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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESIS OF UNSATURATED MONOESTERS OF α-GLYCOLS, PRODUCTION OF COMPLEX ESTERS OF OIL ACIDS BASED ON THEM AND STUDY OF THEIR PROPERTIES

Speciality: 2314.01 – Petrochemistry

Field of science: Chemical Sciences

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GENERAL CHARACTERISTICS OF THE WORK

Relevance and level of development of the dissertation. Esters of carboxylic acids are an important class of organic compounds that are used in a number of chemical reactions and are often found as natural compounds, also widely used in numerous areas of production as solvents, components of various aromatic compositions, flavoring agents in perfumery, additives to synthetic oils and fuels. In addition, they are used in the production of drugs, insecticides, etc. Esters of carboxylic acids are part of fusel oils - by-products of distillation. The traditional method of obtaining esters of carboxylic acids is esterification of the latter with alcohols in the presence of mineral acidic or alkaline catalysts, the use of which requires additional anti-corrosion protection of the used equipment. Expansion, as well as their application, is also very interesting for study.

The possibility of wide variation of the chemical composition of petroleum feedstock, distribution of the molecular weight of the naphthyl radical of acids obtained from petroleum distillate, the amount and composition of the functional components and active centers of the ether derivatives creates prerequisites for a wide promising synthesis of previously unknown functionally substituted compounds based on the above esters and their derivatives containing numerous substituents.[1] In this aspect, the properties of the target compounds will be largely determined by the nature and structural features of the hydrocarbon radicals of alcohols.

The use of the complex ester bond as a fastening building block for the assembly of various functional based on aliphatic, cycloaliphatic, framework polycyclic, aromatic, condensed aromatic synthons and fragments of structures of both natural and synthetic origin can serve as a striking example of molecular design. Natural petroleum acids have a wide range of practical application in various industries. Thus, among the key sources enriched with petroleum acids, one can especially highlight the oils of Azerbaijan, where the

[1] Barros, E.V. Characterization of naphthenic acids in crude oil samples – A literature review / Barros E.V., Filgueiras P.R, Valdemar L.Jr. [et al.]. // Fuel, – 2022. Vol.319, – p. 123775.

content of petroleum acids in oils varies within 0.07-2.4% by weight. Natural petroleum acids, having close boiling ranges, but obtained from different petroleum sources, differ in many ways in their qualitative properties. For this reason, natural petroleum acids are the most practically valuable products.

Petrochemical products synthesized on the basis of natural petroleum acids are distinguished by a wide range of qualitative properties. The presence of a radical of petroleum acids in the molecule of organic substrates contributes to a qualitative change in the physicochemical parameters of the target products of petrochemical synthesis, in particular, ignition and setting temperatures, solidification temperature, thermal-oxidative and hydrolytic stability, inhibitory, plasticizing and other properties.[2]

Development of effective methods for obtaining esters of unsaturated monoethers of glycols (UMEG) based on natural petroleum acids seems to be a very promising direction and expands the possibilities of their practical application.

At the same time, it should be noted that the problem of the appropriate use of cyclopentadiene, which is a by-product of the pyrolysis process, is one of the most pressing problems of problems of modern petrochemistry. Therefore, the synthesis of norbornene derivatives based on cyclopentadiene, as well as finding optimal options for using the obtained compounds are also included in the research topic of this dissertation.

Object and subject of research. The object of research of the dissertation is esters of natural petroleum acids synthesized on the basis of petroleum acids isolated from the composition of Baku oils and unsaturated monoesters of glycols in racemic and optically active form. The subject of the dissertation research is to identify the area of practical application of the obtained compounds, in particular, the presence of high antimicrobial and antifungal activity of the synthesized compounds, which allows them to be recommended for use as local antiseptic drugs, the presence of good antioxidant and

[2] Abbasov, V.M. Müxtəlif funksional qrup tərkibli mürəkkəb efirlərin sintezi/ V.M.Abbasov, L.M. Əfəndiyeva, N.F. Sədiyeva [və b.] // Azərbaycan neft təsərrüfatı jurnalı, – 2015. №10, – s. 37-40.

depressant properties, allowing the use of synthesized esters based on petroleum acids and unsaturated glycol monoesters as additives to hydrotreated diesel fuel.

In order to solve the problems of the appropriate use of cyclopentadiene derivatives, as a by-product of the pyrolysis process, as additives to diesel fuel, the following compounds of the norbornene series were studied: 5-methoxycarbonylnorborn-2-ene (IS-1); 5-carboxylnorborn-2-yl acrylate (IS-2); 5-acetoxymethylnorborn-2-ene (IS-3); norbornenemethanol (IS-4), and also allyl esters of natural petroleum acids (AENPA) for comparison.

The purpose and objectives of the dissertation. The main purpose of the dissertation is to develop effective methods for the synthesis of racemic and chiral unsaturated monoethers of glycols (RUMEG and CUMEG), the synthesis of esters of natural petroleum acids on their basis, as well as the synthesis of norbornene compounds based on cyclopentadiene with further study of new areas of application of the obtained compounds. The implementation of the goal set in the dissertation work was associated with the solution of the following problems:

- development of methods for the synthesis of new representatives of UMEG;
- synthesis of esters based on NPA and UMEG by esterification;
- synthesis of esters based on NPA and UMEG by the Mitsunobu reaction;
- selection of effective heterogeneous and ionic-liquid catalysts, namely piperidine hydrosulfate $[C_5H_{10}HN^+]HSO_4$- and N-methylpyrrolidone hydratsulfate, as well as selection of optimal conditions for the synthesis of esters based on natural petroleum acids and UMEG;
- study of the biological activity of esters synthesized on the basis of natural petroleum acids and UMEG in racemic and optically active forms;
- study of the structure of the synthesized compounds using physicochemical analysis methods (NMR, IR spectroscopy);
- the synthesized compounds were studied as antimicrobial in synthetic oil (diester of succinic acid), T-22 base oil and AI 95

gasoline;

- study of norbornene series compounds, such as 5-methoxycarbonylnorborn-2-ene (IS-1); 5-carboxylnorborn-2-yl acrylate (IS-2); 5-acetoxymethylnorborn-2-ene (IS-3); norbornenemethanol (IS-4), as well as for comparison, allyl esters of natural petroleum acids (AENPA) as additives to diesel fuel.

Research methods. The structure of the synthesized compounds was proven by elemental analysis data and spectral methods: IR, ^{1}H and ^{13}C NMR spectroscopy, and the purity of individual compounds was controlled by thin-layer (TLC) and gel chromatography.

Main scientific provisions presented for defense.

- Enantioselective synthesis of β-hydroxyesters was carried out, and the absolute configuration of esters (diasteromers) was determined, which were obtained by interaction of synthesized β-hydroxyesters with a chiral derivatizing agent (CDA) - α-trifluoromethylphenylacetic acid chloride (MTPA-Cl, Mosher reagent);
- Biological activity of esters synthesized on the basis of natural petroleum acids and UMEG in racemic and optically active forms was studied;
- The obtained esters on the basis of natural petroleum acids and UMEG were studied as antioxidants and depressants for hydrotreated diesel fuel;
- Study of synthesized esters based on natural petroleum acids with UMEG isomers (by Mitsunobu reaction) as antimicrobial additives to synthetic oil (succinic acid diester), T-22 base oil and AI-95 gasoline;
- Compounds of norbornene derivatives based on cyclopentadiene "IS-1", "IS-2", "IS-3", "IS-4" were synthesized and the possibility of using the synthesized compounds as antioxidant additives to diesel fuels was investigated;
- The effect of synthesized allyl esters of natural petroleum acids as dispersing additives to diesel fuels was studied.

Scientific novelty of the work.

• Racemic representatives of UMEG were synthesized for the first time by the interaction of chloromethyl propargyl ether with

chloro(bromo-)-methylbenzaldehydes with the participation of Zn, MeCOOEt and HgCl in the HMPTA medium;

• Chiral representatives of UMEG were synthesized by reacting chloromethyl propargyl ether with chloro(bromo)methylbenzaldehyde in the presence of Zn, MeCOOEt and HgCl in a HMPTA medium and a chiral catalyst – N-ethyl-N-{[(2S)-pyrrolidine-2-methyl]ethanamine;

• An effective method for synthesizing esters of natural petroleum acids by esterification of NPA with UMEG isomers (according to the Mitsunobu reaction) has been developed;

• It was revealed that esters synthesized on the basis of natural petroleum acids and optically active unsaturated oxyesters exhibit more active antimicrobial and antifungal properties compared to its racemic analogues;

• The compounds we obtained were studied as antimicrobial additives in synthetic oil (diester of succinic acid), T-22 base oil and AI-95 gasoline;

• For the first time, the possibility of using the synthesized compounds IS-1-IS-4 as antioxidant additives to diesel fuel in an amount of 1-3% by weight has been demonstrated;

• For the first time, it has been revealed that adding 1-3% by weight of allyl esters of natural petroleum acids to diesel fuel leads to a decrease in the freezing point of the resulting compounds by 2°C, in connection with which allyl esters of natural petroleum acids can be recommended as resource-enhancing and dispersing additives to diesel fuels.

Practical and theoretical significance of the work:

The esters synthesized by us based on natural petroleum acids and racemic, as well as optically active unsaturated oxyesters, can be used as agents exhibiting depressant and antioxidant properties in diesel fuels, as well as agents providing antimicrobial and antifungal properties.

The studied in the work 5-methoxycarbonylnorborn-2-ene (IS-1); 5-carboxylnorborn-2-yl acrylate (IS-2); 5-acetoxymethylnorborn-2-ene (IS-3) norbornenemethanol (IS-4), as well as allyl esters of natural petroleum acids can be used as multifunctional - resource-

enhancing and antioxidant additives to diesel fuels.

