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Reactions of 2-Sulfanylethanol with Mucochloric Acid and Its Derivatives

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Abstract—Mucochloric acid reacted with 2-sulfanylethanol in the presence of triethylamine to give 3-chloro-5-hydroxy-4-(2-hydroxyethylsulfanyl)furan-2(5*H*)-one which underwent acid-catalyzed cyclization to 7-chloro-2,3,4a,6-tetrahydrofuro[2,3-*b*][1,4]oxathiin-6-one. Likewise, reactions of 5-alkoxy-3,4-dichlorofuran-2(5*H*)-ones with 2-sulfanylethanol in the presence of triethylamine involved replacement of chlorine in position *4* of the furan ring with formation of the corresponding 4-(2-hydroxyethylsulfanyl) derivatives. The reaction of mucochloric acid with 2-sulfanylethanol in excess aqueous potassium hydroxide resulted in the formation of an acyclic product, 3-(2-hydroxyethylsulfanyl)-2-chloroprop-2-enoic acid. The structure of 7-chloro-2,3,4a,6-tetrahydrofuro[2,3-*b*][1,4]oxathiin-6-one and 3-(2-hydroxyethylsulfanyl)-2-chloroprop-2-enoic acid was proved by X-ray analysis.

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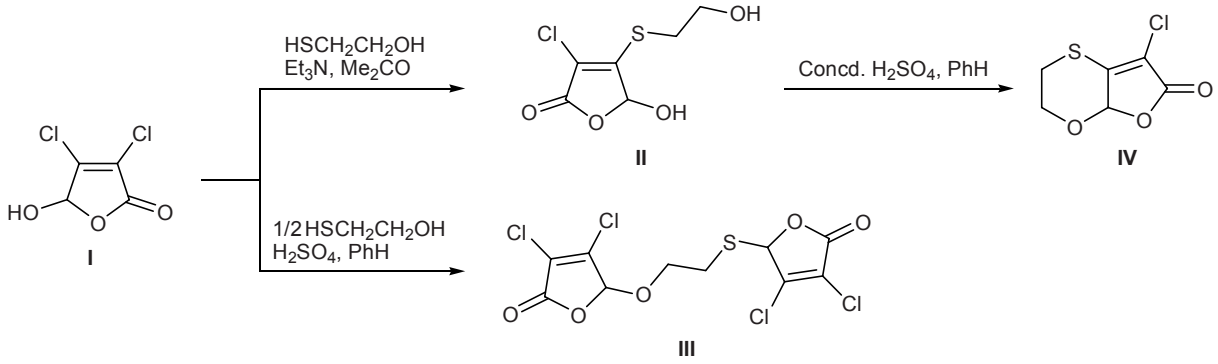
Development of the chemistry of unsaturated γ-lactones is related to their occurrence in nature, vast synthetic potential, and wide scope of application in medicine and agriculture due to their versatile biological activity [1–4]. Mucochloric acid [**I**, 3,4-dichloro-5-hydroxyfuran-2(5*H*)-one] is among such chemically and biologically active heterocyclic compounds. In the recent time, it has attracted considerable attention as an accessible starting material [5–8]. Mucochloric acid (**I**) is capable of undergoing ring–chain tautomerism [9, 10], and its molecule possesses several reaction centers, so that it may be regarded as α,β-unsaturated acid, α,β-unsaturated aldehyde, tetrasubstituted *Z*-olefin, vinyl halide, latent hemiacetal, or pseudolactone. Therefore, the lactone ring in **I** can be modified via introduction of various functional substituents with a view to obtain new heterocyclic compounds possessing practically useful properties.

While studying the synthesis, structure, and properties of sulfur- and selenium-containing derivatives of biologically active heterocycles, we previously reported on the reactions of mucochloric acid (**I**) with aromatic and heterocyclic thiols [11] and selenols [12]. We showed that variation of the reaction conditions (acid or base catalysis), as well as of the order of mixing of the reactants, ensures selective formation of different nucleophilic replacement products, the corresponding α-, β-, and γ-arylsulfanyl derivatives [11].

The goal of the present work was to study reactions of mucochloric acid (**I**) and some its derivatives with 2-sulfanylethanol under different conditions. The use in these reactions of a sulfur-containing binucleophile seemed to be promising from the viewpoint of obtaining new sulfur-containing products having both mono- and bicyclic structure.

Zanker and Reicheneder [13] and Gumulka and Kokosinski [14] previously reported on the formation of different types of substitution products in the reactions of compound **I** with 2-sulfanylethanol under basic and acidic conditions. Under the conditions ensuring replacement of the 4-chlorine atom by the action of aliphatic and aromatic thiols (base catalysis), compound **II** having a free hydroxy group in the side chain was obtained [13] (Scheme 1). The reaction of **I** with 2-sulfanylethanol at a ratio of 2:1 on heating in benzene in the presence of sulfuric acid gave product **III** [14]. Unfortunately, no reliable spectral parameters of compounds **II** and **III** were given in [13, 14].

