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Synthesis and fungicidal activity of methylsulfanylmethyl ether derivatives of levoglucosenone

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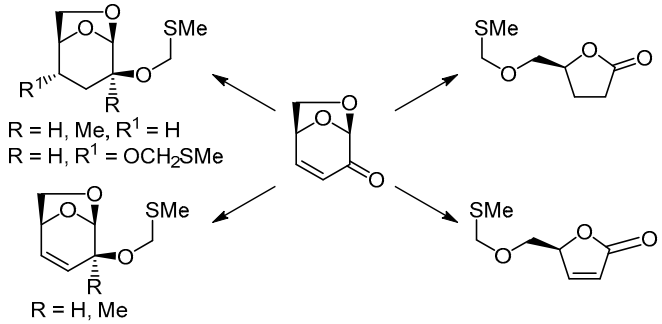


A series of derivatives were synthesized on the basis of levoglucosenone that contained hydroxy groups at the C-4 atom or C-2 and C-4 atoms or a hydroxy and methyl group at the C-4 atom. In addition, 4-hydroxymethylbutanolides were synthesized. Derivatives containing hydroxy groups were obtained as methylsulfanylmethyl ethers. It was established that compounds containing a 6,8-dioxabicyclo[3.2.1]-octane ring exhibited fungicidal activity against *Rhizoctonia solani*. It was shown that the presence of a methylsulfanylmethyl moiety in the ring could increase the fungicidal activity of compounds.

Keywords: γ-butanolides, levoglucosenone, methylthiomethyl ethers, fungicidal activity, *Rhizoctonia solani.*

Levoglucosenone is a unique compound with advantages compared to other materials that are obtained from renewable biological sources: it is readily available *via* pyrolysis of any cellulose-containing materials. The structure of levoglucosenone combines 6,8-dioxabicyclo-[3.2.1]octane framework with an enone system, keto group, and an acetal center. The 1,6-anhydro bridge blocks the acetal center and sterically shields the molecule, providing regio- and stereoselectivity. All of these features combined in one molecule make levoglucosenone a convenient chiral starting material for practical synthesis of various enantiomerically pure derivatives that are used in the chemistry of natural compounds.[1] A wide range of biologically active natural compounds and their analogs have been synthesized on the basis of levoglucosenone: carbohydrates,[2] nucleosides,[3] γ-butyrolactones,[4] pheromones,[5] and prostaglandins.[6] In several cases the levoglucosenone molecule was modified in order to obtain compounds with practically useful biological properties: cytotoxic activity,[7] antimicrobial[8] and herbicidal effects.[9]

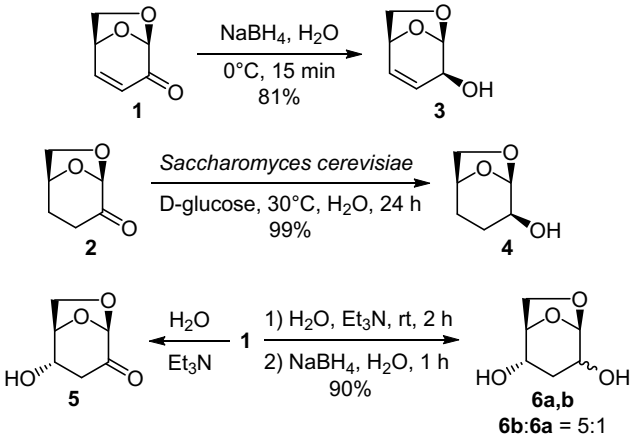
Recent progress in the use of levoglucosenone derivatives as alternative industrial solvents for the replacement of toxic solvents points to the great promise of such renewable chemicals not only in laboratory-scale syntheses but also for industrial applications.[10]

In the current work, we present the results achieved in the synthesis of levoglucosenone derivatives, among which hydroxy derivatives protected with a methylsulfanylmethyl group showed a new type of biological effect – fungicidal activity against the microscopic fungi *Bipolaris sorokiniana*, *Fusarium oxysporum*, and *Rhizoctonia solani*.

We applied several practical methods for the modification of levoglucosenone (**1**): oxa-Michael reaction, 1,2-alkylation, and keto group reduction. It should be noted that dihydrolevoglucosenone (Cyrene™) (**2**)) is easily prepared by hydrogenation[11] and is commercially available. It is known that levoglucosenone (**1**) can be stereo- and regioselectively reduced with $NaBH_4$ in aqueous medium, leading to the formation of carbinol **3**[12] (Scheme 1). Diastereomerically pure alcohol **4** was obtained by

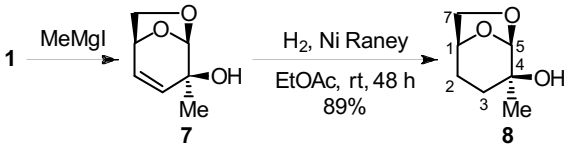
selective reduction of Cyrene (**2**) using baker's yeast (*Saccharomyces cerevisiae*).[13] A Michael reaction was performed by maintaining levoglucosenone (**1**) in water in the presence of Et_3N for 2 h, resulting in hydroxy ketone **5**.[12] We used this reaction in a one-pot procedure where hydroxy ketone **5** obtained by hydration of levoglucosenone (**1**) was immediately reduced with $NaBH_4$ in aqueous medium, giving diols **6a**,**b**.

Scheme 1



The reaction of levoglucosenone (**1**) with MeMgI in CH_2Cl_2–Et_2O system was used to synthesize alcohol **7**[14] (Scheme 2). Since similar methylation of Cyrene (**2**) resulted in a mixture of products,[11b,15] the saturated alcohol **8** was obtained by hydrogenation of alcohol **7** in the presence of Raney nickel catalyst.

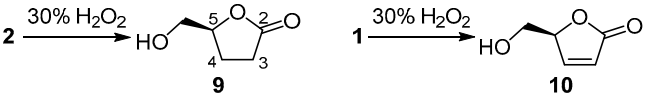
Scheme 2



Another short route for the modification of levoglucosenone derivatives involves Baeyer–Villiger oxidation that leads to butan-4-olides containing a primary hydroxymethyl group protected by a formyl group.[16] Previously we developed an effective method for Baeyer–Villiger oxidation of Diels–Alder adducts obtained from levoglucosenone (**1**) and 1,3-dienes, giving deprotected γ-butanolides in one step by refluxing the adducts with 30% H_2O_2 and acids in *i*-PrOH.[17] We studied the oxidation reaction of Cyrene **2** with 30% H_2O_2 in the presence of *p*-TsOH, which led to the formation of butanolide **9** in 85% yield (Table 1).

