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M. P. Bei, A. P. Yuvchenko, O. V. Sokol

The Institute of Chemistry of New Materials of the Nationa Academy of Sciences of Belarus, Minsk, Republic of Belarus

SYNTHESIS AND PROPERTIES OF NEW DERIVATIVES OF MALEOPIMARIC AND CITRACONOPIMARIC ACIDS

The review article summarizes data on synthesis of new derivatives of maleopimaric acid (the most available diterpenoid acid, isolated from maleated rosin) – esters, amides, imides, imido amides, imido esters, diimido acids etc. and of oxygen- and nitrogen containing derivatives of previously unknown citraconopimaric acid. The article mainly covers the literature data since 2000 year as well as work carried out in the Institute of Chemistry of New Materials of NAS of Belarus.

Keywords: rosin, terpenoids, maleopimaric acid, citraconopimaric acid, esters, amides, imides.

М. П. Бей, А. П. Ювченко, О. В. Сокол

Институт химии новых материалов НАН Беларуси, Минск, Республика Беларусь

СИНТЕЗ И СВОЙСТВА НОВЫХ ПРОИЗВОДНЫХ МАЛЕОПИМАРОВОЙ И ЦИТРАКОНОПИМАРОВОЙ КИСЛОТ

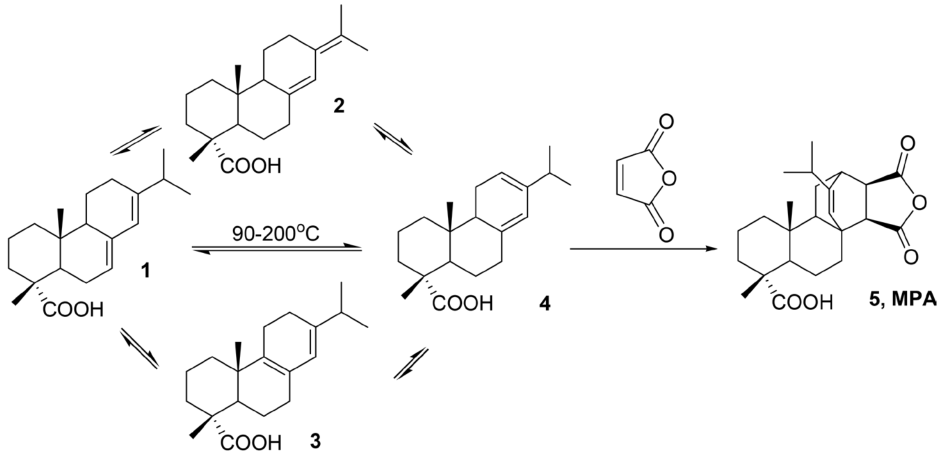
Представлен обобщающий и систематизирующий обзор данных по синтезу производных малеопимаровой кислоты (наиболее доступной дитерпеноидной кислоты, выделяемой из малеинизированной канифоли) – эфиров, амидов, имидов, имидоамидов, имидоэфиров, диимидокислот и др., а также кислород- и азотсодержащих производных ранее неизвестной цитраконопимаровой кислоты. Приведены литературные данные с 2000 г., а также работы, выполненные в Институте химии новых материалов НАН Беларуси.

Ключевые слова: канифоль, терпеноиды, малеопимаровая кислота, цитраконопимаровая кислота, сложные эфиры, амиды, имиды.

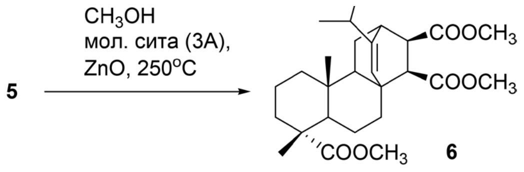
Terpenes from wood resins (essential oils and rosins) constitute one of the valuable part of plant resources and main source of terpene substances. In the last decades, the intensive studies were directed toward the development of new methods for valuable chemical products preparation from renewable raw materials and the individual substances that can be isolated or synthesized from rosin are of special interest. The most promising approach to the preparation of individual diterpene derivatives is to modify rosin in particular by active dienophiles. The most available individual substance thus obtained is maleopimaric acid (MPA), isolated from rosin-maleic anhydride adduct (RMA). This compound is used for the production of printing inks, alkyd resins, lubricants, paper sizing agent, and its derivatives show pronounced biological activity [1−5]. This review article mainly covers the literature data on preparation of new maleo- and citraconopimaric acid derivatives since 2000 year as well as work carried out in the Institute of Chemistry of New Materials NAS of Belarus.

