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Synthesis and Antioxidant Activity of Alkyl 3-(4-Hydroxyaryl)propyl Sulfides

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Abstract—4-Alkylthiopropylphenols were synthesized from corresponding 2,6-dialkylphenols via the allyl derivative. A comparative study of the antioxidant activity of the prepared compounds was carried out in five model systems. The rate constants for the reactions of the test compounds with cumene, styrene, and methyl oleate peroxide radicals were measured. It was shown that 4-thioalkylphenols with methyl and cyclohexyl *ortho*-substituents are powerful inhibitors in the oxidation of mineral oil.

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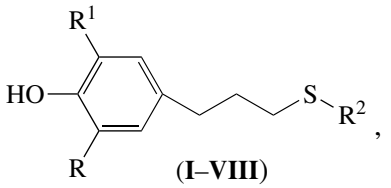
Bis-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl sulfide (SO-3) is a high-performance heat stabilizer of polymer materials [1, 2], mineral oils [3], and edible fats [3, 4] and exhibits a pronounced protective activity in vivo in pathological conditions caused by activation of the peroxide oxidation of lipids [5–7]. We have found that two groups of structural analogues of SO-3 possess a higher antioxidant activity (AOA): bis-(3-(4-hydroxyaryl)propyl sulfides with a sterically less hindered phenolic OH group [3] and alkyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl sulfides with an equal number of phenolic and sulfide moieties in molecules [8].

This work was devoted to the synthesis and comparative study of the antioxidant activity of alkyl 3-(4-hydroxyaryl)propyl sulfides (**I–VIII**):

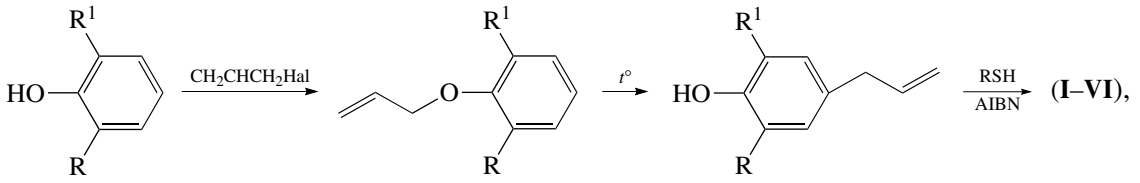


(**I–VIII**)

where R = *cyclo*-C_6H_{11}, R^1 = Me, and R^2 = Bu (**I**); R = R^1 = *cyclo*-C_6H_{11} and R^2 = Bu (**II**) or $C_{12}H_{25}$ (**III**); R = R^1 = Me and R^2 = Bu (**IV**), $C_{12}H_{25}$ (**V**), or $C_{18}H_{37}$ (**VI**); or R = R^1 = *tert*-Bu and R^2 = Bu (**VII**) or $C_{12}H_{25}$ (**VIII**).

EXPERIMENTAL

Sulfides **I–VI** were synthesized from corresponding 2,6-dialkylphenols via intermediate synthesis of allyl derivatives. Allyl phenyl ethers were prepared in the reactions of methyl- and cyclohexyl-substituted phenols with 3-bromo- or 3-chloropropene, and then the Claisen rearrangement was performed with the subsequent free-radical thiylation initiated by azobisisobutyronitrile (AIBN):



(**IX–XI**) (**XII–XIV**)

where Hal = Cl or Br, R = *cyclo*-C_6H_{11} and R^1 = Me (**IX**, **XII**), R = R^1 = *cyclo*-C_6H_{11} (**X**, **XIII**), and R = R^1 = Me (**XI**, **XIV**).

The synthesis of **VII** was described in [9], and sulfide **VIII** was prepared according to a procedure given in [10].

The examples of synthesis of some other sulfides are given below.