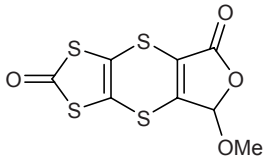
Scheme 1.



Therefore, first of all we made an attempt to reproduce the reactions described therein. In fact, the product obtained in benzene in the presence of sulfuric acid had the structure of 3,4-dichloro-5-[2-(3,4-dichloro-5-oxo-2,5-dihydrofuran-2-ylsulfanyl)ethoxy]furan-2(5*H*)-one (**III**); it was formed as a mixture of two diastereoisomers. When the reaction was performed under basic conditions (triethylamine, acetone), we isolated not only 3-chloro-5-hydroxy-4-(2-hydroxyethylsulfanyl)-furan-2(5*H*)-one (**II**) but also previously unknown bicyclic compound **IV**, depending on the procedure for treatment of the reaction mixture.

The ^{1}H NMR spectrum of **IV** contained a singlet at δ 6.11 ppm from 5-H, while no signals assignable to hydroxy protons were present. Methylene protons in the OCH_2CH_2S fragment resonated as an *ABXY* spin system: the OCH_2 group gave a multiplet in the region δ 4.2–4.5 ppm, while the SCH_2 protons appeared as a multiplet at δ 3.2–3.4 ppm. The structure of bicyclic compound **IV** in crystal was characterized by the X-ray diffraction data (Fig. 1). The six-membered ring in molecule **IV** adopts a *chair* conformation: the $C^4C^5C^6C^7$ fragment is planar within 0.01 Å, and the O^5 and S^4 atoms deviate from that plane by –0.70 and 0.57 Å, respectively.

Compound **IV** is the first representative of a new sulfur-containing fused heterocyclic system, 2,3,4a,6-tetrahydrofuro[2,3-*b*][1,4]oxathiin-6-one. As far as we know, there are no published data on the synthesis of sulfur-containing bicyclic compounds on the basis of mucochloric acid and its derivatives. Hartke and Rauschen [15] reported on the formation of tricyclic sulfur-containing compound in the reaction of 3,4-dibromo-5-methoxyfuran-2(5*H*)-one with disodium 2-oxo-1,3-dithiole-4,5-dithiolate.



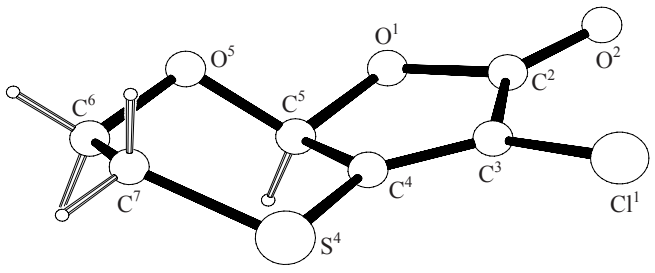
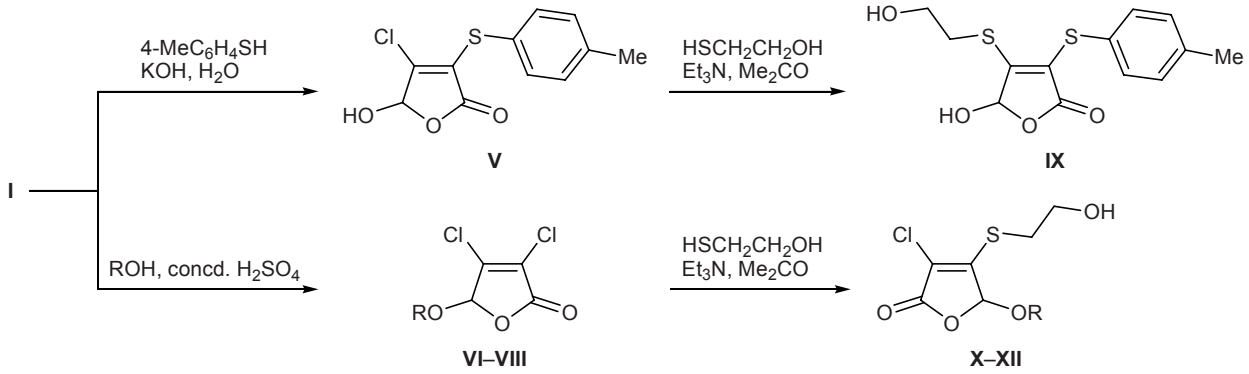


Fig. 1. Structure of the molecule of 7-chloro-2,3,4a,6-tetrahydrofuro[2,3-*b*][1,4]oxathiin-6-one (**IV**) according to the X-ray diffraction data.

