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ABSTRACT

of the dissertation for the degree of
Doctor of Philosophy

**THE SYNTHESIS AND THE STUDY OF GLYCERIDE
ESTERS BY COMBINATION OF GLYCEROL TO
CYCLOOLEPHINES**

Speciality: 2314.01 - Petrochemistry

Field of science: Chemistry

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The work was performed at the laboratory of “Polifunctional monomers and oligomers” of the department “Monomers, oligomers and catalysis” of the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev Azerbaijan National Academy of Sciences.

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GENERAL DESCRIPTION OF WORK

Relevance and elaboration of the topic. Glycerol esters are used in more than 2,000 fields area of industry, technology, medicine and household¹. These esters are obtained on the basis of cheap and easily obtained products of petrochemical synthesis. Various methods for the synthesis of many glycerol derivatives have been developed, and although the properties of these derivatives have been thoroughly studied, they should not be construed as a complete chemical study of glycerol. Although much research has been done on the synthesis of glycerol ethers and esters, we have found out that the synthesis of cyclic esters has not been the focus of researchers.

The synthesis of polycyclic glycerol esters, their various transformations, the study of the properties of these esters, the study of the practical application of cyclic esters containing a carboxyl group are very relevant. These points can also be applied to structures containing ether and ester fragments synthesized on the basis of mono-, bi-, tri- and tetra- cyclic monoesters of glycerol. Thus, these esters are of interest as insecticides used in agriculture against insects in plants.

One of the most important issues in petrochemistry is the selection of the optimal method of synthesis of glycerol esters, the determination of conditions, the study of the relationship between the composition and properties of certain functional groups, cyclic ring with the inclusion of esters, the study of practical applications. The subject of the dissertation is dedicated to the solution of these problems: the synthesis of mono-, bi-, tri-, tetracyclic mono-esters of glycerol and the development of a method for obtaining new structural diesters from the esterification of these esters with monobasic C₁-C₅ carbonic acids, the study of the properties of the obtained target compounds, the study of research areas of applications.

Object and subject of research. Synthesis and study of polycyclic monoesters of glycerol by combination in the presence of

¹ Pagliaro, M. *The Future of Glycerol* / M. Pagliaro, M. Rossi. – Cambridge: Royal Society Of Chemistry, -2010. -170 p.

$\text{BF}_3 \cdot \text{OEt}_2$ and by an esterification reaction in the presence of KU 2-8H^+ .

The synthesis of diesters based on these monoethers, which contain an ether and ether of glycerol, is also the subject of research.

The subject is to study the application of the obtained ethers in scientifically based fields.

The purpose and objectives of the study. The purpose of the dissertation research is to develop new suitable methods for the synthesis of new functional derivatives-diesters of polycyclic monoesters of glycerol based on cyclohexene, norbornene, dicyclopentadiene, tetracyclododene - to study the application of physical and chemical properties of these diesters. To achieve the set goal, the dissertation reflected the solution of the following specific issues:

-Synthesis and study of the properties of monocyclic glyceride monoesters of glycerol based on the reaction of glycerol with cyclohexene, its methyl, ethyl, propyl substituents in the presence of the catalyst $\text{BF}_3 \cdot \text{OEt}_2$;

-Study of the reaction of glycerol binding to norborne and its alkyl ($\text{C}_1\text{-C}_6$) derivatives in the presence of a triple fluorine boron ether complex based on the activity of double bonds in the Norbornene ring and the synthesis of bicyclic glyceride monoether;

-Study of the reaction of catalytic binding of glycerol to the double bond of dicyclopentadiene- the by-product of the C_5 fraction in the presence of a triple fluorine boron ether complex, and the synthesis of tricyclic glyceride monoester;

-Study of the reaction of glycerol binding to tetracyclododesene and its alkyl ($\text{C}_1\text{-C}_6$) derivatives in the presence of boron trifluoride ether complex ethyl ether and the production of tetracyclic glyceride monoesters;

-Study of esterification reactions of $\text{C}_1\text{-C}_5$ aprotic monobasic carbonic acids in the presence of the catalyst KU 2-8 H^+ of synthesized polycyclic monoglycerides, synthesis of polycyclic glyceride diesters containing simple and complex ether fragments.

Research methods. The results of the research on the dissertation are based on the accepted standard methods of analysis

and the study of the structure and composition of the obtained substances by IR-, NMR ^1H and ^{13}C spectroscopy, elemental analysis methods.

The main provisions for the defense. Determination of the synthesis conditions for the diethers based on different structured mono-, di-, tri-, tetracyclic simple esters of glycerol in the presence of homogeneous and heterogeneous catalysts and etherification reaction of these esters with monobasic acids.

The scientific novelty of the work. For the first time:

-Cyclohexyl-, norbornyl-, dicyclopentadienyl-, tetracyclododesenylglycerine monoethers was prepared by combining glycerol in the presence of homo- and hetero- catalysts to double π -bonds of cyclohexene, norbornene, dicyclopentadiene and tetracyclododesen hydrocarbons. It has been proved that $\text{BF}_3 \cdot \text{OEt}_2$ plays the role of an effective catalyst in the system and provides the production of mono-, bi-, tri-, tetracyclic monoesters of glycerol with a high yield.

-A method for the synthesis of polycyclic glyceride diesters based on the esterification reaction of $\text{C}_1\text{-C}_5$ monobasic carbonic acids with synthesized polycyclic glyceride monoethers has been developed and its properties have been studied. It is shown that the composition of saturated acid glycerol with polycyclic monoethers in the presence of KU 2-8 H^+ forms simple and complex ethereal fractions.

The theoretical and practical significance of the work. Synthesized bicyclic norbornylglycerine and tricyclic dicyclopentadienylglycerine monoesters are recommended for use as insecticides against pests that reduce crop yields.

Tricyclo[5.2.1.0^{2,6}]des-3-en-8-ylglyceridebutyrate ester has been studied as a plasticizing component and has been recommended as an effective plasticizer for PVC.

Personal participation of the author. The main directions and purpose of the research work were determined by the bidder by examining the literature materials, the solution of the problem has been shown to achieve the set goal, and the obtained results were discussed. The applicant was also directly involved in each stage of laboratory research, writing theses, articles and dissertations.

Accuracy of results. It is determined using modern analytical methods (NMR-, IR-, element analysis, gas-liquid chromatogram) in the performance of research.

Publications. 17 scientific works on the materials of the dissertation, including 8 articles and abstracts of reports at 9 international and national conferences were published.

Approbation. The results of the dissertation were presented and discussed at the following conferences: At the I International Conference on Chemistry and Chemical Engineering dedicated to the 90th anniversary of Heydar Aliyev (Baku, 2013), Scientific conference dedicated to the 105th anniversary of academician M.F.Nagiyev (Baku, 2013), Republican scientific-practical conference dedicated to the 100th anniversary of academician S.C.Mehdiyev (Baku 2014), III International Conference on Chemistry and Chemical Engineering dedicated to the 92nd anniversary of Heydar Aliyev (Baku, 2015), III Republican Conference on "Modern Problems of Monomers and Polymer Chemistry" (Sumgayit-2015), IX International Scientific Conference named after Y.H. Mammadaliyev (Baku, 2016), International scientific-technical conference "Petrochemical synthesis and catalysis in complex condensed systems" dedicated to the 100th anniversary of academician B.K.Zeynalov (Baku, 2017), The International Scientific conference "Actual Problems of Modern Chemistry" dedicated to the 90th Anniversary of the Academician Y.H. Mammadaliyev Institute of Petrochemical Processes (2019), XXIII International Scientific and Practical Conference "Russian Science in the Modern World" (2019), "Theses and materials of the international scientific conference" Prospects for innovative development of chemical technology and engineering "dedicated to the 70th anniversary of Sumgayit city (Sumgayit 2019).

Name of the organization where the dissertation work is performed. The dissertation work implemented in the laboratory "Polifunctional monomers and oligomers" according to the research work plan of the Institute of Petrochemical Processes named after acad. Y.H. Mammadaliyev (State registration № 0111 Az 2071).

