

СИНТЕЗ И ИЗУЧЕНИЕ СВОЙСТВ ПРОИЗВОДНЫХ МЕТИЛФЛОРОГЛЮЦИНА И ФЛОРОГЛЮЦИНА В КАЧЕСТВЕ АНТИОКИСЛИТЕЛЬНЫХ ПРИСАДОК К МАСЛАМ

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В настоящее время существует необходимость поиска новых органических соединений с выраженной антиокислительной способностью. В данной работе были изучены показатели антиокислительной стабильности соединений, полученных на основе флороглюцина и метилфлороглюцина, и были выявлены основные принципы синтеза. Механизм действия этих присадок похож на принцип действия пространственно-затрудненных фенолов в качестве антиокислительной присадки в топливе. Также синтезированные соединения могут выступать в качестве деактиваторов металлов. Они позволяют снизить расход ингибитора окисления за счет их синергизма. Данные деактиваторы представляют собой соединения фенольного типа, содержащие функциональные группы, которые приводят к деактивации иона металла через образование устойчивых комплексов. Анализ литературных данных показал, что для достижения намеченной цели необходимо ввести в молекулу иминогруппу. Необходимо отметить, что это может понизить растворимость соединения в углеводородном материале. Для решения этой проблемы в молекулу вводят высшие алкильные радикалы, что решает возникшую проблему без ущерба основной задаче. В данной работе был синтезирован ряд антиокислительных присадок типа аминокфенолов. Для получения антиокислителей типа пространственно-затрудненных фенолов, способных связывать катионы металлов в хелатные комплексы, то есть потенциально являться так же деактиваторами металлов, был синтезирован ряд оснований Шиффа через промежуточный продукт ацилирования. В ходе работы были получены соответствующие замещенные триаминобензолы из флороглюцина и метилфлороглюцина. Полученные соединения проявляют высокую антиокислительную активность. Синтезированные соединения охарактеризованы методами ¹H ЯРМ, ИК-спектроскопии и масс-спектрометрии. Испытания соединений на основе флороглюцина и метилфлороглюцина показали, что некоторые из них проявляют хорошую антиокислительную способность и могут быть рекомендованы для дальнейшего их более детального исследования, а также синтеза структуроподобного ряда с различными заместителями.

Ключевые слова: присадки к маслам, пространственно-затрудненные фенолы, присадки аминного типа, метилфлороглюцин, флороглюцин, деактиваторы металлов

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**SYNTHESIS AND STUDY OF PROPERTIES OF DERIVATIVES
OF PHLOROGLUCINOLMETHYLVIOLGEN AS ANTIOXIDANT ADDITIVES TO OILS**

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At the present time there is a need to search for new organic compounds with pronounced antioxidant activity. In this work, we studied indicators of antioxidant stability of the compounds obtained by the modification of the phloroglucinol and methylviologen, and identified the basic principles of the synthesis of antioxidant additives. Moreover, the synthesized compounds can act as metal deactivator. These deactivators are phenolic compounds containing functional groups, for example, the iminogroup, which lead to the deactivation of the metal ion through the formation of stable complexes. A literature review showed that in order to achieve it, iminogroup should be introduced. It is worth mentioning that it can reduce the solubility of the compound in hydrocarbon. To solve this problem, it is necessary to introduce higher alkyl radicals to the molecule. In this paper, a number of antioxidant additives such as aminophenols were synthesized. To obtain the antioxidants of the type of spatially hindered phenols, also able to bind cations of metals in chelate complexes, that is, potentially able to be metal deactivators, a series of Schiff bases were synthesized via an intermediate product of the acylation. In the course of the work the corresponding substituted triamine benzenes from phloroglucinol methyl and phloroglucinol were obtained. The resulting compounds exhibit high antioxidant activity. The synthesized compounds were characterized via ¹H nuclear magnetic resonance, IR spectroscopy and mass spectrometry. The trials carried out with compounds on the basis of phloroglucinol and methylviologen showed that some of them have good antioxidant properties and can be recommended for the further more details investigation as well as for synthesis of an array with a similar structure with various substituting groups.

Key words: oil additives, spatially hindered phenols, amine-type additives, methyl phloroglucinol, phloroglucinol, metal deactivators

INTRODUCTION

It is known that there is a need to search for new antioxidant additives that work by various mechanisms to increase the chemical stability of fuels and petroleum oils and lubricants during storage and their thermo-oxidative stability during engine operation at high temperatures and exposure to atmospheric oxygen [1, 2].

