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Brominated and Iodinated Thiofluoresceins

V. V. Russkikh, E. V. Vasil'ev, and V. V. Shelkovnikov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: vsh@nioch.nsc.ru

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Abstract—Conditions were found for the synthesis of mono-, di-, tri-, and tetrabromo- and -iodo-substituted thiofluoresceins. Iodination and bromination of thiofluorescein with molecular iodine and bromine in 1 N aqueous sodium hydroxide gave mixtures of the corresponding 2,4,5,7-tetra- and 2,4,5-trihalo derivatives in 71/14 (Y = I) and 73/13% yield (Y = Br), respectively. In the reactions of thiofluorescein with bromine in acetic acid and with iodine in methanol at a substrate-to-halogen ratio of 1:2, 4,5-dibromo- and 4,5-diiodothiofluoresceins were isolated in 56 and 67% yield. Analogous reactions with equimolar amounts of the reactants produced 59% of 4-bromothiofluorescein and 51% of 4-iodothiofluorescein.

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Replacement of the endocyclic oxygen atom in the fluorescein molecule by sulfur sharply increases the yield of triplet states [1]. Additional introduction of heavy bromine or iodine atoms into the molecule of thiofluorescein (**I**) also strongly affects photophysical parameters of the resulting thioxanthene dyes [2]. Up to now, only two halogenated thiofluoresceins have been reported, 2,4,5,7-tetrabromothiofluorescein (**IIa**) [1] and 2,4,5,7-tetraiodothiofluorescein (**IIb**) [3]. These compounds were synthesized by bromination of **I** in acetic acid [1] and by iodination in methanol [3]. However, no data were given on the formation in these reactions of mono-, di-, and trihalo derivatives, and such products were not isolated.

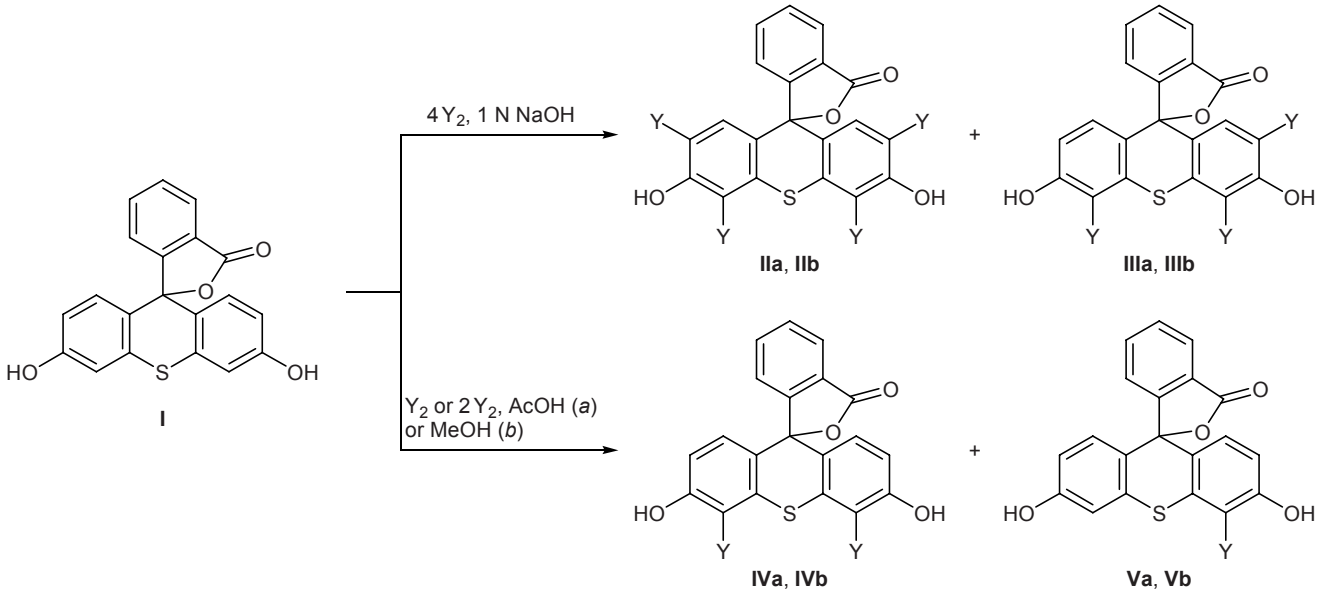
The goal of the present work was to find conditions for selective halogenation of thiofluorescein (**I**) with a view to isolate mono-, di-, tri-, and tetrabromo- and -iodo-substituted thiofluoresceins as individual products. Electrophilic substitution in the molecule of thiofluorescein (**I**), as well as in fluorescein, is favored at positions *2*, *4*, *5*, and *7* that are activated by electronic factors and are spatially accessible. According to quantum-chemical calculations [4], the charges on the C^2/C^7 and C^4/C^5 atoms in the dianions derived from fluorescein (X = O) and thiofluorescein (X = S) are –0.251, –0.309 and –0.255, –0.250, respectively.