Publications and testing of the dissertation. The presented work is carried out on the basis of the thematic program of scientific research of the department "Chemistry of Oil and Industrial Ecology" (Registration number № 2314.01)

On the topic of the dissertation, 14 scientific works were published, including 5 articles (1 WOS indexed scientific journal) and 5 conference materials, 4 thesis. Материалы II Научной Конференции «Динамические процессы в химии элементоорганических соединений», посвященная 75-летию ИОФХ им. А.Е. Арбузова И Казанского научного центра РАН. (Казань,2020). International Conference on "Actual problems of chemical engineering". (Bakı. 2020). 11th World Conference "Intelligent System for Industrial Automation" (WCIS-2020), Advances in Intelligent Systems and Computing (Ташкент, 2021). "Наука. технология. производство–2021" (с международным участием). Материалы Всероссийской научно-технической конференции студентов, аспирантов и молодых ученых, посвященной 65-летию филиала УГНТУ в г. Салавате (Уфа,2021). Integration of Education, Science and Business in Modern Environment: Winter Debates: abstracts of the 2nd International Scientific and Practical Internet Conference. (Ukraine, 2021). Республиканская научная конференция «Современные проблемы химии» Сумгаитский государственный университет. (Сумгаит, 2021). Ümummilli lider Heydər Əliyevin anadan olmasının 98-ci ildönümünə həsr olunmuş gənc tədqiqatçı və doktorantların onlayn Elmi Konfransı. (Bakı, 2021). Their Application As Additives To Diesel Fuels. Journal: News Of Azerbaijan Higher Technical Educational Institutions International Conference On Reconstruction And Recovery In Post-Conflict Situations RRPCS 2021 dedicated to 100th anniversary of ASOIU (Bakı, 2022). Akademik Soltan Cəfər oğlu Mehdiyevin 110 illik Yubileyinə həsr olunmuş Beynəlxalq elmi konfrans "Monomerlər və Neft Kimyasının Müasir Problemləri", Bakı 19-20 dekabr 2024, s.238

Place of the dissertation.

The dissertation was carried out in accordance with the thematic

plan of scientific research works of the department "Chemistry of Oil and Industrial Ecology" of the Azerbaijan State University of Oil and Industry.

Volume, structure and main content of the dissertation. The dissertation is presented on 160 pages of computer text and consists of an introduction (13046 characters), four chapters: literature review (54514 characters), experimental part (50240 characters), discussion of the obtained results (29695 characters), study of the areas of application of the synthesized compounds (30920 characters), conclusions (2790 characters), a list of used literature, consisting of 139 sources, and appendices. The dissertation includes 20 tables, 29 schemes and 26 figures, the total number of characters of the dissertation is 181205 characters (excluding figures, tables and a list of used literature).

The first chapter presents a literature review, which shows modern methods for the synthesis of esters obtained on the basis of natural petroleum acids and UMEG (racemic and optically active forms);

The second chapter presents methods for synthesizing UMEG (racemic and optically active forms), configuration definition, method for the synthesis of compounds IS-1 - IS-4, as well as the allylic ester of NPA.

The third chapter describes the determination of the configuration of synthesized UMEG (racemic and optically active forms).

The fourth chapter presents studies of the obtained esters as depressant and antioxidant additives to diesel fuels, as well as agents providing antimicrobial and antifungal properties to fuels and oils. This chapter also presents studies on the use of such norbornene derivatives as 5-methoxycarbonyl-norborn-2-ene (IS-1); 5-carboxylnorborn-2-yl acrylate (IS-2); 5-acetoxymethylnorborn-2-ene (IS-3); norbornenemethanol (IS-4), as well as allyl ether of natural petroleum acids as multifunctional additives - resource-enhancing and antioxidant additives to diesel fuels.

Personal contribution of the author. The studies, the results of which are reflected in this dissertation, their interpretation and

generalizations are carried out by the author himself. The experimentally obtained research results, in particular spectroscopic and chromatographic data, were analyzed by the author of the dissertation in consultation with specialists in the relevant field. In addition, the writing of articles and preparation of abstracts for conference reports were also carried out by the applicant with the support of the supervisor.

Main content of the work

1. Preparation of raw materials for experiments.

At the first stage of the studies, narrow cut of natural petroleum acids were isolated and purified, for which chlorine anhydrides of NPA were first obtained and their physicochemical properties were studied (Table 1).

Table 1.

Technical characteristics of natural petroleum acids of the kerosene fraction and their acid chlorides

Component	Boiling range, °C at 0.27-4.0 kPa, kg/m^3	ρ_4^{20}, kg/m^3	n_d^{20}	Acid number, mg KOH/g	Yield per fr., % (mass)	Chlorine content, % (mass)	Molecular weight
1.Naphthenic acids of kerosene fractions	88-175	959,7	1,4810	287,5	-	-	195,2
2.Chlorine anhydrides of naphthenic acids	100-115	1008,3	1,4919		15,3	15,2	229,3
	115-130	1040,5	1,4925		18,3	14,3	-
	130-145	1085,7	1,4940		36,4	12,7	233,0
	145-185	1099,0	1,4965		28,1	11,5	
	remainder >186	-	-		19,0	-	

As can be seen from Table 1, the highest yield of natural petroleum acids is observed for the 130-145^{0}C fraction / at 0.27-0.4 kPa and is 36.4% by weight. This fraction was subsequently used to synthesize aromatic NPA esters.

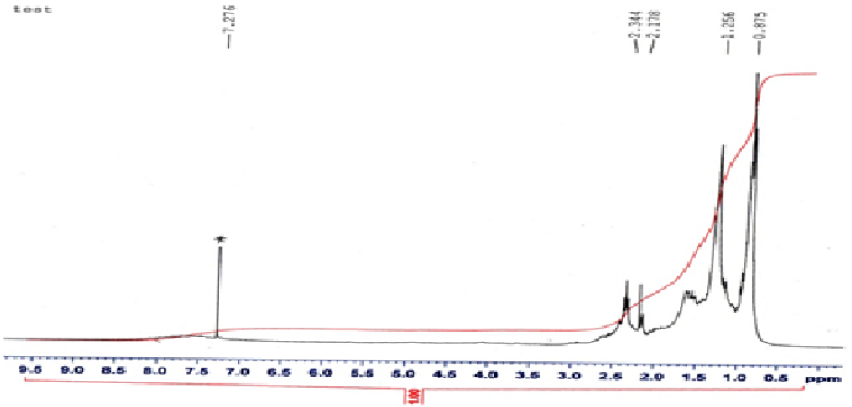


Figure 1. ^{1}H NMR spectrum of NPA halogen anhydrides of the 130-145°C fraction / at 0.27-0.4 kPa

After this, methyl esters of NPA chlorides were obtained by the reaction.

$$RCOCl + CH_3OH \xrightarrow[HCl]{} RCOOCH_3$$

In order to purify natural petroleum acids from unsaponifiable impurities and simplify further transesterification reactions, the elemental and approximate average composition of the used NPA were determined (Table 2).

Table 2.

Elemental and approximate general average composition of petroleum acids and their methyl esters

№	Boiling range of methyl esters, °C at 1.8-2.0 kPa	Content %(mass.)			Molecular weight	Molecular refraction R_m	Gross formula	General formula
		C	H	O				
1	120-130	1,09	10,54	18,18	173	0,0471	$C_{10,41}H_{18,6}O_{2,04}$	$C_{10}H_{18}O_2$
2	130-140	1,96	10,80	17.23	190,1	0,0532	$C_{11,51}H_{21,03}O_{2,07}$	$C_{11}H_{20}O_2$
3	140-150	4,13	10,64	15,12	201,1	0,0621	$C_{13,17}H_{23,64}O_{2,08}$	$C_{13}H_{24}O_2$
4	150-160	5,15	10,57	14,47	231,4	0,1194	$C_{14,47}H_{24,74}O_{2,06}$	$C_{14}H_{24}O_2$

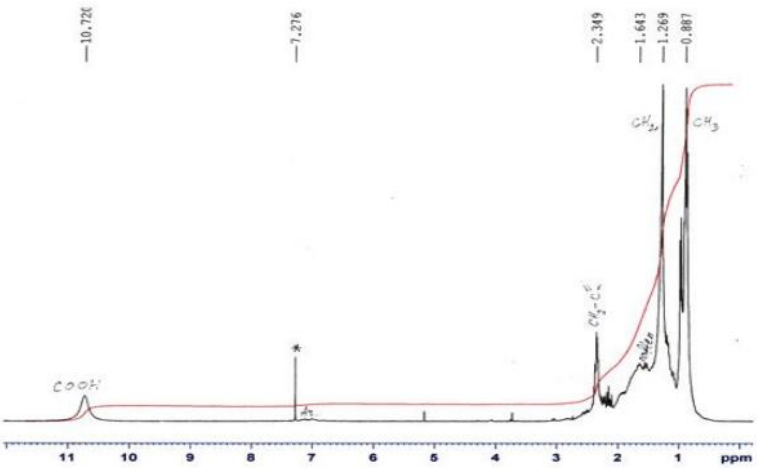


Figure 2. ^{1}H NMR spectrum of NPA

The ^{1}H NMR spectrum contains signals with chemical shifts of δ=0.5-1.0 ppm and 1.0-2.0 ppm. The first resonance band is due to the protons of the terminal methyl groups (H_y = 41.2), and the second one is due to the protons of the methylene and methine groups (H_β), with the exception of the methylene protons located in the -position to the aromatic ring. The downfield signals δ = 2.0-2.8 ppm and δ=6.5-8.0 ppm. correspond to the proton of the alkyl groups located in the α-position to the aromatic ring, and the protons of the aromatic nucleus $(H_\alpha - 0,6; H_a - 0,2)$, and in the $\sigma = 1,40 - 1,90$ ppm region correspond to the resonance absorption of hydrogen in naphthenic structures (H_β). The signals at 11.0 ppm are characteristic of the carboxyl group protons. The purity of the obtained fractions of natural petroleum acids was also tested using IR spectroscopy (Fig. 3)

In the IR spectrum of the obtained NPAs, absorption bands were found at the following wavelengths: 1376, 1411, 1457, 2865, 2929, 2953 cm^{-1} - deformation vibrations of the C-H bonds in the methylene and methyl groups of aliphatic and naphthenic structures, including the C-H bonds located at the carbonyl groups; the band 937 cm^{-1} is characteristic of deformation vibrations of the C-H bond in the naphthenic fragment; 1175, 1236 cm^{-1} - stretching vibrations of the C-O bond. The absorption band at 3321 cm^{-1} is responsible for the

stretching vibrations of the acid fragments OH group.