1-Allyloxy-2-methyl-6-cyclohexylbenzene (IX). 3-Bromopropene-1 (0.53 mol, 46 ml) was added dropwise to a mixture of 2-methyl-6-cyclohexylphenol (0.26 mol, 50 g), NaOH (0.32 mol, 13 g), and DMF (100 ml) at 40°C. The mixture was stirred for 2 h, cooled, and treated with benzene. The extract was washed with water and dried over Na_2SO_4, and the solvent was removed by distillation. The residue was distilled in vacuum. The yield of desired ether **IX** was 57.5 g (95%).

4-Allyl-2-methyl-6-cyclohexylphenol (XII). Allyloxybenzene **IX** (15 g, 65 mmol) was heated and held at 200°C for 2 h and then distilled in vacuum. The yield of allylphenol **XII** was 13.95 g (93%).

Butyl 3-(3-methyl-5-cyclohexyl-4-hydroxyphenyl)propyl sulfide (I). Butanethiol-1 (8.9 g, 85 mmol) was added dropwise to a mixture of allylphenol **XII** (13 g, 56 mmol) and AIBN (2.41 g, 14.7 mmol) at 60°C. The mixture was stirred for 4 h, cooled, and treated with benzene. The extract was successively washed with 20% an aqueous NaOH solution and water dried with Na_2SO_4; then the solvent was distilled off. The residue was distilled in vacuum. The yield of desired sulfide **I** was 7.94 g (44%).

1-Allyloxy-2,6-dialkylbenzenes **X** and **XI**, 4-allyl-2,6-dialkylphenols **XIII** and **XIV**, and alkyl 3-(4-hydroxyaryl)propyl sulfides **II–VI** were synthesized in a similar manner.

^{1}H NMR spectra of the prepared compounds were recorded in $CDCl_3$on a Bruker DRX500 spectrometer operating at a frequency of 500.13 MHz. The melting points were measured with a PTP device.

White oil (KPKhFO Tatkhimpharmpreparaty, Kazan), lard (Novosibirsk meat-packing plant), cumene (Acros Organics), styrene (Russia), and methyl oleate (Acros Organics) were used as model oxidation substrates. Cumene, styrene, and methyl oleate were doubly distilled in vacuum before use. AIBN (Acros Organics) was used as an initiator. Rate curves were plotted and processed with the use of the Origin 6.0 software.

In kinetic studies, the value of k_7 was determined by manometric method [11] with the use of a Warburg setup or a volumetric system similar to that described in [12]. The k/k_7 ratio was determined from the experimental dependence $[O_2]/[RH] = -k/k_7 \ln(1 - t/\tau)$ (where k is the rate constant of the chain propagation reaction $ROO^\bullet + RH \longrightarrow ROOH + R^\bullet$). The absolute values of k_7 were calculated with the use of the literature values of k [13]. All measurements were repeated five to seven times with the mean-square deviations being less than 20%.

Cumene oxidation was carried out at 60°C and the AIBN concentration of 3–6 mmol l^{-1}, with the initiation rate w_i being $(0.38–1.44) \times 10^{-7}$ mol l^{-1} s^{-1} and the oxidation chain lengths being longer than 76. The antioxidant concentration was $(2.5–5.0) \times 10^{-5}$ mol l^{-1}. Styrene was oxidized at 50°C, [AIBN] = 0.07–0.12 mol l^{-1}, w_i – $(2.53–4.10) \times 10^{-7}$ mol l^{-1} s^{-1}, an oxidation chain length of ≥116, and [Ar OH] = 0.27–0.44 mmol l^{-1}. Methyl oleate oxidation was carried out in chlorobenzene (1 : 1 by volume) at 60°C, [AIBN] = 12 mmol l^{-1}, w_i – 5.12×10^{-8} mol l^{-1} s^{-1}, an oxidation chain length of ≥ 56, [ArOH] = 0.3–0.6 mmol l^{-1}. White oil was oxidized in a gasometric unit similar to that described in [12] at 180°C, an oxygen pressure of 1 atm, a sample volume of 5 ml, and [ArOH] = 1.75 μmol per gram of oil (0.875 μmol per 1 g for binuclear phenol SO-3). The induction time was determined as a point of intersection of two tangents to the rate curve corresponding to the initial and final oxidation rates for white oil. Lard was oxidized under conditions of oxygen bubbling at 130°C with the use of the procedure and the oxidation cell described in [14]. The oxygen flow rate was 1 l/min, the mass of the sample subjected to oxidation was 50 g, [ArOH] = 2.75 μmol/g (1.375 μmol/g for SO-3). During an experimental run, ~1-g aliquots were taken, and the concentration of peroxide compounds was determined by iodometry [15]. The time of lard oxidation to have a peroxide number of 0.1 (the initial peroxide number was 0.003) was taken as an induction period.