1. The synthesis and application of maleopimaric acid and its derivatives. The MPA, **5** was firstly obtained independently by Arbuzov and Ruzicka et al. in 1932 in the course of studies of resin acids structure [6, 7]. Two main groups of methods have been proposed for the MPA synthesis. The first group consists of methods using reaction of levopimaric acid **4** (content up to 53% in wood resin [8]) and maleic anhydride at 30–80 ºC [9, 10]. The disadvantage of these methods is that abietic-type acids (abietic **1,** neoabietic **2**, palustric **3**) except levopimaric acid **4** stay intact decreasing MPA yield.

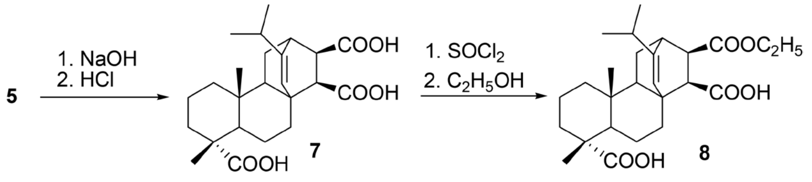
The second group of methods is based on reaction of abietic-type acids (abietic **1,** neoabietic **2**, palustric **3**) of rosin with maleic anhydride at 90–200 ºC or MW-irradiation including the application of catalysts followed by isolation of MPA from mixture [11–13]. These methods are the most often used for individual MPA synthesis.



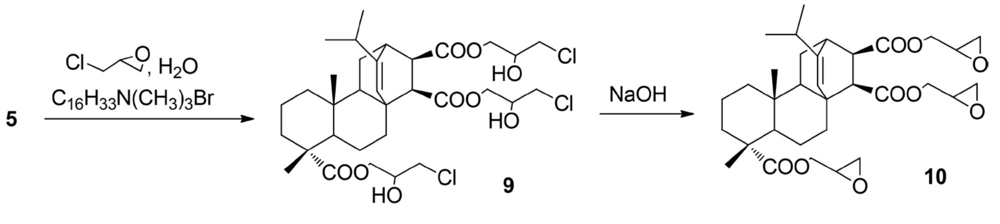
MPA is a tribasic acid anhydride, as a result its derivatives on carboxyl groups, in particular mono-, di-, tri- and polyesters are among the most important. MPA methyl ester was firstly obtained by treatment of MPA with diazomethane [14] and monoethyl-, propyl- and butyl esters were prepared by reaction of MPA with PCl_3 followed by treatment with the correspondent alcohol [15]. The MPA vinyl ester was synthesized by reaction of MPA and vinyl acetate catalyzed by mercury salt [16]. MPA trimethylester **6** was prepared by reaction of MPA and methyl alcohol in autoclave at the presence of molecular sieves (3Å) at 250 °C for 4 h in 98% yield [17].



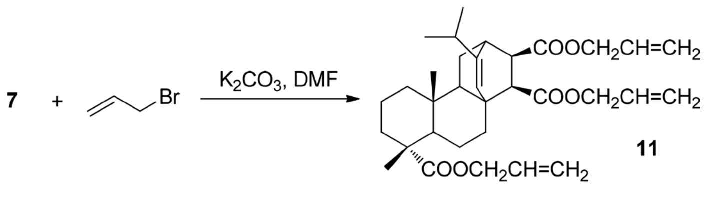
The treatment of MPA with 30% NaOH solution and subsequent acidification gave triacid **7**. Reaction of the acid **7** with $SOCl_2$ followed by the treatment with ethyl alcohol led to the regioselective formation of monoethyl ester **8** in 73% yield [18].