Also, in the spectrum there is a band at 1704 cm^{-1}, which corresponds to the C=O group of the acid. It can be concluded that the obtained spectrum fully proves the structure of the NPA.

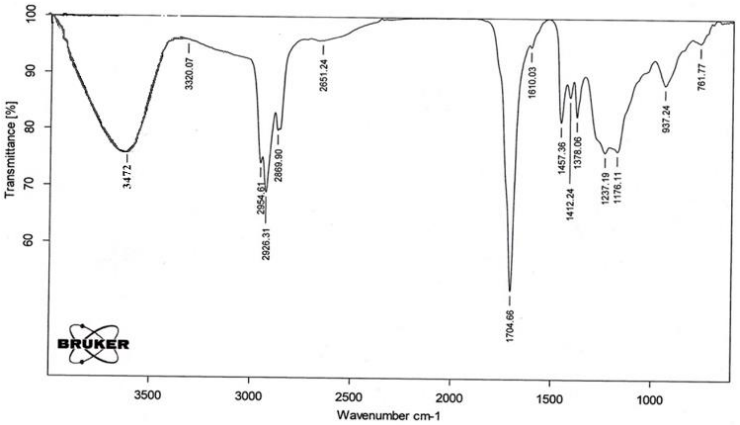
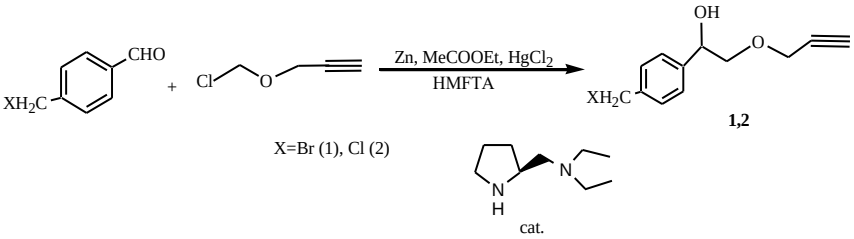


Figure 3. IR spectrum of the obtained NPA

2. Synthesis of unsaturated oxyesters

2.1 Synthesis of 1-[4-chloro(bromo)methylphenyl]-2-[prop-2-yn-1-yl)oxy]ethan-1-ols

The synthesis of 1-[4-chloro(bromo)methylphenyl]-2-[prop-2-yn-1-yl)oxy]ethan-1-ols was carried out according to the following scheme:



General procedure for the synthesis of unsaturated oxyesters: A mixture of 1.0 g (15 mg-atom) finely chopped zinc metal turnings, 0.27 g (0.01 mol) $HgCl_2$, 0.6 g (6 mmol) chloromethyl propargyl ether, 0.04 g (2 mmol) 4-bromomethylbenzaldehyde, 0.5 g N-ethyl-N-{[(2S)-pyrrolidin-2-yl]methyl}ethanamine, 10 ml anhydrous benzene, 5 ml anhydrous ethyl acetate, and 1 ml HMPTA

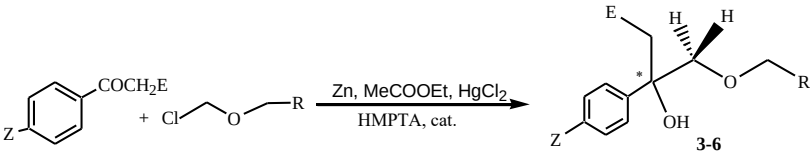
was taken and boiled for 4 h under an inert nitrogen atmosphere and then cooled. The reaction products were extracted from the aqueous layer with ethyl acetate (2×25 ml). After drying the extract with anhydrous sodium sulfate, the solvent was distilled off. Then the reaction mixture was concentrated in vacuo, and the residue was chromatographed on a column with SiO_2 (petroleum ether–ethyl acetate, 2:1).

1-[4-Bromomethylphenyl]-2-[prop-2-yn-1-yl)oxy]ethan-1-ol (1) Yield 78.1%. Selectivity: 93.4% $C_{12}H_{20}BrO_2$. Founded, %: C 53.42, H 4.81, Br 29.72. Calculated, %: C 53.55, H 4.87, Br 29.69. IR spectrum, ν, cm^{-1}: 3603 (O–H), 3287, 3085, 3065, 3030, 2110 (C≡C), 2000-1667, 1071, 1600, 1490, 1350, 1260, 1220, 1100 (C–O–C), 1020, 985, 770 (Ph), 700, 680 (C-Br). ^{1}H NMR spectrum, δ, ppm: 2.51 t (1H, ≡CH, ^{4}J 2.4 Hz), 2.84 a.u. (H, OH), 3.00 d.d (1H, CH_2O, J=16.5, 7.8 Hz), 3.15 d (1H, J=16.5, 7.8 Hz), 3.43 s (3H, CH_3O), 3.83 d.d (1H, ≡CCH_2O, ^{2}J 16.2 Hz, ^{4}J 2.4 Hz), 4.05 d.d (1H, ≡CCH_2O, ^{2}J 16.2 Hz, ^{4}J 2.4 Hz), 4.13 d.d (1H, CHO, ^{2}J 5.7, 7.8 Hz), 4.52 d (1H, CH_2Br, J=10.5 Hz), 4.61 d (1H, CH_2Br, J=10.5 Hz), 7.03 d.d (2H, J=1.5, 8.7 Hz), 7.49 d.d (2H, J=1.5, 8.6 Hz).

1-[4-(Chloromethyl)phenyl]-2-[(prop-2-yn-1-yl)oxy]ethan-1-ol (2) was obtained similarly. Yield 74.3%. $C_{12}H_{20}ClO_2$. Founded, %: C 62.21; H 8.73; Cl 15.29. Calculated, %: C 62.19; H 8.70; Cl 15.30.IR spectrum, ν, cm^{-1}: 3612 (O-H), 3286, 3085, 3065, 3030, 2100 (C≡C), 1600, 1490, 1100 (C-O-C), 985, 770 (Ph), 700, 670 (C-Cl). ^{1}H NMR spectrum, δ, ppm: 2.49 t (1H, ≡CH, ^{4}J 2.5 Hz), 2.82 a.u. (H, OH), 3.02 d.d (1H, CH_2O, J=16.2, 7.7 Hz), 3.15 d (1H, J=16.2, 7.7 Hz), 3.42 s (3H, CH_3O), 3.81 d.d (1H, ≡CCH_2O, ^{2}J 16.1 Hz, ^{4}J 2.5 Hz), 4.04 d.d (1H, ≡CCH_2O, ^{2}J 16.1 Hz, ^{4}J 2.5 Hz), 4.12 d.d (1H, CHO, ^{2}J 5.6, 7.8 Hz), 4.52 d (1H, CH_2Cl, J=10.4 Hz), 4.58 d.d (1H, CH_2Cl, J=10.4 Hz), 7.02 d.d (2H, J=1.5, CH_{Ar}, J=8.7 Hz), 7.48 d.d (2H, CH_{Ar}, J=1.5, 8.6 Hz).

2.2 Synthesis of racemic mixtures of monoesters of α-glycols of unsaturated C_3-alcohols

was carried out according to the scheme:



3-6

Z= Cl (**3,4**), H (**5,6**)
E= Br (**3,4**), Cl (**5,6**)
R= C≡CH (**3,5**), CH=CH_2 (**4,6**)

Compounds 3-6 were synthesized with yields of 74-79% and selectivity of 89.3-92.6%.

(±)1-Bromomethyl-2[4-chlorophenyl]-3-[(prop-2-yn-1-yl)oxy]propan-2-ol (3). Yellow oily substance. NMR spectrum^{1}H, δ, ppm: 2.52 t (1H, ≡CH, ^{4}J=2.4 Hz), 3.06 d (1H, CH, J 15.9 Hz), 3.18 d (1H, CH, J 15.9 Hz), 3.43 s (3H, CH_3O), 3.69 d (1H, CH, J 10.5 Hz), 3.77 d (1H, CH, J 10.5 Hz), 3.83 d.d (1H, ≡CH_2O, ^{2}J 16.2 Hz, ^{4}J=2.4 Hz), 4.05 d.d (1H, ≡CH_2O, ^{2}J 16.2 , ^{4}J 2.4 Hz), 7.28-7.51 m (5H, Ph), 7.38-7.42 m (5H, Ph).

(±)1-Bromomethyl-2[4-chlorophenyl]-3-[(prop-2-en-1-yl)oxy]propan-2-ol (4). Yellow oily substance ^{1}H NMR spectrum, δ, ppm: 3.12 d (1H, CH, J 15.9 Hz), 3.21 d (1H, J 15.9 Hz), 3.49 s (3H, CH_3O), 3.69 d (1H, CH, J 10.5 Hz), 3.77 d (1H, CH, J 10.5 Hz), 4.07 d.d. (2H, CH_2O, ^{3}J=5.67 and ^{4}J=1.47 Hz), 5.21 d.d.t (1H, H_2C=, J^{cis} =10.37, ^{2}J=4^J 1.57 Hz), 5.32 d.d.t (1H, H2C=, J^{trans} =17.31 and ^{2}J=4^J 1.66 Hz), 5.92 d.d.t (1H, CH=, J^{cis}=10.37, ^{2}J=^{4}J 1.57 and J^{trans} 17.31 Hz), 7.22-7.45 m (5H, Ph), 7.42-7.48 m (5H, Ph).