The well-known acidic catalyst Amberlyst 15 has been used for the hydrolysis of formyl group in γ-butanolides[16b,c] and was able to promote the oxidation of Cyrene (**2**) at room temperature. When the reaction was performed in *i*-PrOH over 2 days, the yield of deprotected product **9** was 44%. The reaction proceeded analogously also in aqueous medium. Doubling the amount of Amberlyst 15 allowed to increase the yield of butanolide **9** to 68% while using the same reaction duration.

Table 1. Baeyer–Villiger oxidation of Cyrene (**2**) and levoglucosenone (**1**)*



9 **10**

Compound	Catalyst (amount)	Solvent	Temperature, °C	Time, h	Yield, %
2	*p*-TsOH (1 mol)	*i*-PrOH	80	2	85
2	Amberlyst 15 (1 mol)	*i*-PrOH	25	48	44
2	Amberlyst 15 (1 mol)	H_2O	25	48	46
2	Amberlyst 15 (2 mol)	H_2O	25	48	68
2	Amberlyst 15 (2 mol)	–	50	1	87
2	Amberlyst 15 (2 mol)	H_2O	50	1	87
2	Amberlyst-15 (2 mol)	H_2O	50	2	84**
1	Amberlyst-15 (2 mol)	H_2O	50	1	76
1	Amberlyst 15 (2 mol)	H_2O	50	2	70**

* Reaction conditions: 10 mmol of ketone **1** or **2**, 50 mmol H_2O_2.
** Reaction conditions: 10 mmol of ketone **1** or **2**, 10 mmol H_2O_2.

In order to improve the yield of butanolide **9**, we performed the reaction at 50°C without adding solvent. The product was formed in 87% yield already after 1 h, but the process could not be controlled due to its highly exothermic nature. Diluting the reaction mixture with water in 1:1 ratio enabled better control of the reaction without decreasing the yields.

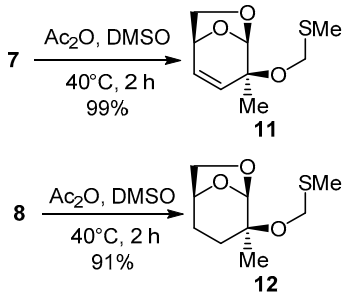
Using an excess of H_2O_2 was effective for achieving complete conversion, but required neutralization of residual reagent in order to prevent explosion during workup of the reaction mixture. In order to decrease the residual amount of H_2O_2, we studied oxidation using 1 equiv of 30% H_2O_2. This change resulted in a slight decrease of conversion and yield but allowed to nearly completely avoid the need for H_2O_2 neutralization step.

Baeyer–Villiger oxidation of levoglucosenone (**1**) in *i*-PrOH in the presence of *p*-TsOH led to the formation of complex product mixture. Oxidation of levoglucosenone (**1**) with 5 equiv of 30% H_2O_2 in aqueous medium in the presence of Amberlyst 15 resin provided lactone **10** in 76% yield (Table 1). Using equimolar amounts of oxidizing agent gave lactone **10** in 70% yield. It should be noted that epimerization at the C-5 carbon atom did not occur under these conditions.

The further direction of work involved protecting the free hydroxy groups in compounds obtained above as methylsulfanylmethyl ethers. This transformation can be achieved using DMSO–Ac_2O,[14,18] DMSO–Ac_2O–AcOH,[19] and Me_2S–$(PhCO_2)_2$–MeCN[20] systems. Synthesis of methylsulfanylmethyl ether **11** was performed in quantitative yield by heating alcohol **7** in Ac_2O–DMSO system to 40°C (Scheme 3).[14] The saturated product **12** was obtained analogously.

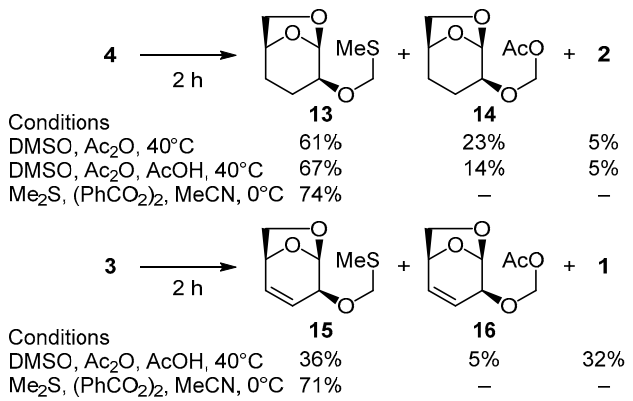
The protection of hydroxy group in alcohol **4** was performed in DMSO–Ac_2O system, leading to the formation of the desired ether **13** as well as acetate **14** and a byproduct from the oxidation of Cyrene (**2**) (Scheme 4). Using DMSO–Ac_2O–AcOH system, which is commonly

Scheme 3



employed in similar cases,[19] gave ether **13** in 67% yield. The reaction of DMSO with allyl alcohol **3** under these conditions increased the yield of levoglucosenone (**1**) oxidation product to 32%, while the yield of the desired ether **15** was 36%. The attempt to synthesize methylthiomethyl ether from alcohol **5** resulted in dehydration, giving levoglucosenone (**1**) in 76% yield. For the purpose of increasing the yield of ethers **13** and **15** we tested a method where alcohols were treated with Me_2S in the presence of $(PhCO_2)_2$. As a result, alcohols **4** and **3** were converted to ethers **13** and **15** in 74 and 71% yields, respectively.

Scheme 4



Synthesis of bismethylsulfanylmethyl ether **17** was achieved starting from 2*S*-isomer **6a** using Me_2S–$(PhCO_2)_2$ mixture (Scheme 5). The hydroxy groups of γ-butanolides **9** and **10** were also protected using Me_2S. The reaction in both cases proceeded easily, with the formation of ethers **18** and **19** in 83 and 80% yields, respectively. It should be noted that this method was more effective for the protection of hydroxy groups in γ-butanolide **9**, compared to the previously described synthesis using chloromethyl methyl sulfide where the yield of product **18** was only 46%.[21]

All methylsulfanylmethyl derivatives **11**–**13**, **15**, **17**–**19**, levoglucosenone (**1**), and alcohol **7** were tested for fungicidal activity against the microscopic fungi *Rhizoctonia solani*, *Bipolaris sorokiniana*, and *Fusarium oxysporum* that affect agricultural crops (Table 2). The compounds were tested as 0.5% solutions in DMF.