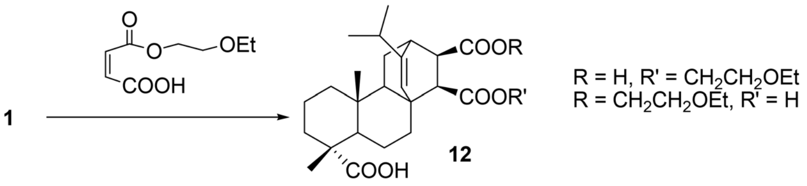
The MPA triglycidyl ester useful for polymer producing was prepared in two stages. Firstly the reaction of MPA with epichlorohydrin in the presence of hexadecyltrimethylammonium bromide gave triol **9**, which was converted into triglycidyl ester **10** in 87% yield under the treatment with sodium hydroxide solution [19].



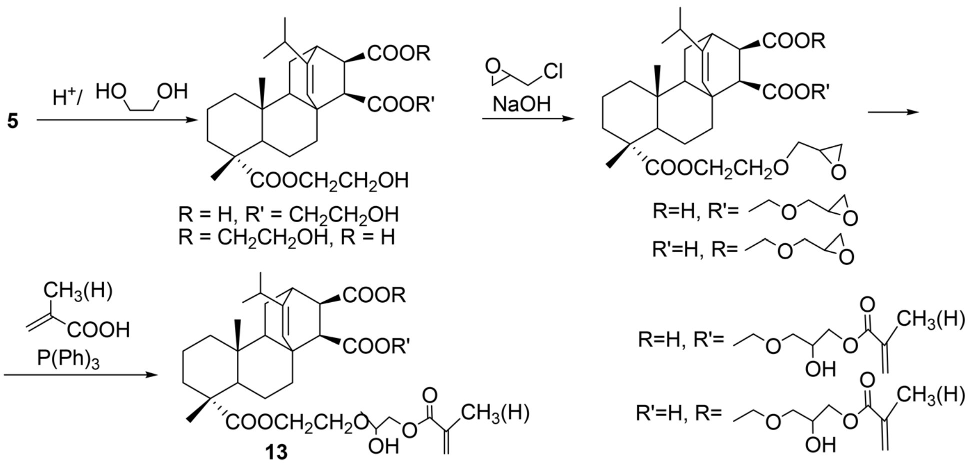
MPA triallyl ester **11** was synthesized by reaction of triacid **7** with allyl bromide in 91% yield and used for preparation of bio-based thermosetting resins [20].



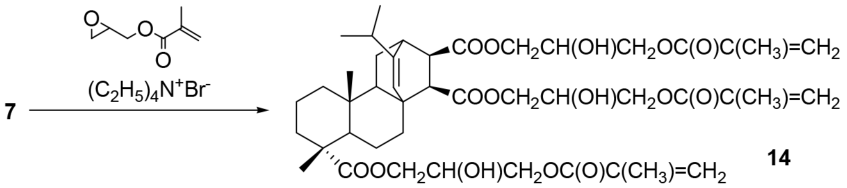
The mixture containing the isomeric MPA 2-ethoxyethyl esters **12** was prepared by reaction of tall rosin with 2-ethoxyethylmaleat and used as paper sizing agent [21].