The basic principles of the synthesis of antioxidant additives were revealed [3]. Thus, the main provisions of the synthesis of additives operating on the principle of hindered phenols, alkylated aminophenols, and also metal deactivators were identified. In this regard, it can be concluded that antioxidants used in fuels and lubricants, should contain bulky substituents at the

radical in their structure and have a powerful electron-donor effect [4].

The influence of mesomeric and inductive effects which distribute the unpaired electron of the resulting radical over the entire molecule of the antioxidant should be noted. Amino and hydroxy groups in the range of aromatic hydrocarbons have this influence [5,17,18]. The presence of small amounts of such dissolved metals as copper, vanadium, and iron in the fuel, petroleum oils and lubricants can accelerate the oxidation reactions [6]. As it was mentioned earlier, one of the types of antioxidants are metal deactivators. It is known that metal deactivators allow to decrease at least by 30-35% the demand of oxidation inhibitor due to their synergism [6].

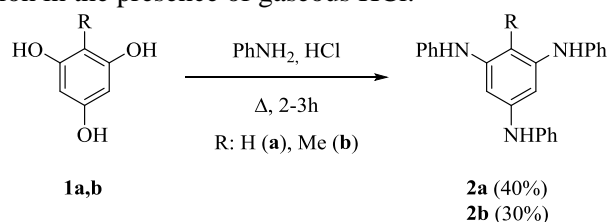
Moreover, their concentration in fuels and lubricants is much less. The concentration of metal deactivators varies up to 0.1%, whereas the concentration of antioxidants reaches 1-2.5% on average [7, 13, 14]. These deactivators are phenolic compounds containing functional groups, for example, the imino group, which lead to the deactivation of the metal ion through the formation of stable complexes [8, 15]. For this purpose, an imino group is often introduced, but it should be noted that it can decrease the solubility of a compound in petroleum oils and lubricants. On the other hand, the higher alkyl radicals present in the molecule increase its solubility. In this work, a number of aminophenol-type antioxidant additives were synthesized [6].

DISCUSSION OF RESULTS

In our research as the starting material we used 2 triatomic phenols: 2,4,6-trihydroxybenzene **1a** (phloroglucinol) and 2,4,6-trihydroxytoluene **1b** (methylphloroglucinol).

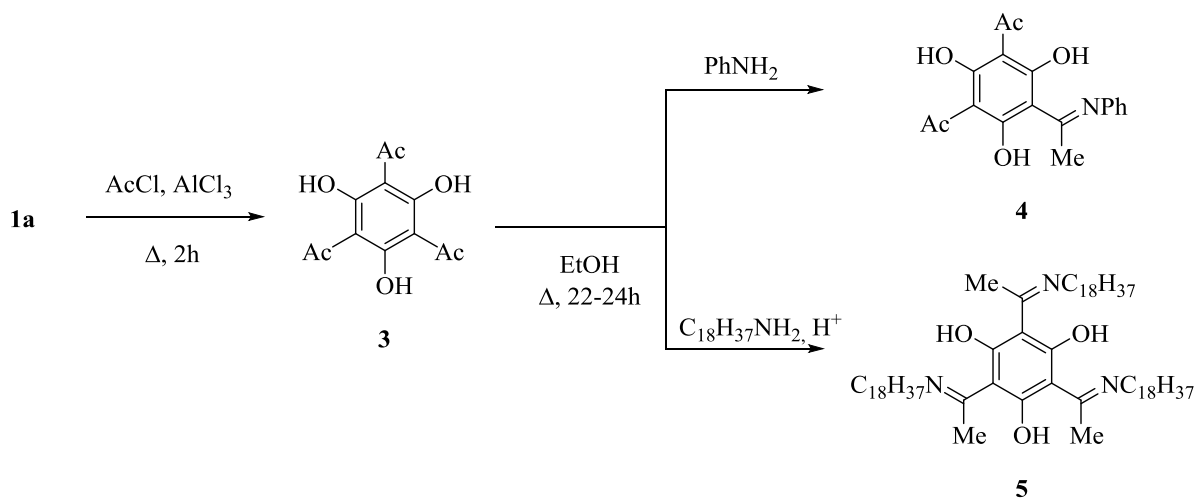
Both these substances possess high antioxidant potential and appear as affordable raw material [16]. It is worth mentioning that these phenols may be obtained by reduction with the following hydrolysis of 1,3,5-trinitrobenzene and 1,3,5-trinitrotoluene on the methodology, developed in Zelinsky Institute of Organic Chemistry of Russian Academy of Sciences [9, 10].