The results of biological testing allowed to conclude that the majority of the studied compounds at 0.5% concentration showed pronounced fungicidal activity against *Rhizoctonia solani*, resulting in nearly complete growth suppression. Lactone **19** exhibited fungicidal

Scheme 5

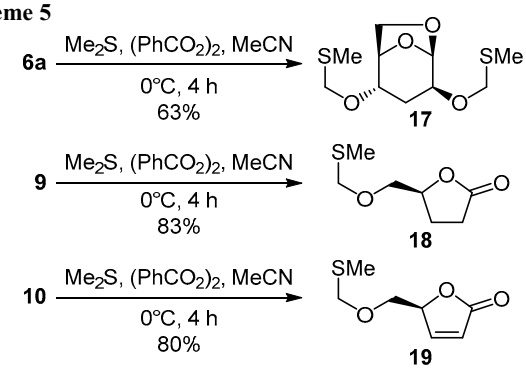


Table 2. The effects of compounds on the development of fungal test cultures (aerial mycelium development suppression in the zone of compound action, mm)

Compound	*Rhizoctonia solani*	*Bipolaris sorokiniana*	*Fusarium oxysporum*
1	13.0 ± 3.0	13.0 ± 1.0	14.0 ± 3.0
7	31.6 ± 3.2	Delay in fungal development	13.3 ± 0.7
11	No growth of micromycetes	Delay in fungal development	15.0 ± 3.0
12	–*	–	–
13	30.1 ± 4.7	Delay in fungal development	–
15	No growth of micromycetes	–	–
17	No growth of micromycetes	–	–
18	No growth of micromycetes	–	–
19	No growth of micromycetes	No growth of micromycetes	–

* No activity or insignificant zone of growth suppression.

activity against the microscopic fungus *Bipolaris sorokiniana*, suppressing its development. The rest of the methylthiomethyl ethers showed different levels of fungistatic activity against *Bipolaris sorokiniana* and *Fusarium oxysporum*.

Remarkably, compounds not containing sulfur, such as levoglucosenone (**1**) and alcohol **7**, also suppressed the growth of microscopic fungi, while the saturated ether **12** bearing a methyl group at the C-4 carbon atom was the least active among the tested compounds.

In addition, testing according to analogous method revealed bactericidal activity of levoglucosenone (**1**) at 0.5% concentration against actinobacteria *Streptomyces xanthophaeus* and *Streptomyces atroolivaceus.*

Thus, compounds containing 6,8-dioxabicyclo[3.2.1]-octane ring in their structures may exhibit fungicidal activity against *Rhizoctonia solani* and fungistatic effects on micromycetes *Bipolaris sorokiniana* and *Fusarium oxysporum.* The presence of methylsulfanylmethyl group in molecule can result in enhanced fungicidal activity of these compounds.

Experimental

IR spectra were recorded for Nujol mulls on Shimadzu IR Prestige-21 and Bruker Tensor 27 spectrometers. ^{1}H and

^{13}C NMR spectra were acquired on a Bruker Avance III 500 MHz spectrometer (500 and 125 MHz, respectively) for $CDCl_3$ solutions (the use of other solvents is indicated in each separate case), internal standard – residual solvent signals ($CDCl_3$: 7.27 ppm for ^{1}H nuclei, 77.1 ppm for ^{13}C nuclei; CD_3OD: 3.30 ppm for ^{1}H nuclei, 49.0 ppm for ^{13}C nuclei). The majority of ^{13}C NMR spectra were acquired in DEPT or J-MOD modes. In the case of compound **4**, additional two-dimensional COSY, ^{1}H–^{13}C HSQC, and NOESY spectra were acquired. Mass spectra were recorded on a Shimadzu LCMS-2010 EV single quadrupole mass spectrometer in positive and negative ion modes at 4.5 and –3.5 kV capillary potentials, respectively, using electrospray ionization, the eluent was MeCN–H_2O system (MeOH–H_2O system was used as eluent for compound **19**). Elemental analysis was performed on a EuroVector EA2000 CHNS(O)-analyzer. The optical rotation angles were measured on a PerkinElmer-341 polarimeter. Melting points were determined on a Boetius apparatus equipped with an RNMK 05 viewing adapter. TLC analysis was performed on Sorbfil PTSKh-AF-A plates (Sorbpolymer, Russia). Column chromatography was performed on Silica gel 60 from Macherey-Nagel (particle size 0.063–0.2 mm).

Alcohols **5**[12] and **7**[14] were obtained according to published procedures.

(1*S*,4*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]oct-2-en-4-ol (3). A solution of levoglucosenone (**1**) (1.00 g, 7.93 mmol) in H_2O (20 ml) was cooled to 0°C and treated by the addition of 98% $NaBH_4$ (0.31 g, 7.93 mmol). The excess of $NaBH_4$ was destroyed after 15 min by adding acetone (2 ml). The aqueous layer was extracted with $CHCl_3$, the organic layers were combined and dried over anhydrous $MgSO_4$. The solvent was removed by distillation, the residue was separated chromatographically using petroleum ether – EtOAc as eluent, gradient from 2:1 to 1:1. Yield 0.82 g (81%), mp 67–68°C, $[\alpha]_D^{20}$ –33.7°(*c* 1.0, $CHCl_3$). Recrystallization from petroleum ether – CH_2Cl_2 system gave crystals with mp 70–71°C, $[\alpha]_D^{20}$ –29.4 (*c* 1.0, $CHCl_3$) (mp 70–70.5°C, $[\alpha]_D^{20}$ –30° ($CHCl_3$)[12]). R_f 0.35 (petroleum ether – EtOAc, 1:1). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.55 (1H, br. s, OH); 3.67 (1H, dd, *J* = 6.6, *J* = 4.2) and 3.78 (1H, d, *J* = 6.6, 7-CH_2); 4.25 (1H, br. s, 4-CH); 4.58 (1H, t, *J* = 4.2, 1-CH); 5.43 (1H, d, *J* = 2.0, 5-CH); 5.63 (1H, dt, *J* = 9.9, *J* = 2.1, 3-CH); 6.04 (1H, dd, *J* = 9.9, *J* = 4.2, 2-CH). ^{13}C NMR spectrum, δ, ppm: 68.7 (C-7); 70.7 (C-1); 71.1 (C-4); 101.3 (C-5); 129.1, 130.6 (C-2,3). Mass spectrum, *m*/*z* (I_{rel}, %): 129 $[M+H]^+$ (100). Found, %: C 56.31; H 6.36. $C_6H_8O_3$. Calculated, %: C 56.24; H 6.29.