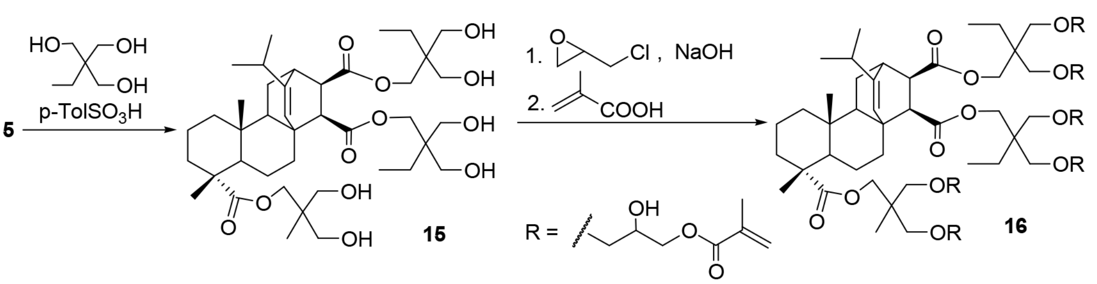
MPA was used for the synthesis of acrylic esters. The esterification of MPA with ethylene glycol gave a mixture of diesters that on treatment with epichlorohydrin followed by reaction with acrylic or methacrylic acids in the presence of $P(Ph)_3$ provided the mixture of acrylic esters **13** useful for corrosion protection of metals [22].



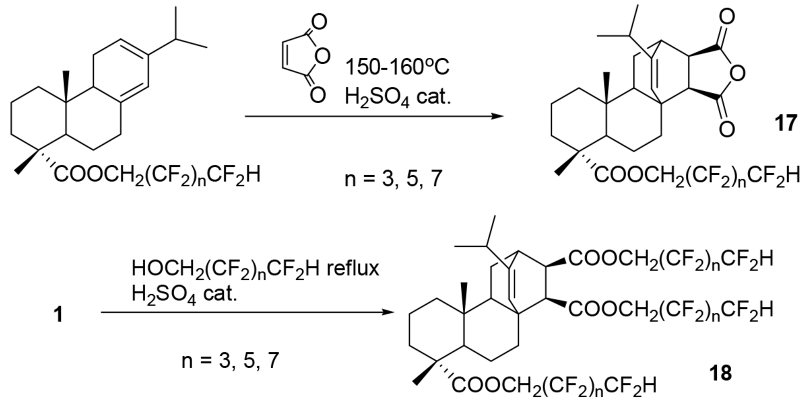
The MPA triacrylic ester **14** was prepared in two stages. MPA was converted into triacid **7**, and subsequent treatment of the latter one with glycidyl methacrylate in the presence of tetraethylammonium bromide gave triester **14** useful for producing of methyl methacrylate and stirol copolymers [23].



RMA was esterified by trimethylol propane to give mixture containing polyol **15**. Reaction of polyol **15** successively with epichlorohydrin and methacrylic acid afforded polyacrilic ester **16**. Thermal, mechanical and chemical performance of vinyl ester resins based on ester **16** as high performance coatings materials were found to be comparable to those of conventional petroleum based coating materials [24].

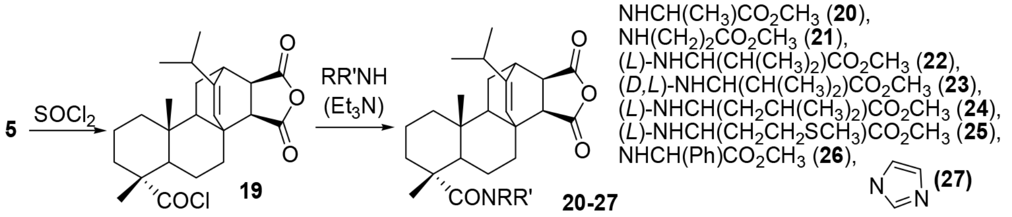


The perfluoroalkyl esters of MPA **17** were prepared by Diels-Alder reaction of rosin perflouroalkyl esters with maleic anhydride at 150–160 ºC under acidic catalysis [25]. The refluxing of MPA in the corresponding alcohol at the presence of sulfuric acid gave MPA perfluoroalkyl triesters **18** in 55–70% yield [26].

