as two distinctive doublets of doublets (δ 3.19 and 3.44) with coupling constants of $J_{AX} = 7.8$ Hz and $J_{BX} = 6.0$ Hz. These values are a typical feature of all *S*-substituted cysteine sulfoxide derivatives that have the sulfoxide oxygen and the amino group on the same face of the molecule. On the basis of the above data, the structure and absolute configuration of the derivative were unambiguously assigned as (S_SR_C)-*S*-*n*-butylcysteine sulfoxide (BCSO, **1**). The correct structural assignment of **1** was further verified by comparing its specific optical rotation value ($[\alpha]^{20}_D$ +20°) with those of synthetic (S_SR_C)-*S*-*n*-butylcysteine sulfoxide ($[\alpha]^{20}_D$ +23°) and (R_SR_C)-*S*-*n*-butylcysteine sulfoxide (**1b**) ($[\alpha]^{20}_D$ −27°). The geometric arrangement of the substituents about the sulfur in **1** is thus identical with that of the other *S*-substituted cysteine sulfoxides that have so far been isolated from other alliaceous species.

Hörhammer et al. were the first to report the occurrence of *S*-*n*-butylcysteine sulfoxide in nature.[5] They reported detection of BCSO in garlic (*A. sativum* L.) using a fairly nonsensitive TLC procedure in which a spot with an R_f

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Table 1. Content and Relative Ratios of *S*-Substituted Cysteine Sulfoxides in Different Parts of *A. siculum*

	relative proportions (%) and total content (mg 100 g^{-1} fr wt)			
	MCSO[a] (**1**)	PeCSO[b] (**2**)	BCSO[c] (**3**)	content
stem[d]	18	64	18	3.5 ± 0.2
leaves[d]	23	48	29	3.1 ± 0.4
flowers[d]	73	11	15	n.d.[e]
bulbs[d]	62	15	23	34.6 ± 1.4
bulbs[f]	58	17	26	10.1 ± 1.5

[a] MCSO (**2**), *S*-methylcysteine sulfoxide. [b] PeCSO (**3**), (*E*)-*S*-(1-propenyl)cysteine sulfoxide. [c] BCSO (**1**), *S*-*n*-butylcysteine sulfoxide. [d] Grown in NY. [e] Not determined due to insufficient amount of material. [f] Grown in VA.

value identical with that of synthetic BSCO was identified as BSCO, without any further verification by spectral methods. Their finding has never been confirmed. Thus, it is likely that Hörhammer et al.[5] confused BSCO with an amino acid that coincidentally had the same R_f value. Indeed, it has been shown in numerous subsequent studies utilizing more sensitive GC and HPLC techniques that BCSO does not occur in garlic at levels > 0.01 mg g^{-1} fresh weight.[4,7−14] It may however be present in some other alliaceous species in trace quantities, as indicated by the finding of several *n*-butyl-containing sulfides in onion (*Allium cepa* L.)[15] and Chinese chive (*Allium tuberosum* L.)[16] volatiles.

No attempt was made to isolate the remaining two major cysteine derivatives detected by GC. That these cysteine derivatives are most probably sulfoxide forms with absolute configurations analogous to **1**, i.e., (S_SR_C)-*S*-methylcysteine sulfoxide (**2**, MCSO, methiin) and (R_SR_C)-(*E*)-*S*-(1-propenyl)cysteine sulfoxide (**3**, PeCSO, isoalliin), is supported by previous reports[10,17] in which the presence of **2** in a closely related species, *A. tripedale*, was confirmed. It should be noted that the difference in the *R*,*S* nomenclature of **3** is merely a consequence of the reversed priority assignments of the substituents. Thus, although **3** has the opposite *R*,*S* designation, the geometric arrangement of its substituents about the sulfur remains analogous to that observed in **1** and **2**. That **2** and **3** are indeed present was further verified by detection of various methyl- and 1-propenyl-containing thiosulfinates (shown later). Thiosulfinates are typical enzymatic breakdown products of *S*-alk(en)ylcysteine sulfoxides, but are not formed from *S*-alk(en)ylcysteines. Both **2** and **3** are common secondary metabolites occurring in the majority of *Allium* species,[4,7−14] with **2** also occurring abundantly in other families (e.g., Brassicaceae[18] and Leguminosae[19,20]).

