DOI: https://doi.org/10.24297/jac.v19i.9479

# Synthesis of Heptylalkanoyldisulfides and Investigation of Their Antimicrobial Properties

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**Abstract**

The paper describes the results of the research of some heptylalkanoyldisulfides as antimicrobial additives to the lubricating oils. Heptylalkanoyldisulfides were synthesized and studied. The synthesized compounds were characterized by spectroscopic techniques. Study of antimicrobial properties of the studied heptylalkanoyldisulfides revealed effective bactericidal and fungicidal activities in suppression of fungi and bacteria allowing them to be used as biocides in storage and transportation of oil products. Antimicrobial efficacy of the studied compounds was determined by zonal diffusion method using the following microorganisms: bacteria, fungi and yeast. The test compounds were added to M-8 oil in mass percent. It is established that their antimicrobial activity is at the level of effectiveness of the widely used industrial additive sodium pentachlorophenolate. Sodium pentachlorophenolate, widely applied as an antimicrobial additive in lubricating oils, was used for comparison. It was determined that they may be used as antimicrobial additives for M-8 engine oil (0.25-1%). As a result of the studies carried out on heptylalkanoyldisulfides, distinct patterns of dependence of antimicrobial efficacy on the structure of alkyl radical were determined. Antimicrobial activity increases by an increase in alkyl radical, i.e., each subsequent member of the disulfide series is biologically more active than the previous one. The increase in antimicrobial activity seems to be due to the fact that the adding each new $CH_2$ group gives one more van der Waals bond, increasing adsorption forces that bind the compound to the receptor in the microorganism. As a result of the studies carried out on heptylalkanoyldisulfides, distinct patterns of dependence of antimicrobial efficacy on the structure of alkyl radical were determined

**Keywords:** disulfides, lubricating oils, biodeterioration, bacteria, antimicrobial activity, additive

## Introduction

Development of modern technology is associated with increased requirements for operation of machines and quality of lubricating oil, accordingly [1, 2]. It is known that the properties and chemical composition of oils vary by storage and transportation, mucus and sediments are formed in them [3]. This is due to the vital activity of microorganisms that leads to microbiological corrosion of parts and mechanisms [4-6]. As a result, activity of microorganisms causes decomposition of oils, as well as damage to materials and structures in contact with them [7, 8]. Thus, lubricating oils become unusable for their intended purpose.

Various mechanical and physicochemical methods are used for prevention of microbiologically influenced corrosion [9]. However, these methods aren't applicable in all cases, and, besides, none of them provides such effective protection of oil as antimicrobial additives. Despite the fact that many substances belonging to different classes of chemical compounds have been studied and recommended as antimicrobial additives, microorganisms adapt to the biocides by prolonged use of the same preparation [10]. Therefore, it is important to study antimicrobial properties of the most well-known organic compounds.

Antimicrobial additives stabilize bacterial situation in lubricating oils. Adding antimicrobial additives causes inhibition of unrelated microorganisms [11, 12].

Antimicrobial additives are toxic to humans and fauna. Among the wide variety of available biocides, only a few can be used as additives to lubricating oils [13]. Therefore, studies are being carried out to search for new antimicrobial low-toxic and non-toxic additives [14].

Due to the lack of literature data on antimicrobial properties of unsymmetrical disulfides, it was interesting to study the compounds which we had synthesized earlier from these positions.
Organic sulfur compounds containing various functional groups and other fragments in their structures are the object of systematic research, due to their valuable properties, allowing use of them in oil compositions [15]
The purpose of the work is to study antimicrobial properties of a number of heptylalkanoyldisulfides (HADs) synthesized by us.
Therefore, we studied and showed new antimicrobial properties of the known compounds that had positive effects.
Synthesis of heptylalkanoyldisulfides was carried out by the interaction of mercaptides with sulfur and carboxylic acid chlorides according to the scheme [16]:

$$RSH + KOH \rightarrow RSK + S + ClC(O)R' \rightarrow RSSC(O)R'$$

where R– $C_7H_{15}$;
R'– $CH_3$; $C_2H_5$; $C_3H_7$; $C_5H_{11}$; $C_9H_{19}$; $C_{11}H_{23}$.