The results of halogenation of compound **I** in acetic acid [1] and methanol [3] indicate that the reactivity of positions *2*, *4*, *5*, and *7* in the neutral lactone form toward electrophilic bromination and iodination remains sufficient due to the presence of electron-donating hydroxy groups and endocyclic sulfur atom. Therefore, the iodination can be performed with molecular iodine in the absence of oxidants.

However, we failed to obtain compound **IIa** as the major product in our attempts to reproduce the bromination of compound **I** in acetic acid under the conditions described in [1]. The crystalline product formed in acetic acid contained dibromo-substituted thiofluorescein rather than tetrabromo derivative. By bromination of **I** in 1 N aqueous sodium hydroxide at 25°C we succeeded in isolating tetrabromothiofluorescein **IIa** in 73% yield (Scheme 1). The long-wave absorption maximum in the electronic spectrum of **IIa** was located at λ 533 nm (cf. λ 525 nm [2]). Tribromothiofluorescein **IIIa** isolated in 13% yield during purification of **IIa** was characterized by absorption maximum at λ 523 nm (for dianion).

The bromination of **I** in acetic acid favors formation of dibromothiofluorescein **IVa**. When the reactant ratio **I**–Br_2 was changed from 1:4 to 1:2, we obtained

Scheme 1.



Y = Br (**a**), I (**b**).

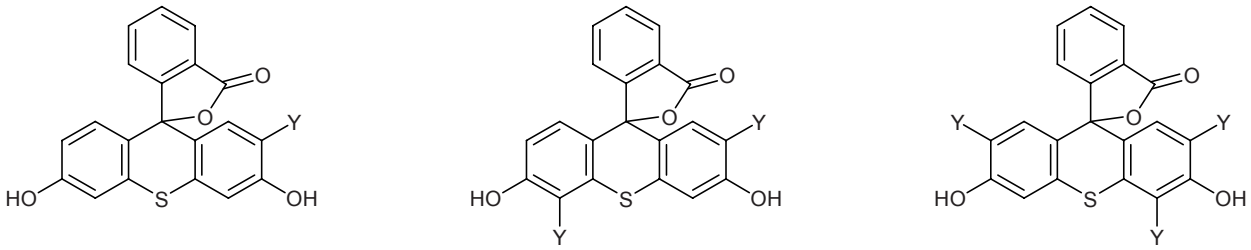
56% of compound **IVa** under the conditions described in [1]. Monobromothiofluorescein **Va** was isolated in 59% yield when the reaction was performed with equimolar amounts of the reactants.