(1*S*,4*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]octan-4-ol (4). A round-bottom flask equipped with a magnetic stirrer, thermometer, and bubble counter was charged with D-glucose (39 g) and water (390 ml). Baker's yeast (*Saccharomyces cerevisiae*) (50 g) was added to the solution and the mixture was stirred for 1 h at 30°C. After 1 h, Cyrene (**2**) (5.00 g, 39.0 mmol) was added. The mixture was stirred at the same temperature for additional 24 h. The reaction mixture was filtered, the filtrate was evaporated, the residue was separated chromatographically using petroleum ether – EtOAc as eluent, gradient from 2:1 to 1:1. Yield 5.02 g (99%), partially crystallizing oil, $[\alpha]_D^{20}$ –134.2° (*c* 1.0, $CHCl_3$), $[\alpha]_D$ –132.8° (*c* 1.0, H_2O) (mp ~28°C (not sharp), $[\alpha]_D^{25}$ –133° (*c* 0.6, H_2O)[22]). R_f 0.3 (petroleum ether – EtOAc, 1:1). IR spectrum, ν, cm^{-1}: 3418, 1131, 1070, 985, 900. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.49 (1H, dtd, *J* = 12.9, *J* = 10.0, *J* = 6.1, 3-CH_{endo}); 1.57 (1H, dd, *J* = 13.9, *J* = 6.1) and 1.82–1.91 (1H, m, 2-CH_2); 1.98–2.04 (1H, m, 3-CH_{exo}); 2.18 (1H, br. s, OH); 3.58 (1H, dd, *J* = 10.0, *J* = 6.2, 4-CH); 3.79 (1H, dd, *J* = 7.1, *J* = 5.4) and 3.83 (1H, d, *J* = 7.1, 7-CH_2); 4.46–4.49 (1H, m, 1-CH); 5.30 (1H, s, 5-CH). ^{13}C NMR spectrum, δ, ppm: 26.0 (C-3); 27.8 (C-2); 68.2 (C-7); 70.0 (C-4); 72.8 (C-1); 102.9 (C-5). Mass spectrum, *m*/*z* (I_{rel}, %): 131 $[M+H]^+$ (100). Found, %: C 55.45; H 7.79. $C_6H_{10}O_3$. Calculated, %: C 55.37; H 7.74.

(1*R*,2*S*,4*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]octane-2,4-diol (6a) and (1*R*,2*S*,4*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octane-2,4-diol (6b). A solution of levoglucosenone (**1**) (1.00 g, 7.93 mmol) and triethylamine (0.55 ml, 3.96 mmol) in H_2O (60 ml) was stirred at room temperature for 2 h. The mixture was then treated with 98% $NaBH_4$ (0.31 g, 7.93 mmol) and stirred for approximately 1 h. The excess of $NaBH_4$ was decomposed with AcOH (3 ml). The solvent was removed by evaporation on rotary evaporator, the residue (mixture of alcohols **6a**,**b**) was separated chromatographically, eluent EtOAc.

Compound 6a. Yield 0.87 g (75%), white amorphous material, $[\alpha]_D^{20}$ –156° (*c* 1.0, H_2O) ($[\alpha]_D^{20}$ –156° (*c* 0.73, H_2O)[23]). R_f 0.2 (EtOAc). IR spectrum, ν, cm^{-1}: 3374, 1181, 1091, 971, 902. ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 1.70 (1H, ddd, *J* = 14.3, *J* = 10.7, *J* = 4.5) and 1.91 (1H, dddd, *J* = 14.3, *J* = 6.0, *J* = 3.1, *J* = 1.7, 3-CH_2); 3.71 (1H, dd, *J* = 7.6, *J* = 5.5) and 3.76 (1H, d, *J* = 7.6, 7-CH_2); 3.74–3.80 (1H, m, 2-CH); 3.79 (1H, ddd, *J* = 10.7, *J* = 6.0, *J* = 1.1, 4-CH); 4.36–4.40 (1H, m, 1-CH); 5.22 (1H, s, 5-CH). ^{13}C NMR spectrum (CD_3OD), δ, ppm: 32.6 (C-3); 66.0 (C-7); 66.1 (C-4); 67.4 (C-2); 76.6 (C-1); 102.8 (C-5). Mass spectrum, *m*/*z* (I_{rel}, %): 188 $[M+MeCN+H]^+$ (100). Found, %: C 49.43; H 6.83. $C_6H_{10}O_4$. Calculated, %: C 49.31; H 6.90.

Compound 6b. Yield 0.17 g (15%), white amorphous material, $[\alpha]_D^{24}$ –78° (*c* 0.5, H_2O) ($[\alpha]_D^{20}$ –79.9° (H_2O)[24]). R_f 0.25 (EtOAc). IR spectrum, ν, cm^{-1}: 3370, 1179, 1091, 975, 905. ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 1.74 (1H, d, *J* = 16.2) and 2.13 (1H, dt, *J* = 16.2, *J* = 4.8, 3-CH_2); 2.15 (1H, br. s, OH); 3.65–3.68 (1H, m, 2-CH); 3.78–3.86 (2H, m, 7-CH_{exo}, 4-CH); 3.91 (1H, d, *J* = 7.9, 7-CH_{endo}); 3.96 (1H, br. s, OH); 4.57–4.62 (1H, m, 1-CH); 5.41 (1H, s, 5-CH). ^{13}C NMR spectrum (D_2O), δ, ppm: 29.5 (C-3); 65.3 (C-7); 65.7, 65.9 (C-2,4); 77.0 (C-1); 101.6 (C-5). Mass spectrum, *m*/*z* (I_{rel}, %): 188 $[M+MeCN+H]^+$ (100). Found, %: C 49.46; H 6.80. $C_6H_{10}O_4$. Calculated, %: C 49.31; H 6.90.