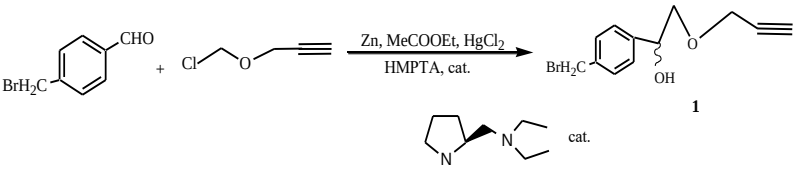
(±)1-Chloromethyl-2-phenyl-3-[(prop-2-yn-1-yl)oxy]propan-2-ol (5). Yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 2.51 t (1H, ≡CH, ^{4}J=2.4 Hz), 3.05 d (1H, CH, J 15.9 Hz), 3.17 d (1H, CH, J 15.9 Hz), 3.43 s (3H, CH_3O), 3.69 d (1H, CH, J 10.5 Hz), 3.77 d (1H, CH, J 10.5 Hz), 3.83 d.d (1H, ≡CCH2O, ^{2}J 16.2 Hz, ^{4}J=2.4 Hz), 4.05 d.d (1H, ≡CCH_2O, ^{2}J 16.2, ^{4}J 2.4 Hz), 7.28-7.51 m (5H, Ph), 7.38-7.42 m (5H, Ph)

(±)1-Chloromethyl-2-phenyl-3-[(prop-2-en-1-yl)oxy]propan-2-ol (6). Yellow oily substance ^{1}H NMR spectrum, δ, ppm: 3.05 d (1H, CH, J 15.9 Hz), 3.17 d (1H, CH, J 15.9 Hz), 3.43 s (3H, CH_3O), 3.69 d (1H, CH, J 10.5 Hz), 3.77 d (1H, J 10.5 Hz), 4.00 d.d. (2H, CH_2O, 3J 5.67 and ^{4}J 1.47 Hz), 5.17 d.d.t (1H, H_2C=, J^{cis} =

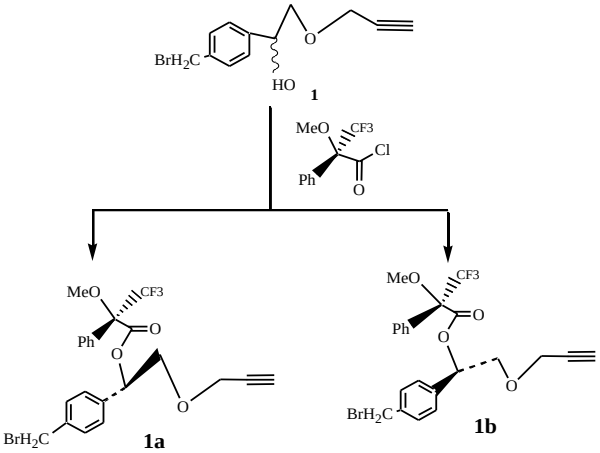
10.37, $^{2}J=^{4}J$ 1.57 Hz), 5.26 d.d.t (1H, $H_2C=$, J^{trans} =17.31 and $^{2}J=^{4}J$ 1.66 Hz), 5.89 d.d.t (1H, CH=, J^{cis}=10.37, $^{2}J=4^{J}$ 1.57 and J^{trans} 17.31 Hz), 7.28-7.51 m (5H, Ph), 7.38-7.42 m (5H, Ph).

2.3 Determination of the absolute configuration of o α-glycols monoethers of unsaturated C_3-alcohols

The implementation of the synthesis of oxyesters in a stereoselective form contributes to the increase of the practical aspect of this process. The use of chiral ligands leads to the enantioselective synthesis of optically active propargyl oxyester. When using the optically active catalyst N-ethyl-N-{[(2S)-pyrrolidin-2-yl]methyl}ethanamine, the reaction occurs according to the scheme below.



In order to determine the absolute configuration, compound **(1)** was subjected to interaction with a chiral derivatizing reagent (CDR) - α-methoxytrifluoromethylphenylacetic acid chloride (MTPA-Cl, Mosher reagent), converting it according to the following scheme into the corresponding diastereoisomers **(1a, 1b)**.



General procedure for the synthesis of MTPA esters (1a, 1b). $C_{21}H_{20}BrO_3$. To a mixture of 4.1 g (17 mmol) of unsaturated alcohol **(1)** in thoroughly dried pyridine (2.5 ml, 31 mmol) and CH_2Cl_2 (20 ml), MTPA-Cl (3.2 g, 16 mmol) was slowly added dropwise at 0ºC in a nitrogen environment and the resulting mixture was thoroughly stirred for 5 h at room temperature. Excess pyridine formed after evaporation of the solvents was removed azeotropically with dry toluene (20 ml×2) to give the crude product. The two diastereomeric esters were separated by column chromatography on silica gel + CH_2Cl_2, yielding the (S)-MTPA ester from **(1a)** (1.7 g, 44%), selectivity 81.3% and the (R)-MTPA ester from **(1b)** (2.0 g, 53%), selectivity 87.8%.

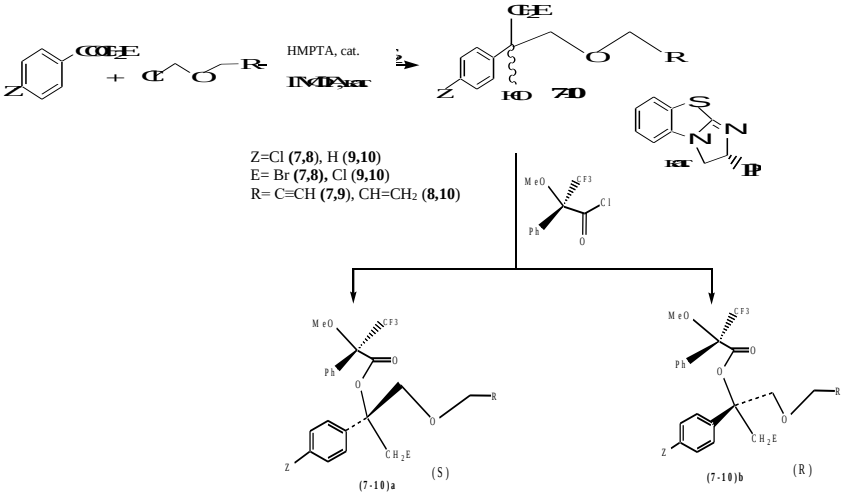
(1R)-1-[4-(Bromomethyl)phenyl]-2-[(prop-2-yn-1-yl)oxy]ethyl (4S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanate (1a). $C_{21}H_{20}BrO_3$. The resulting product is an oily liquid with [α]D=+32.75 (c 2.00, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3603 (O–H), 3287, 3085, 3065, 3030, 2110 (C≡C), 1600, 1490, 1100 (C–O–C), 985, 770 (Ph), 700. NMR spectrum 1H, δ, ppm: 2.51 t (1H, ≡CH, ^{4}J 2.4 Hz), 3.00 d.d (1H, CH_2O, J=16.5, 7.8 Hz), 3.15 d (1H, J=16.5, 7.8 Hz), 3.43 s (3H, CH_3O), 3.83 d.d (1H, ≡CH_2O, 2J 16.2 Hz, ^{4}J 2.4 Hz), 4.05 d.d (1H, ≡CCH_2O, ^{2}J 16.2 Hz, ^{4}J 2.4 Hz), 4.13 d.d (1H, CHO, ^{2}J 5.7, 7.8 Hz), 4.52 d (1H, CH_2Br, J=10.5 Hz), 4.61 d. (1H, CH_2Br, J=10.5 Hz), 7.03 d.d (2H, J=1.5, 8.7 Hz), 7.38-7.42 (5H, Ph), 7.49 d.d (2H, J=1.5, 8.6 Hz).

(1R)-1-[4-(Bromomethyl)phenyl]-2-[(prop-2-yn-1-yl)oxy]ethyl (4R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanate (1b). $C_{21}H_{20}BrO_3$. Oily liquid [a]D=-14.0 (c 2.26, $CHCl_3$); IR spectrum, ν, cm^{-1}: 3603 (O-H), 3287, 3085, 3065, 3030, 2110 (C≡C), 1600, 1490, 1100 (C–O–C), 985, 770 (Ph), 700. NMR spectrum 1H, δ, ppm: 2.55 t (1H, ≡CH, ^{4}J 2.4 Hz), 3.08 d.d (1H, CH_2O, J=16.5, 7.8 Hz), 3.22 d (1H, J=16.5, 7.8 Hz), 3.89 s (3H, CH_3O), 4.08 d.d (1H, ≡CH_2O, ^{2}J 16.2 Hz, ^{4}J 2.4 Hz), 4.19 d.d (1H, ≡CCH_2O, ^{2}J 16.2 Hz, ^{4}J 2.4 Hz), 4.18 d.d (1H, CHO, ^{2}J 5.7, 7.8 Hz), 4.48 d (1H, CH_2Br, J=10.5 Hz), 4.55 d.

(1H, CH_2Br, J=10.5 Hz), 6.97 d.d (2H, J=1.5, 8.7 Hz), 7.34-7.37 (5H, Ph), 7.42 d.d (2H, J=1.5, 8.6 Hz).

2.4 Determination of the absolute configuration of α-glycols monoesters of unsaturated C_3-alcohols by ^{1}H NMR spectroscopy

Diastomeric monoesters of α-glycols of unsaturated C_3-alcohols (7-10 S/R) were obtained by esterification of α-trifluoromethylphenylacetic acid chloride (MTPA-Cl) with alcohols.