Likewise, the iodination of thiofluorescein (**I**) with iodine in 1 N aqueous sodium hydroxide at 100°C gave 71% of tetraiodothiofluorescein **IIb** and 14% of triiodothiofluorescein **IIIb**. When the iodination was carried out in methanol, a mixture of tri-, di-, and monoiodo-substituted thiofluoresceins **IIIb**, **IVb**, and **Vb** was formed rather than tetraiodothiofluorescein **IIb** as reported in [3]. By iodination in methanol at **I**-to-I_2 molar ratios of 1:2 and 1:1 we obtained compounds **IVb** and **Vb** in 67 and 51% yield, respectively.

The long-wave absorption maxima in the electronic spectra of dianions of **IIa**–**Va** and **IIb**–**Vb** shift to the red region as the number of halogen atoms in the molecule increases: λ_{max} 512 nm for **I**, 533 nm for tetrabromothiofluorescein **IIa**, and 542 nm for tetraiodothiofluorescein **IIb** (see table). The IR spectra of halogenated thiofluoresceins contained absorption bands at 1721–1738 cm^{-1} due to stretching vibrations of the lactone carbonyl group and at 1664–1689 cm^{-1}; the latter were assigned to stretching vibrations of carbonyl group in the quinoid form, by analogy with fluorescein [5]. Tetrahalo-substituted derivatives **IIa** and **IIb** are most prone to formation of colorless lactones in the solid state. In the IR spectra of **IIa** and **IIb** the carbonyl absorption bands are observed at 1722 and

Bromo- and iodo-substituted thiofluoresceins

Compound no.	Thiofluorescein (**I**)-to-halogen molar ratio	Solvent	Temperature, °C	Reaction time, h	λ_{max}, nm (log ε)
I					512 (4.68) [9]
IIa	1:4	1 N aq. NaOH	25	2	533 (4.71)
IIb	1:4	1 N aq. NaOH	100	8	542 (4.88)
IIIa	1:4	1 N aq. NaOH	25	2	523 (4.71)
IIIb	1:4	1 N aq. NaOH	100	8	532 (4.42)
IVa	1:2	AcOH	25	24	520 (4.80)
IVb	1:2	MeOH	25	6	523 (4.49)
Va	1:1	AcOH	25	0.2	515 (4.69)
Vb	1:1	MeOH	25	6	514 (4.50)



Y = Br, I.

1733 cm^{-1}, respectively. As the degree of halogen substitution decreases, stabilization of the lactone form requires formation of a molecular complex. It is known [5] that the lactone form of fluorescein is stabilized by dioxane at a fluorescein-to-dioxane molar ratio of 2:1. We isolated a 1:1 molecular complex of dibromothiofluorescein **IVa** with diethyl ether as a white powder with $\nu_{C=O}$ 1730 cm^{-1}. Removal of diethyl ether changes the color to red ($\nu_{C=O}$ 1664 cm^{-1}).

The structure of the isolated products was confirmed by the ^{1}H NMR spectra. It should be noted that the formation of regioisomeric halogen derivatives is possible, but their ^{1}H NMR spectra should differ considerably from those having the assumed structures. The formation of isomeric iodinated fluoresceins was discussed in [6], and attempts to isolate them were made [7]. Impurities of isomeric 2,4,5- and 2,4,7-triiodofluoresceins in commercial samples of Erythrosin were quantitated by HPLC and capillary electrophoresis [8]. In most samples, the concentration of the 2,4,5-triiodo isomer exceeded the concentration of the 2,4,7-triiodo isomer by a factor of 10. TLC analysis of the mother liquors obtained during purification of the products revealed weak spots as satellites to spots of compounds **IIIa**–**Va** and **IIIb**–**Vb**. However, in most cases isolation of concomitant isomeric halogenated thiofluoresceins seems to be inexpedient, for they can be obtained by reductive dehalogenation of the isolated products. The conditions for synthesis of brominated and iodinated thiofluoresceins and long-wave absorption maxima in the electronic spectra of their dianions are given in table.