Structure of the obtained compounds was confirmed by the determination of their physicochemical properties, elemental analyses, IR and NMR spectroscopy [17].

**Experimental Part**

A three-necked flask was equipped with a stirrer, dropping funnel and Dean-Stark nozzle, 100 ml of isopropyl alcohol was added, it followed by adding 16.8 g (0.3 mol) of potassium hydroxide at 60°C and stirring until dissolved. 39.6 g (0.3 mol) of heptylmercaptan were added dropwise to the mixture and stirred at 60-70°C for 1 hour. 9.6 g (0.3 mol) of finely ground sulfur was added in portions to the mixture after cooling, heated to 60-70°C and stirred for 4 hours. Then 0.3 mol of carboxylic acid chloride was added dropwise to the mixture at room temperature and stirred for another 2 hours at the same temperatures.
The reaction mass was acidified by hydrochloric acid, washed with water, dried, and dissolved in benzene. After distillation of benzene, the residue was distilled in vacuum. Physicochemical properties of the obtained compounds are set into Tab. 1.

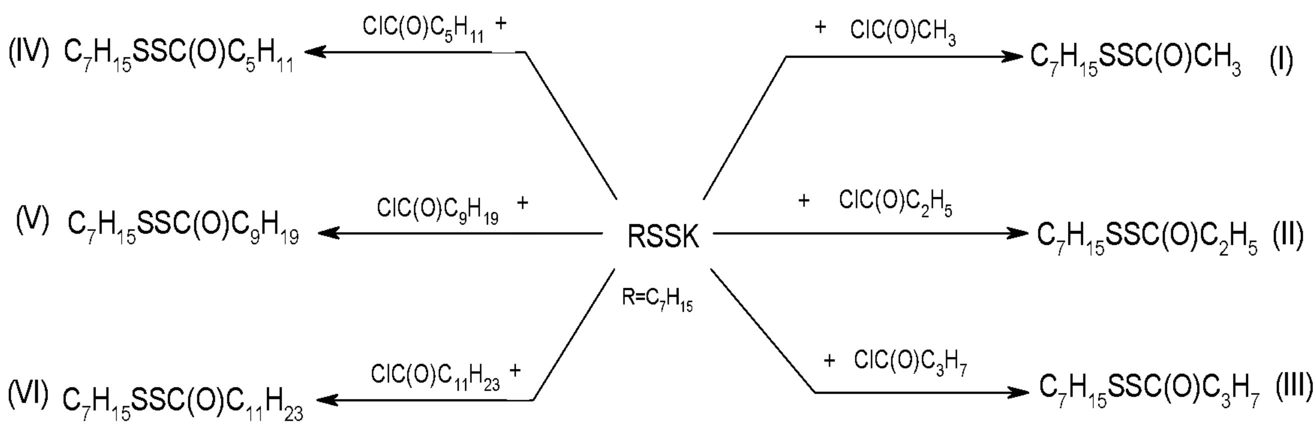

**Table 1.** Physico-chemical properties of HAD ($C_7H_{15}SSC(O)$ R')

| No. of comp. | R' | Yield, % | $T_{boil.}$ (C/0.2 mm Hg) or $T_{melt.}$ (°C) | $n_D^{20}$ | $d_4^{20}$ | Gross formula | Mol. weight | $MR_D$ found<br>calculated | Found, %<br>Calculated | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | C | H | S |
| I | $CH_3$ | 64.3 | 92-94 | 1.5276 | 1.0727 | $C_9H_{18}OS_2$ | 206 | 59.42<br>59.71 | 53.41<br>52.47 | 7.96<br>8.87 | 30.72<br>31.09 |
| II | $C_2H_5$ | 61.7 | 102-103 | 1.5198 | 1.0388 | $C_{10}H_{20}OS_2$ | 220 | 64.49<br>64.32 | 53.64<br>54.60 | 10.07<br>9.18 | 29.86<br>29.14 |
| III | $C_3H_7$ | 58.4 | 120-122 | 1.5067 | 1.0166 | $C_{11}H_{22}OS_2$ | 234 | 68.71<br>68.94 | 55.82<br>56.46 | 10.35<br>9.53 | 28.12<br>27.47 |
| IV | $C_5H_{11}$ | 63.4 | 132-134 | 1.4919 | 1.9629 | $C_{13}H_{26}OS_2$ | 262 | 79.28<br>78.12 | 60.35<br>59.57 | 8.56<br>9.89 | 25.34<br>24.53 |
| V | $C_9H_{19}$ | 58.1 | 68-69 | - | - | $C_{17}H_{34}OS_2$ | 318 | - | 63.89<br>64.7 | 9.76<br>10.65 | 21.11<br>20.23 |
| VI | $C_{11}H_{23}$ | 56.8 | 82-83 | - | - | $C_{19}H_{38}OS_2$ | 346 | - | 65.27<br>65.74 | 10.84<br>11.09 | 19.04<br>18.48 |