(1*S*,4*S*,5*R*)-4-Methyl-6,8-dioxabicyclo[3.2.1]octan-4-ol (8). A solution of alcohol **7** (1.00 g, 7.04 mmol) in EtOAc (10 ml) was treated by the addition of activated Raney nickel (0.1 g). The reaction mixture was stirred under hydrogen atmosphere. The reaction mixture was filtered after 48 h, the filtrate was concentrated, the residue was separated chromatographically, using petroleum ether – EtOAc as eluent, gradient from 3:1 to 1:1. Yield 0.90 g (89%), colorless oil, $[\alpha]_D^{20}$ –77.1° (*c* 1.0, $CHCl_3$). R_f 0.3 (petroleum ether – EtOAc, 2:1). IR spectrum, ν, cm^{-1}:

3443, 1131, 1085, 988, 892. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.17 (3H, s, CH_3); 1.45–1.54 (1H, m, 2-CH_{exo}); 1.56–1.70 (2H, m, 3-CH_2); 1.75–1.90 (1H, m, 2-CH_{endo}); 2.48 (1H, br. s, OH); 3.70–3.75 (1H, m) and 3.80 (1H, d, *J* = 6.7, 7-CH_2); 4.41–4.48 (1H, m, 1-CH); 4.93 (1H, s, 5-CH). ^{13}C NMR spectrum, δ, ppm: 21.8 (CH_3); 27.3 (C-2); 31.9 (C-3); 67.4 (C-7); 70.5 (C-4); 73.2 (C-1); 105.9 (C-5). Mass spectrum, *m*/*z* (I_{rel}, %): 127 $[M–H_2O+H]^+$ (100). Found, %: C 58.23; H 8.46. $C_7H_{12}O_3$. Calculated, %: C 58.32; H 8.39.

Baeyer–Villiger oxidation of levoglucosenone (1) and Cyrene (2) (General procedure). Method I (oxidation with 5 equiv of 30% H_2O_2 in the presence of Amberlyst 15 resin). A mixture of ketone **1** or **2** (10.0 mmol) and Amberlyst 15 (42 mg, 2.0 mmol, ion exchange capacity ≥4.7 equiv/kg) in water (1.5 ml) was cooled to 0°C and treated by dropwise addition of 30% H_2O_2 solution (5.1 ml, 5 mmol). After the addition of H_2O_2 was complete, the reaction mixture was heated to 50°C and stirred for 1 h, then cooled to room temperature and quenched with saturated Na_2SO_3 solution until complete removal of peroxides (determined with 10% KI solution). Water was then removed by distillation at reduced pressure, the precipitate was filtered off and washed with EtOH. The filtrate was evaporated on a rotary evaporator, the residue was separated by chromatography on silica gel, using petroleum ether – EtOAc as eluent, gradient from 2:1 to 1:1.

Method II (oxidation with 1 equiv of 30% H_2O_2 and Amberlyst 15). A mixture of ketone **1** or **2** (10.0 mmol) and Amberlyst 15 (42 mg, 2.0 mmol, ion exchange capacity ≥4.7 equiv/kg) in water (1.5 ml) was cooled to 0°C and treated by dropwise addition of 30% H_2O_2 solution (1.02 ml, 1 mmol). After the addition of H_2O_2 was complete, the reaction mixture was heated to 50°C and stirred for 2 h. The reaction mixture was then cooled to room temperature. The residual peroxides, if present, were neutralized with Na_2SO_3. Amberlyst 15 resin was removed from the reaction mixture by filtration, washed with water, the filtrate was concentrated at reduced pressure, the residue was separated by chromatography on silica gel, using petroleum ether – EtOAc as eluent, gradient from 2:1 to 1:1 (or distilled at reduced pressure of 0.7–0.9 mbar).

(*S*)-5-(Hydroxymethyl)dihydrofuran-2(3*H*)-one (9) was obtained from Cyrene (**2**) (1.28 g, 10.0 mmol) according to method I or II. Yield 1.01 g (87%, method I), 0.97 g (84%, method II), colorless oil, $[\alpha]_D^{26}$ +57.0° (*c* 1.0, $CHCl_3$) ($[\alpha]_D^{20}$ +52.9° (*c* 0.01, $CHCl_3$)[16c]). R_f 0.2 (petroleum ether – EtOAc, 1:1). IR spectrum, ν, cm^{-1}: 3409, 1761, 1188, 1062, 936, 653. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.09 (1H, dddd, *J* = 18.1, *J* = 10.0, *J* = 8.0, *J* = 7.2) and 2.22 (1H, dddd, *J* = 18.1, *J* = 9.8, *J* = 7.6, *J* = 5.9, 4-CH_2); 2.47 (1H, ddd, *J* = 17.9, *J* = 9.8, *J* = 8.0) and 2.56 (1H, ddd, *J* = 17.9, *J* = 10.0, *J* = 5.9, 3-CH_2); 3.58 (1H, br. s, OH); 3.58 (1H, dd, *J* = 12.5, *J* = 4.6) and 3.82 (1H, dd, *J* = 12.5, *J* = 3.7, C$\underline{H}_2$OH); 4.55–4.60 (1H, m, 5-CH). ^{13}C NMR spectrum, δ, ppm: 23.1 (C-4); 28.7 (C-3); 63.9 (CH_2OH); 81.0 (C-5); 178.2 (C-2). Mass spectrum, *m*/*z* (I_{rel}, %): 158 $[M+MeCN+H]^+$ (100). Found, %: C 51.62; H 6.99. $C_5H_8O_3$. Calculated, %: C 51.72; H 6.94.

(*S*)-5-(Hydroxymethyl)furan-2(5*H*)-one (10) was obtained from levoglucosenone (**1**) (1.26 g, 10.0 mmol). Yield 0.88 g (76%, method I), 0.80 g (70%, method II); colorless partially crystallizing oil, $[\alpha]_D^{26}$ –113.5° (*c* 1.0, $CHCl_3$) ($[\alpha]_D^{20}$ –114.5° (*c* 0.1, $CHCl_3$)[16b]). R_f 0.2 (petroleum ether – EtOAc, 1:1). IR spectrum, ν, cm^{-1}: 3415, 2941, 1728, 1170, 1050. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.74 (1H, dd, *J* = 12.3, *J* = 4.9) and 3.94 (1H, dd, *J* = 12.3, *J* = 3.8, C$\underline{H}_2$OH); 5.10–5.16 (1H, m, 5-CH); 6.15 (1H, dd, *J* = 5.8, *J* = 1.9, 3-CH); 7.50 (1H, dd, *J* = 5.8, *J* = 1.4, 4-CH). ^{13}C NMR spectrum, δ, ppm: 62.0 (CH_2OH); 84.4 (C-5); 122.7 (C-3); 154.2 (C-4); 173.7 (C-2). Mass spectrum, *m*/*z* (I_{rel}, %): 115 $[M+H]^+$ (100). Found, %: C 52.73; H 5.28. $C_5H_6O_3$. Calculated, %: C 52.63; H 5.30.

