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Structural diversity of interaction products of mucochloric acid and its derivatives with 1,2-ethanedithiol

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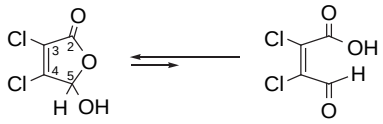
ABSTRACT

The synthesis and characterization of previously unknown sulfur-containing products from the reaction of mucochloric acid (3,4-dichloro-5-hydroxy-2(5*H*)-furanone) and its 5-alkoxy derivatives with 1,2-ethanedithiol is reported. Under basic and acidic conditions both SH-groups of the reagent show nucleophilic activity, leading to the formation of substitution products of different structural types. Novel fused (7-hydroxy-2,3-dihydro[1,4]dithiino[2,3-*c*]furan-5(7*H*)-one) and spiro (9-chloro-6-methoxy-7-oxa-1,4-dithiaspiro[4.4]nonan-8-one) bicyclic compounds, as well as various bis-thioethers have been obtained and characterized by NMR spectroscopy and single crystal X-ray diffraction.

1. Introduction

2(5*H*)-Furanone derivatives are naturally occurring and extremely useful heterocyclic compounds in various branches of medicine, agriculture, technology, and organic synthesis.[1] One of the most important representatives of unsaturated γ-lactones is mucochloric acid **1** (3,4-dichloro-5-hydroxy-2(5*H*)-furanone), well-known as a commercially available starting material with a range of reactivity.[2] Due to the propensity of compound **1** for cycle-chain tautomerism[2,3] (Fig. 1) and the presence of different reaction centers, this heterocycle is widely used as a versatile building block for the preparation of a variety of interesting compounds.

Despite the large number of publications devoted to reactions of **1** and its derivatives with *O*-, *N*-, *C*-, and *P*-nucleophiles, the reactivity toward sulfur-containing reagents is scarcely explored.[4–8] Recently, in connection with our ongoing projects related to the synthesis and investigation of the structure and properties of sulfur- and selenium-containing derivatives of chemically and biologically active heterocycles, we have studied reactions of **1** and some of its ethers and thioethers with various thiols,[9–11] and selenophenols.[12] It was shown that by conducting reactions of **1** with thiols under basic or acidic conditions it is possible to selectively introduce different SR groups into specific positions of the γ-lactone ring (atoms C(3), C(4), and C(5)) and to obtain pure regioisomers of thioethers of the 2(5*H*)-furanone series.[9,12]



1a **1b**

Fig. 1. Cycle-chain tautomerism of mucochloric acid **1**.

In a further effort to reveal the potential of **1** as a useful building block for the synthesis of new sulfur heterocycles, we initiated a study into the reactivity of **1** toward sulfur-containing

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binucleophilic reagents, which are very attractive for the synthesis of both mono- and bicyclic 2(5*H*)-furanone based products. To the best of our knowledge there are only a few reports in the literature of the use of 3,4-dihalo-2(5*H*)-furanones in the construction of sulfur-containing heterocyclic compounds (Fig. 2).[10,13,14]

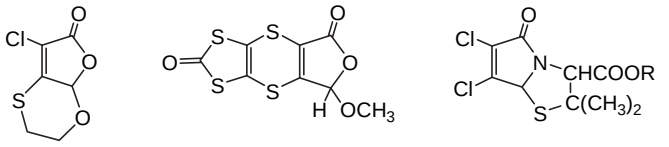


Fig. 2. Sulfur-containing fused heterocycles derived from substituted 2(5*H*)-furanones.

In this study, we have allowed **1** and its 5-alkoxy derivatives to react with 1,2-ethanedithiol under basic and acidic catalytic conditions, and observed the formation of previously unknown sulfur-containing compounds.

2. Results and discussion

Previously, it was shown that in the presence of acids, mucochloric acid **1** and some of its derivatives react with *S*-nucleophiles with the substitution of the hydroxy group at the C(5) atom of the lactone ring.[6,8,9] Reaction of **1** with 1,2-ethanedithiol was examined in the presence of concentrated sulfuric acid (from 2 to 30 mol %) and *p*-toluenesulfonic acid, as well as in polyphosphoric acid medium. We also conducted a series of experiments using various proportions of reagents and different heating times in order to optimize the reaction conditions. Two stable products **2** and **3** were isolated in all cases in nearly the same yields (Scheme 1).

(6.45 ppm), a broad signal for the proton of the hydroxy group (4.0–5.5 ppm), and a multiplet for the methylene protons, characteristic for the AA′BB′ spin system in the range of 3.1–3.5 ppm. Structure determination by single crystal X-ray diffraction identified **3** as 2,3-dichloro-3-(1,3-dithiolan-2-yl)prop-2-enoic acid (Fig. 3). According to the X-ray data the five-membered ring of **3** in the crystal has an 'envelope' conformation: the S(8)C(4)S(5)C(6) fragment is planar within 0.02 Å, the atom C(7) deviates from the plane by 0.648(7) Å. In the crystal, pairs of molecules are linked through strong hydrogen bonds between the carboxyl groups to form dimers. The parameters of the O(2)–H(2)…O(1) hydrogen bonds are: O(2)–H(2) 0.91(9) Å, O(2)…O(1) 2.621(8) Å, H(2)…O(1) 1.72(10) Å, ∠O(2)–H(2)…O(1) 172(10)°.

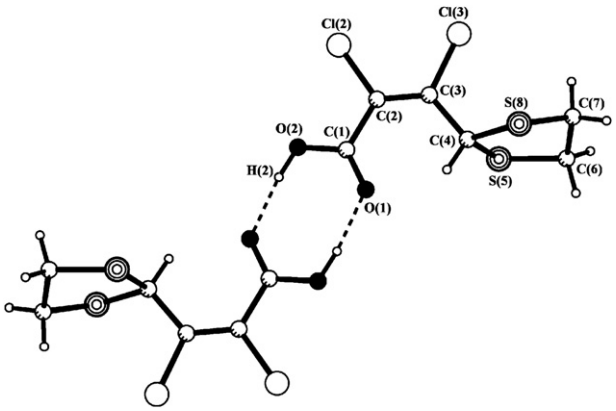
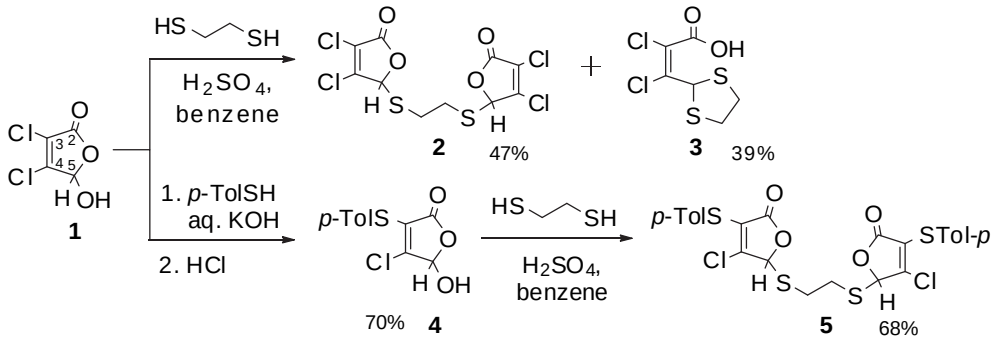


Fig. 3. A fragment of crystal packing in the crystal of compound **3**.