As the result were obtained polyaminobenzenes with nitrogen atoms containing phenyl radical which improves oil solubility of the substance. 1,3,5-tri(aminophenyl)benzene **2a** and 1,3,5-tri(aminophenyl)toluene **2b** were synthesized with good yield from the corresponding phenols by boiling in aniline solution in the presence of gaseous HCl.



Scheme 1
Схема 1

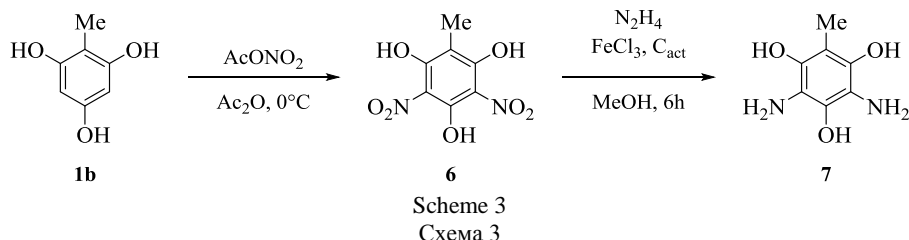
To obtain antioxidants of sterically hindered phenols type which are able to bond metal cations into chelate complexes, what means potentially serve as metal deactivators, some amount of Schiff bases was synthesized with obtaining of intermediate product of acylation **3**. Long-term boiling in aniline-ethanol solution resulted in formation of a monosubstituted product **4** with 95% yield. Substitution with *n*-octadecylamine for the purpose of improvement of tribological behavior resulted in formation of a trisubstituted product **5** in similar conditions, though the yield rate decreased to 64%.



Scheme 2
Схема 2

It is known that phenols may show antioxidizing activity [10]. Diamino derivative of methylphloroglucinol **7** was obtained from the corresponding dinitro derivative. Dinitromethylphloroglucinol **6** was obtained by its exposure to acetyl nitrate in acetic anhydride at 0 °C.

The following reduction was conducted by hydrazine hydrate in the presence of iron (III) chloride hexahydrate and activated carbon. The obtained compound remains aromatic structure, which may be proved by ¹H NMR spectroscopy.



The obtained compounds were tested on anti-oxidizing ability of oils. The test is named “acid number”. For comparison we have chosen the industrial additives, widely produced both in Russian and abroad: ionol (Agidol-1), A-22 (Agidol-2), DF-11. As the test samples were taken the industrial oils of viscosity classes 40 and 20 at 50 °C (I-20A and I-40A respectively) without additives. The tests were conducted on “APSM-1M” device on the methodology described in GOST 5985-79.

The obtained compounds were tested on anti-oxidizing ability and the results of the tests are presented in tables 1-3.

During the 1st stage of the test dinitromethylphloroglucinol **6** and diaminomethylphloroglucinol **7** were examined. The place of acidifiable oil was taken by I-40A. The comparison was conducted with A-22 (Agidol-2) and DF-11 additives. The results of the test are presented in Table 1.

Table 1

Results of tests on the first group of additives

Таблица 1. Результаты испытаний по первой группе присадок

Name of additive	Per cent by weight, %	Acid number, mg KOH/g	Efficiency in regard to oil without additives, %
DF-11	0.05	1.288	17
A-22	0.05	1.232	9
6	0.05	0.829	55.55
7	0.05	0.901	41.31
Oil without additives	-	1.387	-

The obtained compounds may be used as anti-oxidizing additives. Dinitromethylphloroglucinol **6** appeared to show more efficiency than A-22 and DF-11: the chemical stability of oil increases by almost 55%, so the compound **6** turned out to be 38 and 44% more effective than A-22 and DF-11 respectively. Diaminomethylphloroglucinol **7** showed 41,31% more efficiency in comparison to oil without additives and 24

and 28% more efficiency in comparison to A-22 and DF-11 respectively.

During the 2nd stage of the test the compounds **4** and **5** were examined. The place of acidifiable oil was taken by I-22A. The comparison was conducted with DF-11 additive. The results of the test are presented in Table 2.

Table 2

Results of tests on the second group of additives

Таблица 2. Результаты испытаний по второй группе присадок

Name of additive	Per cent by weight, %	Acid number, mg KOH/g	Efficiency in regard to oil without additives, %
DF-11	0.84	0.39	31.16
4	0.84	0.41	29.31
5	0.84	0.46	20.69
Oil without additives	-	0.58	-

The compounds possess good oil solubility. The obtained results prove that the synthesized compounds may be used as the new type of industrial anti-oxidizing additives.