The structure and scope of the dissertation. The dissertation

consists of 166 pages, introduction, 5 chapters, results, 243 bibliography, appendices and descriptions of abbreviations. The dissertation includes 42 tables and 25 figures. The structure of the dissertation consists of 5497, introduction 9840, first chapter 40192, second chapter 6524, third chapter 28711, fourth chapter 24329, fifth chapter 45795, results 2711, bibliography 43401, list of abbreviations 1542 characters. The total volume of the dissertation is 165532 characters (excluding figures, tables, graphs, appendices and bibliography).

In the Introduction, the relevance of the presented dissertation is substantiated; the purpose and objectives of the study, scientific novelty, practical value and application of the results are formulated.

In the first chapter given the literature review in accordance with the topic of the dissertation, a detailed analysis of the literature on the production of ethers and esters as well as cyclic, polycyclic esters of glycerol, the field of application is given.

The second chapter gives an experimental part of the work, the initial compounds, their physical and chemical characteristics, degree of purity, as well as determination and confirmation of the composition and structure of the obtained main substances by modern analytical methods, equipment used for experiments and their working methods.

The third chapter deals with the synthesis reactions of glycerol with cyclohexene and its alkyl derivatives in the presence of various (homo- and hetero-) catalysts. This chapter also explains the synthesis of alkyl cyclohexyl glyceride and describes the synthesis of cyclohexyl glyceride ether by esterification of cyclohexanol with glycerol through a cross-synthesis reaction. The study of the properties and acquiring diesters as a result of the esterification reaction of aprotic carbonic acids with monoethers of cyclic glycerides in the presence of the catalyst $KU\ 2-8\ H^+$ are also widely described in this chapter.

The fourth chapter deals with the synthesis of monoethers of bicyclic glycerides from combining of glycerol with bicyclo[2.2.1]hept-2-ene and its alkyl derivatives in the presence of $BF_3 \cdot OEt_2$ catalyst, the probable mechanism of the reaction and the

synthesis of of these esters as a result of the esterification reaction with norborneol and methyl norborneol alcohols with glycerol. The chapter also covers the preparation and study of the properties of diethers based on the esterification reaction of monoethers with aprotonic carbonic acids in the presence of the catalyst KU 2-8 H⁺

In the fifth chapter the synthesis of tri- and tetracyclic glyceride ethers by the addition of glycerol with tricyclo[5.2.1.0^{2,6}]deca-3-diene, tetracyclododesene and its alkyl derivatives, as well as the esterification reaction of polycyclic alcohols with glycerol has been extensively studied. Obtaining and properties of diesters based on the esterification reaction of polycyclic glyceride monoethers with aprotonic carbonic acids in the presence of KU 2-8 H⁺ catalyst were studied.

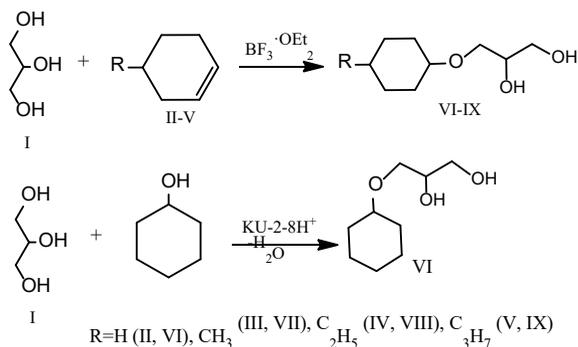
The dissertation concludes with a summary of the research work, a list of references and appendices.

MAIN CONTENT OF THE WORK

1. Synthesis of cyclic ethers and diesters of glycerol

Due to the lack of information in the literature on the study of polycyclic glycerides, extensive research is needed to synthesize new glycerin (Gl)-based compounds. The work is aimed at studying the synthesis simple polycyclic simple mono ethers by catalytic binding of Gl to mono-, bi-, tri- and tetracyclic olefins, as well as the study of catalytic esterification reactions of monobasic saturated carbonic acids with these ethers. In the first direction, the synthesis of cyclic ethers of glycerine was carried out in two ways: on the basis esterification of the reaction of Gl with cyclic alcohol and on the basis of the addition of glycerin with cyclic olefins. It was found out that the presence of the catalyst BF₃·OEt₂ addition of glycerine to the double bond of cyclohexene (CH) and the formation of cyclohexylglyceride (CHGl).

The reaction follows the following scheme:



The interaction of GI with CH was studied and the optimal synthesis conditions of CHGI monoether were determined (Figure 1).

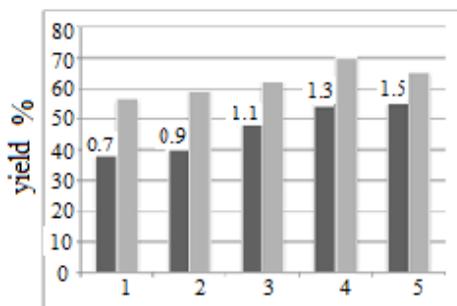


Figure 1. The effect of catalyst amount and duration on the yield of CHGI ether

catalyst, % mass.
 duration, hour

Mole ratio of CH to GI - 1: 1.2, temperature - 90°C, catalyst amount $\text{BF}_3 \cdot \text{OEt}_2$ - 1.3% mass. According to CH, the reaction duration is 4 hours, the yield of CHGI ether is 70%.

The IR spectrum of CHGI showed specific absorption bands to the groups (OH) in the 3408 cm^{-1} area, (-CH) in the $2872\text{-}2951 \text{ cm}^{-1}$, (-CH₂) groups in the 1407 cm^{-1} and (C-O-C) group in the 1232 cm^{-1} .

The NMR ¹H and ¹³C spectra of the monoether sample studied are: ¹H spectrum, δ , ppm: 1.25-1.70 (m, 10H, 5CH₂), 2.69 (m, H, CH-O), 3.48-4.40 (d, 4H, 2CH₂, J 10.9 Hz), 3.55-3.60 (s, 2H, 2OH), 3.64 (m, H, CH). ¹³C spectrum, δ_c , ppm.: 23.8 (C^{3,5}), 25.40 (C⁴), 31.10 (C^{2,6}), 62.7 (C⁹), 71.50 (C⁸), 71.92 (C⁷), 81.80 (C¹).

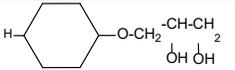
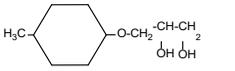
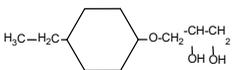
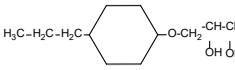
Synthesis of glyceride esters on the basis of C₁-C₃ alkyl derivatives of glycerol and cyclohexene was carried out under the conditions of optimal synthesis of monocyclic glyceride ether,

physical and chemical parameters of the obtained monoether were determined, the results are given in Table 1. As can be seen from the table, the yield of monoether decreases with the elongation of the alkyl radical attached to the cyclohexene ring, and the boiling point rises significantly.

The optimal conditions for the synthesis of CHGI in the presence of the catalyst KU 2-8 H⁺ by the esterification reaction of cyclooxanol (CHol) with GI were determined: CHol:GI molar ratio 1:1.1 reaction temperature 110 °C; amount of catalyst 5.0%; reaction duration is 5 hours.

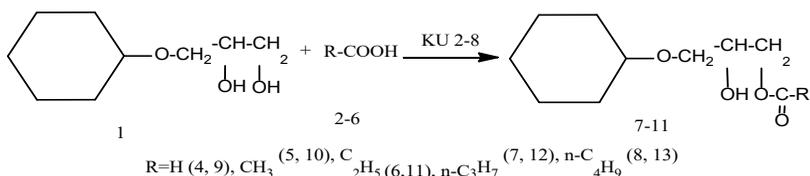
Table 1.