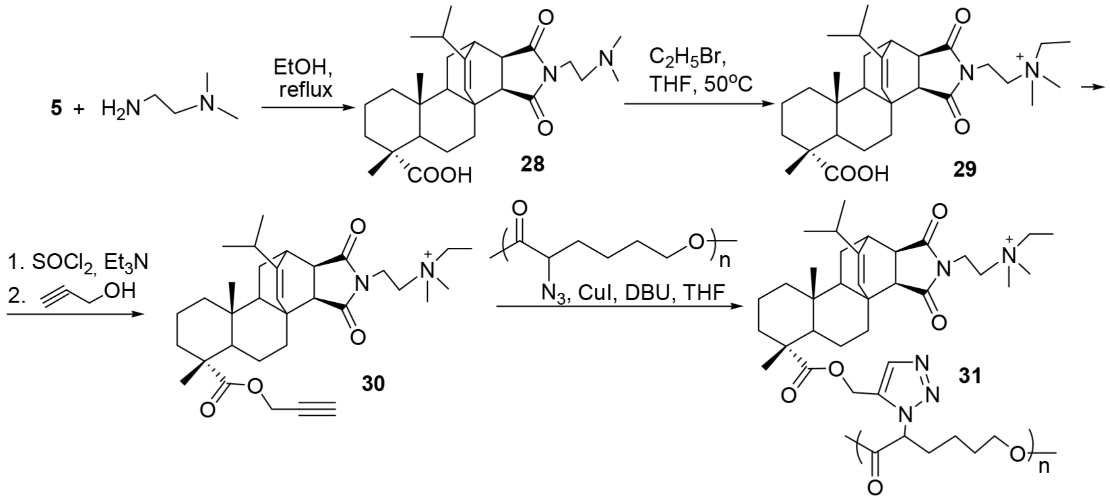


Amide compounds from MPA were firstly synthesized by treatment of MPA vinyl ester with cyclohexylamine [16]. It was found substituted MPA amides show pronounced hepatoprotective [27], antimicrobial [5] and fungicidal properties [28], and MPA based polyamides are suitable for applications as protective films, printing inks, thermo stable polymers [29–31].

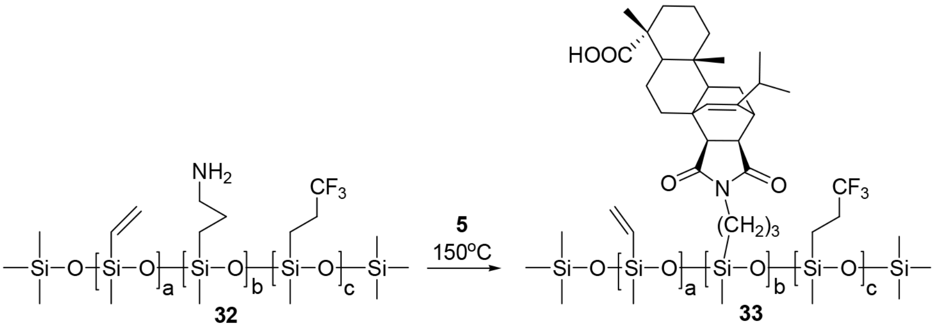
MPA amides **20–27** with anti-inflammatory and antiulcer properties were synthesized by reaction of MPA chloride **19** with amino acids and imidazole. It was established that amide **24** prepared from L-leucine has the highest anti-inflammatory properties and show low toxicity [32].



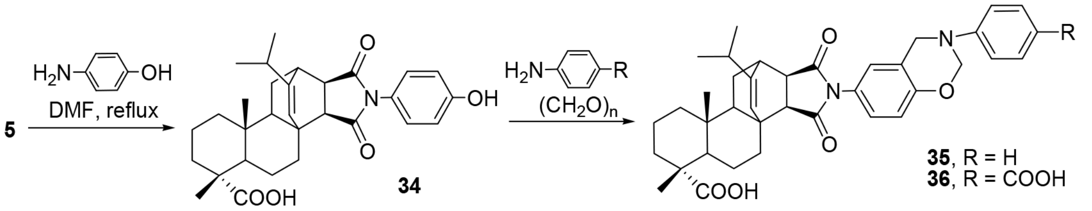
Wang et al. synthesized antimicrobial polymers **31** based on MPA N-(2-N,N-dimethylethyl)imide and azide substituted poly(ε-caprolactone). MPA N-(2-N,N-dimethylethyl)imide after quaternization and esterification with propargyl alcohol was grafted on polymer by click-reaction with the use of CuI/DBU as catalysts [33].