The relative proportions as well as total content of sulfoxides **1**−**3** were determined in the leaves, stem, flowers, and bulbs of the plant. Bulbs from two different sources were examined. As shown in Table 1, the total amount of the amino acids ranged between 0.03 and 0.35 mg g^{-1} fresh weight, being highest in the bulbs. Interestingly, although the total content of **1**−**3** in the bulbs grown in different areas varied by a factor of 3, the relative proportions of **1**/**2**/**3** were almost identical in both samples. On the other hand, these ratios varied significantly in different parts of the plant. Similar variations in the mutual ratios of *S*-alk(en)ylcysteine sulfoxides have also been observed between various parts of Chinese chive (*A. tuberosum* L.)[21] and ramsom (*A. ursinum* L.).[22]

Freeman and Whenham[23] were the first to study the *S*-substituted cysteine sulfoxides in *A. siculum*. They observed *S*-methyl- and *S*-propylcysteine sulfoxides (PCSO) in a ratio of 92.5:7.5. The authors did not look for the presence of **1**, although it may have been present. More surprising, however, is the absence of **3** in the sample they analyzed, with PCSO being present instead.

The second member of the subgenus, *A. tripedale*, was also recently examined for the presence of *S*-substituted cysteine sulfoxides.[10] Although the authors were looking for the presence of BCSO, surprisingly only *S*-methylcysteine sulfoxide (**2**) was detected in the bulbs (0.1 mg g^{-1} fresh weight). If present, it is possible that **1** might have been overlooked due to the less sensitive HPLC method used. The detection limit of the HPLC method was 0.01 mg g^{-1} fresh weight, which makes it 10 times less sensitive compared to the GC method employed in the present study. Unfortunately, despite great effort, we were unable to obtain a sample of *A. tripedale* to confirm the absence of **1** in this very rare species.

S-Substituted cysteine sulfoxides are readily cleaved by C−S lyases upon disruption of the tissue, forming *S*-alkyl alkanethiosulfinates as the primary breakdown products. The latter compounds are responsible for the aroma of freshly prepared homogenates. In theory, three *S*-substituted cysteine sulfoxides should give rise to nine thiosulfinates (three symmetrical and six unsymmetrical ones). However, in the case of PeCSO, the situation is different. The symmetrical thiosulfinate arising from PeCSO, (*E*)-*S*-(1-propenyl) (*E*)-1-propenethiosulfinate [(*E*,*E*)-CH_3CH=$CHS(O)SCH$=$CHCH_3$], was found to be very unstable above −70 °C, rapidly rearranging into several other compounds.[8] On the other hand, (*E*)-*S*-(1-propenyl) alkanethiosulfinates [(*E*)-CH_3CH=$CHSS(O)R$] were shown to undergo rapid *cis*/*trans* isomerization, giving a mixture of both stereoisomers. Considering the above facts, one would expect up to 10 thiosulfinates (**4**−**13**) to be formed in *A. siculum* (Figure 1). Of these, six should contain an *n*-butyl moiety (**4**−**9**). Thus, to facilitate their HPLC detection and subsequent isolation from a plant homogenate, thiosulfinates **4**−**9** were synthesized. An HPLC method employing a C-8 column was developed. Excellent separation was achieved for the regioisomers **4**/**5** and **7**/**8** as well as for the stereoisomers **6**/**7**. Indeed, all six of the *n*-butyl-containing thiosulfinates were detected in a CH_2Cl_2 extract of a bulb homogenate. The thiosulfinates **4**, **5**, and **9** were subsequently isolated by preparative C-8 HPLC and fully characterized by spectroscopic methods (NMR, IR, MALDI/MS, and UV). The content of **6**−**8** in the extract was too low to permit preparative scale isolation. However, their presence was detected by comparison of their retention times and UV spectra with those of authentic compounds. To the best of our knowledge, this represents the first report of the occurrence of *n*-butyl-containing thiosulfinates in nature.

Since thiosulfinates are known to exhibit a variety of physiological effects, including antitumor, antimicrobial, and antifungal activity, as well as insect attractive/repulsive activity,[8,24,25] the antimicrobial properties of the thiosulfinates **4**−**7** and **9** were tested against a panel of both Gram-negative and Gram-positive bacteria, as shown in Table 2. The thiosulfinates exhibited modest activity against most of the microorganisms tested. There was no significant difference observed between the antimicrobial activities of **4**−**7** and **9** using the agar diffusion test.