Scheme 1. Reactions of **1** and thioether **4** with 1,2-ethanedithiol in an acidic medium.

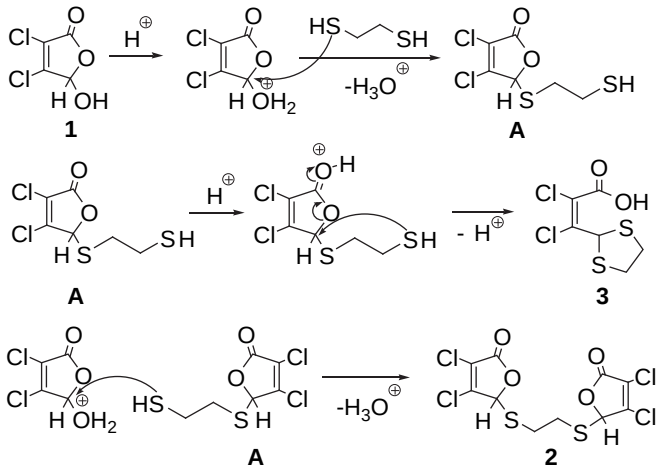
IR and NMR spectroscopic analysis indicated the absence of free OH- and SH-groups in product **2**. The ^{1}H NMR spectrum of **2** in acetone-d_6 displays two singlets of equal intensity for the methine proton at 6.59 and 6.60 ppm and two AA′BB′ multiplets for the methylene protons in the range of 2.99–3.10 ppm, that provides evidence for the formation of two diastereomers in a 1:1 ratio. The results of the elemental analysis and mass spectrometry confirmed the proposed structure of the bis-thioether **2**. It is notable that the similar compound with the –O–CH_2–CH_2–S– chain, connecting two 2(5*H*)-furanone units, has been described previously as the only product of the reaction of **1** with 2-mercaptoethanol under acidic conditions.[6,10]

There is no furanone ring in the second product **3** according to the spectroscopic data. In the IR spectrum of compound **3**, the absorption band of the γ-lactone carbonyl group is not observed and instead, a narrow intense band appeared at 1688 cm^{-1} typical for the stretching vibrations of the C=O group of carboxylic acids in the dimer state. In the ^{1}H NMR spectrum of the compound **3** in DMSO-d_6 there is a singlet for the proton at the saturated carbon

We assume that the reaction of **1** with 1,2-ethanedithiol in an acidic medium proceeds according to the following mechanism (Scheme 2):

Under acidic conditions, the increasing electrophilicity of atom C(5) in the protonated form of mucochloric acid directs the nucleophilic attack of 1,2-ethanedithiol to this position of the lactone ring, which is followed by the elimination of a water molecule and of a proton to form the product of monosubstitution (**A**). Presumably, after the protonation of the carbonyl oxygen of compound (**A**) an attack of the second sulfur atom onto the electron deficient carbon atom and proton elimination occur, thus, dithiolanylprop-2-enoic acid **3** may be formed. Bis-thioether **2** may be generated as the result of the attack of the thiol group in the compound (**A**) at the carbon atom C(5) in the protonated form of mucochloric acid (Scheme 2).

Interestingly, a similar reaction of 1,2-ethanedithiol with furanone **4**, obtained from the reaction of **1** with 4-methylthiophenol in alkaline medium,[9] required more prolonged heating; the only product isolated from this reaction was bis-thioether **5** (Scheme 1).



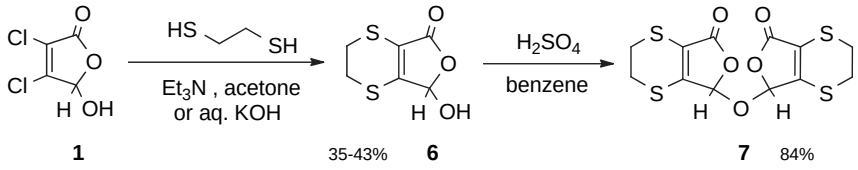
Scheme 2. Proposed mechanism of the reaction in an acidic medium.

It is known that reactions of **1** with aliphatic and aromatic thiols,[4,7,9] 2-mercaptoethanol,[10] and 2-mercaptoacetic acid,[11] carried out in acetone or diethyl ether in the presence of triethylamine, lead to the formation of the products resulting from substitution of the chlorine atom in the 4-position of the γ-lactone ring. Under the same conditions, reaction with 1,2-ethanedithiol results in substitution of both of the chlorine atoms in the molecule of mucochloric acid **1** and forms a novel bicyclic compound **6** (Scheme 3).

It should be noted that bicyclic product **6** was also isolated from the reaction of compound **1** with 1,2-ethanedithiol under conditions in which phenols,[15] thiophenols,[9] and 2-mercaptoacetic acid[11] give substitution of the chlorine atom in the 3-position of the γ-lactone ring (aqueous solution of potassium hydroxide and subsequent acidification of the reaction mixture). However, the reactions carried out in the presence of base (triethylamine or potassium hydroxide) are accompanied by considerable polymerization, that decreases the yield of pure final product **6**. The TLC analysis of reaction mixtures showed that the only reaction product is compound **6**.

Bicycle **6** undergoes an intermolecular dehydratation by heating in benzene in the presence of catalytic amounts of sulfuric acid and gives the compound **7** (Scheme 3). The IR spectrum of **7** shows the absorption band of the lactone carbonyl group at 1748 cm^{-1} and a band of medium intensity at 1618 cm^{-1}, assigned to the stretching vibrations of the C=C bond of the furanone ring. As evidenced by ^1H NMR spectrum, which displays two singlets for the methine proton at C(5) at 6.35 and 6.40 ppm, and two multiplets for the two different ABCD spin systems of the methylene protons in the range of 3.33–3.50 ppm, the compound **7** is present as a 1:1 mixture of diastereomers.

Interesting results were obtained in the reactions of 1,2-ethanedithiol with 5-alkoxy derivatives of mucochloric acid **8**–**10** in the presence of triethylamine. While mucochloric acid **1** itself gives bicyclic compound **6**, reactions of **8**–**10** resulted in the formation of **11**–**13** that combine a bis-thioether moiety and two 2(5*H*)-furanone fragments bridged through their carbon atoms C(4) (Scheme 4). Judging from the ^1H and ^{13}C NMR spectra of the reaction mixtures, bis-thioethers **11**–**13** are formed as 1:1 mixtures of diastereomers. The ratio can be clearly evaluated from the ^1H NMR spectra of the methine protons at carbon atom C(5) of the lactone ring by integration of the respective signals.



Scheme 3. Synthesis of 7-hydroxy-2,3-dihydro[1,4]dithiino[2,3-*c*]furan-5(7*H*)-one (**6**) and its anhydride **7**.

In the ^1H NMR spectrum of product **6** there are two doublets for the proton of the hydroxy group and for the methine proton at 7.00 and 6.13 ppm, respectively, as well as a multiplet for the ABCD spin system of the methylene protons in the range of 3.2–3.5 ppm. Compound **6** is the first representative of a new type of the sulfur-containing fused bicyclic systems—2,3-dihydro[1,4]dithiino[2,3-*c*]furan-5(7*H*)-ones. The structure was also determined by single crystal X-ray diffraction. According to the X-ray data, the six-membered ring of the molecule **6** is characterized by the half-chair conformation (Fig. 4a). The S(1)C(8)C(9)S(4) fragment is planar, the deviation of C(2) and C(3) atoms from the plane is −0.290(4) Å and 0.477(4) Å, correspondingly. The molecules of **6** in the crystal form infinite chains via hydrogen bonds H(1)…O(5) 2.09(5) Å, O(7)…O(5) 2.811(4) Å, ∠O(7)–H(1)…O(5) 162(4)° (Fig. 4b).