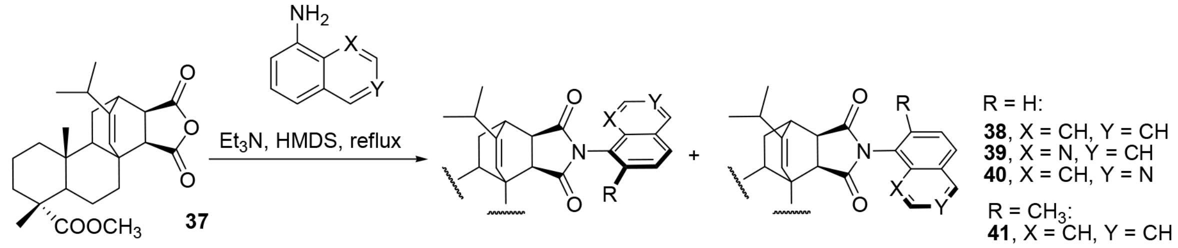
The MPA imide modified fluorosilicone resin **33** was prepared by heating of MPA and amine containing fluorosilicone resin **32** at 150°C for 4 h. This novel crosslinker was added into high temperature vulcanization rubber composition to prepare a series of MPA modified fluorosilicone rubbers with increased mechanical properties [34, 35].



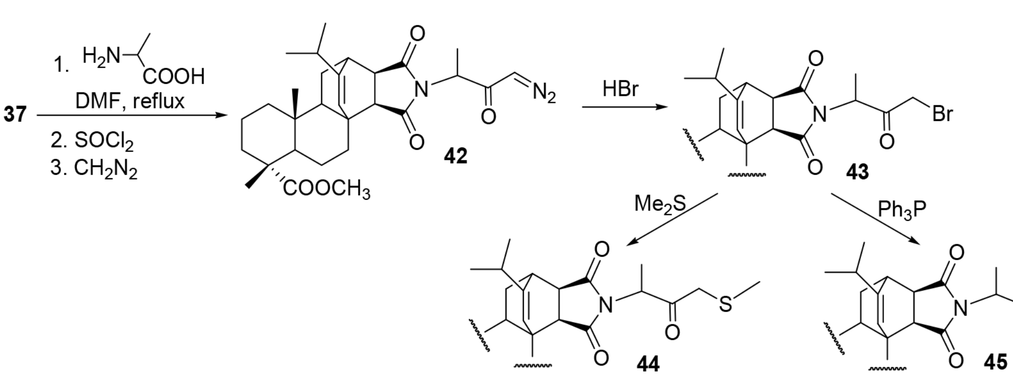
The benzoxazine monomers **35, 36** were synthesized from MPA in two steps. The reaction of MPA and 4-aminophenol afforded MPA N-(4-hydroxy)phenyl imide **34** that on reaction with paraformaldehyde and aniline (or 4-aminobenzoic acid) gave benzoxazines **35, 36.** The polybenzoxazines were prepared by polymerization of compound **35, 36** and showed high thermal stability [36].



Reactions of MPA methyl ester **37** with 1-naphtylamine, 8-aminoquinoline, 5-aminoisoquinoline [37] and 2-methy-1-naphtylamine [38] in refluxing triethylamine in the presence of hexamethyldisilazane (HMDS) give MPA imides **38–41** as the mixture of atropisomers. It was found N-(2-methylnaphtyl-1) imide of MPA methyl ester **41** has anti-proliferative properties and a significant difference in the level of cytotoxicity was observed between R- and S-conformers [38].