Experimental Section

General Experimental Procedures. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 HC spectrometer and IR spectra on a Perkin-Elmer RX I FTIR spectrometer. UV spectra were measured on a Shimadzu UV-1601PC

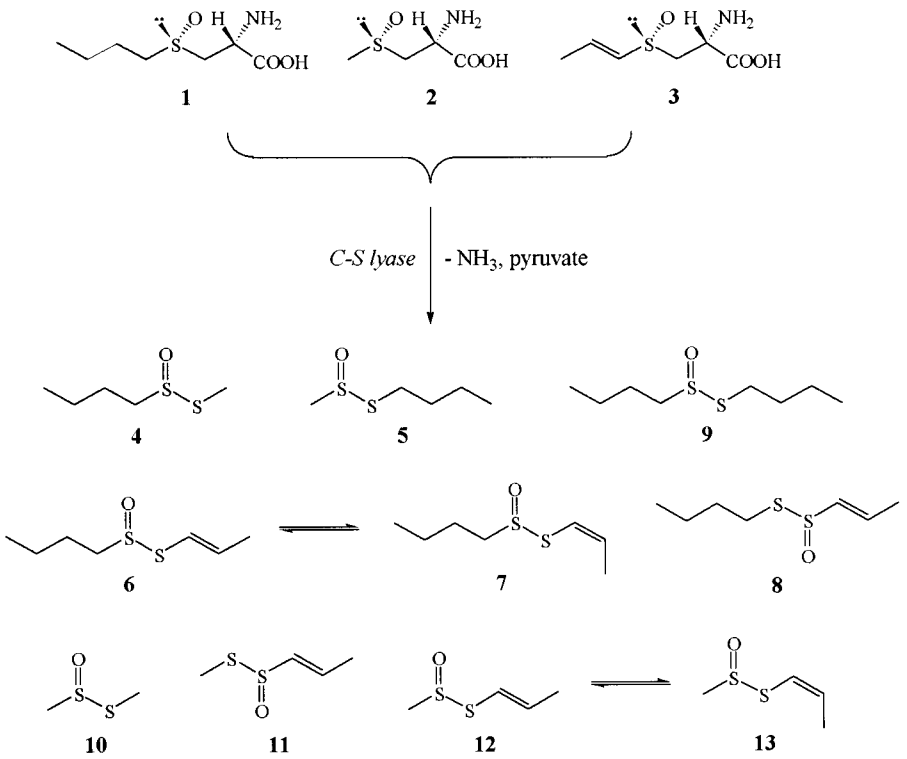

Figure 1. Structures and enzymatic decomposition of the cysteine sulfoxides found in *A. siculum*.

Table 2. Antimicrobial Activity of Isolated *n*-Butyl-Containing Thiosulfinates

tested compound	dose (μg/disk)	*B. cereus*	*S. aureus*	*S. agalactiae*	*E. coli*	*P. aeruginosa*	*S. maltophila*	*K. pneumoniae*
4	10	0[a]	8	0	0	0	0	0
	250	30	30	0	22	0	12	16
	500	34	38	0	24	8	14	18
5	10	0	0	0	0	0	0	0
	250	22	20	16	14	0	12	12
	500	28	26	24	20	0	17	20
6/7	10	0	0	0	0	0	0	0
	250	30	19	0	12	0	12	10
	500	38	38	0	18	7	14	14
9	10	8	10	0	0	0	0	0
	250	34	34	30	10	0	8	8
	500	40	38	34	16	0	16	8
gentamicin	10	22	22	18	18	18	20	22
chloramphenicol	30	20	18	23	20	0	22	24
tetracycline	30	27	20	28	18	10	13	18
ampicillin	10	7	38	30	18	0	0	0

[a] Diameter of the zone of inhibition (in mm).

spectrophotometer and CD spectra on an Aviv 62DS circular dichroism spectrometer. Specific rotation values were determined by means of a Perkin-Elmer 243B polarimeter. Melting points (uncorr) were determined using a Köfler hot stage. HPLC separations were performed on a Dynamax SD-200 binary pump system, employing a Varian PDA 330 detector and analytical C-18 or C-8 columns (Rainin Microsorb-MV 100 Å, 250 × 4.6 mm, 5 μm). Alternatively, preparative C-18 or C-8 columns (Rainin Dynamax-100 Å, 250 × 21.4 mm, 8 μm) were used. GC analyses were performed on a Varian 3800 gas chromatograph equipped with a Saturn 2000 GC/MS/MS detector, using a Rtx-1 fused silica capillary column (30 m × 0.25 mm; 25 μm; Restek Corp.). Matrix-assisted laser desorption/ionization (MALDI) FTMS experiments were performed on an IonSpec FTMS mass spectrometer.