The composition and the structure of the compounds were confirmed by elemental analysis and spectral data (Table 1). According to the search in the STN International Database, sulfides **I–VI** and allyl derivatives **IX**, **X**, **XII**, and **XIII** are novel compounds, which have not been described in the literature.

RESULTS AND DISCUSSION

Compounds **I–VIII** contain two antioxidant centers in their structure. Therefore, their antioxidant activity is determined by three factors: the antiradical activity (ARA) of the phenol moiety, the antiperoxide activity of the sulfide group, and the synergistic effect due to the presence of both these functions in the antioxidant molecule. The differences in the structure of *ortho*-substituents in the series of compounds **I–VIII** must be reflected in both the reactivity of the phenolic OH group and in the total antioxidant activity. Therefore, the antioxidant properties of the synthesized compounds with respect to model hydrocarbon and lipid substrates were studied under different oxidation conditions.

The antiradical activity of the compounds was judged from the values of the rate constants of their reaction (k_7) with cumene, styrene, and methyl oleate peroxyl radicals:

$$ArOH + ROO^\bullet \longrightarrow ArO^\bullet + ROOH, \quad (1)$$

as measured in the initiated-oxidation mode. The total antioxidant activity was determined from the duration of the induction period in the autooxidation of white oil and lard. 2,6-Di-*tert*-butyl-4-methylphenol (ionol, Acros