Acyclic product **II** was isolated when the reaction mixture was treated with water, while bicyclic compound **IV** was isolated by treatment of the reaction mixture (in another experiment) with butanol. We presumed that compound **IV** is formed via intramolecular cyclization of **II** in the presence of traces of triethylamine hydrochloride. This assumption was based on the known ability of mucochloric acid to undergo nucleophilic attack on C^5 in the presence of mineral acids [11, 14] and was confirmed by special experiments. By heating compound **II** in boiling benzene in the presence of sulfuric acid we obtained furo[2,3-*b*][1,4]oxathiine **IV**, whereas no intramolecular cyclization occurred when pure sulfide **II** was recrystallized from anhydrous butanol. Facile intramolecular dehydration of **II** with formation of bicyclic compound **IV** also follows from the results of quantum-chemical calculations. The Gibbs energy $\Delta\Delta G_{298}$ of this reaction was estimated at –1.29 kkal/mol in terms of the density functional theory [B3LYP/6-31G(*d*,*p*)].

2-Sulfanylethanol reacted with 3-(*p*-tolylsulfanyl)-substituted furanone **V** and 5-alkoxy derivatives **VI**–**VIII** in the presence of triethylamine to give the corresponding sulfides **IX**–**XII** as a result of nucleophilic

Scheme 2.



VI, **X**, R = Me; **VII**, **XI**, R = Et; **VIII**, **XII**, R = *i*-Pr.

replacement of chlorine in position *4* of the furan ring (Scheme 2). Compounds **X**–**XII** characteristically showed in the ^{1}H NMR spectra a group of multiplets from protons in the SCH_2CH_2OH fragment (*ABMXY* system, Fig. 2).

The reactions of furanones **V**–**VII** with 2-sulfanylethanol (heating in boiling acetone in the presence of triethylamine) required a longer time than analogous reaction of mucochloric acid (**I**). We also found that recrystallization of compounds **X** and **XI** from water is accompanied by dealkylation with formation of compound **II**. Dealkylation of compounds **X**–**XII**, followed by intramolecular cyclization, also occurred on heating in benzene in the presence of a catalytic amount of concentrated sulfuric acid; in these cases, bicyclic product **IV** was isolated.

As we showed previously [11], mucochloric acid (**I**) reacted with 4-methylbenzenethiol in excess aqueous potassium hydroxide to give product of chlorine replacement at C^3. According to [9–11], alkaline medium promotes cleavage of the lactone ring in molecule **I**, nucleophilic attack is directed at the α-carbon atom with respect to the carboxy group, and cyclic product is isolated after acidification of the reaction mixture. In

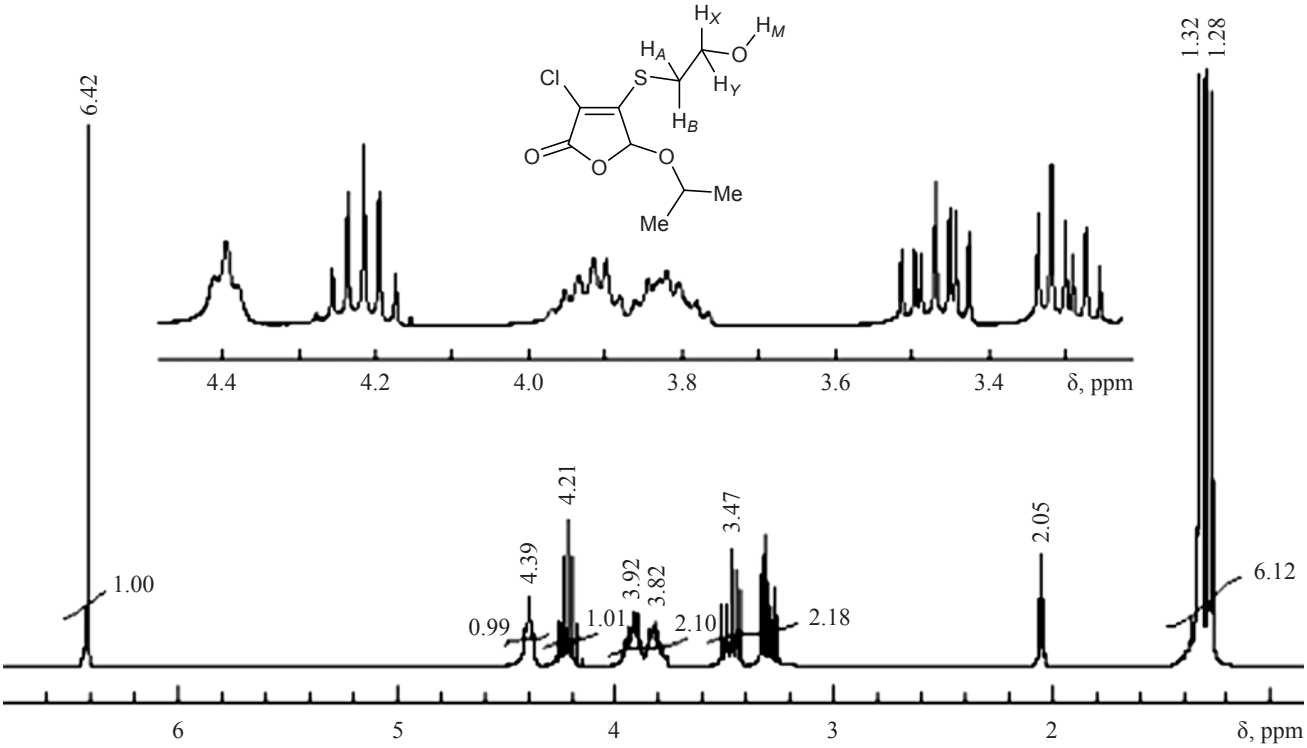


Fig. 2. ^{1}H NMR spectrum of 3-chloro-4-(2-hydroxyethylsulfanyl)-5-isopropoxyfuran-2(5*H*)-one (**XII**) in acetone-d_6.