In the case of products **11** and **12**, the diastereomeric mixtures were separated into the individual components (*meso* **11a**, **12a**, and DL **11b**, **12b**) by fractionated crystallization from tetrachloromethane. The *meso* isomer **13a** of isopropoxy derivative was also separated; however, we have not managed to isolate the DL isomer **13b** in pure form. The individual diastereomeric forms of bis-thioethers **11**–**13** were characterized by ^1H and ^{13}C NMR spectroscopy; the chemical shifts and all spin–spin coupling constants are given in Section 3.3.

The methylene protons of the $-SCH_2CH_2S-$ moiety form an AA′BB′ spin system, giving rise to a pair of complex multiplets in the ^1H NMR spectra of compounds **12** and **13**. Spin–spin coupling

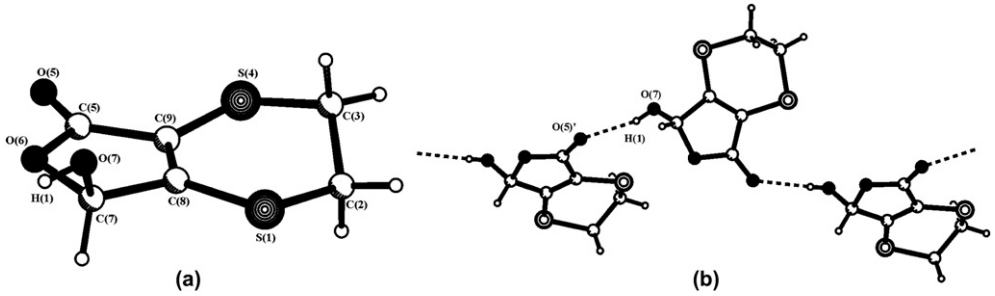
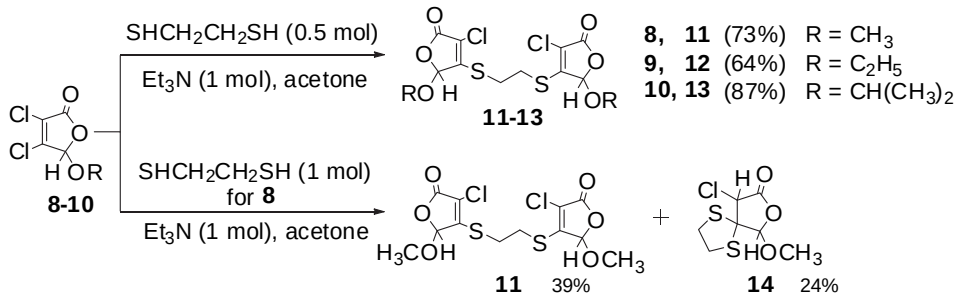


Fig. 4. a) Molecular structure of compound **6** in the crystal. (b) The hydrogen bonding scheme for **6**.



Scheme 4. Reactions of 5-alkoxy derivatives **8**–**10** with 1,2-ethanedithiol.

constants observed for *meso* isomers **12a** and **13a** are equal to $J_{AA'}=J_{BB'}=9.0$ Hz, $J_{AB}=J_{A'B'}=-13.9$ Hz, $J_{A'B}=J_{AB'}=6.0$ Hz; and non-equivalence of the diastereotopic methylene protons A and B is $\Delta\delta=0.03$ ppm. It is noteworthy that the ^{1}H NMR spectra of the methoxy derivatives **11**, **11a**, and **11b** contain signals for the $-SCH_2CH_2S-$ protons in the form of a broad singlet due to very small nonequivalence of the diastereotopic protons. A comparison of the ^{1}H NMR spectroscopic data for the two diastereomeric forms of bis-thioethers **11**–**13** indicates that in the *meso* isomers, the observed chemical shift of the methine proton at C(5) in the range 6.32–6.42 ppm is slightly lower than those of the DL isomers.

Isolated diastereomers of bis-thioethers **11**–**13** were crystallized and their crystal structures were studied in detail by X-ray single diffraction. Molecules of five isomers **11a**, **11b**, **12a**, **12b**, and **13a** were crystallized in different conformations, and the crystals were of different shape and symmetry. Unusually the *meso* diastereomer **11a** forms a clathrate with carbon tetrachloride in the trigonal crystal system (space group *R*–3), in contrast bis-thioethers **11b**, **12a**, **12b**, and **13a** crystallize without incorporation of solvent in the triclinic or monoclinic system (space groups *P*–1, $P2_1/c$, C2/*c*, $P2_1/n$, respectively).

The crystals of individual diastereomers grown under identical conditions from the tetrachloromethane solution have different forms: compound **11a** crystallizes in the form of hexagonal prisms, **11b**—plates, **12a**—plates, **12b**—cubic prisms and **13a**—rounded plates. Photographs of the crystals obtained are shown in Fig. 5.

associated with the sulfur atom; at the same time corresponding bond lengths and bond angles are equal in all three molecules.

There are no centrosymmetric conformations for DL diastereomers, therefore they crystallize in a different way to that of the *meso* isomers. Thus, **11b** occupies the general position in the crystal, and **12b** is in a special position on the two-fold axis. Unlike the other four isomers, **12b** in the crystal adopts a *gauche* conformation around the central C(6)–C(6)' bond with the heterocyclic fragments spatially close to each other (Fig. 7).

X-ray structure analysis revealed that *meso* diastereomer **11a** in contrast to the other studied molecules has unusual packing in the crystal, forming a true clathrate with tetrachloromethane in host/guest ratio=3:1 (Fig. 8). The host molecules via C–H…O hydrogen bonds form a three-dimensional associate with threefold symmetric channels, parallel to the *c*-axis, and the guest molecules are situated on the trigonal axis and disordered over two equal positions, one atom of chlorine is exactly at the center of inversion.

The literature contains a few examples of similar three-dimensional associates, having a cavity filled with guest molecules, including CCl_4, $CHCl_3$, however, host molecules are connected by classical hydrogen bonds.[16–18] The major difference between clathrate CCl_4/**11a** and the structures described earlier, is that the walls of the 3D channels in clathrate CCl_4/**11a** are linked together via C–H…O interactions. The hydrogen atom at atom C(5) and the oxygen atom O(2) of the carbonyl group participate in hydrogen bonding, each bis-thioether molecule is found to be connected with four neighboring molecules,

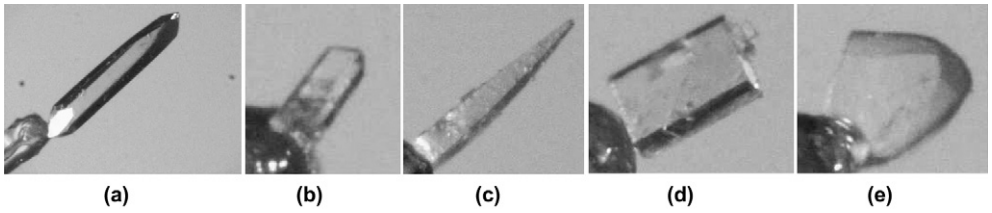


Fig. 5. Photographs of the crystals of individual diastereomers grown from the tetrachloromethane solution: (a) **11a**, (b) **11b**, (c) **12a**, (d) **12b**, (e) **13a**.