Plant Material. A whole fresh plant of *A. siculum* subsp. *bulgaricum* was obtained from the *Allium* garden of Professor E. Block (Schenectady, NY) while in full bloom in June 2001 and immediately analyzed. For subsequent preparative work, additional bulbs of the plant were obtained from Brent and Becky's Bulbs (Gloucester, VA). These were harvested in September 2001 and immediately analyzed. Voucher specimens (A33085 and A33086) have been deposited in the New York State Museum Herbarium in Albany, NY.

Isolation of Amino Acids. Fresh bulbs (1485 g) were carefully peeled, homogenized in MeOH using a blender, and extracted with boiling MeOH (2 × 1500 mL). The extracts were combined, concentrated to ca. 150 mL by vacuum evaporation (40 °C), and adjusted to 300 mL by addition of 3% HCl. The precipitate that appeared on acidification was filtered off, and the filtrate was passed through a cation-exchange column (19 × 2.1 cm; Amberlite 200, H^+ form, 20−50 mesh). After washing the column with 3% HCl (300 mL) and H_2O (300 mL), the amino acid-containing fraction was eluted with 500 mL of 1 M NH_4OH. The eluent obtained was concentrated to ca. 20 mL, filtered, and subjected to preparative HPLC, using a C-18 column and 10 mM KH_2PO_4 buffer (pH 5.5, solvent A) with acetonitrile (solvent B) as the mobile phase. The gradient was as follows: A/B 99/1 (0 min), 90/10 (in 20 min), and 50/50 (in 30 min), with a flow rate of 18 mL min^{-1}. The fraction eluting at 8.9 min was collected and evaporated to dryness, and the residue recrystallized from boiling H_2O to yield 23 mg of white crystalline **1**.

Quantitative Analysis. An amino acid fraction was isolated from each part of the plant (leaves, stem, flowers, and bulbs) in a manner similar to that described above. Due to the limited amount of material, only one extract of each part was prepared. Extracts were analyzed by GC in triplicate, after derivatization with methyl chloroformate.[4] *S*-Benzylcysteine sulfoxide, added to the samples before extraction, was used as an internal standard.

Isolation of Thiosulfinates. The bulbs (2180 g) were carefully peeled and homogenized with 800 mL of H_2O using a blender. The slurry was allowed to stand at room temperature for 15 min and filtered, and the filtrate was extracted with cold CH_2Cl_2 (2 × 600 mL). After centrifugation, the organic layers were combined and evaporated, yielding a yellow viscous oil with an intense alliaceous odor. It was redissolved in 20 mL of acetonitrile, filtered, and subjected to preparative HPLC, using a C-8 column. The gradient was as follows: H_2O/CH_3CN 75/25 (0 min), 60/40 (in 20 min), 25/75 (in 30 min), and 5/95 (in 45 min), with a flow rate of 21 mL min^{-1}. The fractions eluting at 12.1, 12.7, and 29.8 min were collected, affording **4**, **5**, and **9** respectively.

Synthesis of Reference Compounds. *S*-Alk(en)yl-substituted L-cysteines and their sulfoxides were synthesized as described by Stoll and Seeback.[26] Their identities were confirmed by NMR and IR spectroscopy. Pure diastereomers of *S*-*n*-butyl-L-cysteine sulfoxide (**1** and **1b**) were obtained by repeated fractional recrystallization (H_2O−acetone−acetic acid, 70:30:1 v/v/v) and in combination with preparative C-18 HPLC coupled with diode array detection.

Dimethyl and di-*n*-butyl disulfides were purchased (Aldrich). *n*-Butyl methyl and *n*-butyl 1-propenyl disulfides were prepared according to McAllan et al.[27] and Wijers et al.,[28] respectively. The thiosulfinates were prepared by oxidation of the corresponding disulfides with 3-chloroperoxybenzoic acid (MCPBA, 1 equiv) in CH_2Cl_2 (−20 °C, 30 min) and purified by preparative C-8 HPLC.