The yield and physicochemical parameters of synthesized monocyclic glycerol ethers

Monocyclic glycerol ethers	Yield %	T _{boil.} , °C/45 mm Hg	d ₄ ²⁰	n _D ²⁰
	70.0	180	1.0031	1.4608
	65.2	198	1.0189	1.4614
	59.8	223	1.0425	1.4626
	52.4	260	1.0713	1.4650

The physicochemical properties of the ether of glycerol synthesized by this method have been studied and it has been determined that these values are practically the same as those of the simple CHGI ester obtained from the reaction of CH with GI.

In the second direction, the process of synthesis of 1,3-glyceride diesters on the basis of the esterification reaction of CHGI monoether with monobasic saturated C₁-C₅ series carbonic acids was studied. KU 2-8 H⁺ has been used as a catalyst in the researches. The reaction equation is given below:



In order to determine the optimal conditions for the reaction to obtain cyclohexyl-1-glyceride-3-formate diesters, the effect of various factors on the process: molar ratios of raw materials, catalyst amount, reaction duration to yield of diesters has been studied and optimal conditions for 91% mass yield of the target product have been determined: CHGI:formic acid molar ratio 1:1, KU 2-8 H⁺ amount 2.5% by weight, temperature 80°C, reaction duration 3 hours.

Physico-chemical parameters of diesters obtained by the reaction of CHGI with saturated acids with the participation of the catalyst KU 2-8 H⁺ were studied and shown in Table 2.

Table 2.

Esterification of THQI with C₁-C₅ monobasic saturated carbonic acid reaction conditions and physicochemical parameters of synthesized diesters

CHGI 87 g, KU 2-8 H⁺ 2.5% mass, duration of reaction 3 hour

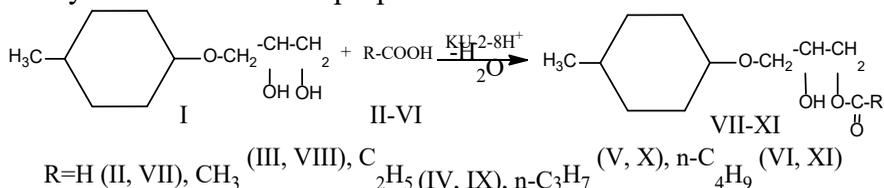
Taken in reaction, g	Boil point, 2°C/8 mm hg	d_4^{20}	n_D^{20}	Diesters	
				№	Yield %
FA – 23.0	145-146	1.1733	1.4685	9	91.0
AA -30.0	150-152	1.1356	1.4686	10	85.2
PA -37	159-161	1.0961	1.4687	11	80.8
n-BA-44	169-170	1.0735	1.4696	12	72.4
n-VA-51	178-179	1.0586	1.4709	13	70.6

The structure of the synthesized diesters was confirmed by IR-, NMR ¹H and ¹³C analysis methods and specific absorption bands to the groups 3414 cm⁻¹ (OH), 2857-2932 cm⁻¹ (-CH), 1448 cm⁻¹ (-CH₂) are observed in the IR spectrum and 1738 cm⁻¹ (C=O) and 1229 cm⁻¹ absorption bands prove the presence of (-COO⁻) group in the composition.

NMR ¹H chemical shift δ. ppm.: 1.31-1.73 m (10H, 5CH₂), 2.88 m (H, CH-O), 3.59-4.15 d (4H, 2CH₂, J 10.9 Hs), 4.02 m (H, CH), 3.55 s (H, OH), 7.85 d (H, HCOO, J 8.3 Hs)

NMR ^{13}C chemical shift δ . ppm.: 31.88 ($\text{C}^{1,3}$), 82.08 (C^2), 23.7 ($\text{C}^{4,6}$), 23.97 (C^5), 72.0 (C^7), 68.40 (C^8), 67.91 (C^9), 159.7 (C^{10})

In order to synthesize new representatives of diesters, researches were carried out in the field of esterification of saturated acids with methylcyclohexyl glycerol (MCHGI) and corresponding diesters were synthesized and their properties were studied.



Finding the optimal conditions for the reaction to obtain diesters was studied on the example of the synthesis of 4-methylcyclo-hexylglyceride-3-acetate (MCHGIAc), a representative of this class, the effect of various factors (molar ratio of reactants, catalyst amount) was studied and the optimal temperature 80°C , MCHGI:As mole ratios 1:1.2, catalyst amount- 2.5%, reaction duration is 4 hours. Under the optimal conditions: esterification of formic, propionic, fatty and valeric acids with MCHGI was also carried out, their physicochemical parameters and element composition were determined (Table 3).

Table 3.

Physicochemical properties and element composition of monocyclic glyceride diesters.

Sequence number of diesters №	Boil point, $^\circ\text{C}/8$ mm Hg	Yield of diesters %	d_{4}^{20}	n_D^{20}	Found, %		Calculated, %	
					C	H	C	H
VII	154-156	86.4	1.1223	1.4786	60.47	9.81	60.69	9.92
VIII	166-168	80.0	1.0794	1.4774	62.39	9.43	62.58	9.63
IX	175-177	73.2	1.0635	1.4783	63.70	9.75	63.91	9.90
X	184-186	68.5	1.0412	1.4796	64.87	10.02	65.09	10.14
XI	190-192	63.1	1.0247	1.4813	66.05	10.25	66.14	10.36

The structure of the synthesized monocyclic diethers was confirmed by modern analysis methods IR-, NMR ^1H and ^{13}C . Results of IR-spectroscopic analysis: deformation and valence oscillations of CH bonds of CH, CH_2 and CH_3 groups 1374, 1448,

2837, 2921 cm^{-1} , OH group valence shift 3416 cm^{-1} , absorption band of COO^- group of ether 1740 cm^{-1} and the mathematical oscillation of the COC group of simple ether is observed in the area of 1223 cm^{-1} .

MCHGIAC NMR ^1H vø ^{13}C chemical landslides are shown below: ^1H chemical shift δ . ppm.:

1.29-1.70 m (8H, 4 CH_2), 1.59 22m (H, CH), 0.93 t (3H, CH_3), 2.80 m (H, CH-O), 3.67-4.37 d (4H, 2 CH_2 , J 10.9 Hs), 4.10 m (H, CH), 3.60 s (H, OH), 2.22 s (3H, CH_3), ^{13}C chemical shift δ . ppm.: 32.01 ($\text{C}^{1,3}$), 81.98 (C^2), 28.99 ($\text{C}^{4,6}$), 31.54 (C^5), 19.58($\text{C}^{7,12}$), 72.33 (C^8), 68.93 (C^9), 65.32 (C^{10}). 176.5 (C^{11}).

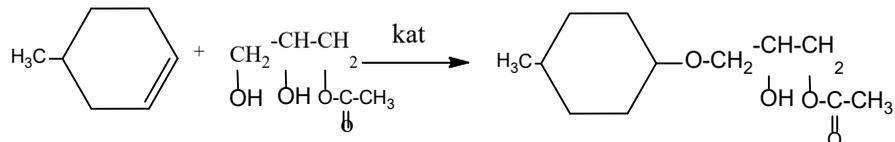
Research on the synthesis of monocyclic glycerol diethers has been expanded by us and their production has also been carried out through a cross-synthesis reaction.

For this purpose, we first synthesized 2,3-dihydroxypropylacetate (DHPA) ether from the reaction of GI esterification with acetic acid. The esterification reaction was carried out in a benzene medium at a temperature of 80°C in a ratio of GI:SA 1.2:1 mol for 3 hours.