The molecules of all three *meso* forms (**11a**, **12a**, **13a**) in the crystals were in the special position in the center of symmetry (in the center of bonds C(6)–C(6)'), and as a result one half of molecules was crystallographically independent. The conformational flexibility of the $-SCH_2CH_2S-$ fragments allows the molecules **11a**, **12a**, **13a** to adopt different conformations in the crystal (Fig. 6).

Atoms Cl(1) and C(6) of the molecules **11a** and **13a** are in an *anti*-orientation, in the case of molecule **12a** a *syn*-orientation is observed. Considering the spatial arrangement of structural fragments relative to the plane of one of the five-membered rings, the alkoxy-group and second 2(5*H*)-furanone ring lie on one side of the plane in the molecule **11a**, and on the other side in the molecule **12a**. In the molecule **13a** both five-membered rings and the bis-thioether fragment are all situated in one plane. The aforementioned conformational differences become apparent only in a variation of the torsion angles

that apparently provide sufficient stabilization of the channel walls. The parameters of the C(5)–H(5)…O(2) hydrogen bonds are as follows: C(5)–H(5) 0.92 Å, C(5)…O(2) 3.426(4) Å, H(5)…O(2) 2.47 Å, ∠C(5)–H(5)…O(2) 164°.

Reactions of 5-alkoxy derivatives of mucochloric acid **8**–**10** with 1,2-ethanedithiol in the presence of triethylamine were carried out under different ratios of reagents. Bis-thioethers **11**–**13** were the only products formed using a ratio of ether/1,2-ethanedithiol/triethylamine of 2:1:2. The same compounds were isolated from the reactions of ethers **9** and **10** with 1,2-ethanedithiol with reagents in a 1:1:1 ratio. However, two products, bis-thioether **11** and the novel spiro compound **14**, were obtained in the case of the methoxy derivative **8** and an equimolar reagent ratio (Scheme 4).

The ^{1}H NMR spectrum of the isolated compound **14** shows the presence of one diastereomer. Since other possible diastereomer

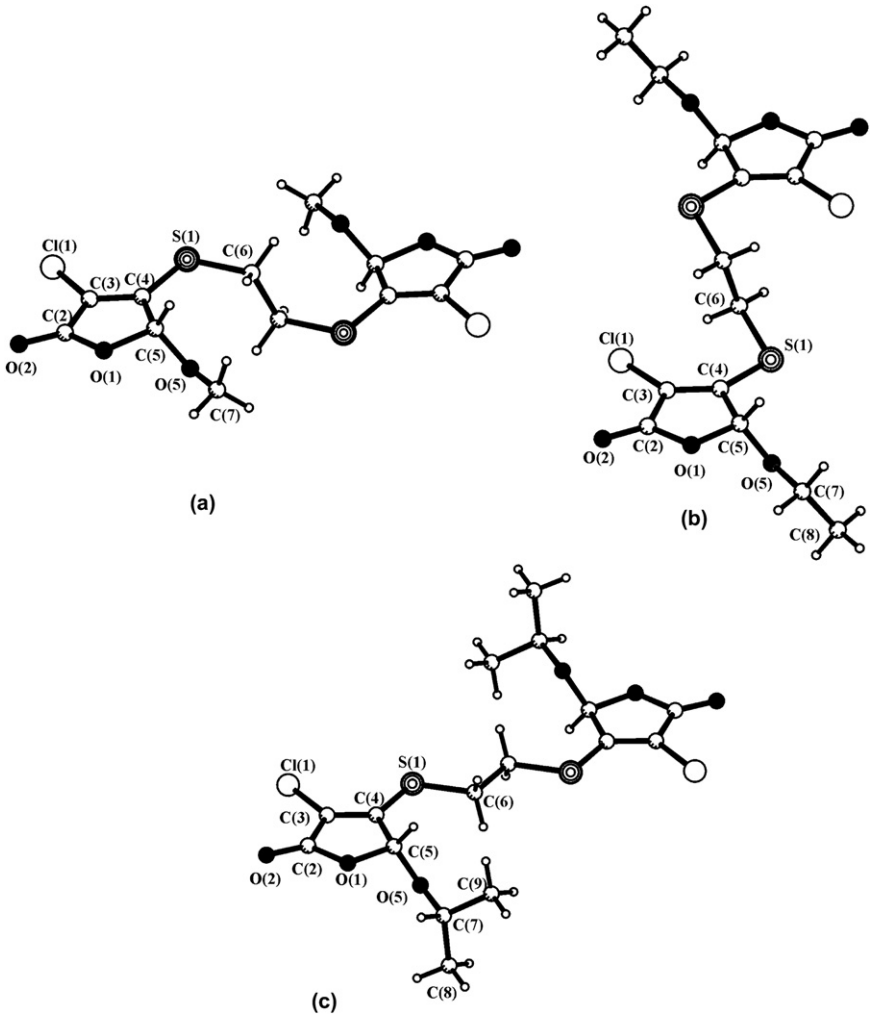


Fig. 6. Molecular structure of *meso* isomers in the crystal: (a) **11a**, (b) **12a**, (c) **13a**.

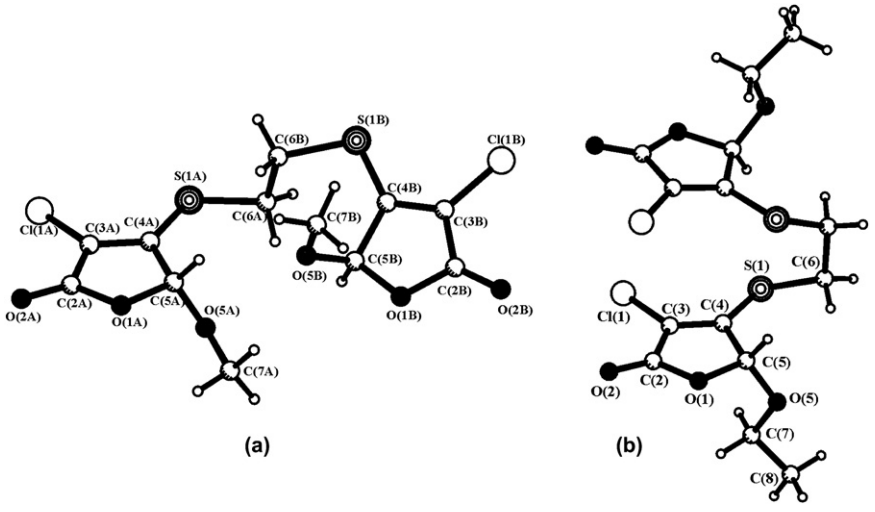


Fig. 7. Molecular structure of DL isomers in the crystal: (a) **11b**, (b) **12b**.

was not detected in the reaction mixture, the formation of spirocyclic compound **14** is likely to occur stereospecifically.