Antimicrobial Assays. The tested compounds were dissolved in EtOH, and a 10 μL aliquot of each solution was placed on a 6 mm disk (Becton Dickinson Microbiology Systems). The disks containing the test compounds (10, 250, and 500 μg, respectively) were placed on agar plates that had been seeded with selected microorganisms. After overnight incubation at 37 °C, the zones of inhibition surrounding the disks were measured. Disks with several common antibiotics were used as a control (Becton Dickinson Microbiology Systems). The following bacteria were used: *Bacillus cereus* (ATCC 11778), *Staphylococcus aureus aureus* (ATCC 27853), *Streptococcus agalactiae* (ATCC 13813), *Escherichia coli* (ATCC 25922), *Pseudomonas aeruginosa* (ATCC 27853), *Stenotrophomonas maltophila* (ATCC 13637), *Klebsiella pneumoniae pneumoniae* (ATCC 13833).

(S_SR_C)-*S*-*n*-Butylcysteine sulfoxide (1): white solid; mp 171−173 °C; $[\alpha]^{22}_D$ +23° (*c* 0.24, H_2O); CD $\Delta\epsilon_{max}$ (*c* 0.02, 25 °C, H_2O) +4.98 (212 nm); UV (H_2O) λ_{max} nm (log ϵ) 192 (3.64), 212 (3.18); IR (KBr) ν_{max} 3423 (m, br), 3445 (m, br), 3082 (m, br), 2958−2864 (m), 1612 (s), 1590 (vs), 1432 (m), 1360 (m), 1323 (m), 1020 (vs) cm^{-1}; ^{1}H NMR (D_2O, 300 MHz) δ 0.92 (3H, t, J = 7.4 Hz, H-8), 1.47 (2H, m, H-7), 1.73 (2H, quintet, J = 7.6 Hz, H-6), 2.97 (2H, m, H-5), 3.19 (1H, dd, J = 7.8, 13.8 Hz, H-3a), 3.44 (1H, dd, J = 6.0, 13.8 Hz, H-3b), 4.21 (1H, J = 6.0, 7.8 Hz, dd, H-2); ^{13}C NMR (D_2O, 75 MHz) δ 12.9 (C-8), 21.2 (C-7), 23.9 (C-6), 50.9 (C-3), 51.1 (C-2), 52.0 (C-5), 171.5 (C-1); MALDI-HRMS [MH^+] 194.0846 (calcd for $C_7H_{16}NO_3S$, 194.0845).

(R_SR_C)-*S*-*n*-Butylcysteine sulfoxide (1b): white solid; mp 168−170 °C; $[\alpha]^{22}_D$ −27° (*c* 0.94, H_2O); CD $\Delta\epsilon_{max}$ (*c* 0.046, 25 °C, H_2O) −2.57 (216 nm); UV (H_2O) λ_{max} nm (log ϵ) 192 (3.61), 214 (3.12); IR (KBr) ν_{max} 3440 (w, br), 2958−2864 (m), 1612 (vs), 1592 (vs), 1529 (m), 1394 (s), 1353 (m), 1026 (vs) cm^{-1}; ^{1}H NMR (D_2O, 300 MHz) δ 0.94 (3H, t, J = 7.5 Hz, H-8), 1.47 (2H, m, H-7), 1.74 (2H, quintet, J = 7.6 Hz, H-6), 3.01 (2H, m, H-5), 3.38 (2H, d, J = 6.0 Hz, H-3), 4.25 (1H, t, J = 6.0, H-2); ^{13}C NMR (D_2O, 75 MHz) δ 12.9 (C-8), 21.2 (C-7), 23.9 (C-6), 50.4 (C-3), 50.6 (C-2), 51.3 (C-5), 171.5 (C-1).

***S*-Methyl *n*-butanethiosulfinate (4):** viscous yellow oil; UV (EtOH) λ_{max} (log ϵ) 204 (3.56), 250 (3.28) nm; IR (neat) ν_{max} 2962−2875 (s), 1461 (m), 1428 (m), 1085 (vs), 1053 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.98 (3H, t, J = 7.4 Hz, H-1), 1.50 (2H, m, H-2), 1.82 (2H, m, H-3), 2.67 (3H, s, H-7), 3.12 (2H, m, H-4); ^{13}C NMR ($CDCl_3$; 75 MHz) δ 13.7 (C-1), 14.4 (C-7), 21.9 (C-2), 25.5 (C-3), 55.9 (C-4); MALDI-HRMS [MH^+] 153.0406 (calcd for $C_5H_{13}OS_2$, 153.0402).