Then the configuration was determined using 1H NMR spectroscopic differentiation data (ΔδR/S) of diastereomers **(7-10) a** and **(7-10) b.** The signals of the protons of the propargyl(allyl)oxymethyl group are shifted to low fields, and the signals of the protons of the phenyl group are shifted to the high field region. No significant shift of the halogen methylene protons at 3.69 d (1H, J = 10.5 Hz), 3.77 d (1H, J = 10.5 Hz) is observed.

The physicochemical properties of the obtained esters are given in table 3.

Table 3.

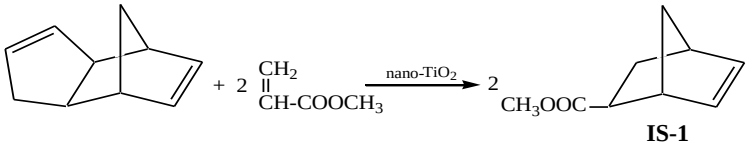
Qualitative characteristics of UMEG esters

Compaund	Boiling point 1,33· 10^{-4} MPa, °C	Yield, %	ρ_4^{20}	n_D^{20}	Saponification number, mq KOH/q		Freezing T-ru, ° C	Flash point T-ru, °C	Volatility, %
					Founded	Calculated			
7(a,b) (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-yn-1-yl)oxy] propan-2-yl (5(S,R) -3,3,3-trifluoro-2-methoxy-2-phenylpropanate (S,R)	250-262	44,1; 52,1	0,9030; 0.9044	1,4570; 1.4586	174,2 172,1	170,5; 172,7	-30; -28	220; 225	0,65; 0,70
8(a,b) (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-en-1-yl)oxy] propan-2-yl (5(S,R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanate (S,R)	264-270	46,6; 53,3	0,9012; 0.9020	1,4564; 1,4655	160,0 162,1	163,6; 166,5	-26; -24	225; 232	0,51; 0,52
9(a,b) (2R)-1-Chloromethyl-2-phenyl-3-[(prop-2-yn-1-yl)oxy]propan-2-yl (5(S,R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanate (S,R)	272-285	43.7; 53,4	0,9008; 0.9010	1,4552; 1,4553	152,1 155.1	157,1; 158,1	-22; -21	233; 234	0,48; 0,47
10(a,b) (2R)-1-Chloromethyl-2-phenyl-3-[(prop-2-en-1-yl)oxy]propan-2-yl (5(S,R))-3,3,3-trifluoro-2-methoxy-2-phenylpropanate (S,R)	292-300	45,1; 52,2	0,8955; 0.8961	1,4544; 1,4553	149,3 148,4	151,2; 153,5	-17; -18	237; 243	0,46; 0,45

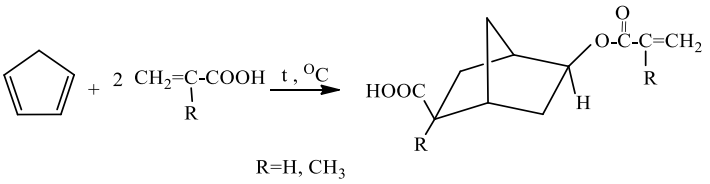
2.5 Synthesis of 5-methoxycarbonylnorborn-2-ene (IS-1); 5-carboxylnorborn-2-yl acrylate (IS-2); 5-acetoxymethylnorborn-2-ene (IS-3); norbornenemethanol (IS-4), and allyl esters of natural petroleum acids (AENPA)

The synthesis of the above-listed additives to diesel fuels was

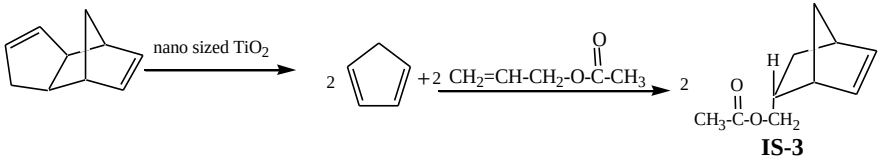
carried out using known methods according to the following reactions:



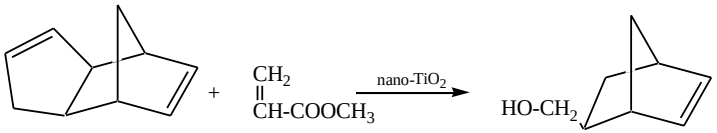
IS-1



IS-2



IS-3



IS -4

$$R\text{-}COOH + CH_2{=}CH\text{-}CH_2\text{-}OH \rightarrow R\text{-}COO\text{-}CH_2\text{-}CH{=}CH_2 + H_2O$$

AENPA

The study of the purity of the synthesized compounds was carried out using ^{1}H-NMR spectroscopy (Figs. 4-8).

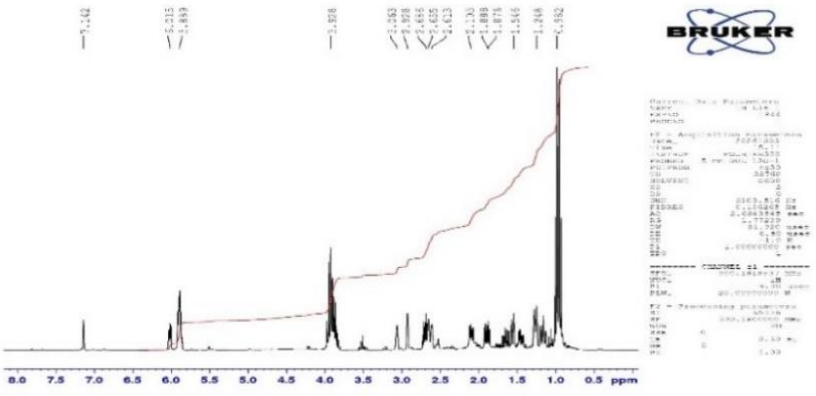


Figure 4. ^{1}H-NMR spectrum of IS-1

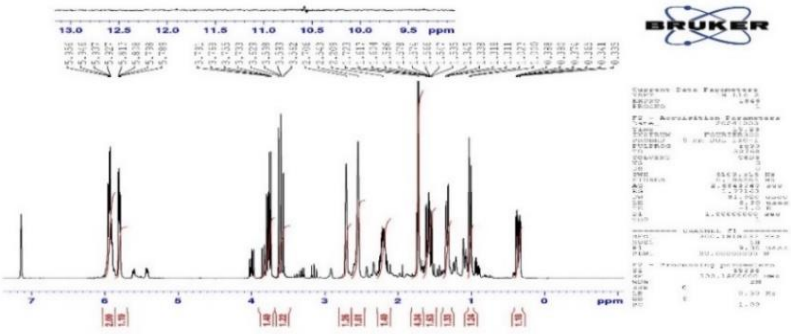


Figure 5. ^{1}H-NMR spectrum of IS-2

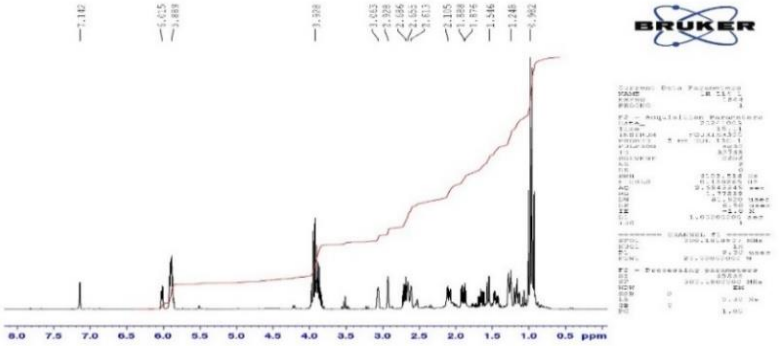


Figure 6. ^{1}H-NMR spectrum of IS-3

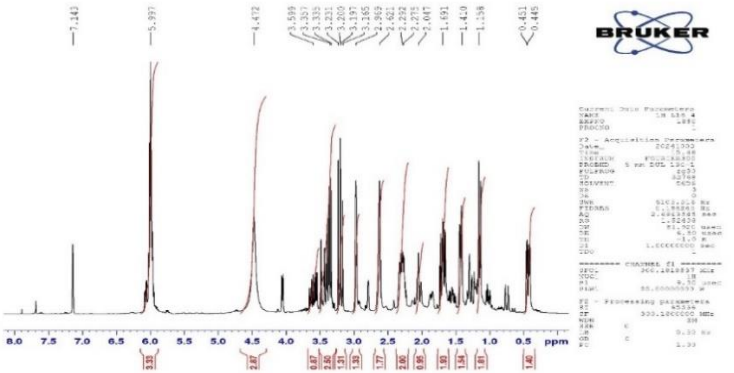


Figure 7. ^{1}H-NMR spectrum of IS-4

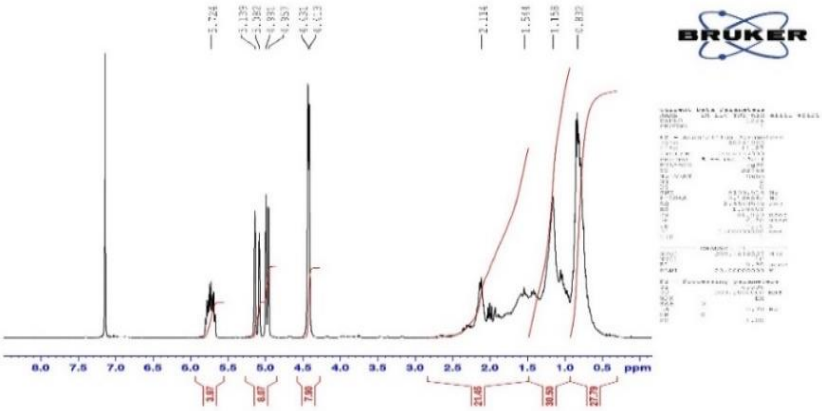


Figure 8. ^{1}H-NMR spectrum of AENPA

Summary material balance of the process for obtaining 5-methoxycarbonylnorborne-2-ene.