In the reaction, KU 2-8 H^+ was used as a heterogeneous catalyst with a 2.5% mass (relative to the mass of GI). The yield of synthesized DHPA was 65%. Its physical and chemical properties are as follows:

T_{boil} 129-130°C/3mm, d_4^{20} 1.206, n_D^{20} 1.4500, T_{igni} .145°C, $M=134\text{g/mol}$

In the second phase of the study, the synthesis of DHPA synthesized to 4-methylcyclohexene (MCH) was studied. The scheme of the reaction is as follows:



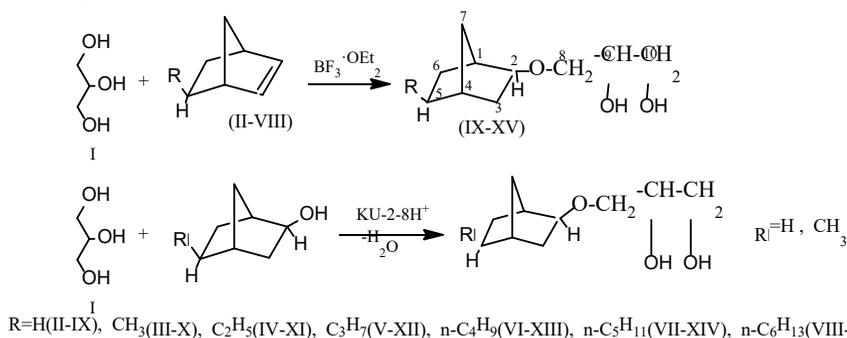
Experiments were carried out at the temperature range of 80-120°C, MCH:DHPA molar ratio was 1:1-1:1.6, the amount of catalyst 1-2%, the reaction duration in the range of 2-6 hours, based on the reaction of methylcyclohexene with dihydropropylacetate, the optimal synthesis conditions of MCHGIAC diesters were determined: Molar ratio of MCH to DHPA 1:1.5, temperature 120°C, catalyst

$\text{BF}_3 \cdot \text{OEt}_2$ amount 2% mass. According to MCH, the reaction duration is 5 hours. In this case, the yield of the synthesized diester is 74.2%.

The structure of the synthesized MCHGI was confirmed by IR-, NMR ^1H and ^{13}C analysis methods. The structure of MCHGIAc synthesized by this method was similar to the physicochemical properties and structure of glyceride diester obtained by other methods. Thus, on the basis of the conducted researches, glycerol was combined with cyclohexene and its methyl derivative, cyclohexanol esterification, cyclohexyl glycerol and $\text{C}_1\text{-C}_5$ series of methylcycloglyceride esterification with saturated carboxylic acids.

2. Obtaining of norbornylglycerid diethers and diesters from their reaction with saturated acids

In accordance with the purpose of the dissertation, in order to synthesize bicyclic ethers of glycerol, the combination of NB and alkyl derivatives with glycerol in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ catalysts, taking into account the active double bond in the norbornene molecule and also was synthesized of norbornylglyceride (NBGI) ethers as a result of esterification reaction of norborneol and methylnorborneol alcohols in the presence of catalyst KU 2-8 H^+ . The equation of the reaction is as follows:



According to the obtained results, under the determined optimal conditions of the catalytic addition reaction of GI to Nb temperature, 80°C , NB:GI molar ratio 1:1.25, the amount of catalyst GI % mass 1.25, the reaction duration is 4.0 hours, the yield of bicyclic

monoether is 86.5%. The combination reactions of GI to C₁-C₅ alkyl derivatives of NB to under optimal conditions for the synthesis of NBGI monoether were studied and the results obtained are given in Table 4. As the length of the alkyl chain in the NB ring increases, the yield of bicyclic glycerides based on them decreases in part. Thus, the yield of methylbicyclohexyl glycerine (MBHGI) is 84.6%, while the yield of hexylnorbornyl glycerine is 70.1%. The explanation for this is related to spatial conformation. Thus, electrodonor alkyl radicals weaken the activity of the double π bond in the NB ring, resulting in a decrease in the yield of ethers.

Table 4.

Elemental composition and physicochemical properties of synthesized bicyclic glyceride monoether.

Mono ethers	Molar mass	Boiling Point C/ 1 mmHg	d_4^{20}	n_D^{20}	Found, %		Calculated, %	
					C	H	C	H
IX	186.1	110-111	1.2556	1.4730	64.49	9.61	64.54	9.67
X	200.1	122-123	1.1816	1.4800	65.91	9.81	66.02	10.00
XI	214.1	131-133	1.1309	1.4818	67.26	10.21	67.31	10.28
XII	228.1	146-148	1.1209	1.4820	68.35	10.42	68.45	10.52
XIII	242.1	151-155	1.1190	1.4844	69.25	10.54	69.45	10.74
XIV	256.2	160-161	1.1065	1.4900	7.12	10.73	70.32	10.93
XV	270.2	169-170	1.1021	1.5051	70.92	10.91	71.12	11.10

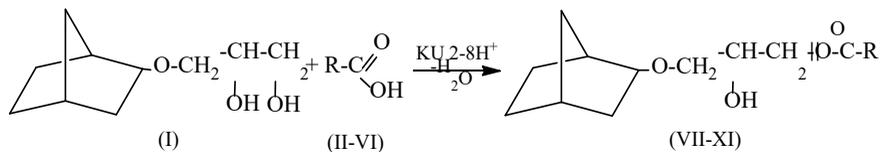
The structure of the synthesized bicyclic monoether was confirmed by IR-, NMR ¹H and ¹³C analysis methods. The following absorption bands were observed in the IR spectrum of monoether: absorption bands with single and double OH-groups in the molecule 3327-3378 cm⁻¹, 2875-2943 cm⁻¹ - CH, 1450-1453 cm⁻¹ -CH₂ and 1182 of the simple ether group -1199 cm⁻¹ was observed. The presence of these absorption bands in the IR spectrum directly confirms the structure of bicyclic glycerides.

Chemical shifts of NBGI in the NMR ¹H and ¹³C spectra are shown below: NMR ¹H chemical shift, δ , ppm: H¹- 2.23, H²- 2.80, H³- 1.49-1.83, H⁴- 1.43, H⁵- 1.49, H⁶-1.20-1.46, H⁷- 1.83-2.10, H^{8,9}- 3.38-4.23, H¹⁰- 3.62, OH - 3.50-3.61. NMR ¹³C chemical shift, δ , ppm.: 86.2 (C²), 72.3 (C⁹), 65.8 (C¹⁰), 71.9 (C⁸), 41.4 (C¹), 39.9 (C⁴), 36.7 (C³), 24.8 (C⁶), 36.7 (C⁷), 29.3 (C⁵).

The yield of norbornyl and methylnorbornylglycerides obtained by esterification reaction is 76.5% and 78.0% by weight, respectively. The physicochemical parameters of the obtained norbornyl- and 5-methylnorborn-2-ylglycerine ethers were compared with the corresponding values of the ethers obtained by the combination of GI to NB and methylnorbornene and complete conformity was determined.

The structure of the obtained NBGI was studied by IR- and NMR ^{13}C and ^1H analysis methods.

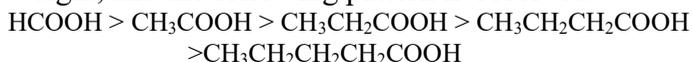
In order to synthesize new representatives of glyceride diesters, the esterification reaction of saturated acids to NBGI with the participation of the catalyst KU 2-8 H^+ was studied, the relevant diesters were synthesized and their physicochemical parameters were determined:



R=H(II, VII), CH_3 (III, VIII), C_2H_5 (IV, IX), C_3H_7 (V, X), C_4H_9 (VI, XI)

The optimal conditions for the esterification reaction of formic acid with NBGI were determined: temperature 80°C , NBGI: molar ratio of formic acid 1:1, the amount of catalyst 2.0% mass. According to NBGI, the reaction duration was 3 hours. The yield of the synthesized norbornylglycerolidformate diesters was 87.4%.

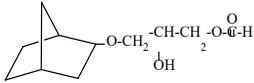
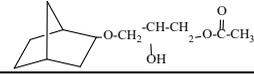
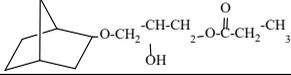
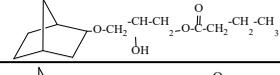
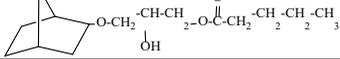
Acetic, propionic, butiric, and valeric acids were combined with NBGI under optimal conditions for formate diesters, and the corresponding diesters were synthesized. The synthesis conditions and yields of bicyclic diethers are shown in Table 5. The yield of diesters depends on the degree of dissociation of monobasic saturated acids. Thus, as the molecular weights of acids increase from formic acid to n-valeric acid, the yield of diesters decreases from 87.4% to 76.4% by weight, and the following pattern is observed.