IR spectra of the obtained compounds were taken on an "Alpha" spectrometer (Bruker, Germany) in the range from 400 to 4000 $cm^{-1}$. KBr tablets were used for liquid samples, but vaseline - for solid samples.
NMR spectra were taken on the device "Bruker" (USA), solvent - $CCl_4$, standard - tetramethylsilane (TMS).
The IR spectrum of individual compounds I–VI shows absorption bands at 465–549 $cm^{-1}$, which are characteristic of the –S–S– group. There are also absorption bands at 1641, 1710, 1798 $cm^{-1}$, which are characteristic of the C=O group.
The NMR spectra of the studied compounds confirm the structure indicated for them. The spectrum contains signals of protons of methylene groups in the form of a singlet at 4.84 ppm. The $–C–CH_2–$ proton signals give a triplet at 2.45 ppm, while the –CH– proton signals appear in the region of 1.61 ppm. in the form of a sextet. Signals of $CH_3–$ protons are found in the region of 0.95 ppm. in the form of a triplet.
We carried out experimental studies on antimicrobial activity of the studied HADs. M-8 oil was used for studying antimicrobial properties of the synthesized disulfides, that was tested for resistance to mold fungi (in accordance with GOST 9.052–88) and bacteria (in accordance with GOST 9.082-77).
Antimicrobial efficacy of the studied compounds was determined by zonal diffusion method using the following microorganisms: bacteria - *Mycobacterium lacticolium, Pseudomonas aeruginosa*; fungi - *Aspergillus niger, Penicillium chrysogenum*; yeast - *Candida tropicalis*. Meat-and-peptone agar (MPA) was used for the growth of bacterial cultures, but wort-agar (WA) was used for fungi and yeast cultures.
The essence of the method lies in keeping the lubricating oil contaminated by microorganisms and placed in a nutrient medium for microorganisms under conditions favorable for their growth.
Sodium pentachlorophenolate, widely applied as an antimicrobial additive in lubricating oils, was used for comparison.
The test compounds and the standard were added to M-8 oil in mass percent. The tests were carried out as follows. The nutrient medium was poured into Petri dishes in a volume of 20-30 ml and allowed to solidify. Sowing of microorganisms was carried out superficially. Then, holes of 4-6 mm deep were made on the surface of the medium using a sterile drill with a diameter of 10 mm, into which 0.1-0.3 ml of the test sample solution was added. Petri dishes were placed in thermostat and kept at 30±2°C for 2 days for bacteria and 3-4 days for fungi.

**Result and Discussion**

Antimicrobial efficacy of the studied compounds was determined by the size of the diameter of the inhibition zone of microorganisms growth (cm) around the hole with and without the additive: the larger it is, the more effective antimicrobial effect of the compound. The results of microbiological tests are set into Tab. 2.