Stage I – Interaction of DCPD with MAK

Taken:	Mass, g	Mass, %
Dicyclopentadiene (0.1 mol)	13.2	43.4
Methyl acrylate (0.2 mol)	17.2	56.6
Total: 30.4	100.0	

Received:	Mass, g	Mass, %
Reaction products	29.8	98.0
Losses	0.6	2.0
Total: 30.4	100.0	

Stage II – Rectification

Taken:	Mass, g	Mass, %
Reaction products	29.8	100.0
Total: 29.8	100.0	

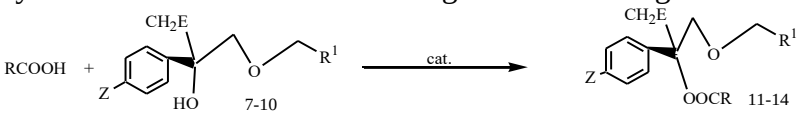
Received:	Mass, g	Mass, %
DCPD return	1.2	4.0
MAK return	3.5	11.7
Target product	21.7	76.2
Unidentified products	1.1	3.7
Residue	0.6	2.1
Losses	0.7	2.3
Total:	**29.8**	**100.0**

As can be seen from the material balance of the process for obtaining 5-methoxycarbonylnorborne-2-ene, 22.7 g of the target product is obtained, the yield is 74.6% for the taken DCPD, and the selectivity for the target product is 93.0%. Conversion for DCPD is 90.9%. Conversion for MAK is 79.7%.

3. Synthesis of esters based on unsaturated monoesters of glycols with natural petroleum acids in the presence of an ionic-liquid catalyst.

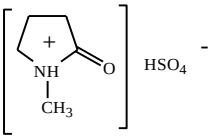
3.1. Synthesis of esters based on UMEG with NPA.

Synthesis was carried out according to the following scheme:



Z= Cl (**11,12**), H (**13,14**)
E=Br (**11,12**), Cl (**13,14**)
R^1= C≡CH (**11,13**), $CH=CH_2$ (**12,14**)

R - naphthenic radical C_5H_{11}-

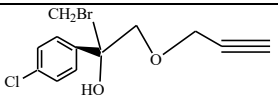
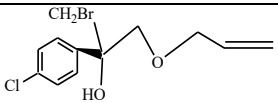


The corresponding quantities of UMEG (see tab. 4) and NPA acid chlorides were taken in molar ratios of 1:1, and benzene (100 ml) was also added as a solvent. The temperature was maintained at 70-75°C, and the stirring duration was 20-25 min.

The physicochemical parameters of the esters obtained on the basis of UMEG and NPA are given in Table 4.

Table 4.

Esters based on UMEG and NPA

№	quantity NPA(g)	quantity of UMEG (g)	Output,%
1	2	3	4
1	RCOOH 42,4	 36,2	87
2	RCOOH 42,4	 31,7	86

Continue

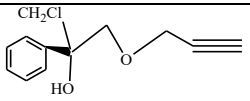
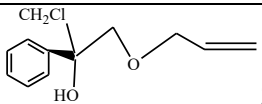
1	2	3	4
3	RCOOH 42,4	 24,1	69
4	RCOOH 42,4	 28,1	65

Table 5

Physicochemical properties of esters obtained based on UMEG and NPA

Esters obtained from UMEG and naphthenic acids	Boiling point, °C/kPa	Yield per fraction, % (mass.)	ρ_4^{20}, kg/m^3	n_D^{20}	Saponification number, mg KOH/g		Acid number, mg KOH/g
					Practical	Theoretical	
11	255-332/0,7	87,0	960,2	1,4794	297,2	305,1	0,75
12	220-300/0,61	76,2	1035,1	1,4928	201,1	205,11	0,72
13	202-270/0,5	72,8	958,7	1,4700	277,6	279,3	0,63
14	195-307/0,61	73,0	1031,2	1,4983	268,8	267,8	0,84

Physicochemical properties of esters obtained based on UMEG and NPA were given in the table 5 and 6.

Complex ether obtained on the basis of naphthenic acid and (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-in-1-yl)oxy]propan-2-ol (11). Spectrum NMR ^{1}H, δ, ppm: 0.87-1.39 m (n CH_3, nCH_2), 1.48-2.1 (cyclo-nCH_2), 2.31 m(nCH_2COO), 2.51 t (1H, ≡CH, ^{4}J 2.4 Hs), 3.03 d (1H, CH, J 16.2 Hs), 3.18 d (1H, CH, J 16.2 Hs), 3.57 d (1H, CH, J 10.8 Hs), 3.64 d (1H,CH, J 10.8 Hs), 3.83 d.d (1H, ≡CCH_2O, ^{2}J 16.2 Hs, ^{4}J 2.4 Hs), 4.05 d.d (1H, ≡CCH_2O, ^{2}J 16.2 Hs, ^{4}J 2.4 Hs), 7.03 d.d (2H, J 1.5, 8.7 Hs), 7.49 d.d (2H, J 1.5, 8.6 Hs).

Table 6.

Physicochemical parameters of esters of NMEG and NPA

Esters of UMEG and NPA	Boiling point, °C/kPa	Yield per fraction, % mass.	ρ_4^{20} kg/m^3	n_D^{20}	Boiling point, °C/kPa		Yield per fraction, % (mass.)
					Pract.	Theor	
15(a) (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-in-1-il)oksi]propan-2-il(5S)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (S)-7	249-332/0,8	84,0	955,4	1,4881	295,5	308,0	0,70
15(b) (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-in-1-il)oksi]propan-2-il(5R)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (R)-7	221-285/0,53	73,2	928,4	1,4610	290,5	296,06	0,60
16(a) (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-en-1-il)oksi]propan-2-il(5S)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (S)-8	230-296/0,53	76,0	1031,0	1,4521	200,0	208,64	0,70
16(b) (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-en-1-il)oksi]propan-2-il(5R)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (R)-8	199-264/0,4	69,5	955,4	1,4494	275,0	284,8	0,60
17(a) (2R)-1-Chloromethyl-2-(4-phenyl)-3-[(prop-2-in-1-il)oksi]propan-2-il(5S)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (S)-9	195-299/0,53	71,0	1031,0	1,4823	270,5	265,52	0,80
17(b) (2R)-1-Chloromethyl-2-(4-phenyl)-3-[(prop-2-in-1-il)oksi]propan-2-il(5R)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (R)-9	221-290/0,53	73,5	1017,0	1,4820	275,0	281,6	0,70
18(a) (2R)-1-Chloromethyl-2-(4-phenyl)-3-[(prop-2-en-1-il)oksi]propan-2-il(5S)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (S)-10	190-280/0,8	70,8	998,5	1,4769	267,5	284,3	0,75
18(b) (2R)-1-Chloromethyl-2-(4-phenyl)-3-[(prop-2-en-1-il)oksi]propan-2-il(5R)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (R)-10	200-300/0,53	74,0	970,6	1,4860	256,5	262,15	0,80

Complex ether obtained on the basis of naphthenic acid and (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-en-1-yl)oxy]propan-2-ol (12). Spectrum NMR ^{1}H, δ, m.h.: 0.87-1.40 m (n CH_3, nCH_2), 1.48-2.1 (cyclo-nCH_2), 2.31 m (nCH_2COO), 3.03 d (1H, CH, J 16.1 Hs), 3.18 d (1H, CH, J 16.1 Hs), 3.57 d (1H, CH, J 10.8 Hs), 3.63 d (1H, CH, J 10.8 Hs), 4.01 d.d (2H, CH_2O, ^{3}J 5.67 и ^{4}J 1.47 Hs), 5.16 d.d.т (1H, H_2C=, J^{sis} 10.37, ^{2}J=^{4}J 1.57 Hs), 5.25 d.d.d (1H, H_2C=, J^{trans}=17.31 и ^{2}J=^{4}J=1.66 Hs), 5.88 d.d.t (1H, CH=, J^{sis} 10.37, ^{2}J=^{4}J =1.57 и J^{trans}=17.31 Hs), 7.02 d.d (2H, J 1.5, J 8.7 Hs), 7.48 d.d (2H, J 1.5, 8.6 Hs).

Complex ether obtained on the basis of naphthenic acid and (2R)-1-Chloromethyl-2-phenyl)-3-[(prop-2-in-1-yl)oxy]propan-2-ol (13). Spectrum NMR ^{1}H, δ, m.h.: 0.87-1.39 m (n CH_3, nCH_2), 1.48-2.1 (cyclo-nCH_2), 2.31 m (nCH_2COO), 2.51 t (1H, ≡CH, ^{4}J=2.4 Hs), 3.06 d (1H, CH, J 15.9 Hs), 3.16 d (1H, CH, J 15.9 Hs), 3.69 d (1H, CH, J 10.5 Hs), 3.77 d (1H, CH, J 10.5 Hs), 3.83 d.d (1H, ≡CCH_2O, ^{2}J 16.2 Hs, ^{4}J=2.4 Hs), 4.05 d.d (1H, ≡CCH_2O, ^{2}J 16.2 , ^{4}J 2.4 Hs), 7.38-7.42 m (5H, Ph).