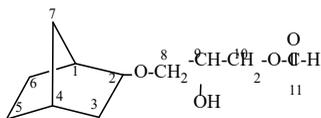
Physicochemical parameters of the synthesized bicyclic glyceride diesters were determined and given in Table 5.

Table 5.

Physicochemical properties of synthesized bicyclic glyceride diesters

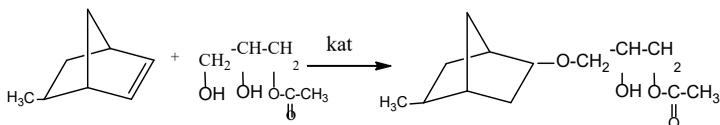
The structure of bicyclic diesters	Boil point °C/1 mmHg	d_4^{20}	n_D^{20}	Yield, %
	131-132	1.2647	1.4516	87.4
	148-149	1.2476	1.4533	84.1
	165-166	1.2281	1.4598	81.6
	182-183	1.2078	1.4621	79.1
	195-196	1.1905	1.4645	76.4

The structure of the synthesized bicyclic diesters was confirmed by IR-, NMR H^1 and ^{13}C spectral analysis methods. The following absorption bands were observed in the IR spectrum: 705 cm^{-1} is mathematical oscillation of CH_2 group, 1017 cm^{-1} , 1056 cm^{-1} , 1233 cm^{-1} , 1292 cm^{-1} are valence oscillation of C-O-C bond of ether, 1440 cm^{-1} is of C-H bond deformation oscillation of CH_2 group, valence oscillation of CH bond of CH_3 group is 2938 cm^{-1} , C = O group of ester is 1730 cm^{-1} , 3414 cm^{-1} is OH group of alcohol.



1H (δ , ppm.); H^1 -2.30; H^2 -2.75; H^3 -1.60-1.81; H^4 -1.45; $H^{5,6}$ -1.30-1.55; H^7 -1.86-2.15; H^8 -3.42-3.60; H^9 -4.12; H^{10} -4.15-4.40; OH-3.52; H^{11} -8.01. ^{13}C (δ , ppm); C^1 -42.49; C^2 -86.94; C^3 -39.0; C^4 -34.5; C^5 -29.1; C^6 -24.8; C^7 -35.2; C^8 -72.56; C^9 -68.79; C^{10} -70.1; C^{11} -160.06.

In the possibility of DHPA's integration into the double-bond of the MBH in the bicyclic ring, we have expanded our research and achieved some positive results in this area. The equation of the reaction can be written as follows:



Triple fluorine boron ether complex was used as a catalyst in the reaction. In order to synthesize the maximum amount of methylbornylglyceridasetate from the combination reaction of DHPA with MBH, we conducted a number of experiments to find the optimal reaction conditions and studied the effect of various reaction factors on the yield of the target product. Examples of these factors are temperature, the molar ratio of the initial compounds entering the reaction, the amount of catalyst, and the reaction duration. The optimal conditions for the synthesis of methylbornylglyceridasetate from the combination of DHPA to MBH were determined as follows: the mole ratio of MBH to DHPA was 1:1.4, the reaction temperature was 100°C, the amount of catalyst $\text{BF}_3 \cdot \text{OEt}_2$ was 2% by weight of methylbornorene, the reaction duration is 4 hours. Under such conditions, the yield of methylbornylglyceryl acetate diester was 77.4%.

The obtained substance was separated by evaporation under vacuum conditions and its purity was determined with the help of GLC. The physicochemical parameters of this substance were almost the same as those of the diester obtained from the reaction of acetic acid with MNBGL.

3. Synthesis of tri- and tetracyclic glycerine ethers and diesters based on them

In order to expand the field of application of glycerol as a by-product in the production of biodiesel fuels based on vegetable oils, the reaction of glycerol with the presence of a catalyst in the dimer of cyclopentadiene obtained as a by-product of petroleum pyrolysis was studied and dihydrocyclopentadienyl glycerine. KU-2, KU 2-8, $\text{BF}_3 \cdot \text{OEt}_2$, p-toluene sulfuric acid and naphthalene-1,5-disulfuric acid were used as catalysts. As a result of the research, it was determined that the catalyst KU 2-8 and NDSA are 5.0%, respectively; relatively good results are obtained when 3.0% is taken. Catalyst $\text{BF}_3 \cdot \text{OEt}_2$ showed a higher result (70.5%) than the mentioned catalysts in the

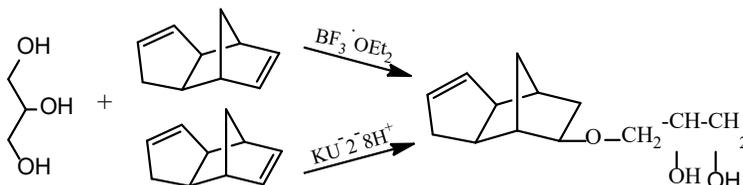
amount of 1% (Table 6).

Table 6.

**The yield of ether in the presence of various catalysts.
Reaction temperature 100 ° C, duration 3 hours.**

Catalyst,% for Gl	Taken in reaction, g		The yield of TCDGI, %
	TCD	Gl	
p-TST -5.0%	132.0	92.0	35.5
KU-2 -6%	132.0	92.0	40.6
BF ₃ O(C ₂ H ₅) ₂ -1%	132.0	92.0	70.5
KU 2-8 -5.0%	132.0	92.0	65.0
NDSA -3.0%	132.0	92.0	58.4

The reaction of the addition of Gl to tricyclo[5.2.1.0^{2,6}] deca-3.8-diene (TCD) to was studied as a catalyst in the presence of BF₃·OEt₂, KU 2-8 H⁺. The reaction proceeds according to the following scheme:

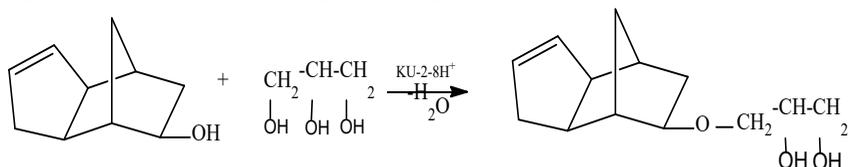


The optimal conditions for the synthesis of tricyclo[5.2.1.0^{2,6}]des-3-en-8(9)-ilglycerine (TCDGI) in the presence of the catalyst BF₃·OEt₂ are as follows: temperature 100°C, molar ratio of initial materials TCD:Gl 1:1.5, the amount of catalyst is 1.4 mass %, the reaction duration is 4 hours.

Under these conditions, the yield of TCDGI is 84.2%. Physicochemical parameters of the synthesized glycerine ether were determined. Boiling point 165-166°C/2 mmHg, d_4^{20} -1.1429 g/cm³, irradiance coefficient n_d^{20} -1.5138, structure was confirmed by IR-, NMR ¹H and ¹³C spectral analysis methods. In the IR spectrum, 1158-1206 cm⁻¹ is characteristic of the C-O-C group, 3044-3396 cm⁻¹ is characteristic of the single and double-OH groups, 2844-2946 cm⁻¹ is characteristic of the -CH- and 1636 cm⁻¹ is characteristic of the CH=CH- absorption bands characteristic of double communication fragment were observed.

In the NMR ^1H spectrum of the sample, the absorption band characteristic of the endo-H isomer was observed at 4.2 ppm. The chemical shift observed at 3.5-3.8 ppm. in the molecule of synthesized glyceride monoether belongs to the protons of the second hydroxyl group. Based on the preliminary results, the process of obtaining monoglycerine ether was studied in the form of $\text{KU } 2\text{-}8 \text{H}^+$ as a catalyst, the optimal conditions of the reaction were determined: molecular ratio of TCD to Gl 1:1.2, catalyst amount 5%, reaction temperature 120°C , reaction duration 5 hours. Under optimal conditions, the yield of TCDGl is 70%.