**Table 2.** Antimicrobial efficacy of HAD ($C_7H_{15}SSC(O)$ R') in the composition of oil M-8

| Compound No. | Compound (R') | Concentration, % | Zone of inhibition of microorganisms growth, $cm^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Bacteria mixture in MPA medium | Fungi mixture in WA medium | Candida tropicalis (yeast) WA |
| I | $CH_3$ | 1<br>0.5<br>0.25 | 1.0-1.2<br>0.8-0.6<br>+ + | 1.4-1.2<br>1.2-1.0<br>0.8-0.6 | 1.2-1.0<br>1.0-0.8<br>0.8-0.8 |
| II | $C_2H_5$ | 1.0<br>0.5<br>0.25 | 0.5-0.4<br>+ +<br>+ + | 0.7-0.9<br>+ +<br>+ + | 0.4-0.4<br>+ +<br>+ + |
| III | $C_3H_7$ | 1<br>0.5<br>0.25 | 1.0-1.0<br>0.8-0.8<br>0.5-0.4 | 1.2-1.2<br>1.0-0.7<br>0.6-0.6 | 0.9-0.9<br>0.6-0.4<br>+ + |

**Cont. of Tab. 2**

| Compound No. | Compound (R') | Concentration, % | Bacteria mixture in MPA medium | Fungi mixture in WA medium | Candida tropicalis (yeast) WA |
|---|---|---|---|---|---|
| IV | $C_5H_{11}$ | 1<br>0.5<br>0.25 | 1.3-1.0<br>0.8-0.6<br>0.4-0.4 | 1.4-1.2<br>1.0-0.9<br>0.6-0.7 | 1.0-0.8<br>0.7-0.7<br>0.4-0.6 |
| V | $C_9H_{19}$ | 1<br>0.5<br>0.25 | 1.4-1.2<br>1.0-0.8<br>0.6-0.6 | 1.6-1.7<br>1,4-1.2<br>0.8-0.7 | 1.2-1.0<br>0.9-0.9<br>0.7-0.6 |
| VI | $C_{11}H_{23}$ | 1<br>0.5<br>0.25 | 1.4-1.5<br>1.2-1.1<br>1.0-0.7 | 1.8-1.9<br>1.5-1.3<br>1.2-1.0 | 1.4-1.4<br>1.0-0.8<br>0.7-1.0 |
| VII | Sodium pentachlorophenolate | 1<br>0.5 | 1.3-1.5<br>0.7-1.0 | 1.4-1.6<br>0.8-1.2 | 1.4-1.4<br>0.7-0.9 |
| VIII | Oil M-8 (without biocide) | - | + + | + + | + + |

**Note:** + + - abundant growth of microorganisms around the hole in Petri dish

As is seen from Tab. 2, at a concentration of 0.25-1% (wt.) the studied HAD compounds effectively inhibit the growth of microorganisms (except for compound 2) that infect lubricating oil M-8. Their antimicrobial activity is at the level of effectiveness of the widely used industrial additive sodium pentachlorophenolate.

To reveal the relationship between the structure and antimicrobial activity of the synthesized compounds, it is convenient to consider their dependence on the structure of the alkyl part of the molecule.

As a result of the studies carried out on heptylalkanoyldisulfides, distinct patterns of dependence of antimicrobial efficacy on the structure of alkyl radical were determined. Antimicrobial activity increases by an increase in alkyl radical, i.e., each subsequent member of the disulfide series is biologically more active than the previous one. The increase in antimicrobial activity seems to be due to the fact that the adding each new $CH_2$ group gives one more van der Waals bond, increasing adsorption forces that bind the compound to the receptor in the microorganism [18].

Analysis of the test results showed that antimicrobial additives possess high efficiency, especially dodecanoylheptyldisulfide is an effective inhibitor of microbiological oil damage. It has high antimicrobial properties - both bactericidal and fungicidal at a certain concentration (0.25-1 wt. %).

As a result of the tests, it was determined that compounds IV and V are at the level of the standard in terms of antimicrobial efficacy. Simultaneously, bactericidal properties are inferior to fungicidal ones. Other compounds are close to the standard. The compound III has good fungicidal properties at a concentration in 1% and protects the lubricating oil from fungal attack.

Thus, analysis of antimicrobial properties of the studied disulfides (HAD) made it possible to establish the dependence of activity on the structure of alkyl radical.

**Conclusion**

The test compounds havn't adverse effect on the physicochemical properties of M-8 oil and may be used as biocides for storage and transportation of lubricating oils.

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