Further on, the ability to inhibit oxidizing processes proved 1,3,5-tri(phenylamino)benzene **2a** and 2-methyl-1,3,5-tri(phenylamino)benzene **2b**. The results of the test are presented in Table 3.

Table 3

Results of tests on the third group of additives

Таблица 3. Результаты испытаний по третьей группе присадок

Name of additive	Per cent by weight, %	Acid number, mg KOH/g	Efficiency in regard to oil without additives, %
Ionol	0.25	2.795	10
2b	0.25	2.273	27
2a	0.25	2.030	35
Oil without additives	0.25	3.112	-

The compounds presented the perfect antioxidizing ability, appeared to be more effective in comparison to ionol and, in addition, possess good solubility.

EXPERIMENTAL STAGE

The structure of the synthesized compounds is verified by Fourier-transform infrared spectroscopy (FTIR) and ^1H NMR spectroscopy, mass spectrometry. IR-spectrum data was obtained from Fourier-transform infrared spectrometer FSM-1201 with 2 cm^{-1} resolution with number of scans equal to 32 in KBr pellet. ^1H -NMR spectra solutions in DMSO- d_6 were registered on Bruker AM-300 device. All the experiments were conducted according to the standard methodics of Bruker company. The chemical shifts are presented relative to Me $_4$ Si. The values of coupling constant are presented in Hz. Mass spectra were registered on MS-30 Kratos device (EI, 70 eV). For all of the synthesized compounds parent peak M $^+$ was observed. The melting point of the obtained compounds was measured on the open capillary method. Monitoring of reaction was conducted on TLC method on Silufol plates.

1,3,5-Tri(aminophenyl)benzene 2a

0.3 g (2.378 mmol) of **1a** and 0.10 ml of aniline were added into a 3-neck flask. The solution had been boiled for 2 h while being stirred with gaseous HCl being passed through. Monitoring of reaction was conducted on TLC method (PhMe:i-PrOH, 10:1). Then aniline was distilled, the solution was cooled and 3 ml of concentrated hydrochloric acid were added. Then the precipitate was filtered and rinsed several times with ethanol. As the result 0.334 g of light-purple powder were obtained (yield 40%). Tm = 193-194 °C.

^1H NMR (300 MHz, DMSO- d_6 , δ , м.д.): 7.99 (s, 3H, NH), 7.23 (t, 6H, Ar, $J = 7.7$ Hz), 7.09 (d, 6H, Ar, $J = 8.0$ Hz), 6.80 (t, 3H, Ar, $J = 7.2$ Hz), 6.36 (s, 3H, Ar). MS: m/z 351.

2-Methyl-1,3,5-tri(phenylamino)benzene 2b

0.3 g (2.141 mmol) of **1b** were dissolved in 10 ml of aniline. The solution had been boiled for 3 h while being stirred with gaseous HCl being passed through. Then aniline was distilled. After that the product was precipitated with i-PrOH mixture: petroleum ether (3:2). Then the precipitate was filtered, rinsed with hot water and air dried. As the result 0.235 g of green crystals were obtained (yield 30%). Tm = 165-166 °C.

^1H NMR (300 MHz, DMSO- d_6 , δ , м.д.): 10.51 (s, 2H, NH), 8.43 (s, H, NH), 7.4 (s, 3H, Ar), 7.2-7.4 (m, 6H, Ar), 6.5 (s, 2H, Ar), 5.5 (s, 6H, Ar), 2.3 (s, 3H, CH $_3$). MS: m/z 365.

2,4,6-Triacetyl-1,3,5-trihydroxybenzene 3

To the stirred suspension of 8 g of anhydrous AlCl $_3$ in 20 ml of acetyl chloride being cooled slowly

2 g (15,859 mmol) of **1a** dehydrate were added. The obtained mixture had been boiled for 2 h. To the reaction mass 5 ml of 10% HCl solution and 90 ml of water were added. The produced precipitate was filtered and rinsed with water and EtOH. As the result 2,86 g of white needle-like crystals were obtained (yield 71%). Tm = 202-203 °C (EtOH).

IR (cm $^{-1}$ -KBr): 3428.0, 1621.2, 1578.8, 1297.7; ^1H NMR (300 MHz, DMSO- d_6 , δ , м.д.): 17.17 (s, 3H, OH), 2.73 (s, 9H, C(O)CH $_3$). MS: m/z 252.