***S*-*n*-Butyl methanethiosulfinate (5):** a viscous yellow oil; UV (EtOH) λ_{max} (log ϵ) 204 (3.62), 250 (3.43) nm; IR (neat) ν_{max} 2962 (s), 1413 (m), 1260 (s), 1085 (vs), 1027 (vs), 867 (m), 798 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (3H, t, J = 7.2 Hz, H-7), 1.46 (2H, hex, J = 7.5 Hz, H-6), 1.77 (2H, m, H-5), 3.00 (3H, s, H-1), 3.15 (2H, m, H-4); ^{13}C NMR ($CDCl_3$; 75 MHz) δ 13.5 (C-7), 21.8 (C-6), 32.7 (C-5), 32.8 (C-4), 42.8 (C-1); MALDI-HRMS [MH^+] 153.0404 (calcd for $C_5H_{13}OS_2$, 153.0402).

(*E*)-*S*-(1-Propenyl) *n*-butanethiosulfinate (6): a viscous yellow oil; UV (EtOH, mixture with **7**) λ_{max} (log ϵ) 208 (3.92), 256 (3.51) nm; IR (neat, mixture with **7**) ν_{max} 2958−2869 (m), 1721 (w), 1613 (w), 1464 (m), 1442 (m), 1379 (w), 1331 (w), 1089 (vs), 1056 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (3H, t, J = 7.4 Hz, H-1), 1.49 (2H, m, H-2), 1.81 (2H, m, H-3), 1.91 (3H, m, H-9), 3.12 (2H, m, H-4), 6.35 (1H, m, H-7), 6.35 (1H, m, H-8); ^{13}C NMR ($CDCl_3$; 75 MHz) δ 13.7 (C-1), 15.2 (C-9), 21.9 (C-2), 25.5 (C-3), 55.9 (C-4), 117.2 (C-8), 136.6 (C-7); MALDI-HRMS [MNa^+] 201.0377 (calcd for $C_7H_{14}OS_2Na$, 201.0378).

(*Z*)-*S*-(1-Propenyl) *n*-butanethiosulfinate (7): a viscous yellow oil; UV and IR see **6**; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.98 (3H, t, J = 7.2 Hz, H-1), 1.49 (2H, m, H-2), 1.81 (2H, m, H-3), 1.86 (3H, m, H-9), 3.16 (2H, m, H-4), 6.29 (1H, m, H-7), 6.44 (1H, m, H-8); ^{13}C NMR ($CDCl_3$; 75 MHz) δ 13.7 (C-1), 19.0 (C-9), 21.9 (C-2), 25.5 (C-3), 55.5 (C-4), 115.9 (C-8), 143.5 (C-7); MALDI-HRMS [MNa^+] 201.0377 (calcd for $C_7H_{14}OS_2Na$, 201.0378).

***S*-*n*-Butyl (*E*)-1-propenethiosulfinate (8):** a viscous yellow oil; UV (EtOH) λ_{max} (log ϵ) 208 (3.97), 262 (3.62) nm; IR (neat) ν_{max} 2962−2873 (m), 1620 (m), 1441 (m), 1095 (vs), 1079 (vs), 952 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (3H, t, J = 7.3 Hz, H-9), 1.46 (2H, hex, J = 7.4 Hz, H-8), 1.79 (2H, m, H-7), 1.98 (3H, d, J = 6.3 Hz, H-1), 3.14 (2H, m, H-6), 6.33−6.61 (2H, m, H-2, H-3); ^{13}C NMR ($CDCl_3$; 75 MHz) δ 13.5 (C-9), 17.4 (C-1), 21.7 (C-8), 32.7 (C-7), 32.9 (C-6), 133.0 (C-3), 135.8 (C-2); MALDI-HRMS [MNa^+] 201.0377 (calcd for $C_7H_{14}OS_2Na$, 201.0378).

***S*-*n*-Butyl *n*-butanethiosulfinate (9):** a viscous yellow oil; UV (EtOH) λ_{max} (log ϵ) 206 (3.56), 250 (3.35) nm; IR (neat) ν_{max} 2960−2876 (s), 1466 (m), 1381 (w), 1271 (w), 1225 (w), 1085 (vs), 1050 (s) cm^{-1}; MALDI-HRMS [MH^+] 195.0867 (calcd for $C_8H_{18}OS_2$, 195.0872).

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