TCDGl was also carried out by esterification of glycerol with tricyclodesenol (TCDol) by cross-synthesis reaction:

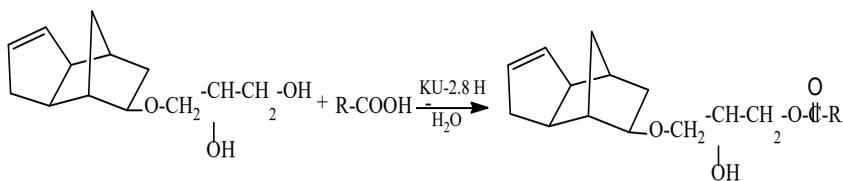


It was found that the toluene medium is more efficient for removing water from the system during the esterification reaction, as the yield of dihydrodicyclopentadienyl glycerine ether is higher because the reaction temperature is higher than that of the benzene medium. The resulting water is separated from the reaction mixture in the form of an azeotrope for 4 hours.

Thus, in the ratio of TCDol: Gl 1:1.2 mol, at a temperature of 110°C , in the presence of 6% by mass catalyst $\text{KU } 2\text{-}8\text{H}^+$, the etherification reaction is completed in 4 hours, and when it reaches the yield of the target product ether is 64.7%.

The properties of the synthesized bicyclic norbornylglycerine and tricyclic dicyclopentadienylglycerine monoether were tested at the Vegetable Research Institute of the Ministry of Agriculture of the Republic of Azerbaijan and used as an insecticide in the fight against pests that reduce productivity in potato crops.

The addition reaction of $\text{C}_1\text{-C}_5$ carbonic acids to TCDGl monoether was carried out in the presence of $\text{KU } 2\text{-}8 \text{H}^+$ heterogeneous catalyst and mixed, ether and ester 1.3-glyceride diesters were synthesized.



R= H(II-VII); -CH₃(III, VIII); -CH₃-CH₂(IV, IX); -CH₃-CH₂-CH₂(V, X); -CH₃-CH₂-CH₂-CH₂ (VI-XI)

The effect of various factors - molar ratios of initial materials, the amount of KU 2-8 H⁺ catalyst - was studied in order to obtain high yields of diesters obtained by the esterification reaction of dicyclopentadienyl glyceride monoethers with C₁-C₅ carbonic acids (Figure 2).

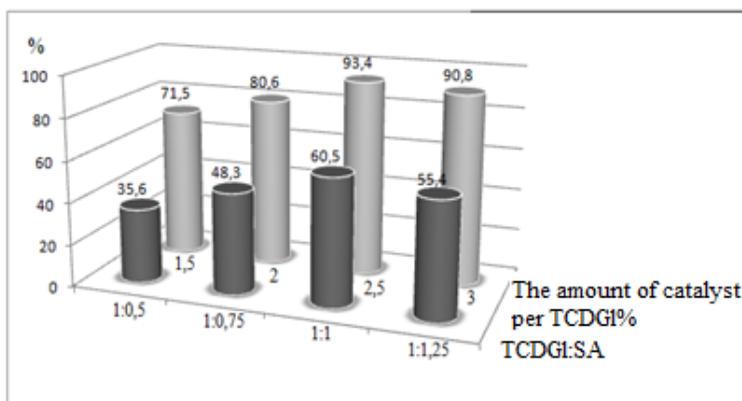


Figure 2. Dependence of the yield of the TCDGIAc diester on the molar ratio of the initial substances to the amount of catalyst

Under the specified optimal conditions, the temperature is 80-85°C, TCDGI: SA molar ratio 1:1, catalyst KU 2-8 H⁺ 2.5%, reaction duration is 4 hours, yield of TCDGIAc diester is 93.4%.

Addition reactions of other representatives of saturated aliphatic acid acids under the specified optimal conditions: formic acid, propionic acid, butiric acid, and valeric acid to TCDGI were studied, high-yield synthesis of 1-3 glyceride diesters with appropriate tricyclic structure was carried out. The results of the research are given in Table 7.

Table 7.

**Synthesis of diesters from the esterification reaction of
TCDGI with saturated acids**

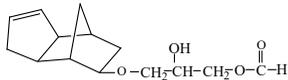
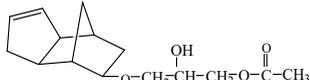
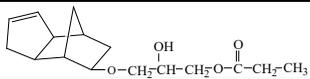
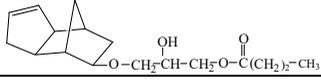
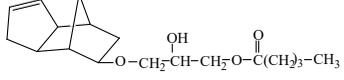
Taken in reaction, g		Catalyst, KU 2-8 H ⁺ , g	Duration, hour	Received	
Saturated Acids	TCDGI			Diester	Yield %
FA - 46.0	224.3	5.6	4	VII	98.0
SA - 60.0	224.3	5.6	4	VIII	93.4
PA-74.1	224.3	5.6	4	IX	89.6
n-BA-88.1	224.3	5.6	5	X	81.4
n-VA-100.1	224.3	5.6	5	XI	79.5

Studies have shown that the yield of tricyclic 1-3 glyceride diesters varies depending on the monobasic saturated carbonic acid, and that the yield of diesters decreases from 98% to 79.5% as the molecular weight increases with the transition from formic acid to valeric acid.

Physicochemical parameters of the synthesized tricyclic 1-3 glyceride diesters were studied and given in Table 8.

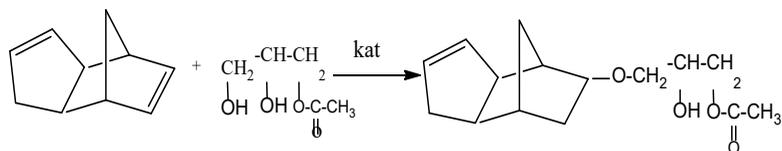
Table 8.

**Physicochemical properties of 1-3 glyceride diesters with
tricyclic structure**

The structure of diesters	Molecular weight	Boil point °C/ 1 mmHg	d ₄ ²⁰	n _D ²⁰
	252.3	126-127	1.2315	1.5069
	266.3	135-136	1.1377	1.5110
	280.3	140-141	1.1211	1.5165
	294.4	150-151	1.1190	1.5178
	308.4	158-160	1.0739	1.5198

The following absorption bands were observed in the IR spectrum of all obtained diester samples: 698, 739 cm^{-1} – absorption bands reflecting the mathematical oscillation specific to the C-H bond of the CH_2 group; 874, 946, 985 cm^{-1} –CH=CH- group C-H bond; 1048, 1072, 1092 cm^{-1} - deformation dance of the OH group; 1158, 1234 cm^{-1} -C-O-C- absorption band of ether group; 1369 cm^{-1} CH_3 -, 1440 cm^{-1} CH_2 - deformation and valence oscillations; 1740 cm^{-1} C=O of carbonyl group; 2947, 2885 cm^{-1} CH_2 , CH_3 - valence oscillation; valence oscillation of the group 3418 cm^{-1} OH-.

The tricyclic acetate diester of glycerol was obtained by cross-synthesis reaction using the addition reaction of glycerol monoacetate ether with DTPD in the presence of a catalyst, the scheme of the reaction can be shown as follows:



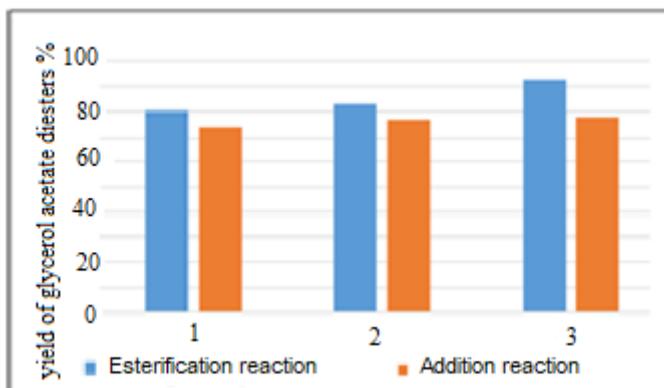
$\text{BF}_3 \cdot \text{OEt}_2$ was used in experiments as a catalyst. The results of our research showed that the catalyst provides the addition of glycerol monoacetate ether to the double bond of dicyclopentadiene in the bicyclic ring.