Table 1. Characterization of the synthesized compounds

Compound	Bp, °C (1–2 mmHg)	Mp, °C	Yield, %	Elemental analysis, found/calcd, %			Empirical formula	1H NMR, δ, ppm
				C	H	S		
I	191–192	Tar	44	75.06/74.94	10.07/10.06	10.03/10.00	$C_{20}H_{32}OS$	0.96 t (3H, $CH_2\underline{Me}$), 1.31 m (1H, *cyclo*-C_6H_{11}), 1.46 m (4H, *cyclo*-C_6H_{11}; 2H, $C\underline{H}_2Me$), 1.60 m (2H, $C\underline{H}_2Et$), 1.80 m (1H, *cyclo*-C_6H_{11}), 1.89 m (4H, *cyclo*-C_6H_{11}; 2H, $ArCH_2C\underline{H}_2$), 2.25 s (3H, $Ar\underline{Me}$), 2.55 t (4H, SCH_2), 2.64 t (2H, $ArC\underline{H}_2$), 2.81 m (1H, *cyclo*-C_6H_{11}), 4.70 s (1H, OH), 6.81 d (1H, H_{arom}, J 2 Hz), 6.88 d (1H, H_{arom}, J 2 Hz)
II	230	Tar	64	77.13/77.26	10.33/10.37	8.33/8.25	$C_{25}H_{40}OS$	1.02 t (3H, $CH_2\underline{Me}$), 1.37 m (2H, *cyclo*-C_6H_{11}), 1.51 m (8H, *cyclo*-C_6H_{11}; 2H, $C\underline{H}_2Me$), 1.65 m (2H, $C\underline{H}_2Et$), 1.86 m (2H, *cyclo*-C_6H_{11}), 1.94 m (8H, *cyclo*-C_6H_{11}; 2H, $ArCH_2C\underline{H}_2$), 2.56 m (4H, SCH_2), 2.68 t (2H, $ArC\underline{H}_2$), 2.80 m (2H, *cyclo*-C_6H_{11}), 4.79 s (1H, OH), 6.85 s (2H, H_{arom})
III		Tar	58	78.93/79.13	11.07/11.27	6.45/6.40	$C_{33}H_{56}OS$	0.88 t (3H, $CH_2\underline{Me}$), 1.26 m (16H, $(C\underline{H}_2)_8Me$), 1.37 m (2H, *cyclo*-C_6H_{11}), 1.42 m (8H, *cyclo*-C_6H_{11}; 2H, $C\underline{H}_2C_9H_{19}$), 1.56 m (2H, $C\underline{H}_2C_{10}H_{21}$), 1.76 m (2H, *cyclo*-$C_6H_{11}$), 1.85 m (8H, *cyclo*-$C_6H_{11}$; 2H, $ArCH_2C\underline{H}_2$), 2.50 m (4H, SCH_2), 2.61 t (2H, $ArC\underline{H}_2$), 2.71 m (2H, *cyclo*-C_6H_{11}), 4.64 s (1H, OH), 6.82 s (2H, H_{arom})
IV	169–170	Tar	63	71.24/71.38	9.56/9.60	12.87/12.70	$C_{15}H_{24}OS$	0.91 t (3H, $CH_2\underline{Me}$), 1.40 m (2H, $CH_2\underline{Me}$), 1.55 m (2H, $C\underline{H}_2Et$), 1.85 m (2H, $ArCH_2C\underline{H}_2$), 2.22 s (6H, $Ar\underline{Me}$), 2.51 t (4H, SCH_2), 2.58 t (2H, $ArC\underline{H}_2$), 4.56 s (1H, OH), 6.79 s (2H, H_{arom})
V		46	55	75.61/75.76	10.92/11.06	8.97/8.79	$C_{23}H_{40}OS$	0.89 t (3H, CH_2Me), 1.26 m (16H, $(CH_2)_8Me$), 1.36 m (2H, $CH_2C_9H_{19}$), 1.54 m (2H, $CH_2C_{10}H_{21}$), 1.80 m (2H, $ArCH_2CH_2$), 2.19 s (6H, $Ar\underline{Me}$), 2.44 m (4H, SCH_2), 2.54 t (2H, $ArCH_2$), 4.30 s (1H, OH), 6.71 s (2H, H_{arom})
VI		63	75	77.46/77.59	11.63/11.68	7.29/7.14	$C_{29}H_{52}OS$	0.87 t (3H, $CH_2\underline{Me}$), 1.26 m (30H, $(C\underline{H}_2)_{15}Me$), 1.55 m (2H, $C\underline{H}_2C_{16}H_{33}$), 1.83 m (2H, $ArCH_2C\underline{H}_2$), 2.21 s (6H, $Ar\underline{Me}$), 2.48 m (4H, CH_2SCH_2), 2.56 t (2H, $ArC\underline{H}_2$), 4.48 s (1H, OH), 6.78 s (2H, H_{arom})
IX	102–106	Tar	95	83.57/83.43	9.64/9.63		$C_{16}H_{22}O$	1.41 m (1H, *cyclo*-C_6H_{11}), 1.53 m(4H, *cyclo*-C_6H_{11}), 1.89 m (1H, *cyclo*-C_6H_{11}), 1.95 m (4H, *cyclo*-C_6H_{11}), 2.42 s (3H, $Ar\underline{Me}$), 3.08 m (1H, *cyclo*-C_6H_{11}), 4.40 m (2H, OCH_2), 5.39 m (1H, =CH), 5.78 m (1H, =CH), 6.24 m (1H, =CH), 7.11 m (2H, H_{arom}), 7.19 m (1H, H_{arom})
X		Tar	96	84.21/84.51	9.83/10.13		$C_{21}H_{30}O$	1.27 m (2H, *cyclo*-C_6H_{11}), 1.40 m (8H, *cyclo*-C_6H_{11}), 1.75 m (2H, *cyclo*-C_6H_{11}), 1.82 m (8H, *cyclo*-C_6H_{11}), 2.93 m (2H, *cyclo*-C_6H_{11}), 4.26 m (2H, OCH_2), 5.30 m (1H, =CH), 5.47 m (1H, =CH), 6.14 m (1H, =CH), 7.07 m (3H, H_{arom})

Table 1. (Contd.)