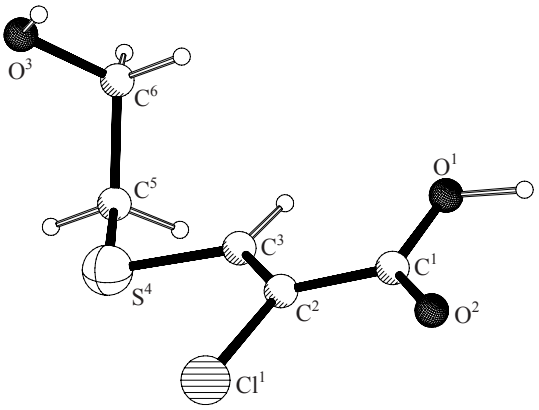


Fig. 3. Structure of the molecule of 2-chloro-3-(2-hydroxyethylsulfanyl)prop-2-enoic acid (**XIII**) according to the X-ray diffraction data.

the reaction of mucochloric acid with 2-sulfanylethanol in aqueous potassium hydroxide, after treatment of the reaction mixture with dilute hydrochloric acid, we isolated compound **XIII** which (according to the spectral data) had acyclic structure (Scheme 3). The IR spectrum of **XIII** lacked absorption band assignable to stretching vibrations of γ-lactone carbonyl, but a strong sharp peak was present at 1686 cm^{-1}; such absorption is typical of stretching vibrations of the carbonyl group in carboxylic acid dimers [16]. In the ^1H NMR spectrum of **XIII** we observed an olefinic proton singlet at δ 8.14 ppm, a broadened signal at δ 4.0–4.5 ppm (OH), and a multiplet at δ 3.0–4.0 ppm, typical of methylene protons. The structure of compound **XIII** as 2-chloro-3-(2-hydroxyethylsulfanyl)prop-2-enoic acid was finally proved by X-ray analysis (Fig. 3).

The presence of hydroxy and carboxy groups in molecule **XIII** determines specificity of crystal packing of this compound. Intermolecular hydrogen bonds in crystal give rise to twinned chains along the *a* crystallographic axis (Fig. 4). The oxygen atom in the hydroxy group of one molecule interacts with the

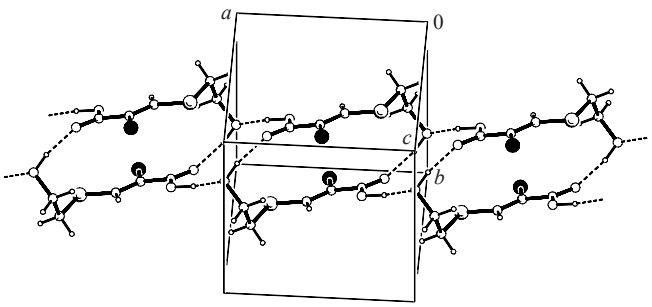
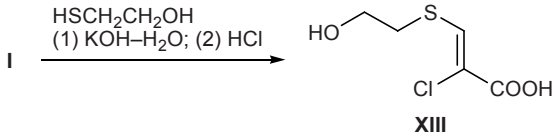


Fig. 4. Crystalline structure of 2-chloro-3-(2-hydroxyethylsulfanyl)prop-2-enoic acid (**XIII**) according to the X-ray diffraction data.

Scheme 3.



carboxy hydrogen atom of the neighboring molecule (O^1–$H^1\cdots O^3$: $H^1\cdots O^3$ 1.59 Å, $\angle O^1H^1O^3$ 166°), while the carbonyl oxygen atom is involved in hydrogen bonding with hydrogen atom in the hydroxy group (O^3–$H^3\cdots O^2$: $H^3\cdots O^2$ 1.77 Å, $\angle O^3H^3O^2$ 166°).

Although it is still difficult to discuss the mechanism of formation of acyclic compound **XIII**, we believe that it can be formed as shown in Scheme 4.

Excess aqueous alkali promotes generation of thiolate ion from 2-sulfanylethanol and anion from the open-chain tautomer of mucochloric acid. Reaction of these species gives product **A** as a result of nucleophilic replacement of the chlorine atom on C^3. Intermediate **A** takes up hydroxide ion at the carbonyl group to form adduct **B**, and subsequent transformations of the latter may follow two pathways. One of these involves first decarboxylation of **B** into **C** and then disproportionation of **C** into **E**, while the second, Cannizzaro reaction of **B** to **D** and decarboxylation of **D** into **E**. Acidification of **E** gives acid **XIII**.