Thus the main products in the bromination and iodination of thiofluorescein are its 4-mono-, 4,5-di-, 2,4,5-tri-, and 2,4,5,7-tetrahalo derivatives whose ratio depends on the solvent nature and initial reactant ratio.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hewlett–Packard 8453 spectrophotometer. The IR spectra (mineral oil) and diffuse reflectance spectra were recorded on a Bruker Vector 22 instrument. The ^{1}H NMR spectra were obtained on Bruker WP-200 SY (200.13 MHz) and AM-400 (400 MHz) spectrometers. Column chromatography was performed using KSK silica gel (0–140 μm). The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates.

Thiofluorescein (**I**, 3′,6′-dihydroxyspiro[2-benzofuran-1,9′-thioxanthen]-3-one) was synthesized according to the procedure described in [9].

2′,4′,5′,7′-Tetrabromo-3′,6′-dihydroxyspiro-[2-benzofuran-1,9′-thioxanthen]-3-one (IIa). Thiofluorescein (**I**), 0.348 g (1 mmol), was dissolved in 15 ml of 1 N aqueous sodium hydroxide, 0.64 g (4 mmol) of bromine was added dropwise, and the mixture was kept for 2 h at room temperature. If abundant solid separated, the thick reaction mixture was diluted with a solution of sodium hydroxide. The progress of the reaction was monitored by TLC using chloroform–diethyl ether (9:1 by volume) as eluent. The chromatographic plates were deactivated with acetic acid vapor, and the sample spot was neutralized with trifluoroacetic acid and dried before elution. The chromatograms were developed by treatment with gaseous ammonia. The R_f value of initial compound **I** was 0.1–0.2 (yellow–orange spot), and the R_f value of **IIa** was 0.8–0.9 (crimson spot). The spot due to compound **I** disappeared, spots due to mono-, di-, and tribromo derivatives (R_f 0.3–0.7) decreased in intensity, and that belonging to tetrabromothiofluorescein (**IIa**) increased up to a maximal intensity. The reaction mixture was treated with concentrated hydrochloric acid (to pH 1), and the red precipitate was filtered off, washed with water, dried, and extracted with boiling chloroform (3×25 ml). The brown extract was filtered through a layer of silica gel (25 mm), the colorless filtrate was evaporated to dryness, the residue was treated with carbon tetrachloride, and the undissolved material was filtered off, washed with carbon tetrachloride, and dried under reduced pressure over P_2O_5 at 100°C. Yield 73%, white–pink powder, mp 296–298°C. Electronic absorption spectrum (0.1 N NaOH):

λ_{max} 533 nm (log ε 4.71); published data [2]: λ_{max} 525 nm (log ε 4.83). IR spectrum (mineral oil): ν 1722 cm^{-1} (C=O, lactone). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.1 br.s (2H, OH), 7.35 s (2H, 1′-H, 8′-H), 7.56–7.64 m (3H, 5-H, 6-H, 7-H), 7.94 m (1H, 4-H). Found, %: C 36.42; H 1.27; Br 48.37; S 4.77. $C_{20}H_8Br_4O_4S$. Calculated, %: C 36.18; H 1.21; Br 48.14; S 4.83.

2′,4′,5′-Tribromo-3′,6′-dihydroxyspiro[2-benzofuran-1,9′-thioxanthen]-3-one (IIIa) was isolated from the residue obtained after extraction of compound **IIa** into chloroform. The residue was dissolved in chloroform–acetone (19:1 by volume) and subjected to chromatography on silica gel using chloroform–acetone (19:1) as eluent. The process was monitored by TLC (R_f 0.6–0.7, red spot). The eluate was evaporated to dryness, and the residue was washed with chloroform and dried under reduced pressure over P_2O_5 at 100°C. Yield 13%, dark red powder, mp 335–337°C. Electronic absorption spectrum (0.1 N NaOH): λ_{max} 523 nm (log ε 4.71). IR diffuse reflectance spectrum, ν, cm^{-1}: 1738 (C=O, lactone), 1668 (C=O, quinoid). ^1H NMR spectrum (CF_3COOD), δ, ppm: 7.09 m (1H, 7-H), 7.19 d (1H, 7′-H, J = 9.6 Hz), 7.48 d (1H, 8′-H, J = 9.6 Hz), 7.63 m (2H, 5-H, 6-H), 7.76 s (1H, 1′-H), 8.25 m (1H, 4-H). Found, %: C 41.12; H 1.49; Br 41.01; S 5.54. $C_{20}H_9Br_3O_4S$. Calculated, %: C 41.06; H 1.55; Br 40.97; S 5.48.