As a mechanism for the observed formation of the unexpected product **14**, we can propose an initial nucleophilic substitution of the chlorine atom at the 4-position by the 1,2-ethanedithiol, followed by addition of the free sulfhydryl group to the olefinic double bond of furanone ring to give spiro bicyclic compound **14** (Scheme 5). Understandably, bis-thioethers **11**–**13** are formed as a result of interaction of both SH-groups of *S*,*S*-binucleophile with two molecules of alkoxy derivatives **8**–**10**.

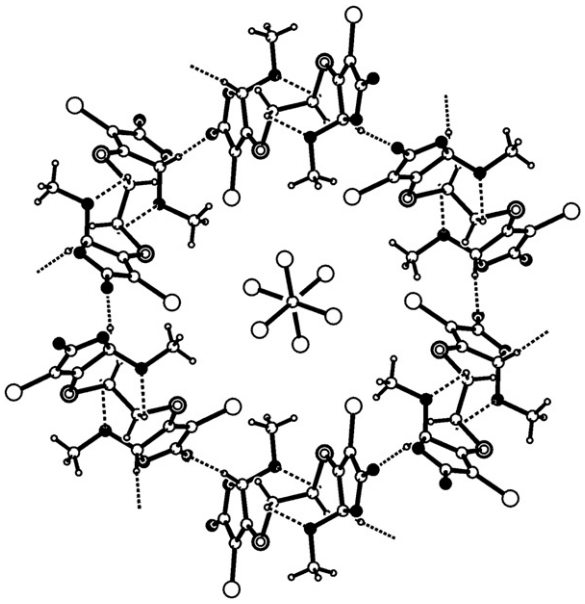


Fig. 8. The fragment of the crystal packing of **11a**; projection is on the *z*0 plane. The C–H…O interactions are shown as dashed lines.

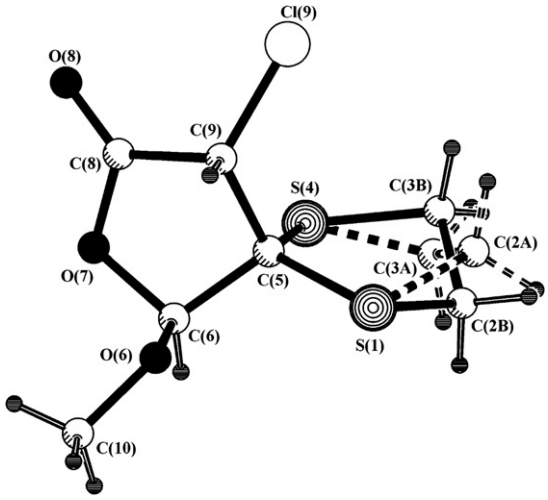
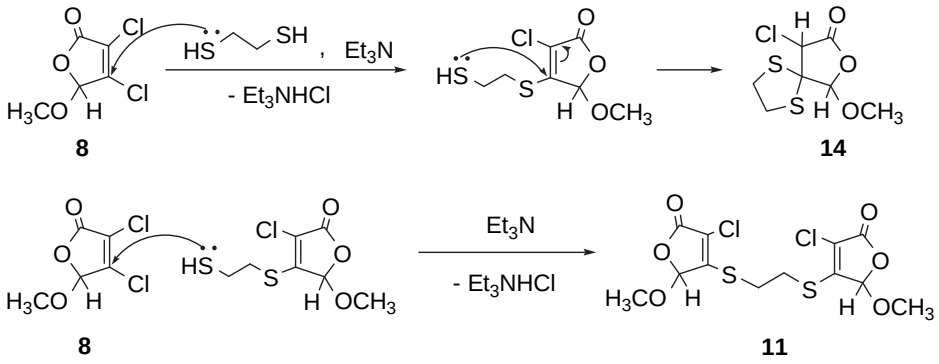


Fig. 9. Molecular structure of bicycle **14** in the crystal (*R*,*R*-isomer is shown).

11–**13** were obtained under basic and acidic conditions. The diastereomeric mixtures **11**–**13** were separated into the individual components by fractional crystallization. The molecular and crystal structure of eight sulfur-containing compounds derived from mucochloric acid were studied by single crystal X-ray diffraction.



Scheme 5. A possible mechanism for the formation of compounds **11**–**13** and **14**.

According to the X-ray data, spiro adduct **14** is represented by the *RR*,*SS*-diastereomer in the examined crystal. The five-membered lactone exists in an 'envelope' conformation, the C(6)O(7)C(8)C(9) fragment is planar within 0.002(3) Å, the atom C(5) deviates from the plane by 0.675(3) Å (Fig. 9). The atoms C(2) and C(3) of the sulfur-containing heterocycle are disordered over two positions with equal occupancy, that correspond to the coexistence of two 'envelope' conformations for this five-membered cycle in the crystal. One conformation is characterized by the planar S(1)C(5)S(4)C(3B) fragment (within 0.016(3) Å) with deviation of C(2B) atom from the plane of 0.77(2) Å, and second one has the planar S(4)C(5)S(1)C(2A) fragment (within 0.042(3) Å) with deviation of C(3A) atom of 0.64(2) Å.

In conclusion, we have reported that the utilization of 1,2-ethanedithiol in the reactions with **1** and its derivatives allows us to significantly expand the synthetic resources of mucochloric acid and to obtain previously unknown sulfur heterocycles. In all experiments performed under various conditions, both SH-groups of the reagent show a nucleophilic activity, leading to the formation of substitution products of different structural types; compounds with free thiol group have not been detected. Novel sulfur-containing fused **6**, **7** and spiro **14** bicyclic compounds, and the product of the lactone ring-opening reaction **3** were described. Several bis-thioethers with a $-SCH_2CH_2S-$ chain, connecting two 2(5*H*)-furanone units **2**, **5**,

3. Experimental section

3.1. General

IR spectra were recorded on a Specord–M80 spectrometer in a solid state (in Nujol); the thickness of cell was d=0.1–0.12 mm. NMR spectra were obtained on a Varian Unity–300 spectrometer at 299.94 MHz (^{1}H) and a Bruker Avance–400 spectrometer at 400.13 MHz (^{1}H), and 100.62 MHz (^{13}C) at 25°C with acetone-d_6 taken as internal standard. Thin-layer chromatography was performed using Silufol UV-254 plates (Kavalier, Czech Republic), acetone–benzene 1:5 mixture was used as the eluent. Spots were visualized with a UV lamp at 254 nm or iodine vapor. Silica gel 60 (Fluka, 70–230 mesh, 0.063–0.200 mm) was used for open column chromatography. The melting points were measured on a Boetius hot stage and were not corrected. Mucochloric acid **1** (Shostka Chemical Reagents Plant, Ukraine) was commercially available and was further recrystallized from water, mp 127 °C. TLC R_f 0.62. 4-Chloro-5-hydroxy-3-(4-methylphenylsulfanyl)-2(5*H*)-furanone[9] (**4**), 3,4-dichloro-5-methoxy-2(5*H*)-furanone[19] (**8**), 3,4-dichloro-5-ethoxy-2(5*H*)-furanone[20] (**9**), 3,4-dichloro-5-isopropoxy-2(5*H*)-furanone[19] (**10**) were synthesized according to the known methods. All solvents were purified and distilled by standard procedures.