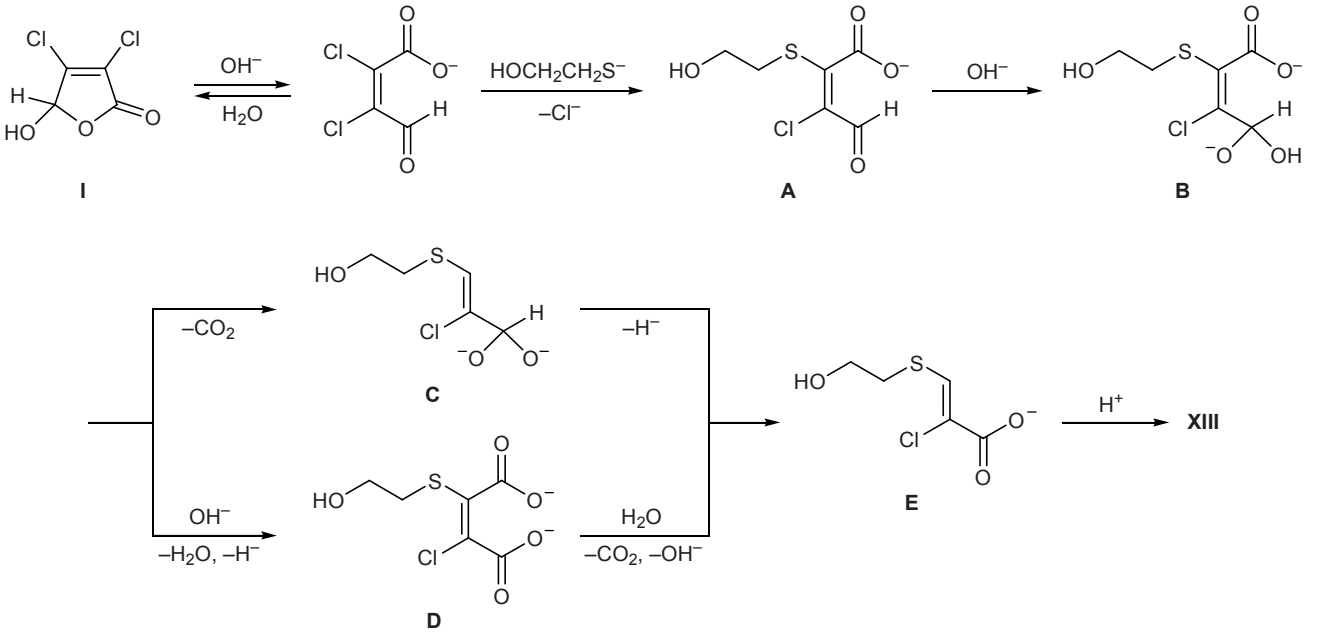
Thus, depending on the conditions (acid or base catalysis), reactions of mucochloric acid and some its derivatives with 2-sulfanylethanol result in the formation of different products, 3-chloro-5-hydroxy(alkoxy)-4-(2-hydroxyethylsulfanyl)furan-2(5*H*)-ones, 2,3,4a,6-tetrahydrofuro[2,3-*b*][1,4]oxathiin-6-one, or 2-chloro-3-(2-hydroxyethylsulfanyl)prop-2-enoic acid.

EXPERIMENTAL

Commercial mucochloric acid (**I**) was recrystallized from water, mp 127°C [17]. 4-Chloro-5-hydroxy-3-(4-methylphenylsulfanyl)furan-2(5*H*)-one (**V**) [11], 3,4-dichloro-5-methoxyfuran-2(5*H*)-one (**VI**), 3,4-dichloro-5-ethoxyfuran-2(5*H*)-one (**VII**) [18], and 3,4-dichloro-5-isopropoxyfuran-2(5*H*)-one (**VIII**) [19] were synthesized by known methods.

The IR spectra (4000–400 cm^{-1}) were recorded from samples dispersed in Nujol and placed between KBr plates on a Bruker Tensor-27 spectrometer with Fourier transform at the Optical Research Laboratory, Federal Collective Use Center. The NMR spectra were measured at 25°C from solutions in acetone-d_6 on a Varian Unity-300 instrument at 299.94 MHz for ^1H

Scheme 4.



and 75.13 MHz for ^{13}C. The ^{1}H chemical shifts were determined relative to the residual proton signal of the solvent. Thin-layer chromatography was performed on Silufol UV-254 plates using acetone–benzene (1:4 by volume) as eluent.