Methylsulfanylmethylation of hydroxy groups in alcohols 3, 4, 6a, 7–10 (General procedure). Method III (methylsulfanylmethylation with DMSO and Ac_2O). A solution of alcohol **3**, **4**, **7**, or **8** (5 mmol) in DMSO (10 ml) and Ac_2O (10 ml) was stirred for 2 h at 40°C. The reaction mixture was quenched by adding ice and saturated $NaHCO_3$ solution until the evolution of gas ceased. The aqueous phase was extracted with EtOAc, the combined extracts were washed with $NaHCO_3$ solution, water, dried over anhydrous $MgSO_4$, evaporated, the residue was separated by chromatography on silica gel, using petroleum ether – EtOAc as eluent, gradient from 5:1 to 2:1.

Method IV (methylsulfanylmethylation with DMSO, Ac_2O, and AcOH). A solution of alcohol **3** or **4** (1.0 mmol) in a mixture of DMSO (1.5 ml), Ac_2O (1.0 ml), and AcOH (0.4 ml) was stirred for 2 h at 40°C. The reaction mixture was quenched by adding ice and saturated $NaHCO_3$ solution until the evolution of gas ceased. The aqueous phase was extracted with EtOAc, the combined extracts were washed with $NaHCO_3$ solution, water, dried over anhydrous $MgSO_4$, evaporated, and the residue was separated by chromatography on silica gel, using petroleum ether – EtOAc as eluent, gradient from 5:1 to 2:1.

Method V (methylsulfanylmethylation with Me_2S, $(PhCO_2)_2$, MeCN). A solution of alcohol **3**, **4**, **6a**, **9**, or **10** (1.0 mmol) in anhydrous acetonitrile (4.0 ml) was cooled to 0°C and treated by adding Me_2S (0.58 ml, 8 mmol). After that, benzoyl peroxide (986 mg, 4 mmol) was added in 4 portions over 30 min intervals. The mixture was stirred for 2 h at 0°C, diluted with Et_2O, and then washed with saturated $NaHCO_3$ solution. The aqueous phase was extracted with Et_2O, dried over anhydrous $MgSO_4$, evaporated, the residue was separated by chromatography on silica gel, using petroleum ether – EtOAc as eluent, gradient from 5:1 to 2:1.

(1*S*,4*S*,5*R*)-4-Methyl-4-[(methylsulfanyl)methoxy]-6,8-dioxabicyclo[3.2.1]oct-2-ene (11) was obtained from alcohol **7** (710 mg, 5.0 mmol) according to method III. Yield 999 mg (99%). The spectral characteristics of ether **11** were identical to those described in the literature.[14]

(1*S*,4*S*,5*R*)-4-Methyl-4-[(methylsulfanyl)methoxy]-6,8-dioxabicyclo[3.2.1]octane (12) was obtained from alcohol **8** (720 mg, 5.0 mmol) according to method III. Yield 928 mg (91%), colorless oil, $[\alpha]_D^{20}$ –45.8° (*c* 1.0, $CHCl_3$). R_f 0.35 (petroleum ether – EtOAc, 3:1). IR spectrum, ν, cm^{-1}: 1484, 1095, 1045, 987, 931. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 (3H, s, CH_3); 1.51–1.56 (1H, m) and 1.65–1.69 (1H, m, 2-CH_2); 1.83–1.91 (1H, m) and 1.93 (1H, dd, *J* = 12.7,

J = 5.4, 3-CH_2); 2.18 (3H, s, CH_3); 3.76 (1H, dd, J = 7.1, J = 4.8) and 3.85 (1H, d, J = 7.1, 7-CH_2); 4.43–4.49 (1H, m, 1-CH); 4.61 (1H, d, J = 11.1) and 4.64 (1H, d, J = 11.1, CH_2S); 5.17 (1H, s, 5-CH). ^{13}C NMR spectrum, δ, ppm: 14.2 (CH_3); 19.5 (CH_3); 27.2 (C-2); 28.3 (C-3); 67.3 (CH_2S); 67.7 (C-7); 73.4 (C-1); 76.7 (C-4); 104.2 (C-5). Mass spectrum, m/z (I_{rel}, %): 205 $[M+H]^+$ (100). Found, %: C 52.99; H 7.73; S 15.56. $C_9H_{16}O_3S$. Calculated, %: C 52.91; H 7.89; S 15.70.

(1*S*,4*S*,5*R*)-4-[(Methylsulfanyl)methoxy]-6,8-dioxabicyclo-[3.2.1]octane (13) and [((1*S*,4*S*,5*R*)-6,8-dioxabicyclo-[3.2.1]octan-4-yloxy)methyl]acetate (14) were obtained as a mixture containing also Cyrene (**2**), starting from alcohol **4** (650 mg, 5.0 mmol, method III or 130 mg, 1.0 mmol, methods IV, V).