4′,5′-Dibromo-3′,6′-dihydroxyspiro[2-benzofuran-1,9′-thioxanthen]-3-one (IVa). *a. Molecular complex* ***IVa*·*Et₂O***. A solution of 0.32 g (2 mmol) of bromine in 1 ml of acetic acid was added to a solution of 0.348 g (1 mmol) of compound **I** in 5 ml of acetic acid. The mixture was stirred for 10 min, kept for 24 h at room temperature, and filtered, and the precipitate was washed with 7 ml of acetic acid, dried at 100°C under reduced pressure, and extracted with diethyl ether (R_f 0.5–0.6, red spot). The weakly colored solution was evaporated, and the residue was washed with anhydrous diethyl ether and dried under reduced pressure over P_2O_5 at 25°C. Yield 56%, white–pink powder, mp 322–324°C. Electronic absorption spectrum (0.1 N NaOH): λ_{max} 520 nm (log ε 4.80). IR diffuse reflectance spectrum: ν 1730 cm^{-1} (C=O, lactone). ^1H NMR spectrum (CF_3COOD), δ, ppm: 0.91 t (6H, CH_3, J = 7.2 Hz), 3.40 q (4H, CH_2, J = 7.2 Hz), 7.08 m (1H, 7-H), 7.17 d (2H, 2′-H, 7′-H, J = 9.6 Hz), 7.48 d (2H, 1′-H, 8′-H, J = 9.6 Hz), 7.61 m (2H, 5-H, 6-H), 8.23 m (1H, 4-H). Found, %: C 49.39; H 3.49; Br 27.67; S 5.61. $C_{24}H_{20}Br_2O_5S$. Calculated, %: C 49.68; H 3.47; Br 27.54; S 5.52.

b. Molecular complex **IVa**·Et_2O thus obtained was dissolved in 1 N aqueous sodium hydroxide and precipitated with 1 N hydrochloric acid. The red precipitate was filtered off, washed with water, and dried under reduced pressure over P_2O_5 at 100°C. Red powder, mp 322–324°C. Electronic absorption spectrum (0.1 N NaOH): λ_{max} 520 nm (log ε 4.80). IR diffuse reflectance spectrum: ν 1664 cm^{-1} (C=O, quinoid). ^1H NMR spectrum (CF_3COOD), δ, ppm: 7.06 m (1H, 7-H), 7.17 d (2H, 2′-H, 7′-H, J = 9.6 Hz), 7.48 d (2H, 1′-H, 8′-H, J = 9.6 Hz), 7.61 m (2H, 5-H, 6-H), 8.23 m (1H, 4-H). Found, %: C 47.24; H 1.91; Br 31.61; S 6.42. $C_{20}H_{10}Br_2O_4S$. Calculated, %: C 47.46; H 1.98; Br 31.57; S 6.33.