X-Ray analysis was performed at the X-Ray Department, Spectral Analytical Collective Use Center, Russian Foundation for Basic Research, on a Smart Apex diffractometer at 20°C (MoK_α irradiation, multi-scan mode). The structures were solved by the direct method using SIR program [20] and were refined first in isotropic and then in anisotropic approximation (SHELXL97 [21], WinGX [22]). Hydrogen atoms were visualized from difference electron density series, and their positions were refined in isotropic approximation in the final step. The structures were plotted, and intermolecular contacts were analyzed, using PLATON program [23]. X-Ray diffraction data: compound **IV**: $C_6H_5ClO_3S$, M 192.61; rhombic crystals, space group $P2_12_12_1$ (no. 19); unit cell parameters: a = 4.1995(5), b = 11.335(1), c = 16.228(2) Å; V = 772.5(2) Å^3; compound **XIII**: $C_5H_7ClO_3S$, M 182.62; monoclinic crystals, space group $P2_1/c$ (no. 14); unit cell parameters: a = 8.352(5), b = 7.290(5), c = 12.785(5) Å; β = 93.510(5)°; V = 777.0(8) Å^3.

Quantum-chemical calculations were performed at the DFT B3LYP/6-31G(*d*,*p*) level using Gaussian-98 software package [24]; the geometric parameters were optimized without symmetry restrictions; second derivative matrix was calculated for all stationary points; the optimized structures were characterized by only positive vibration frequencies.

3-Chloro-5-hydroxy-4-(2-hydroxyethylsulfanyl)-furan-2(5*H*)-one (II). A solution of 0.42 ml (5.9 mmol) of 2-sulfanylethanol in 8 ml of acetone was added dropwise under vigorous stirring to a solution of 1 g (5.9 mmol) of mucochloric acid in 10 ml of acetone. A solution of 0.8 ml (5.9 mmol) of triethylamine in 4 ml of acetone was then added, the mixture was heated for 2 h under reflux, the precipitate of triethylamine hydrochloride was filtered off and washed with acetone, the filtrate was evaporated under reduced pressure, and the oily residue was crystallized twice from water. Yield 53%, colorless crystals, mp 123°C; published data [13]: mp127–128°C; R_f 0.25. IR spectrum, ν, cm^{-1}: 3362, 3152 (OH), 1742 (C=O), 1578 (C=C). ^{1}H NMR spectrum, δ, ppm: 3.37 m (1H, SCH$_A$, J_{AB} = –13.5, J_{AX} = 5.4, J_{AY} = 5.4, J_{AM} = 0.0 Hz), 3.55 m (1H, SCH$_B$, J_{AB} = –13.5, J_{BX} = 7.2, J_{BY} = 5.7, J_{BM} = 0.0 Hz), 3.86 m (1H, OCH$_X$, J_{AX} = 5.4, J_{BX} = 7.2, J_{XY} = –11.3, J_{XM} = 5.3 Hz), 3.94 m (1H, OCH$_Y$, J_{AY} = 5.4, J_{BY} = 5.7, J_{XY} = –11.3, J_{YM} = 5.3 Hz), 4.43 t (1H, OH$_M$, J_{AM} = 0.0, J_{BM} = 0.0, J_{XM} = 5.3, J_{YM} = 5.3 Hz), 6.49 d (1H, 5-H, J = 8.7 Hz), 7.32 d (1H, 5-OH, J = 8.7 Hz). Found, %: C 34.50; H 3.23; Cl 16.81; S 15.19. $C_6H_7ClO_4S$. Calculated, %: C 34.21; H 3.35; Cl 16.83; S 15.22. Recrystallization of the oily residue from butanol gave bicyclic compound **IV**.

3,4-Dichloro-5-[2-(3,4-dichloro-5-oxo-2,5-dihydrofuran-2-ylsulfanyl)ethoxy]furan-2(5*H*)-one (III). Concentrated sulfuric acid, 0.16 ml, was added to a solution of 5.0 g (29.6 mmol) of mucochloric acid (**I**) and 1.04 ml (14.8 mmol) of 2-sulfanylethanol in 100 ml of benzene, and the mixture was heated under reflux until mucochloric acid disappeared completely (34 h, TLC). The mixture was cooled, washed with water until neutral washings, dried over magnesium sulfate, and evaporated under reduced pressure. The yellow oily residue was crystallized first from carbon tetrachloride and then from petroleum ether–benzene. Yield 36%, mp 97–98°C; published data [14]: mp 127–129°C; R_f 0.69. IR spectrum, ν, cm^{-1}: 1788 (C=O), 1624 (C=C). ^1H NMR spectrum, δ, ppm: 2.9–3.1 m (2H, SCH_2), 4.0–4.2 m (2H, OCH_2), 6.23 s and 6.24 s (1H, 5′-H), 6.58 s and 6.58 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 29.70, 29.72 (SCH_2); 70.07, 70.11 (OCH_2); 87.07 ($C^{5'}$); 101.75 (C^5); 123.13, 123.18, 124.00, 124.05 (C^3, $C^{3'}$); 148.27, 148.35, 150.81, 150.91 (C^4, $C^{4'}$); 163.50, 164.46 (C^2, $C^{2'}$). Found, %: C 31.45; H 1.88; Cl 37.66; S 8.68. $C_{10}H_6Cl_4O_5S$. Calculated, %: C 31.60; H 1.59; Cl 37.32; S 8.44.