(1*S*,4*S*,5*R*)-4-[(Methylsulfanyl)methoxy]-6,8-dioxabicyclo-[3.2.1]octane (13). Yield 580 mg (61%, method III), 127 mg (67%, method IV), 141 mg (74%, method V), colorless oil, $[\alpha]_D^{20}$ –73.0° (*c* 1.0, $CHCl_3$). R_f 0.3 (petroleum ether – EtOAc, 3:1). IR spectrum, ν, cm^{-1}: 1437, 1134, 1072, 970, 902, 680. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.57 (1H, dd, J = 13.0, J = 6.1, 2-CH_{exo}); 1.65 (1H, ddd, J = 12.6, J = 10.5, J = 6.1, 3-CH_{endo}); 1.82–1.88 (1H, m, 2-CH_{endo}); 1.90–1.95 (1H, m, 3-CH_{exo}); 2.10 (3H, s, CH_3); 3.67 (1H, dd, J = 9.3, J 6.1, 4-CH); 3.76 (1H, dd, J = 7.2, J = 6.0) and 3.84 (1H, d, J = 7.2, 7-CH_2); 4.59–4.64 (1H, m, 1-CH); 4.60 (1H, d, J = 11.7) and 4.64 (1H, d, J = 11.7, CH_2S); 5.37 (1H, s, 5-CH). ^{13}C NMR spectrum, δ, ppm: 13.5 (CH_3); 22.5 (C-3); 27.8 (C-2); 68.3 (C-7); 73.0 (C-1); 73.1 (CH_2S); 73.5 (C-4); 101.2 (C-5). Mass spectrum, m/z (I_{rel}, %): 191 $[M+H]^+$ (100). Found, %: C 50.60; H 7.49; S 16.76. $C_8H_{14}O_3S$. Calculated, %: C 50.50; H 7.42; S 16.85.

[((1*S*,4*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]octan-4-yloxy)methyl]-acetate (14). Yield 232 mg (23%, method III), 28 mg (14%, method IV), colorless oil, $[\alpha]_D^{20}$ –81.3° (*c* 1.0, $CHCl_3$). R_f 0.3 (petroleum ether – EtOAc, 2:1). IR spectrum, ν, cm^{-1}: 1739, 1216, 1122, 1013, 943, 756. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.61 (1H, dd, J = 13.6, J = 5.9, 2-CH_{exo}); 1.71 (1H, ddd, J = 12.8, J = 10.4, J = 5.9, 3-CH_{endo}); 1.84–1.89 (1H, m, 2-CH_{endo}); 1.94–2.00 (1H, m, 3-CH_{exo}); 2.07 (3H, s, CH_3); 3.62 (1H, dd, J = 10.1, J = 6.0, 4-CH); 3.79 (1H, dd, J = 7.1, J = 6.0) and 3.87 (1H, d, J = 7.1, 7-CH_2); 4.44–4.49 (1H, m, 1-CH); 5.24 (1H, d, J = 6.4) and 5.34 (1H, d, J = 6.4, OCH_2O); 5.39 (1H, s, 5-CH). ^{13}C NMR spectrum, δ, ppm: 21.1 (CH_3); 22.7 (C-3); 27.7 (C-2); 68.3 (C-7); 72.9 (C-1); 77.0 (C-4); 87.9 (OCH_2O); 101.2 (C-5); 170.3 (C=O). Mass spectrum, m/z (I_{rel}, %): 220 $[M–OAc+2H_2O+MeCN]^+$ (100). Found, %: C 53.49; H 7.07. $C_9H_{14}O_5$. Calculated, %: C 53.46; H 6.98.

(1*S*,4*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]octan-4-ol (2). Yield 32 mg (5%, method III), 6 mg (5%, method IV).

(1*S*,4*S*,5*R*)-4-[(Methylsulfanyl)methoxy]-6,8-dioxabicyclo-[3.2.1]oct-2-ene (15) and [((1*S*,4*S*,5*R*)-6,8-dioxabicyclo-[3.2.1]oct-2-en-4-yloxy)methyl]acetate (16) were obtained as a mixture containing also levoglucosenone (**1**), starting from alcohol **3** (128 mg, 1.0 mmol) according to method IV. Ether **15** was also obtained from alcohol **3** (128 mg, 1.0 mmol) according to method V.

(1*S*,4*S*,5*R*)-4-[(Methylsulfanyl)methoxy]-6,8-dioxabicyclo-[3.2.1]oct-2-ene (15). Yield 68 mg (36%, method IV), 133 mg (71%, method V), colorless oil, $[\alpha]_D^{20}$ +9.1° (*c* 1.0, $CHCl_3$). R_f 0.3 (CH_2Cl_2). IR spectrum, ν, cm^{-1}: 1216, 1074, 967, 757. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.08 (3H, s, CH_3); 3.67 (1H, m) and 3.85 (1H, d, J = 6.6, 7-CH_2); 4.44 (1H, s, 4-CH); 4.53–4.57 (1H, m, 1-CH); 4.62 (1H, d, J = 11.8) and 4.69 (1H, d, J = 11.8, CH_2S); 5.54 (1H, d, J = 1.5, 5-CH); 5.60 (1H, dd, J = 9.9, J = 1.5, 3-CH); 6.03 (1H, dd, J = 9.9, J = 4.1, 2-CH). ^{13}C NMR spectrum, δ, ppm: 13.5 (CH_3); 71.3 (C-7); 71.4 (C-4); 73.9 (C-1); 74.0 (CH_2S); 100.2 (C-5); 126.0 (C-2); 131.2 (C-3). Mass spectrum, m/z (I_{rel}, %): 189 $[M+H]^+$ (100). Found, %: C 51.12; H 6.47; S 16.93. $C_8H_{12}O_3S$. Calculated, %: C 51.04; H 6.43; S 17.03.

[((1*S*,4*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]oct-2-en-4-yloxy)-methyl]acetate (16). Yield 10 mg (5%), colorless oil, $[\alpha]_D^{20}$ –11.2° (*c* 1.0, $CHCl_3$). R_f 0.2 (CH_2Cl_2). IR spectrum, ν, cm^{-1}: 1730, 1226, 1117, 975, 831. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.07 (3H, s, CH_3); 3.75 (1H, dd, J = 6.6, J = 4.2) and 3.93 (1H, d, J = 6.6, 7-CH_2); 4.44 (1H, br. s, 4-CH); 4.63 (1H, t, J = 4.2, 1-CH); 5.27 (1H, d, J = 6.4) and 5.45 (1H, d, J = 6.4, OCH_2O); 5.57 (1H, t, J = 2.1, 5-CH); 5.65 (1H, dt, J = 9.9, J = 2.1, 3-CH); 6.13 (1H, ddd, J = 9.9, J = 4.1, J = 1.0, 2-CH). ^{13}C NMR spectrum, δ, ppm: 21.7 (CH_3); 71.9 (C-4); 72.0 (C-7); 78.0 (C-1); 89.1 (OCH_2O); 101.0 (C-5); 126.4 (C-2); 132.3 (C-3); 170.9 (CO). Mass spectrum, m/z (I_{rel}, %): 218 $[M–OAc+2H_2O+MeCN]^+$ (100). Found, %: C 54.08; H 5.95. $C_9H_{12}O_5$. Calculated, %: C 54.00; H 6.04.