Compound	Bp, °C (1–2 mmHg)	Mp, °C	Yield, %	Elemental analysis, found/calcd., %			Empirical formula	1H NMR, δ, ppm
				C	H	S		
XI	(67–68/2 mmHg [19])	Tar	82	81.40/81.44	8.73/8.70		$C_{11}H_{14}O$	2.40 s (6H, ArMe), 4.40 m (2H, OCH_2), 5.35 m (1H, =CH), 5.55 m (1H, =CH), 6.19 m (1H, =CH), 6.98 m (1H, H_{arom}), 7.19 m (1H, H_{arom}, J 7 Hz)
XII	130–137	49–51	93	83.55/83.43	9.64/9.63		$C_{16}H_{22}O$	1.28 m (1H, *cyclo*-C_6H_{11}), 1.43 m (4H, *cyclo*-C_6H_{11}), 1.77 m (1H, *cyclo*-C_6H_{11}), 1.86 m (4H, *cyclo*-C_6H_{11}), 2.23 s (3H, ArMe), 2.76 m (1H, *cyclo*-C_6H_{11}), 3.29 d (2H, $ArCH_2$, J 7 Hz), 4.55 s (1H, OH), 5.04 m (1H, =CH), 5.07 m (1H, =CH), 5.95 m (1H, =CH), 6.80 m (1H, H_{arom}, J 2 Hz), 6.86 m (1H, H_{arom}, J 2 Hz)
XIII	185–190	Tar	96	84.31/84.51	9.93/10.13		$C_{21}H_{30}O$	1.28 m (2H, *cyclo*-C_6H_{11}), 1.43 m(8H, *cyclo*-C_6H_{11}), 1.77 m (2H, *cyclo*-C_6H_{11}), 1.87 m (8H, *cyclo*-C_6H_{11}), 2.72 m (2H, *cyclo*-C_6H_{11}), 3.31 m (2H, $ArCH_2$), 4.65 s (1H, OH), 5.04 m (1H, =CH), 5.07 m (1H, =CH), 5.96 m (1H, =CH), 6.84 s (2H, H_{arom})
XIV	(90.5–91.4/2–3 mmHg [19])	30	97	81.39/81.44	8.74/8.70		$C_{11}H_{14}O$	2.24 s (6H, ArMe), 3.27 d (2H, $ArCH_2$, J 7 Hz), 4.43 s (1H, OH), 5.04 m (1H, =CH), 5.07 m (1H, =CH), 5.93 m (1H, =CH), 6.76 s (2H, H_{arom})

Table 2. Antioxidant activity of alkyl-3-(4-hydroxyaryl)propyl sulfides and their structural analogs

Compound	Induction period (τ), min		$k_7 \times 10^{-4}$, $mol^{-1}s^{-1}$		
	white oil, 180°C	lard, 130°C	cumene, 60°C	styrene, 50°C	methyl oleate in chlorobenzene, 60°C
I	366 ± 10	100 ± 5	19.4	16	2.9
II	233 ± 20	120 ± 5	19.1	15	4.0
III	237 ± 8	90 ± 4	19.5	15.2	3.8
IV	416 ± 10	110 ± 5	15.0	18.8	4.0
V	386 ± 20	98 ± 3	15.2	13.7	3.3
VII	119 ± 5	277 ± 7	2.5	2.3	2.5
VIII	126 ± 10	265 ± 13	2.2	2.2	1.8
SO-3	72 ± 5	287 ± 6	2.2	2.9	2.1
Ionol	43 ± 5	162 ± 8	2.4	2.8	2.6
TMP	40 ± 5	80 ± 5	10.0	18.0	3.6
DCMP	21 ± 5	108 ± 5	12.0	17.0	4.7

Organics), 2,4,6-trimethylphenol (TMP, Lancaster), and 2,6-dicyclohexyl-4-methylphenol (DCMP synthesized according to [16]) were used as reference antioxidants.