7-Chloro-2,3,4a,6-tetrahydrofuro[2,3-*b*][1,4]oxathiin-6-one (IV). Concentrated sulfuric acid, 0.01 ml (20 mol %), was added to a solution of 0.214 g (0.102 mmol) of compound **II** in 25 ml of benzene. The mixture was heated for 3 h under reflux, cooled, and washed with water until neutral washings. The benzene solution was dried over $MgSO_4$ and evaporated to dryness, and the residue was recrystallized from petroleum ether–benzene. Yield 52%, colorless needles, mp 81°C, R_f 0.63. IR spectrum, ν, cm^{-1}: 1773 (C=O), 1602 (C=C). ^1H NMR spectrum, δ, ppm: 3.28 m (1H, SCH_A, J_{AB} = 13.1, J_{AX} = 9.4, J_{AY} = 2.6 Hz), 3.29 m (1H, SCH_B, J_{AB} = 13.1, J_{BX} = 1.7, J_{BY} = 7.2 Hz), 4.32 m (1H, SCH_X, J_{AX} = 9.4, J_{BX} = 1.7, J_{XY} = 12.4 Hz), 4.45 m (1H, SCH_Y, J_{AY} = 2.6, J_{BY} = 7.2, J_{XY} = 12.4 Hz), 6.11 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 28.66 (SCH_2), 67.13 (OCH_2), 97.73 (C^5), 119.12 (C^3), 154.31 (C^4), 164.19 (C^2). Found, %: C 37.15; H 2.68; Cl 18.41; S 16.61. $C_6H_5ClO_3S$. Calculated, %: C 37.41; H 2.62; Cl 18.41; S 16.65.

5-Hydroxy-4-(2-hydroxyethylsulfanyl)-3-(4-methylphenylsulfanyl)furan-2(5*H*)-one (IX). A solution of 0.18 ml (2.65 mmol) of 2-sulfanylethanol in 8 ml of acetone was added dropwise under vigorous stirring to a solution of 0.68 g (2.65 mmol) of compound **V** in 10 ml of acetone, and a solution of 0.36 ml (2.65 mmol) of triethylamine in 4 ml of acetone was then added. The mixture was heated for 30 h under reflux (TLC), the precipitate of triethylamine hydrochloride was filtered off and washed with acetone, and the filtrate was evaporated to dryness under reduced pressure. The oily residue was dissolved in chloroform, and the solution was washed with several portions of water, dried over anhydrous magnesium sulfate, and evaporated to dryness under reduced pressure. The residue was ground with hexane on cooling, and the precipitate was filtered off and recrystallized from petroleum ether–benzene. Yield 46%, mp 101°C, R_f 0.31. IR spectrum, ν, cm^{-1}: 3327, 3194 (OH), 1740 (C=O), 1548 (C=C), 1490 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 2.29 s (3H, CH_3), 3.2–3.6 m (2H, SCH_2), 3.7–4.0 m (2H, OCH_2), 4.35 t (1H, OH, J = 5.2 Hz), 6.48 s (1H, 5-H), 7.13 m and 7.22 m (4H, *AA′BB′*, H_{arom}, J = 8.3 Hz), 7.17 s (1H, OH). Found, %: C 51.99; H 4.49; S 21.59. $C_{13}H_{14}O_4S_2$. Calculated, %: C 52.33; H 4.73; S 21.49.

3-Chloro-4-(2-hydroxyethylsulfanyl)-5-methoxyfuran-2(5*H*)-one (X) was synthesized in a similar way from 0.74 g (4.04 mmol) of compound **VI** and 0.28 ml (4.04 mmol) of 2-sulfanylethanol in the presence of 0.57 ml (4.04 mmol) of triethylamine. Reaction time 60 h. The oily residue obtained after evaporation of the filtrate under reduced pressure was purified by column chromatography using hexane–diethyl ether (1:3) as eluent. The light yellow oily product did not crystallize. Yield 58%. ^1H NMR spectrum, δ, ppm: 3.29 m (1H, SCH_A, J_{AB} = 13.6, J_{AX} = 5.2, J_{AY} = 4.6, J_{AM} = 0.0 Hz), 3.46 m (1H, SCH_B, J_{AB} = 13.6, J_{BX} = 7.6, J_{BY} = 5.1, J_{BM} = 0.0 Hz), 3.56 s (3H, CH_3), 3.81 m (1H, OCH_X, J_{AX} = 5.2, J_{BX} = 7.6, J_{XY} = 11.5, J_{XM} = 5.3 Hz), 3.92 m (1H, OCH_Y, J_{AY} = 4.6, J_{BY} = 5.1, J_{XY} = 11.5, J_{YM} = 5.3 Hz), 4.38 t (1H, OH_M, J_{AM} = J_{BM} = 0.0, J_{XM} = J_{YM} = 5.3 Hz), 6.31 s (1H, 5-H). Recrystallization of liquid compound **X** from water gave furanone **II**.