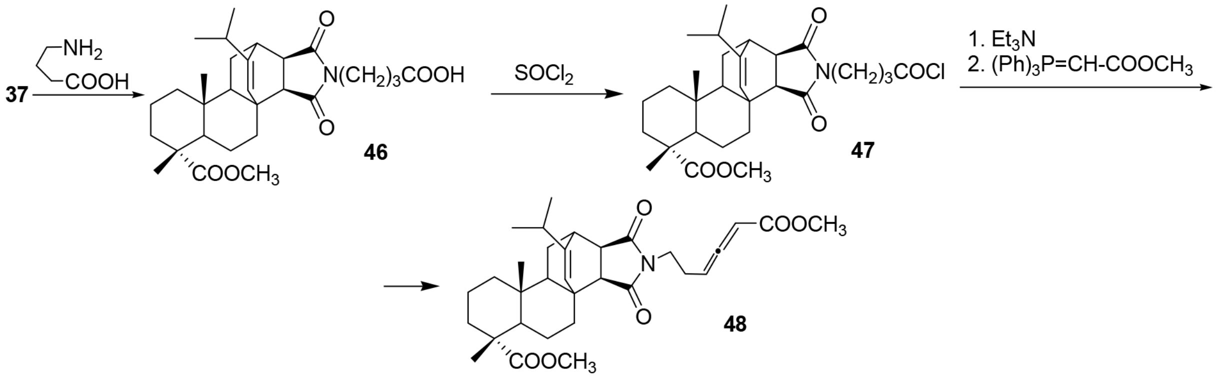


The bromomethylketone **43** was synthesized for the first time under Arndt–Eistert reaction conditions via condensation of ester **37** and alanine. Treatment of ketone **43** with Me_2S or Ph_3P led to the formation of methylsulfide **44** or to reduction into ketone **45**, presumably due to the traces of water [39].

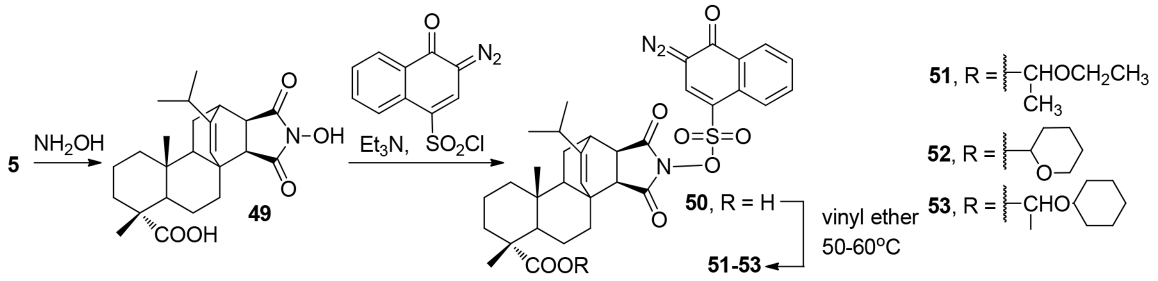


The allene **48** was synthesized from methyl maleopimarate **37** and γ-aminobutyric acid (GABA). Direct fusion or condensation of ester **37** with GABA gave the imide **46** in 52 or 72% yields, respectively, which was converted into the corresponding acid chloride **47** by reaction with $SOCl_2$ excess.

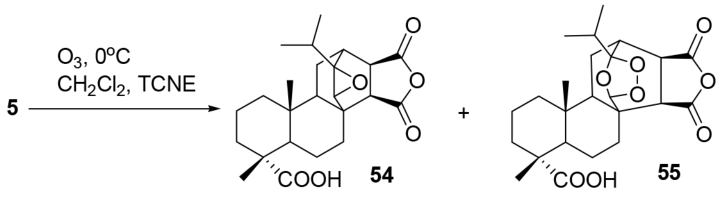
Treatment of chloride with Et_3N and subsequent reaction with methyl(triphenylphosphoranylidene)acetate provided the corresponding allenoate **48** in 66% yield [40].