Optimal conditions for the synthesis of TCDGIAc were determined: temperature 110°C, molar ratio of primary components DTPD: DHPA 1:1.5, amount of catalyst 1.5%, reaction duration is 3 hours. Under optimal conditions, the yield of glycerol tricyclic diester is 78.7%.

The physicochemical parameters of the tricyclic diester of glycerol synthesized by this method are as follows: B.p.135-136°C d_4^{20} 1.1377, n_D^{20} 1.5110. These values correspond to the values of the diester obtained by the previous method.

At the Institute of Polymer Materials of ANAS, the plasticizer properties of tricyclo [5.2.1.0^{2,6}]des-3-en-8-ilglyceridebutyrate ester were studied and tested in detail.

As a result, it proved to be an effective plasticizer for PVC, and the developed composite materials were found out to be suitable for practical application in various industries.



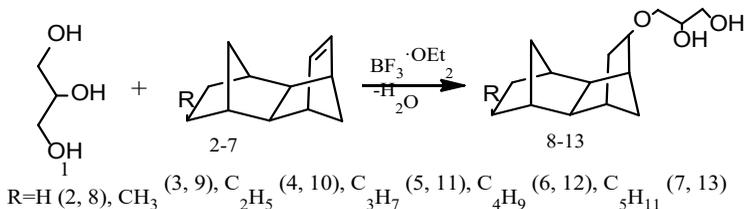
1. Monocyclic acetate diester of glycerol
2. Bicyclic acetate ester of glycerol
3. Tricyclic acetate ester of glycerol

Figure 3. Synthesis of mono-, bi-, tricyclic acetate glycerol diesters by esterification and addition reactions.

The following (Figure 3) shows the comparative yields of mono-, bi-, and tricyclic diesters of GI synthesized by esterification as well as addition reactions. It is clear from the figure that the yield of the polycyclic acetate diester of GI is higher through the esterification reaction. These results can be evaluated as a comparison of synthesis in the presence of both homogeneous and heterogeneous catalysts. Repeated use of the catalyst $KU\ 2-8\ H^+$, a heterogeneous ion exchange resin used in the esterification reaction, in the form of regeneration, also confirms the advantage of this method.

Synthesis of glycerides with tetracyclic structure

The addition of GI to tetracyclic hydrocarbons was studied in order to synthesize new, tetracyclododesylglycerides (TCDDGI) ethers. $BF_3 \cdot OEt_2$ triple fluorine boron ether complex was used as a catalyst in the researches. The production of the corresponding tetracyclododesyl monoethers of GI follows the scheme:



Influence of various factors: temperature (50-110°C), molar ratio of initial components (1:1-2.5), amount of catalyst (1.1-1.7% by weight of GI), reaction duration (1-7 hours) on the yield of TCDDGI was studied in the example of the addition reaction in GI to TCDD (Figure 4).

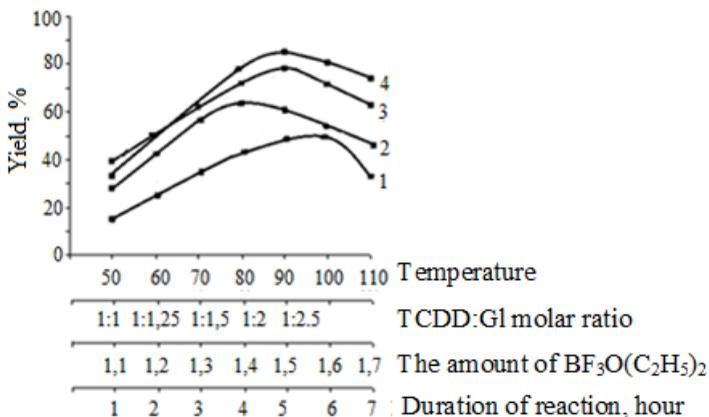


Figure 4. Temperature dependence curves of TCDDGI yield (1), TCDD: GI mol ratio (2), $\text{BF}_3 \cdot \text{OEt}_2$ catalyst amount (3), reaction duration (4).

Based on the results obtained, the optimal conditions for the synthesis of TCDDGI are as follows: reaction temperature 100°C, TTDD:GI molar ratio 1:2, amount of $\text{BF}_3 \cdot \text{OEt}_2$ 1.5% by mass of GI, reaction duration 5 hours. The structure of the synthesized ethers was confirmed by IR, NMR ^1H and ^{13}C spectral analysis methods. Under the optimal conditions, the process of addition of GI to alkyl derivatives of TCDD was carried out. The results are shown in table 9.

The synthesized ethers are clear liquids and have a characteristic odor.

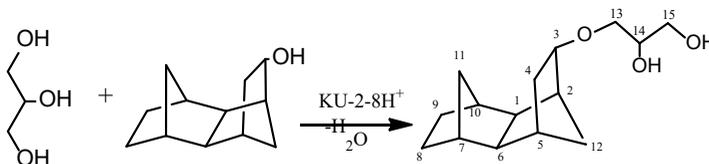
Table 9.

Physicochemical properties and yield of synthesized tetracyclic glycerine monoether

Tetracyclic glycerine ethers	Boil point °C/1 mmHg	d_4^{20}	n_D^{20}	Yield %
8	155-156	1.1358	1.5235	83.7
9	165-166	1.1337	1.5248	80.4
10	172-173	1.1311	1.5259	77.5
11	190-191	1.1286	1.5267	74.2
12	196-197	1.1264	1.5274	64.4
13	210-211	1.1242	1.5283	68.4

The structure of these esters was studied by IR and NMR ^1H , ^{13}C analysis methods and the following absorption bands were observed in the spectra. IR spectrum ν , cm^{-1} : 1210 (C-O-C), 1417 (CH_2), 2879-2932 (CH), 3278 (OH).

The synthesis of a glycerin ether with a tetracyclic structure was also carried out by a cross-synthesis reaction by the esterification reaction of glycerin with tetracyclodekanol (TETDoI), a tetracyclic alcohol.



Physico-chemical properties of ether of G1 synthesized by etherification reaction studied and it was determined that these values correspond to the values of TCDG1 ether obtained from the reaction of TCDD with G1: boiling point 186-187°C/40 mmHg, d_4^{20} 1.0033, n_D^{20} 1.4602. The IR spectrum of glyceride ether obtained by this method was the same as the structure of ether obtained by other methods.

Consequently, on the basis of the conducted research, synthetic conditions have been developed for cyclic, polycyclic monoesters containing various fragments based on glycerol and cyclohexene, norbornene, dicyclopentadiene, tetracyclododesene with various raw materials and for diesters. Their application areas have been identified.