4′-Bromo-3′,6′-dihydroxyspiro[2-benzofuran-1,9′-thioxanthen]-3-one (Va). A solution of 0.16 g (1 mmol) of bromine in 1 ml of acetic acid was added to 0.348 g (1 mmol) of compound **I** in 5 ml of acetic acid. The mixture was stirred for 10 min at 25°C, the solvent was distilled off under reduced pressure (20 mm) on a water bath, and the residue was washed with anhydrous diethyl ether and methanol to remove impurities of compounds **I** and **IVa** and dried under reduced pressure over P_2O_5 at 100°C. Yield 59%, dark red powder, mp 275–277°C, R_f 0.3–0.4 (orange spot). Electronic absorption spectrum (0.1 N NaOH): λ_{max} 515 nm (log ε 4.69). IR diffuse reflectance spectrum: ν 1690 cm^{-1} (C=O, quinoid). ^1H NMR spectrum (CD_3OD), δ, ppm: 7.16 d.d (1H, 7′-H, J = 9.2, 2.2 Hz), 7.22 d (1H, 2′-H, J = 9.2 Hz), 7.53 m (3H, 1′-H, 7-H, 8′-H), 7.65 d (1H, 5′-H, J = 2.2 Hz), 7.88 m (2H, 5-H, 6-H), 8.33 d (1H, 4-H, J = 7.6 Hz). Found, %: C 56.31; H 2.49; Br 18.63; S 7.62. $C_{20}H_{11}BrO_4S$. Calculated, %: C 56.22; H 2.60; Br 18.70; S 7.50.

3′,6′-Dihydroxy-2′,4′,5′,7′-tetraiodospiro[2-benzofuran-1,9′-thioxanthen]-3-one (IIb). Compound **I**, 0.348 g (1 mmol), was dissolved in 15 ml of 1 N aqueous sodium hydroxide, 1.02 g (4 mmol) of molecular iodine was added, and the mixture was heated to 100°C and was kept for 8 h at that temperature. The mixture was intermittently diluted with a solution of sodium hydroxide to facilitate stirring. The progress of the reaction was monitored by TLC as described above for the bromination process. When the reaction was complete, the mixture was cooled and treated with concentrated hydrochloric acid (to pH 1.0). The dark red precipitate was filtered off, washed with water, dried, and extracted with boiling chloroform. The extract was filtered through a layer of silica gel (50 mm) (R_f 0.8–0.9, crimson spot). The filtrate was evaporated, and the crystalline product was filtered off, washed

with chloroform, and dried under reduced pressure over P_2O_5 at 100°C. Yield 71%, white–pink crystals (from chloroform), mp 265–267°C. Electronic absorption spectrum (0.1 N NaOH): λ_{max} 542 nm (logε 4.88); published data [2]: λ_{max} 541 nm (logε 4.88). IR spectrum (mineral oil): ν 1733 cm^{-1} (C=O, lactone). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.01 br.s (2H, OH), 7.57 s (2H, 1′-H, 8′-H), 7.58 m (2H, 5-H, 6-H), 7.72 m (1H, 7-H), 7.94 m (1H, 4-H). Found, %: C 28.37; H 0.98; I 59.32; S 3.71. $C_{20}H_8I_4O_4S$. Calculated, %: C 28.20; H 0.95; I 59.58; S 3.76.

3′,6′-Dihydroxy-2′,4′,5′-triiodospiro[2-benzofuran-1,9′-thioxanthen]-3-one (IIIb) was isolated from the residue obtained after extraction of compound **IIb** into chloroform. The residue was dissolved in chloroform–acetone (19:1 by volume), and the solution was subjected to chromatography on silica gel using chloroform–acetone (19:1) as eluent. The purification process was monitored by TLC (R_f 0.6–0.7, red spot). The eluate was evaporated to dryness, and the residue was washed with chloroform and dried under reduced pressure over P_2O_5 at 100°C. Yield 14%, dark red powder, mp 271–273°C. Electronic absorption spectrum (0.1 N NaOH): λ_{max} 532 nm (logε 4.42). IR diffuse reflectance spectrum, ν, cm^{-1}: 1721 (C=O, lactone), 1689 (C=O, quinoid). ^1H NMR spectrum (CD_3OD), δ, ppm: 6.63 d (1H, 7′-H, J = 9.3 Hz), 7.16 d (1H, 8′-H, J = 9.3 Hz), 7.25 m (1H, 7-H), 7.67 m (2H, 5-H, 6-H), 7.80 s (1H, 1′-H), 8.20 m (1H, 4-H). Found, %: C 33.21; H 1.29; I 52.17; S 4.57. $C_{20}H_9I_3O_4S$. Calculated, %: C 33.08; H 1.25; I 52.44; S 4.42.