Complex ether obtained on the basis of naphthenic acid and (2R)-1-Chloromethyl-2-phenyl)-3-[(prop-2-en-1-yl)oxy]propan-2-ol (14). Spectrum NMR ^{1}H, δ, m.h.: 0.85-1.37 m (n CH_3, nCH_2), 1.48-2.1 (cyclo-nCH_2), 2.31 m (nCH_2COO), 3.05 d (1H, CH, J 15.9 Hs), 3.17 d (1H, CH, J 15.9 Hs), 3.68 d (1H, CH, J 10.5 Hs), 3.77 d (1H, J 10.5 Hs), 4.00 d.d (2H, CH_2O, ^{3}J 5.67 и ^{4}J 1.47 Hs), 5.17 d.d.т (1H, H_2C=, J^{sis} =10.37, ^{2}J=^{4}J 1.57 Hs), 5.25 d.d.d (1H, H_2C=, J^{trans} =17.31 и ^{2}J=^{4}J 1.66 Hs), 5.89 d.d.t (1H, CH=, J^{sis}=10.37, ^{2}J=^{4}J 1.57 и J^{trans}17.31 Hs), 7.37-7.41 m (5H, Ph).

4. Study and practical application of esters of petroleum acids and unsaturated chiral oxyesters, as well as compounds “IS-1”-“IS-4” and AENPA

4.1 Use of esters derived from natural petroleum acids and unsaturated chiral oxyesters as additives to diesel fuels

The obtained esters were tested as antioxidants to diesel fuel (Table 7,8).

Table 7

Results of tests of ethers obtained from UCHOE (11-14) as antioxidants

Compounds	HTDF	HTDF + Naphtenat **QDME (11-14)**, 0,004%			
		11 (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-in-1-il)oksi]propan-2-ol	12 (2R)-1-Bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-en-1-il)oksi]propan-2-ol	13 (2R)-1-Chloro-2-phenyl 3-[(prop-2-en-1-il)oksi]propan-2-ol	14 (2R)-1-Chloro-2-phenyl 3-[(prop-2-in-1-il)oksi]propan-2-ol
Thermal-oxidative stability, sediment amount, mg/100 ml of fuel	6,5	2,3	2,2	2,1	2
Temperature, °C:					
cloud point	-9	-10	-12	-14	-16
setting point	-20	-21	-22	-23	-25

As can be seen from the presented results, these esters exhibit good antioxidant properties and can also be recommended as depressants for diesel fuels, since they provide a decrease in the amount of sediment by 3-5 times and a decrease in the freezing temperature by 6-7°C.

Table 8

Results of tests of ethers obtained from UCHOE (15-18)(a,b) antioxidants in diesel fuel

Compounds	Thermal-oxidative stability, sediment amount, mg/100 ml of fuel			Temperature, °C:					
				cloud point			setting point		
HTDF	**6,5**			**-9**			**-20**		
HTDF+ NPA- 15-18(a,b) based esters	0,001	0,004	0,006	0,001	0,004	0,006	0,001	0,004	0,006
15(a) (2R)-1-Brommethyl-2-(4-chlorophenyl)-3-[(prop-2-in-1-il)oksi]propan-2-il(5S)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (S)-7	2.2	1.8	**1.3**	-10	-11	-15	-21	-22	**-25**
15(b) (2R)-1-Brommethyl-2-(4-chlorophenyl)-3-[(prop-2-in-1-il)oksi]propan-2-il(5R)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (R)-7	2.3	1.6	**1.4**	-11	-12	-14	-22	-23	**-24**
16(a) (2R)-1-Brommethyl-2-(4-chlorophenyl)-3-[(prop-2-en-1-il)oksi]propan-2-il(5S)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (S)-8	2.6	1.9	**1.5**	-11	-12	-13	-21	-22	-23
16(b) (2R)-1-Brommethyl-2-(4-chlorophenyl)-3-[(prop-2-en-1-il)oksi]propan-2-il(5R)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (R)-8	2.7	1.7	**1.6**	-10	-11	-14	-22	-24	-25
17(a) (2R)-1-Chloromethyl-2-(4-phenyl)-3-[(prop-2-in-1-il)oksi]propan-2-il(5S)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (S)-9	2.0	1.4	**1.1**	-12	-13	**-17**	-23	-25	**-27**
17(b) (2R)-1-Chloromethyl-2-(4-phenyl)-3-[(prop-2-in-1-il)oksi]propan-2-il(5R)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (R)-9	2.1	1.5	**1.3**	-11	-12	-13	-22	-23	-26
18(a) (2R)-1-Chloromethyl-2-(4-phenyl)-3-[(prop-2-en-1-il)oksi]propan-2-il(5S)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (S)-10	2.3	1.6	**1.2**	-10	-11	-15	-21	-24	-26
18(b) (2R)-1-Chloromethyl-2-(4-phenyl)-3-[(prop-2-en-1-il)oksi]propan-2-il(5R)-3,3,3-trifloro-2-metoksi-2-phenylpropanat (R)-10	2.4	1.7	**1.4**	-11	-12	-14	-21	-23	-24

At the next stage of the conducted research, the synthesized compounds IS-1-IS-4 and allyl ethers of NPA were added to diesel fuel in the amount of 1-3% % mass. The obtained results allow us to recommend them as depressant additives to diesel fuels (Table 9).

Table 9

Physicochemical properties of DF compounds with IS-1-IS-4 and allyl ethers of NPA

Indicators	Names of devices	Method Compounds	Compounds				
			Initial diesel fuel (DF)	DF +1% IS-1	DF +1% IS -2	DF +1% IS -3	DF +1% IS -4
Density, g/cm3 20°C	DMA 4500 M	ASTM D5002	0.8192	0.8192	0.8210	0.8224	0,8219
Iodine number, Jq/lOOq	methodology	GOST 2070-82	0.07	0.11	0.17	0.18	0,12
Refractive index, 20°C	Abbemat500	methodology	1.4689	1.4687	1.4687	1.4685	1,6914
Setting point ,°C	methodology	GOST 20287-91	-40	-42	-42	-42	-42
Acid number	methodology ASTM		0	0	0	5.26	0
Ignition temperature°C	methodology ГОСТ4333-87		+65	+68	+68	+68	+69

Also, compounds IS-1 – IS-4 were tested as antioxidants to the studied diesel fuel in the amount of 0.004% by weight. The results are presented in Table 10.

Table 10

Results of testing compounds IS-1-IS-4 as antioxidant additives to diesel fuels

	Initial diesel fuel	DF+0,004% mass.			
		IS-1	IS -2	IS -3	IS -4
Thermal-oxidative stability, amount of sediment, mg/100 ml of fuel	2,0	0	0	0	0,5

As can be seen from the results obtained, the studied compounds IS-1- IS-4 provide excellent thermal-oxidative stability of the obtained compounds.

5. Study of biological activity of esters obtained on the basis of natural petroleum acids and racemic, as well as optically active unsaturated monoesters of glycols

The biological activity of the compounds we obtained 11-14 was studied using the dispersion contact method (Table 11).

As can be seen from the presented data, 1-bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-yn-1-yl)oxy]propan-2-ol has lower antimicrobial activity compared to its analogue (2R)-1-bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-yn-1-yl)oxy]propan-2-ol. This is clearly observed in relation to *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

The results of the studies allow us to conclude that the compounds we tested are most active against *Pseudomonas aeruginosa* and *Candida* yeast-like fungi. For example, the ester synthesized from NPA and (2R)-1-bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-yn-1-yl)oxy]propan-2-ol can be said to destroy *Pseudomonas aeruginosa* strains by 100% even at high dilution.

The following diagrams show comparative characteristics of the antibacterial properties of 1-bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-yn-1-yl)oxy]propan-2-yl naphthenate in racemic (1) and chiral (2) forms and ethanol (3) against various microorganisms (fig.9-12):

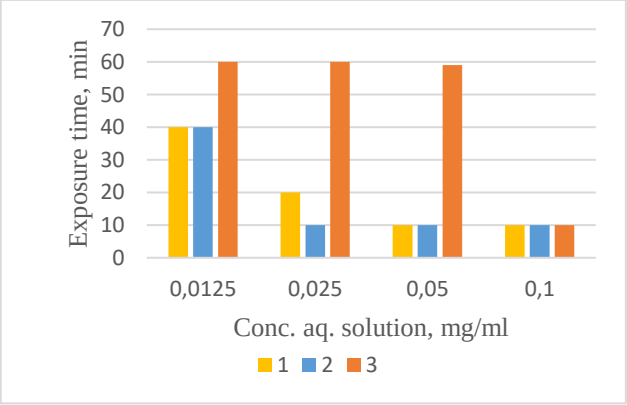
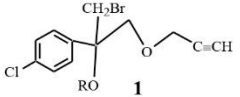
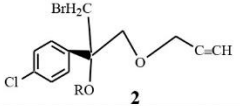
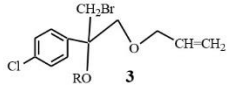
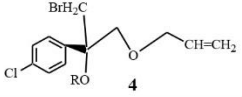


Figure 9. *Staphylococcus aureus*.

Table 11

Comparison of antimicrobial properties of esters obtained from naphthenic acids

Compounds	Dilution degree	Test–culture															
		Staphylococcus aureus				Escherichia coli				Pseudomonas aeruginosa				Fungi Candida			
		Exposure time, min				Exposure time, min				Exposure time, min				Exposure time, min			
		10	20	40	60	10	20	40	60	10	20	40	60	10	20	40	60
 **1**	1:100	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1:200	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1:400	+	–	–	–	+	–	–	–	–	–	–	–	+	–	–	–
	1:800	+	+	–	–	+	+	–	–	–	–	–	–	+	+	–	–
 **2**	1:100	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1:200	+	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1:400	+	+	–	–	+	–	–	–	–	+	–	–	+	–	–	–
	1:800	+	+	–	–	+	+	–	–	–	+	+	+	+	+	–	–
 **3**	1:100	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1:200	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1:400	+	+	–	–	–	+	–	–	+	–	–	–	+	–	–	–
	1:800	+	+	–	–	–	+	–	–	+	+	–	–	+	+	–	–
 **4**	1:100	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1:200	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1:400	+	+	–	–	+	–	–	–	+		–	–	–	–	–	–
	1:800	+	+	–	–	+	+	–	–	+	+	–	–	+	–	–	–

This compound, synthesized by us during the studies, at dilutions of 1:100 and 1:200 has a destructive effect on *Pseudomonas aeruginosa* in just 10 minutes, and at dilutions of 1:400 and 1:800, it takes longer, namely 20 and 40 minutes.