3.2. X-ray structure determinations

The X-ray diffraction data for the crystals of **3**, **6**, and **14** were collected on a CAD 4 Enraf–Nonius automatic diffractometer using graphite monochromated radiation, and for the crystals **11a**, **11b**, **12a**, **12b**, and **13a** on a Smart Apex II automatic diffractometer using graphite monochromated radiation. The structures were solved by direct methods using the SIR[21] program and refined by full-matrix least-squares using SHELXL97[22] program. All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms bonded to carbon were constrained as riding atoms, with C–H set to 0.95 Å. The hydroxy H atoms were located from a difference Fourier map and the O–H bond length set to 0.85 Å. The molecules **11a**, **12a**, **13a** in the crystals are in the special position in the center of symmetry, the molecule **11b** occupies the general position in the crystal, and the molecule **12b** is in a special position on the two-fold axis. The CCl_4 molecules in the crystal **11a** are situated on the trigonal axis and disordered over two equal positions, one atom of chlorine is exactly at the center of inversion. All figures were made using the program PLATON.[23] Crystallographic data (excluding structure factors) for the structures **3**, **6**, **11a**, **11b**, **12a**, **12b**, **13a**, **14** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 611247, 611248, 720830, 720831, 720828, 720832, 720829, and 720827, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

3.3. General procedure of the synthesis of compounds 2, 3, 5–7, 11–14

*3.3.1. 5,5′-(Ethane-1,2-diyldisulfanediyl)bis(3,4-dichlorofuran-2(5H)-one) (**2**) and (2Z)-2,3-dichloro-3-(1,3-dithiolan-2-yl)prop-2-enoic acid (**3**).* A solution of mucochloric acid **1** (1.50 g, 8.9 mmol), 1,2-ethanedithiol (0.74 mL, 8.9 mmol), and concentrated sulfuric acid (0.05 mL) in benzene (35 mL) was heated at reflux for 3 h, the water produced being removed by means of a Dean–Stark apparatus. A purple precipitate was formed during the reaction. After cooling of the reaction mixture to room temperature the purple precipitate was filtered off. The benzene solution was washed with water until neutral, then dried over $MgSO_4$. The solution was concentrated down to a small volume, and a light yellow precipitate was thus obtained. Both isolated precipitates contain two substances according to the TLC analysis. Purple and light yellow precipitates were combined and multiply washed with acetone at room temperature. Thus, practically insoluble in acetone compound **2** as a 1:1 mixture of diastereomers (measured by ^{1}H NMR spectroscopy) and readily soluble in acetone compound **3** were separated from each other.

Compound (**2**). White solid, yield 0.55 g (47%), mp 174–178 °C. TLC R_f 0.83. IR ν: 1792 (C=O), 1628 (C=C$_{lactone}$) cm^{-1}. EIMS: m/z=395.9 [M]$^+$. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.99–3.10 (m, 8H, $-SCH_2-CH_2S-$), 6.59 (s, 2H, C(5)–H), 6.60 (s, 2H, C(5)–H) ppm. $C_{10}H_6Cl_4O_4S_2$ (396.10): calcd. C 30.32, H 1.53, Cl 35.80, S 16.19; found C 30.48, H 1.67, Cl 35.75, S 16.20. When the diastereomeric mixture **2** was heated under reflux with chloroform and the insoluble part was filtered off, one diastereomer as a white powder was obtained from the filtrate. Mp 175–176 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 3.03, 3.06 (m, $^2J_{AB}=^2J_{A'B'}=-13.9$ Hz, $^3J_{AB'}=^3J_{A'B}=6.1$ Hz, $^3J_{AA'}=^3J_{BB'}=9.0$ Hz, 4H, $-SCH_AH_B-CH_{A'}H_{B'}S-$), 6.59 (s, 1H, C(5)–H) ppm.

Compound (**3**). White crystalline solid, yield 0.28 g (39%), mp 166–167 °C (recrystallized from benzene). TLC R_f 0.49. IR ν: 3300–3100 (br, OH), 1688 (C=O), 1548 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.24, 3.40 (m, $^2J_{AB}=^2J_{A'B'}=-9.0$ Hz, $^3J_{AA'}=^3J_{AB'}=^3J_{A'B}=^3J_{BB'}=6.0$ Hz, 4H, $-SCH_AH_B-CH_{A'}H_{B'}S-$), 4.0–5.5 (br s, 1H, OH), 6.45 (s, 1H, C–H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 52.38 (CH_2), 65.38 (CH_2), 101.84 (C(4)–H), 123.41 (C(2)–Cl), 153.12 (C(3)–Cl), 163.31 (C(1)=O) ppm. $C_6H_6Cl_2O_2S_2$ (245.15): calcd. C 29.40, H 2.47, Cl 28.92, S 26.16; found C 29.62, H 2.38, Cl 29.03, S 26.02.

*3.3.2. 5,5′-(Ethane-1,2-diyldisulfanediyl)bis[4-chloro-3-(4-methylphenyl-sulfanyl)furan-2(5H)-one] (**5**).* A solution of compound **4** (1.00 g, 3.9 mmol), 1,2-ethanedithiol (0.16 mL, 1.95 mmol), and concentrated sulfuric acid (0.02 mL) in benzene (35 mL) was refluxed in a round-bottom flask supplied with a reflux condenser and adapter for the azeotropic evaporation of water for 30 h. After cooling, the reaction mixture was evaporated to dryness under reduced pressure, and the brown oily residue was purified by column chromatography (acetone–benzene, 1:5). From the first non-polar fraction, product **5** was obtained as a 1:1 mixture of diastereomers and recrystallized from tetrachloromethane to yield 0.75 g (68%) of a white precipitate. The second fraction contained unreacted starting material 4 (0.12 g, 12% recovery). Mp 147–149 °C. TLC R_f 0.82. IR ν: 1760 (C=O), 1592 (C=C$_{lactone}$), 1491 (C=C$_{arom}$) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.33 (s, 12H, CH_3), 2.91–2.95 (m, 8H, $-CH_2CH_2-$), 6.46 (s, 2H, C(5)–H), 6.47 (s, 2H, C(5)–H), 7.21, 7.40 (AA′BB′, N=8.0 Hz, 16H, H$_{arom}$) ppm. $C_{24}H_{20}Cl_2O_4S_4$ (571.58): calcd. C 50.43, H 3.53, Cl 12.41, S 22.44; found C 50.36, H 3.57, Cl 12.44, S 22.44.

*3.3.3. 7-Hydroxy-2,3-dihydro[1,4]dithiino[2,3-c]furan-5(7H)-one (**6**).* The compound **6** was obtained by two methods:

Method A. To a solution of mucochloric acid **1** (1.00 g, 5.9 mmol) in absolute acetone (10 mL) with intense stirring was added dropwise a solution of 1,2-ethanedithiol (0.50 mL, 5.9 mmol) in acetone (8 mL), and a solution of triethylamine (0.82 mL, 5.9 mmol) in acetone (4 mL). The reaction mixture was refluxed for 6 h and the formation of a white precipitate of $(C_2H_5)_3N\cdot HCl$ was observed. The precipitate was filtered off and washed with acetone. The combined filtrates were evaporated to dryness and the obtained oil was purified by column chromatography (acetone–benzene, 1:4). Evaporation of the main fraction, followed by recrystallization from water gave **6** (0.48 g, 43%) as colorless crystals.