The results obtained (Table 2) indicate that the test compounds exhibit a significant antioxidant activity in the model systems used. In their ability to inhibit the oxidation of white oil, methyl- and cyclohexyl-substituted sulfides **I**–**V** were far superior to their sterically hindered analogues sulfides **VII**, **VIII**, and SO-3. This is consistent with the differences between these compounds in reactivity toward active radicals formed in the free-radical oxidation of cumene and styrene.

It is noteworthy that TMP having a higher value of k_7 than ionol is not superior to the latter in inhibiting activity in the autooxidation of white oil. This behavior agrees with the well-documented fact that trialkylphe-

nols can terminate at most two oxidation chains, regardless of the value of k_7, in accordance with the principle of free valence conservation as a result of consecutive reactions (1) and (2) or (1) and (3) [11]:

$$ArO^{\bullet} + ROO^{\bullet} \longrightarrow \text{Molecular products}, \quad (2)$$

$$ArO^{\bullet} + ArO^{\bullet} \longrightarrow ArOH + \text{Molecular products}. \quad (3)$$

In the autooxidation of hydrocarbon substrates, the antioxidant activity of thiaalkylphenols substantially increases owing to the ability of the sulfide moiety to reduce hydroperoxides:

$$R'–S–R'' + ROOH \longrightarrow R'–SO–R'' + ROH,$$

$$R'–SO–R'' + ROOH \longrightarrow R'–SO_2–R'' + ROH,$$

which prevents the branching of oxidation chains via the thermal homolysis of peroxides: $ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH$.

The combined antioxidant action of the phenolic and sulfide functions leads to a significant increase in the inhibition efficiency, the synergistic effect. Using SO-3 and its *ortho*-dimethyl- and methyl-*tert*-butyl-substituted analogues as an example, we have recently showed [17] that the degree of synergism of this kind increases with a decrease in the degree of sterical hindrance to access to the phenolic OH group.

Hence, the high antioxidant activity of sulfides **I–V** in the oxidation of white oil is due to the bifunctional mechanism of their inhibiting action and to the pronounced synergetic effect.

At the same time, methyl- and cyclohexyl-substituted compounds, both monofunctional (TMP, DCMP) and sulfur-containing (**I–V**), were inferior to corresponding 2,6-di-*tert*-butylphenols in the ability to inhibit the oxidation of lard. 2,6-Di-*tert*-butylphenols had close values of k_7 in the oxidation of cumene, styrene, and methyl oleate, whereas the methyl- and cyclohexyl-substituted compounds were characterized by lower values of k_7 in methyl oleate than in the model hydrocarbons. Such effects were observed earlier [18]. The decrease in the k_7 value in this case is presumably due to the involvement the hydrogen atom of the phenolic OH group in H-bonding with the ester groups of the substrate molecules ArOH…OC(OR)R'. The formation of these bonds is not typical of 2,6-di-*tert*-butylphenols, because its reaction center is sterically hindered.

Another reason for the lower antioxidant activity of sulfides **I–V** in the oxidation of lard is the presence in its molecules of polyunsaturated fatty acid residues containing C–H bonds with a relatively low dissociation energy [19]. This increases the probability of the propagation reaction involving the inhibitor radical:

$$ArO^{\bullet} + RH \longrightarrow ArOH + R^{\bullet}. \quad (4)$$

It is known [11] that the reactivity of phenoxyl radicals in reaction (4) substantially increases when the hindering effect of *ortho*-substituents is reduced.

In general, the results indicate that sulfides **I–V** synthesized in this work hold promise as antioxidants for saturated hydrocarbon substrates (mineral oils, polymers).

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