3′,6′-Dihydroxy-4′,5′-diiodospiro[2-benzofuran-1,9′-thioxanthen]-3-one (IVb). Compound **I**, 0.348 g (1 mmol), was dissolved in 10 ml of methanol, a solution of 0.51 g (2 mmol) of iodine in 10 ml of methanol was added under stirring, and the mixture was kept for 6 h at room temperature until the initial compound disappeared (TLC). The solvent was distilled off to dryness on a rotary evaporator, the residue was extracted with chloroform–diethyl ether (9:1 by volume), the extract was filtered through a layer of silica gel (50 mm) and evaporated, and the residue was washed with chloroform and dried under reduced pressure over P_2O_5 at 110°C. Yield 67%, dark red powder, mp 177–179°C, R_f 0.4–0.5 (red spot). Electronic absorption spectrum (0.1 N NaOH): λ_{max} 523 nm (logε 4.49). IR diffuse reflectance spectrum, ν, cm^{-1}: 1727 (C=O, lactone), 1670 (C=O, quinoid). ^1H NMR spectrum (CD_3OD), δ, ppm: 6.74 d (2H, 2′-H, 7′-H, J = 8.5 Hz), 6.93 d (2H, 1′-H, 8′-H, J = 8.5 Hz), 7.62 m (1H, 7-H), 7.76 m (2H, 5-H, 6-H), 8.02 m (1H, 4-H). Found, %: C 40.31; H 1.65; I 42.11; S 5.17. $C_{24}H_{10}I_2O_4S$. Calculated, %: C 40.02; H 1.68; I 42.29; S 5.34.

3′,6′-Dihydroxy-4′-iodospiro[2-benzofuran-1,9′-thioxanthen]-3-one (Vb). Compound **I**, 0.348 g (1 mmol), was dissolved in 10 ml of methanol, a solution of 0.255 g (1 mmol) of iodine in 10 ml of methanol was added, the mixture was kept for 6 h at room temperature, and the solvent was distilled off. Acetic acid, 0.1 ml, and silica gel, 2.5 g, were added to the residue, and the mixture was thoroughly ground in a mortar and transferred to the top of a column charged with 15 g of silica gel which was preliminarily deactivated with 0.6 ml of acetic acid. The column was eluted with chloroform–diethyl ether (9:1 by volume). Three fractions containing compounds **IVb**, **Vb**, and **I** were collected (R_f 0.3–0.4, orange–red spot). The second fraction was evaporated, and the residue was washed with chloroform and dried under reduced pressure over P_2O_5 at 100°C. Yield 51%, dark red powder, mp 211–213°C. Electronic absorption spectrum (0.1 N NaOH): λ_{max} 514 nm (logε 4.50). IR diffuse reflectance spectrum, ν, cm^{-1}: 1723 (C=O, lactone), 1670 (C=O, quinoid). ^1H NMR spectrum (CD_3OD), δ, ppm: 6.70 d.d (1H, 7′-H, J = 8.7, 2.5 Hz), 6.72 d (1H, 2′-H, J = 8.7 Hz), 6.88 d (1H, 1′-H, J = 8.7 Hz), 6.93 d (1H, 8′-H, J = 8.7 Hz), 7.08 d (1H, 5′-H, J = 2.5 Hz), 7.58 m (1H, 7-H), 7.74 m (1H, 6-H), 7.83 m (1H, 5-H), 8.03 m (1H, 4-H). Found, %: C 50.39; H 2.41; I 27.02; S 6.58. $C_{20}H_{11}IO_4S$. Calculated, %: C 50.65; H 2.34; I 26.76; S 6.76.

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