Method B. To a solution of mucochloric acid (1.50 g, 8.9 mmol) and potassium hydroxide (0.50 g, 8.9 mmol) in water (10 mL) was added slowly with intense stirring a solution of 1,2-ethanedithiol (0.74 mL, 8.9 mmol), and potassium hydroxide (0.50 g, 8.9 mmol) in water (7 mL). An additional amount of KOH (0.25 g, 4.5 mmol) was added to the reaction mixture to bring up the pH ($\approx$10) and the stirring was continued for 2 h at room temperature. The solution was acidified with diluted hydrochloric acid to about pH=2–3 and further evaporated to dryness. The obtained dark oil was washed with acetone and thus isolated precipitate of potassium chloride was filtered off. After evaporating the acetone the resulting residue was recrystallized from carbon tetrachloride to afford **6** (0.59 g, 35%), mp 147–148 °C. TLC R_f 0.52. IR ν: 3344 (OH), 1728 (C=O), 1648 (C=C$_{lactone}$) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 3.25–3.35 (m, 2H, $-CH_2-$S), 3.36–3.45 (m, 2H, $-CH_2-$S), 6.13 (d, $^3J_{H,H}$=8.7 Hz, 1H, C(5)–H), 7.00 (d, $^3J_{H,H}$=8.7 Hz, 1H, OH) ppm. $C_6H_6O_3S_2$ (190.24): calcd. C 37.88, H 3.18, S 33.71; found C 38.11, H 3.08, S 33.65.

*3.3.4. 7,7′-Oxybis(2,3-dihydro[1,4]dithiino[2,3-c]furan-5(7H)-one) (**7**).* A solution containing compound **6** (92 mg, 0.48 mmol) and one drop of concentrated sulfuric acid in benzene (25 mL) was heated at reflux for 2 h, the water produced being removed by means of a Dean–Stark apparatus. The cooled reaction mixture was washed with water until neutral, then dried over $MgSO_4$. The solvent was

evaporated to dryness, and the residue was recrystallized from benzene–petroleum ether mixture to give **7** (74 mg, yield 84%) as a white solid. Mp 165–166 °C. TLC R_f 0.35. IR ν: 1748 (C=O), 1618 (C=$C_{lactone}$) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6): δ 3.33–3.39 (m, 4H, $-CH_2-S$), 3.44–3.50 (m, 4H, $-CH_2-S$), 6.35, 6.40 (s, 2H, (5)–H) ppm. $C_{12}H_{10}O_5S_4$ (362.47): calcd. C 39.76, H 2.78, S 35.39; found C 39.88, H 2.64, S 35.37.

*3.3.5. 4,4′-(Ethane-1,2-diyldisulfanediyl)bis(3-chloro-5-methoxyfuran-2(5H)-one) (**11**).* 1,2-Ethanedithiol (0.23 mL, 2.73 mmol) and triethylamine (0.76 mL, 5.46 mmol) were added to a stirred solution of ether **8** (1.00 g, 5.46 mmol) in acetone (15 mL). The reaction mixture was refluxed for 2 h. The precipitate of $(C_2H_5)_3N\cdot HCl$ was filtered off and washed with acetone. The combined filtrates were evaporated to dryness and the obtained yellow oil was purified by column chromatography (acetone–benzene, 1:5). Evaporation of the main fraction, followed by recrystallization from a mixture of tetrachloromethane and benzene (3:1) afforded a crystal sample of **11** (0.77 g, 73%) as a 1:1 mixture of diastereomers (measured by ^1H NMR spectroscopy). The separation of two diastereomers is described below.

Compound **11** mp 97–100 °C. TLC R_f 0.59. ^1H NMR (400 MHz, acetone-d_6): δ 3.598 (s, 6H, OCH_3), 3.602 (s, 6H, OCH_3), 3.65 (br s, 8H, $-CH_2-CH_2-$), 6.323 (s, 2H, C(5)–H), 6.328 (s, 2H, C(5)–H) ppm. $C_{12}H_{12}Cl_2O_6S_2$ (387.26): calcd. C 37.22, H 3.12, Cl 18.31, S 16.56; found C 37.32, H 3.24, Cl 18.27, S 16.52.

Compound **11a** *meso* isomer, mp 80 °C. IR ν: 1755 (C=O), 1590 (C=$C_{lactone}$) cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ 3.598 (s, 6H, OCH_3), 3.65 (br s, 4H, $-CH_2-CH_2-$), 6.323 (s, 2H, C(5) –H) ppm. ^{13}C {^1H} NMR (100 MHz, acetone-d_6): δ 32.14 (CH_2), 56.82 (CH_3), 103.03 (C(5)), 119.32 (C(3)), 156.58 (C(4)), 165.40 (C(2)) ppm. Compound **11a** forms the clathrate with tetrachloromethane with a 3:1 host/guest ratio. $3(C_{12}H_{12}Cl_2O_6S_2)\cdot CCl_4$ (1315.59): calcd. Cl 26.95; found Cl 27.31.

Compound **11b** DL isomer, mp 99 °C. ^1H NMR (400 MHz, acetone-d_6): δ 3.602 (s, 6H, OCH_3), 3.65 (br s, 4H, $-CH_2-CH_2-$), 6.328 (s, 2H, C(5)–H) ppm. ^{13}C {^1H} NMR (100 MHz, acetone-d_6): δ 32.24 (CH_2), 56.91 (CH_3), 103.08 (C(5)), 119.24 (C(3)), 156.69 (C(4)), 165.39 (C(2)) ppm.

*3.3.6. 4,4′-(Ethane-1,2-diyldisulfanediyl)bis(3-chloro-5-ethoxyfuran-2(5H)-one) (**12**).* Compound **12** was synthesized as described above for compound **11** from ethoxyfuranone **9** (1.00 g, 5.08 mmol) and 1,2-ethanedithiol (0.21 mL, 2.5 mmol) in the presence of triethylamine (0.71 mL, 5.08 mmol). Recrystallization from tetrachloromethane gave a crystal sample of **12** (0.67 g, 64%) as a 1:1 mixture of diastereomers (measured by ^1H NMR spectroscopy).

Compound **12** mp 83–86 °C. TLC R_f 0.65. ^1H NMR (400 MHz, acetone-d_6): δ 1.30 (t, X-part of ABX_3-system, $^3J_{H,H}$=7.1 Hz, 12H, CH_3), 3.60–3.70 (m, 8H, $-CH_2S-$), 3.83–3.98 (m, AB-part of ABX_3-system, 8H, OCH_2), 6.358 (s, 2H, C(5)–H), 6.370 (s, 2H, C(5)–H) ppm. $C_{14}H_{16}Cl_2O_6S_2$ (415.31): calcd. C 40.49, H 3.88, Cl 17.07, S 15.44; found C 40.13, H 3.65, Cl 17.00, S 15.52.

Compound **12a** *meso* isomer, mp 110 °C. ^1H NMR (400 MHz, acetone-d_6): δ 1.30 (t, X-part of ABX_3-system, $^3J_{H,H}$=7.1 Hz, 6H, CH_3), 3.65, 3.68 (AA′BB′, $J_{AA'}=J_{BB'}$=9.0 Hz, $J_{AB}=J_{A'B'}$=−13.9 Hz, $J_{A'B}=J_{AB'}$=−6.0 Hz, 4H, $-CH_2S-$), 3.90, 3.93 (both m, AB-part of ABX_3-system, $^2J_{AB}$=−9.4 Hz, $^3J_{AX}=^3J_{BX}$=7.1 Hz, 4H, OCH_2), 6.358 (s, 2H, C(5)–H) ppm. ^{13}C {^1H} NMR (100 MHz, acetone-d_6): δ 16.34 (CH_3), 32.14 (SCH_2), 66.87 (OCH_2), 102.49 (C(5)), 119.36 (C(3)), 156.64 (C(4)), 165.46 (C(2)) ppm.