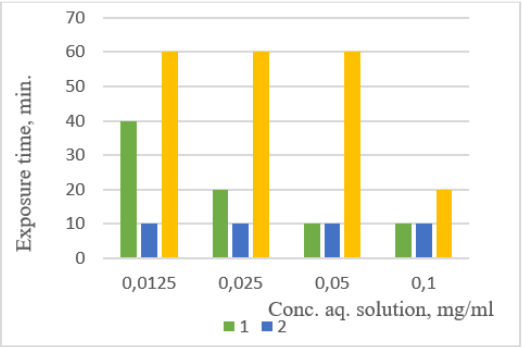


Figure 10. ***Escherichia coli***

Almost the same effect is observed for the complex ester synthesized by the esterification reaction from NPA and 1-bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-yn-1-yl)oxy]propan-2-ol, and this compound causes an antibacterial and antifungal effect also in relation to other pathogenic microorganisms tested, in particular *E. coli* and *Candida* fungi, however, this compound exhibits the greatest effect on *Pseudomonas aeruginosa*, practically ensuring the destruction of this microorganism.

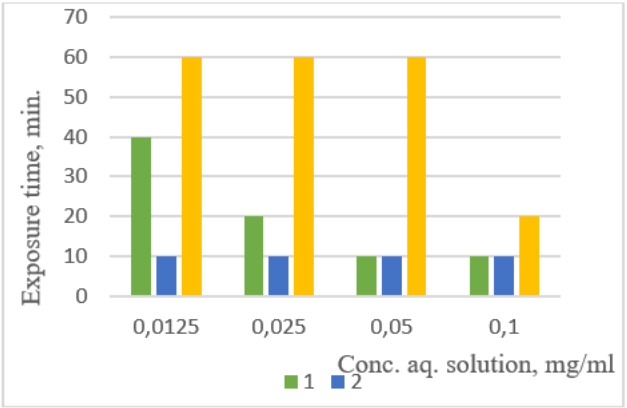


Figure 11. ***Pseudomonas aeruginosa***

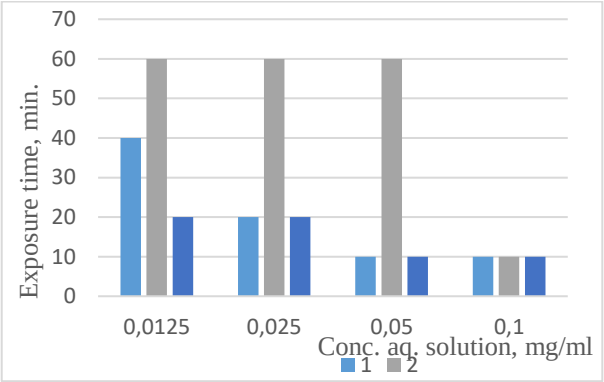
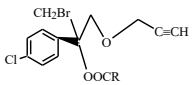


Figure 12. yeast-like fungi of the genus Candida

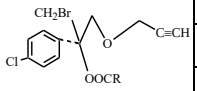
The effectiveness of the antimicrobial action of the studied compounds was determined by the diameter of the zone of inhibition of microorganism growth (Table 12).

Table 12

Efficiency of antimicrobial action of the studied compounds

Compounds	Concentration, %	Zone of inhibition of microorganism growth, cm				
		Synthetic oil (diester of succinic acid)	Oil T-22		Fuel (Gasoline-95)	
		Bacteria (*Pseudomona aeruginosa, Mycobacterium phlei*)	Bacteria (*Pseudomonas aeruginosa, Mycobacterium phlei*)	Fungi (*Aspergillus niger, Penicillium chryso-genum*)	Bacteria (*Pseudomonas aeruginosa, Mycobacterium phlei*)	Fungi (*Cladosporium resinae*)
1	2	3	4	5	6	7
	1,0	2,5-3,0	2,4-2,8	+++	—	—
	0,5	1,0-1,2	1,0-1,0	+++	1,6-1,8	+++
	0,25	+++	+++	+++	1,2-1,2	+++

Continue

1	2	3	4	5	6	7
	1,0	2,1-3,0	2,2-2,9	+++	—	—
	0,5	1,0-1,0	+++	+++	1,5-1,6	+++
	0,25	+++	+++	+++	1,1-1,2	+++
Standard (sodium pentachlorophenolate)	1,0	1,3-1,4	1,3-1,4	1,4-1,6	—	—
Control	0	+++	+++	+++	+++	-

As can be seen from the data in Table 12, the synthesized compounds have antimicrobial activity. Moreover, at a concentration of 1.0% in the synthetic oil (diester of succinic acid), these compounds showed high bactericidal properties (2.5-3.0 cm), which is significantly greater than that of the standard.

Compounds in T-22 oil, along with bactericidal properties, also showed fungicidal properties (1.4-1.6 cm), and in fuel they acted only on bacteria (1.6-1.8 cm).

CONCLUSIONS

1. The enantioselective synthesis of unsaturated β-hydroxy esters was carried out for the first time with an acceptable yield 74.3 - 78.1% and selectivity 91.7-93.4% in the interaction of chloromethyl propargyl ether, 4-bromomethylbenzaldehyde in the presence of metallic zinc and a chiral auxiliary substance - N-ethyl-N-{[(2S)-pyrrolidin-2-yl]methyl}ethanamine [5,9].
2. The absolute configuration of the esters (diasteromers) that were obtained by reacting the synthesized β-hydroxy esters with a chiral derivatizing agent (CDA) - α-trifluoromethyl-phenylacetic acid chloride (MTPA-Cl, Mosher reagent) was determined. (S)-MTBA - 44%, (R)-MTBA - 53%, selectivity of 81.3-87.8% % [3,4].
3. Esters of petroleum acids on the basis of UMEG and NPA were

synthesized by esterification (as well as by the Mitsunobu reaction) with a yield of 67.5%, selectivity of 93.1-95.5% for the target product [2,5].

4. It was revealed that esters of petroleum acids obtained on the basis of UMEG can be used as antioxidants and depressants for diesel fuels when added to the composition of the latter in an amount of 0.001-0.006% by weight. In this case, the best results are achieved when adding to the composition of diesel fuel an ester of NPA based on (2R)-1-Chloromethyl-2-phenyl-3-[(prop-2-yn-1-yl)oxy]propan-2-yl (5S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanate (S)-9, which leads to a decrease in freezing temperature by 7°C, while the amount of sediment decreases by 5 times [5,13].
5. It was revealed that an optically active ester synthesized on the basis of NPA and UMEG, in particular (2R)-1-bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-en-1-yl)oxy]propan-2-ol, inhibits the growth of *Pseudomonas aeruginosa* and yeast-like fungi *Candida* by 98% even at the maximum dilution (0.0125 mg/ml, 1:800) [6,7,11].
6. High bactericidal properties (2.5 – 3.0 cm) of the synthesized compounds of the optically active form of UMEG, (2R)-1-bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-yn-1-yl)oxy]propan-2-ol, as well as its racemic analogue 1-bromomethyl-2-(4-chlorophenyl)-3-[(prop-2-yn-1-yl)oxy]propan-2-ol at a concentration of 1% in synthetic and base oil in comparison with the standard were determined. This study is clearly observed in relation to bacteria *Pseudomonas aeruginosa*, *Mycobacterium phlei* [10,12].
7. It was determined that when adding the obtained compounds "IS-1", "IS-2", "IS-3", "IS-4" to diesel fuel in an amount of 1-3% by weight, the flash point of compounds increase by 3-4°C. The possibility of using the synthesized compounds "IS-1", "IS-2", "IS-3", "IS-4" as antioxidant additives to diesel fuels was revealed. It was shown that their addition to diesel fuel in the amount of 0.004% by weight leads to a decrease in the amount of sediment from 2.0% by weight to 0% by weight.

8. It was revealed that the addition of 1-3% by weight of allyl esters of natural petroleum acids to diesel fuel leads to a decrease in the freezing temperature of the obtained compounds by 2^0C, while their flash point increases by 3-4^0C, in connection with which allyl esters of natural petroleum acids can be recommended as dispersing additives to diesel fuels [14].

The main content of the dissertation work has been published in the following scientific papers:

1. Talybov, G.M., Bagirli, A.N., Study of the reaction of 1-(1-bromomethoxy)-4(bromomethyl)benzene with chloromethyl Csp-phenyl-substituted propargyl ether in diglyme medium // Proceedings of the II Scientific Conference "Dynamic Processes in the Chemistry of Organoelement Compounds" dedicated to the 75th anniversary of the A.E. Arbuzov Institute of Organic Physical Chemistry and the Kazan Scientific Center of the Russian Academy of Sciences. - Kazan: - November 11-13, -2020, -p.169.
2. Bagirli, A.N., Mamedkhanova, S.A., Talybov, G.M. Synthesis of ethers based on chloranhydride of low molecular petroleum acids of Baki oils of marine fields and chiral alcohols // International Conference on “Actual problems of chemical engineering”, - Bakı: – 2020, – p. 122.
3. Talybov, G.M. Synthesis and determination of the absolute configuration of monoethers of α-glycols of allyl and propargyl alcohols by NMR ^{1}H spectroscopy / Talybov, G.M., Baghirli, A.N., Shirinova, N.A. // Ukrainian Chemistry Journal, – 2020. Vol. 86, No. 4, – p. 126–131.
4. Talybov, G.M., Baghirli, A.N. Determination of the absolute configuration of the propargyl oxyether // Russian Journal of Organic Chemistry, – 2020. Vol. 56, No. 4, – p. 628–630.
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