1,1'-(2,4,6-Trihydroxy-5-(1-(phenylamino)ethyl)-1,3-phenylene)bis(ethan-1-one) 4

To the solution of 3 g of aniline in 50 ml of EtOH 0.5 g (1.982 mmol) of **4** were added. The reaction mass had been boiled while being stirred for 22 h. Then the product was cooled and the precipitate was filtered. As the result 0.61 g of material were obtained (yield 95%). Tm = 152-153 °C (EtOH).

^1H NMR (300 MHz, DMSO- d_6 , δ , м.д.): 17.42 (s, 3H, OH), 2.62 (s, 6H, C(O)CH $_3$), 2.42 (s, 3H, CH $_3$ CN), 6.87 (m, 2H, Ar), 7.29 (m, 2H, Ar), 6.96 (m, 1H, Ar). MS: m/z 327.

2,4,6-Tris(1-(octadecylamino)ethyl)benzene-1,3,5-triol 5

To the solution of 11 g (40.815 mmol) of *n*-octadecylamine in 140 ml of EtOH 1 drop of H $_2$ SO $_4$ was added. The solution had been boiled while being stirred for 30 min. Then 3 g (11.894 mmol) of **3** were added. Then the solution had been boiled while being stirred for 23 h. After that the reaction mass was cooled to the room temperature and the produced precipitate was filtered. As the result 3.44 g of white material were obtained (yield 30%). Tm = 131-132 °C (EtOH).

^1H NMR (300 MHz, DMSO- d_6 , δ , м.д.): 17.35 (s, 3H, OH), 2.35 (s, 9H, CH $_3$ CN), 0.87-0.89 (t, 9H, CH $_3$ (CH $_2$) $_{16}$), 1.25-1.28 (m, 68H, (CH $_2$) $_{16}$), 3.68-3.70 (m, 6H, CH $_2$ CN).

2-Methyl-4,6-dinitro-benzene-1,3,5-triol 6

To 10 ml of a cooled to -5 °C acetic anhydride slowly 2 ml of concentrated HNO $_3$ were added dropwise. After that while stirring 0.6 g (4.281 mmol) of **1b** were added in portions. The solution had been stirred for 1,5 h at the temperature of 0 °C. Then the solvent had been distilled under decreased pressure. As the result 0.562 g of dark-orange crystals were obtained (yield 57%). Tm = 145-146 °C (Et $_2$ O).

IR (cm $^{-1}$, KBr) 1626, 1572, 1540, 1510, 1475, 1433, 1352, 1307, 1186, 1154; ^1H NMR (300 MHz, DMSO- d_6 , δ , м.д.): 2.15 (s, 3H, CH $_3$), 11.23 (s, 1H, OH), 10.81 (s, 2H, OH). MS: m/z 230.

2,4-Diamino-6-methylbenzene-1,3,5-triol 7

While stirring 0.5 g (2.938 mmol) of **6** were dissolved in 20 ml of MeOH at 50 °C. To the produced solution 0.2 g of activated carbon and 0.016 g (2% mol)

FeCl₃·6H₂O were added. Then 0.72 ml (14.832 mmol) of N₂H₄·H₂O in 3 ml of MeOH were added dropwise. The solution had been boiled while being constantly stirred for 6 h. After that the reaction mass was cooled and filtered. The filter was boiled out. As the result 0.265 g of white crystals were obtained (yield 53%). T_m = 182-183 °C (EtOH).

¹H NMR (300 MHz, DMSO-d₆, δ, м.д.): 9.58 (s, 1H, OH), 9.42 (s, 2H, OH), 4.66 (s, 4H, NH₂), 2.16 (s, 3H, CH₃). MS: m/z170.

CONCLUSION

In the course of the work the corresponding substituted triamine benzenes were obtained from phloroglucinol methyl and phloroglucinol. Moreover, via a reaction of condensation with aniline and n-octadecylamine Schiff bases were obtained [13].

The previously undocumented nitration reactions of unsubstituted methyl phloroglucinol were

studied and a new method of reduction of nitrated derivative of methyl phloroglucinol was created. The antioxidant properties of the synthesized compounds were investigated. The obtained compounds can be recommended as antioxidant additives to oils on a par with industrial additives [20-21].

RESULTS

A series of previously undocumented derivatives of phloroglucinol and methyl phloroglucinol was described.

All the synthesized compounds were tested for antioxidant properties.

The compounds **2a**, **b**, **6**, **7** proved to be more effective in comparison with the existing industrial additives and can be recommended for further trials as antioxidants for petroleum products and lubricants.

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