3-Chloro-5-ethoxy-4-(2-hydroxyethylsulfanyl)-furan-2(5*H*)-one (XI) was synthesized in a similar way from 1.66 g (8.43 mmol) of compound **VII** and 0.59 ml (8.43 mmol) of 2-sulfanylethanol in the presence of 1.17 ml (8.43 mmol) of triethylamine. Reaction time 10 h. Recrystallization of the yellow oily product from carbon tetrachloride–acetone gave white powder. Yield 65%, mp 45°C, R_f 0.40. IR spectrum, ν, cm^{-1}: 3100–3300 br (OH), 1770 (C=O), 1596 (C=C). ^1H NMR spectrum, δ, ppm: 1.28 t (3H, CH_3, J = 7.1 Hz), 3.30 m (1H, SCH_A, J_{AB} = 13.6, J_{AX} = 5.2, J_{AY} = 5.2, J_{AM} = 0.0 Hz), 3.47 m (1H, SCH_B, J_{AB} = 13.6, J_{BX} = 7.6, J_{BY} = 5.3, J_{BM} = 0.0 Hz), 3.75–3.97 m (4H,

OCH_2, OCH_XH_Y), 4.38 t (1H, OH_M, J = 5.1 Hz), 6.36 s (1H, 5-H). Found, %: C 40.13; H 4.47; Cl 15.12; S 13.74. $C_8H_{11}ClO_4S$. Calculated, %: C 40.26; H 4.65; Cl 14.85; S 13.43. Recrystallization of solid compound **XI** from water gave furanone **II**.

3-Chloro-4-(2-hydroxyethylsulfanyl)-5-isopropoxyfuran-2(5*H*)-one (XII) was synthesized as described above for compound **II** from 1.0 g (4.74 mmol) of isopropoxyfuranone **VIII** and 0.33 ml (4.74 mmol) of 2-sulfanylethanol in the presence of 0.66 ml (4.74 mmol) of triethylamine. Evaporation of the filtrate under reduced pressure gave a solid which was recrystallized from carbon tetrachloride. Yield 83%, colorless crystals, mp 72°C, R_f 0.43. IR spectrum, ν, cm^{-1}: 3509 (OH), 1748 (C=O), 1591 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.28 d (3H, CH_3, J = 6.1 Hz), 1.32 d (3H, CH_3, J = 6.1 Hz), 3.30 m (1H, SCH_A, J_{AB} = –13.5, J_{AX} = J_{AY} = 5.3, J_{AM} = 0.0 Hz), 3.47 m (1H, SCH_B, J_{AB} = –13.5, J_{BX} = 7.7, J_{BY} = 5.3, J_{BM} = 0.0 Hz), 3.82 m (1H, OCH_X, J_{AX} = 5.3, J_{BX} = 7.7, J_{XY} = –11.5, J_{XM} = 5.0 Hz), 3.92 m (1H, OCH_Y, J_{AY} = J_{BY} = 5.3, J_{XY} = –11.5, J_{YM} = 5.0 Hz), 4.21 m (1H, OCH, ^3J = 6.1 Hz), 4.39 t (1H, OH_M, J_{AM} = J_{BM} = 0.0, J_{XM} = J_{YM} = 5.0 Hz), 6.42 s (1H, 5-H). Found, %: C 42.41; H 4.96; Cl 14.32; S 12.52. $C_9H_{13}ClO_4S$. Calculated, %: C 42.77; H 5.18; Cl 14.03; S 12.69.

2-Chloro-3-(2-hydroxyethylsulfanyl)prop-2-enoic acid (XIII). 2-Sulfanylethanol, 0.42 ml (5.9 mmol), was added dropwise under vigorous stirring to a solution of 1 g (5.9 mmol) of mucochloric acid (**I**) and 1.33 g (23.7 mmol) of potassium hydroxide in 10 ml of water. The mixture was stirred for 2 h, acidified with dilute hydrochloric acid to pH 1, and evaporated to dryness under reduced pressure. The semisolid residue was purified by column chromatography using acetone–benzene (1:5) as eluent to obtain a solid which was additionally recrystallized from hexane–benzene. Yield 51%, colorless crystals, mp 147°C, R_f 0.16. IR spectrum, ν, cm^{-1}: 3353 (OH); 2527, 2612, 2682, 2787 m (COOH); 1686 (C=O); 1569 (C=C). ^{1}H NMR spectrum, δ, ppm: 3.14 t (2H, SCH_2, ^3J = 6.00 Hz), 3.84 t (2H, OCH_2, ^3J = 6.00 Hz), 4.0–4.5 br (1H, OH), 8.14 s (1H, 5-H). Found, %: C 33.00; H 3.74; Cl 19.67; S 17.86. $C_5H_7ClO_3S$. Calculated, %: C 32.88; H 3.86; Cl 19.41; S 17.56.

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