Levoglucosenone (1). Yield 40 mg (32%).

Methylthiomethylation of alcohol (**5**) (144 mg, 1.0 mmol) according to method IV gave levoglucosenone (**1**). Yield 96 mg (76%).

(1*R*,2*S*,4*S*,5*R*)-2,4-Bis[(methylsulfanyl)methoxy]-6,8-dioxabicyclo[3.2.1]octane (17) was obtained from alcohol **6a** (146 mg, 1.0 mmol) according to method V. Yield 168 mg (63%), colorless oil, $[\alpha]_D^{20}$ –26.0° (*c* 1.0, $CHCl_3$). R_f 0.4 (petroleum ether – EtOAc, 3:1). IR spectrum, ν, cm^{-1}: 1074, 1036, 975, 903. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.71 (1H, ddd, J = 14.5, J = 10.5, J = 4.4) and 2.11–2.15 (1H, m, 3-CH_2); 2.11 (3H, s, CH_3); 2.15 (3H, s, CH_3); 3.77 (1H, d, J = 7.2) and 3.80 (1H, dd, J = 7.2, J = 5.2, 7-CH_2); 3.83–3.87 (1H, m, 2-CH); 3.87 (1H, dd, J = 10.5, J = 5.0, 4-CH); 4.50–4.54 (1H, m, 1-CH); 4.61 (1H, d, J = 11.8), 4.65 (1H, d, J = 11.8), 4.66 (1H, d, J = 11.8) and 4.74 (1H, d, J = 11.8, $2CH_2S$); 5.46 (1H, s, 5-CH). ^{13}C NMR spectrum, δ, ppm: 13.6 (CH_3); 13.7 (CH_3); 27.7 (C-3); 66.5 (C-7); 71.5 (C-4); 71.9 (C-2); 72.6 (CH_2S); 73.6 (CH_2S); 74.7 (C-1); 101.0 (C-5). Mass spectrum, m/z (I_{rel}, %): 267 $[M+H]^+$ (100). Found, %: C 45.01; H 6.83, S 23.98. $C_{10}H_{18}O_4S_2$. Calculated, %: C 45.09; H 6.81; S 24.07.

(*S*)-5-[(Methylsulfanyl)methoxy]dihydrofuran-2(3*H*)-one (18) was obtained from lactone **9** (116 mg, 1.0 mmol) according to method V. Yield 146 mg (83%), colorless oil, $[\alpha]_D^{20}$ +27.3° (*c* 1.0, $CHCl_3$). R_f 0.3 (petroleum ether – EtOAc, 3:1). IR spectrum, ν, cm^{-1}: 2925, 1769, 1216, 1109, 948, 757. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.06 (3H, s, CH_3); 2.03–2.09 (1H, m) and 2.22–2.28 (1H, m, 4-CH_2); 2.45 (1H, ddd, J = 17.3, J = 9.9, J = 7.3) and 2.51 (1H, ddd, J = 17.3, J = 10.0, J = 6.4, 3-CH_2); 3.58 (1H, dd, J = 10.8, J = 4.4) and 3.70 (1H, dd, J = 10.8, J = 3.0, CH_2O); 4.58 (1H, d, J = 11.7) and 4.61 (1H, d, J = 11.7, CH_2S); 4.61–4.64 (1H, m, 5-CH). ^{13}C NMR spectrum, δ, ppm: 13.8 (CH_3); 24.0 (C-4); 28.4 (C-3); 69.1 (CH_2O); 75.6 (CH_2S); 78.6

(C-5); 177.3 (C-2). Mass spectrum, *m*/*z* (I_{rel}, %): 177 $[M+H]^+$ (100). Found, %: C 47.73; H 6.95; S 18.16. $C_7H_{12}O_3S$. Calculated, %: C 47.71; H 6.86; S 18.19.

(*S*)-5-[(Methylsulfanyl)methoxy]furan-2(5*H*)-one (19) was obtained from lactone **10** (114 mg, 1.0 mmol) according to method V. Yield 139 mg (80%), colorless oil, $[\alpha]_D^{20}$ –112.4° (*c* 1.0, $CHCl_3$). R_f 0.2 (petroleum ether – EtOAc, 3:1). IR spectrum, ν, cm^{-1}: 2922, 1785, 1741, 1164, 1086, 957, 820. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.07 (3H, s, CH_3); 3.73 (1H, dd, *J* = 10.6, *J* = 5.2) and 3.78 (1H, dd, *J* = 10.6, *J* = 4.4, CH_2O); 4.61 (2H, s, CH_2S); 5.14–5.20 (1H, m, 5-CH); 6.12 (1H, dd, *J* = 5.8, *J* = 2.0, 3-CH); 7.46 (1H, dd, *J* = 5.8, *J* = 1.4, 4-CH). ^{13}C NMR spectrum, δ, ppm: 13.8 (CH_3); 66.8 (CH_2O); 75.7 (CH_2S); 81.9 (C-5); 122.7 (C-3); 153.6 (C-4); 172.8 (C-2). Mass spectrum, *m*/*z* (I_{rel}, %): 192 $[M–Me+MeOH+H]^+$ (100). Found, %: C 48.36; H 5.80; S 18.36. $C_7H_{10}O_3S$. Calculated, %: C 48.26; H 5.79; S 18.41.

Evaluation of fungicidal activity was performed by agar diffusion method.[25] The surface of growth medium (potato glucose agar) that was poured in 15 ml portions on 70 mm Petri dishes was inoculated with fungal test culture spore suspension at the density of 10^4 CFU/ml. A 10 mm drill bit was then used to drill wells into the growth medium that were inoculated with solutions (100 μl) of the study compounds. The fungicidal activity was determined from the diameter of zone where the growth of micromycetes was suppressed, as well as by observing the development of test cultures using a Leica Microsystems DM1000 optical microscope at 10× magnification. The experiments were repeated in triplicate. Fungal development on growth medium was used as control. The incubation time was 7 days at 28°C. The test cultures were *Bipolaris sorokiniana*, *Fusarium oxysporum*, and *Rhizoctonia solani.*

A Supplementary information file containing NMR spectra of all synthesized compounds is available at the journal website at http://link.springer.com/journal/10593

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