RESULTS

1. A monocyclic glycerol simple ester with a yield of 70% was synthesized as a result of the combination of cyclohexene glycerol in the presence of a catalyst $\text{BF}_3 \cdot \text{OEt}_2$. It has been proved that in the presence of the given catalyst glycerol combines with cyclohexene $\text{C}_1\text{-C}_3$ alkyl derivatives to form alkylcyclohexyl glyceride simple esters with a yield of 52.4-65.2% under optimal conditions. Synthesis of cyclohexyl glycerol ether with a yield of 63.8% was carried out as a result of the esterification reaction of cyclohexanol with glycerol in the presence of KU 2-8 H^+ [15].
2. Monocyclic glycerol diethers with a yield of 86.4-91% were synthesized by combining $\text{C}_1\text{-C}_5$ saturated monobasic acids with simple cyclohexyl-, methylcyclohexyl glycerol esters in the presence of catalyst KU 2-8 H^+ [13].
3. Bicyclic glycerol esters with a yield of 86.5%, 70.1-84.6%, were synthesized due to the combination of glycerol with norborne and its $\text{C}_1\text{-C}_6$ alkyl derivatives in the presence of 3 $\text{BF}_3 \cdot \text{OEt}_2$ catalyst. As a result of esterification of norborneol and methyl norborneol with glycerol, synthesis of norbornyl glyceride simple ester with 76.5-78% yield was carried out. As a result of combination of $\text{C}_1\text{-C}_5$ saturated monobasic acids in the presence of KU 2-8 H^+ to simple esters of Norbornyl- and methylnorbornyl glyceride, bicyclic glyceride diethers with the yield of 76.4-87.4%, 75.5-85.6% were synthesized, their properties were studied, their structures were confirmed [6, 10, 11, 12].
4. A simple ester of dicyclopentadienyl glycerol with a yield of 84.2% and 70% was synthesized for the first time. It was acquired from the combination of glycerol with dicyclopentadiene in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ and KU 2-8 H^+ and its structure was confirmed by modern methods. The yield of dicyclopentadienyl glycerol ether from the esterification reaction by cross-synthesis reaction was 64.7% [1, 2, 3, 5, 7].
5. Tricyclic glyceride diethers with a yield of 79.5-98% were

synthesized as a result of the combination of C₁-C₅ saturated monobasic acids in the presence of KU 2-8 H⁺ in dicyclopentadienyl glycerol [8, 9].

6. Glyceride diethers with tetracyclic structure were synthesized as a result of combination of glycerol with tetracyclododesene and its C₁-C₅ alkyl derivatives in the presence of catalyst BF₃·OEt₂, with a yield of 83.7% and 68.4-80.4% respectively. Synthesis of tetracyclododesyl glyceride ether as a result of the esterification reaction was carried out with a yield of 60.9% [4, 14, 15, 16].
7. The synthesized norbornyl glycerol and dihydro dicyclopentadiene monoglyceride were tested as insecticides against the Colorado potato beetle at the Vegetable Research Institute of the Ministry of Agriculture of the Republic of Azerbaijan. The tests were carried out in comparison with the German-made Konfidor insecticide as a benchmark and showed the same efficiency (97.5%).
8. Plasticizing properties of tricyclo[5.2.1.0^{2,6}]dec-3-en-8-yl-glyceride butyrate ester were tested at the Institute of Polymer Materials of ANAS. The tests were compared with dioctyl phthalate plasticizer. The results are the same, even some properties are better, so it is recommended to use it as a plasticizer for PVC compositions.

THE MAIN CONTENT OF THE DISSERTATION IS STATED IN THE FOLLOWING PUBLICATIONS:

1. Mammadov, M.K., Mammadova, Kh.M., Piraliyev, A.G. Ditsiklopentadien اساسında gliserid monoefirinin sintezi // H.Aliyev 90 illiyina hasr olunmush I Beynalkhalg Kimya va Kimya Muhandisliyi konfransı, -Bakı: -17-21 aprel, -2013, -s.153.
2. Mammadov, M.K. Sintez tricziklo[5.2.1.0^{2.6}]decz-3-en-8(9)-ilgliczerida/ M.K. Mammadov, Kh.M. Mammadova // Khimicheskie prob., -2013, №1, -s. 59-63.
3. Mammadov, M.K., Mammadova, Kh.M., Piraliyev, A.G. Tritsiklodetsenilgliserid efirinin sintezi // Akademik M.F. Naghıyevin 105 illiyina hasr olunmush elmi konfransın materialları, -Bakı: -2013. -s. 59-61.
4. Mammadov, M.K. Sintez tetracziklododeczena i ego metilzameshhenogo proizvodnogo / M.K. Mammadov, Kh.M. Mammadova, E.G. Makhmudova, V.S. Gadirli // Azerbajdzhanskij Khim. zhur., Baku: -2013. № 4, -s. 96-100.
5. Mammadov, M.K. Optimizacziya proczessa polucheniya tricziklo[5.2.1.0^{2.6}]decz-3-en-8(9)-ilgliczerida/M.K. Mammadov, R.P. Dzhafarov, Kh.M. Mammadova//Trudy molodykh uchenykh, -2013. №8, -s.120.
6. Mammadov, M.K. Sintez bicziklogeptilovykh monoefirov gliczerina / M.K. Mammadov, Kh.M. Mammadova, A.G. Piraliyev, G.N. Mehdiyeva // Scientific works, -2014. №1, -s. 124-128.
7. Mammadov, M.K., Mammadova, Kh.M., Gurbanova, Kh.G. Ditsiklopentadiena gliserinin birlashdirilmesi reaksiyasının tadgigi//Akademik S.J.Mehdiyevin 100 illik yubileyina hasr olunmush respublika elmi-praktiki konfransı,-Bakı:2014. j.1, s.6.
8. Mammadov, M.K, Mammadova, Kh.M., Yusifli, V.S. Sintez smeshannykh diefirov gliczerina // III International scientific conference of young researchers, -Baku: -17-18 aprel, -2015. -p. 272-274.
9. Mammadov, M.K. Sintez smeshannykh diefirov tricziklo[5.2.1.0^{2.6}]decz-3-en-8-il nasyshhenykh C₁-C₅ kislot 1.3-gliczerida/M.K. Mammadov, Kh.M. Mammadova, V.S.

- Yusifli // Mezhdunarodnyj nauchnyj institut «Educatio», №4 (11), -2015. ch. 3, -s. 154-157.
10. Mammadov, M.K., Mammadova, Kh.M. Gliserin اساسında yeni monomerin sintezi // Monomerlar va polimerlar kimyasının muasir problemlari III respublika konfransının materialları, -Sumgayıt: -2015, -s. 16-18.
 11. Mammadova, Kh.M. Gliserin اساسında bitsiklik sada va murakkab diefirlarin sintezi//Neftkimya uzra Beynalkhalg Mammadaliyev konfransının materialları, -Bakı: 4-5 oktyabr, -2016. s. 63.
 12. Mammadov, M.K., Mammadova, Kh.M., Kadyrly, V.S., Ismailova, Dzh.G., Yusifli, V.S Sintez bicziklicheskikh monoe`firov gliczerina // Mezhdunarodnoj nauchno-tekhnicheskoy konferenczii «Neftekhimicheskij sintez i kataliz v slozhnykh kondenczirovannykh sistemakh», posvyashhennoj 100-letnemu yubileyu akademika B.K. Zejnalova, -Baku: -29-30 iyunya, -2017. s. 117.
 13. Mammadova, Kh.M. Monotsiklik qarışığ diefirlarin sintezi // The International Sjientifij jonferenje “Ajtual Problems of Modern Jhemistry” Dedijated to the 90th Anniversary of the Ajademijian Y.H. Mammadaliyev Institute of Petrojhemijal Projesses, -2-4 ojtobor, -2019. -p.127.
 14. Mammadova, Kh.M. Sintez prostyx efirov gliczerina na osnove tetracziklicheskikh olefinov // «Rossijskaya nauka v sovremennom mire» XXIII Mezhdunarodnaya nauchno-prakticheskaya konferenciya, -15 iyulya -2019. c. 39-40.
 15. Mammadova, Kh.M. Preparation of monocyclic diesters of glycerol // Chemical problems, -2019. 4(17), -p.546-550.
 16. Mammadova, Kh.M. Synthesis of tetracyclic ethers of glycerine // Processes of petrochemistry and oil refining, -2020. -vol. 21, № 1, -p. 45-52.
 17. Ibragimova, M.D. Ispolzovanie gliczerina pri sinteze policziklicheskikh gliczeridov / M.D. Ibragimova, Kh.M. Mammadova, R.A. Rasulova, V.S. Kadyrly, E.G. Makhmudova //Khimiya v interesakh ustojchivogo razvitiya, -2020. t. 28, №2, -s. 165-17.

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