Compound **12b** DL isomer, mp 91–92 °C. ^1H NMR (400 MHz, acetone-d_6): δ 1.30 (t, X-part of ABX_3-system, $^3J_{HH}$=7.2 Hz, 6H, CH_3), 3.64, 3.68 (AA′BB′, $J_{AA'}=J_{BB'}$=6.0 Hz, $J_{AB}=J_{A'B'}$=−13.9 Hz, $J_{A'B}=J_{AB'}$=9.0 Hz, 4H, $-CH_2S-$), 3.90, 3.93 (both m, AB-part of ABX_3-system, $^2J_{AB}$=−9.5 Hz, $^3J_{AX}=^3J_{BX}$=7.2 Hz, 4H, OCH_2), 6.370 (s, 2H, C(5)–H) ppm. ^{13}C {^1H} NMR (100 MHz, acetone-d_6): δ=16.34 (CH_3), 32.21 (SCH_2), 66.90 (OCH_2), 102.50 (C(5)), 119.21 (C(3)), 156.78 (C(4)), 165.45 (C(2)) ppm.

*3.3.7. 4,4′-(Ethane-1,2-diyldisulfanediyl)bis(3-chloro-5-isopropoxyfuran-2(5H)-one) (**13**).* Compound **13** was synthesized as described above for compound **11** from isopropoxyfuranone **10** (1.00 g, 4.7 mmol) and 1,2-ethanedithiol (0.20 mL, 2.35 mmol) in the presence of triethylamine (0.66 mL, 4.70 mmol). Recrystallization from mixture of tetrachloromethane and hexane (4:1) afforded a crystal sample of **13** (0.91 g, 87%) as a 1:1 mixture of diastereomers (measured by ^1H NMR spectroscopy).

Compound **13** mp 147–154 °C. TLC R_f 0.71. ^1H NMR (400 MHz, acetone-d_6): δ 1.29 (d, $^3J_{H,H}$=6.1 Hz, 12H, CH_3), 1.34 (d, $^3J_{H,H}$=6.1 Hz, 12H, CH_3), 3.57–3.73 (m, 8H, $-CH_2S-$), 4.25 (septet, $^3J_{H,H}$=6.1 Hz, 4H, OCH), 6.406 (s, 2H, C(5)–H), 6.417 (s, 2H, C(5)–H) ppm. ^{13}C {^1H} NMR (100 MHz, acetone-d_6): δ 23.40, 23.41, 24.53, 24.54 (CH_3), 32.00, 32.05 (SCH_2), 75.73, 75.75 (OCH), 101.82, 101.83 (C(5)), 119.50, 119.64 (C(3)), 156.62, 156.77 (C(4)), 165.52, 165.53 (C(2)) ppm. $C_{16}H_{20}Cl_2O_6S_2$ (443.36): calcd. C 43.34, H 4.55, Cl 15.99, S 14.46; found C 43.31, H 3.49, Cl 15.97, S 14.43.

Compound **13a** *meso* isomer, mp 147–148 °C. IR ν: 1760 (C=O), 1590 (C=$C_{lactone}$) cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ 1.29 (d, $^3J_{H,H}$=6.1 Hz, 6H, CH_3), 1.34 (d, $^3J_{H,H}$=6.1 Hz, 6H, CH_3), 3.64, 3.67 (AA′BB′, $J_{AA'}=J_{BB'}$=9.0 Hz, $J_{AB}=J_{A'B'}$=−13.9 Hz, $J_{A'B}=J_{AB'}$=6.3 Hz, 4H, $-CH_2S-$), 4.25 (septet, $^3J_{H,H}$=6.1 Hz, 2H, OCH), 6.406 (s, 2H, C(5)–H) ppm. ^{13}C {^1H} NMR (100 MHz, acetone-d_6): δ 23.40, 24.53 (CH_3), 32.00 (SCH_2), 75.73 (OCH), 101.82 (C(5)), 119.64 (C(3)), 156.62 (C(4)), 165.53 (C(2)) ppm.

*3.3.8. The separation of diastereomeric bis-thioethers **11**–**13**.* The separation of compounds **11**–**13** was achieved by the method of fractional crystallization in combination with manual sorting of the crystals under a microscope. The sample containing the mixture of two isomers was dissolved in an excess of tetrachloromethane by heating and left for slow evaporation at room temperature. In one to two days the first portion of the crystals were separated by filtration, washed with cold tetrachloromethane, and dried. The isolated crystals appeared under the microscope as well-faceted quite large crystals that have typical forms of hexagonal prisms (**11a**), plates (**12a**) or rounded plates (**13a**). The preferentially grown diastereomer in all three cases of bis-thioethers was the *meso* form as verified by X-ray single diffraction analysis. The subsequent crystallization from mother liquors led to the precipitation of the mixture of two diastereomers (as evidenced by ^1H NMR spectroscopy) that can be sorted out manually under microscope. Thus, the small plates of DL isomer **11b** and the cubic prisms of **12b** were obtained. The last portion of grown crystals represents exclusively the pure DL isomers **11b** and **12b**. Unfortunately, all our attempts to crystallize and isolate the DL diastereomer of isopropoxy bis-thioether **13** were unsuccessful.

*3.3.9. (RR,SS)-9-Chloro-6-methoxy-7-oxa-1,4-dithiaspiro[4.4]nonan-8-one (**14**).* 1,2-Ethanedithiol (0.31 mL, 3.63 mmol) and triethylamine (0.51 mL, 3.63 mmol) were added to a stirred solution of ether **8** (0.66 g, 3.63 mmol) in acetone (20 mL). The reaction mixture was refluxed for 1 h. The precipitate of $(C_2H_5)_3N\cdot HCl$ was filtered off and washed with acetone. The combined filtrates were evaporated to dryness and the obtained yellow oil was purified by column chromatography (hexane–diethyl ether, 1:3). From the first non-polar fraction, product **14** was obtained and recrystallized from a mixture of tetrachloromethane and hexane (2:1) to yield 0.21 g (24%) of colorless crystals. Second fraction contained bis-thioether **11** (0.70 g, 39%). Mp 74–76 °C. TLC R_f 0.65. IR ν: 1790 (C=O) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6): δ 3.37–3.55 (m, 4H, $-CH_2-CH_2-$), 3.61 (s, 3H, OCH_3), 5.25 (s, 1H, C(3)–H), 5.65 (s, 1H,

C(5)–H) ppm. $C_7H_9ClO_3S_2$ (240.73): calcd. C 34.93, H 3.77, Cl 14.73, S 26.64; found C 34.71, H 3.62, Cl 14.78, S 26.55.

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Supplementary data

Supplementary data associated with this article (including single crystal X-ray data and refinement parameters, selected geometrical parameters of the individual isomers of bis-thioethers **11**–**13** and Checkcif Reports of compounds) can be found in online version. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2010.10.047. These data include MOL files and InChiKeys of the most important compounds described in this article.

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