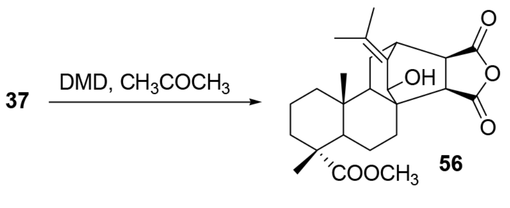
New molecular glass compounds containing 2-diazo-1-naphthoquinone-4-sulfonyl group were designed based on MPA. Reaction of MPA with hydroxylamine gave MPA N-hydroxyimide **49** in 70% yield that on esterification with 2-diazo-1-naphthoquinone-4-sulfonyl chloride provided N-hydroxy maleopimarimide sulfonate **50**. The carboxylic acid group of the acid **50** was then protected by the reaction with vinyl ether compounds (vinylethyl ether, cyclohexylvinyl ether, dihydropiran) to give the corresponding esters **51–53**. The novel one-component molecular glass resists **51–53** have potential to become high-performance i-line photoresists [41].



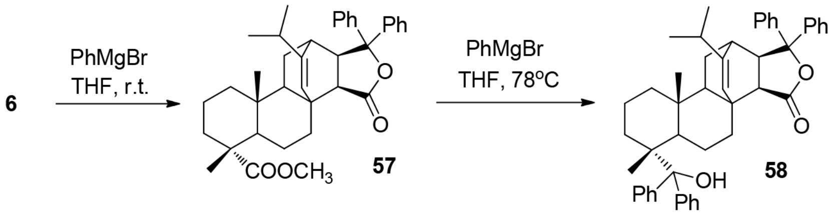
Hess et al. showed that the ozonolysis of MPA in the presence of tetracyanoethylene (TCNE) and subsequent purification lead to isolation of known epoxide **54** in 20% yield and the ozonide **55** in 7% yield [42].



Reaction of the MPA methyl ester **37** and dimethyldioxirane (DMD) resulted in regioselective oxidation of the bridging double bond to form the alcohol **56** [43].

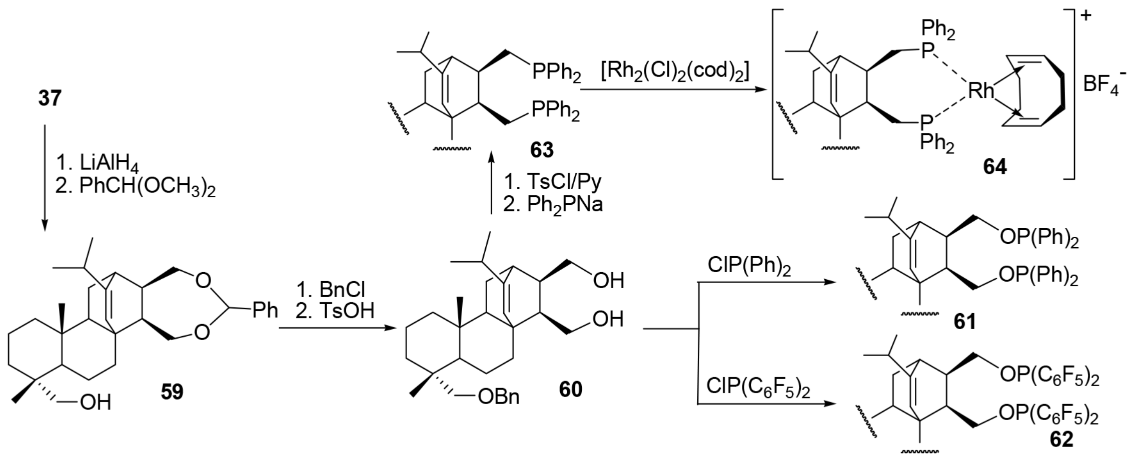


Yao et al. established that reaction of MPA trimethyl ester **6** with PhMgBr proceeds at only one carboxyl group at r. t. to form lactone **57** that on treatment with Grignard reagent at 78°C converts into alcohol **58** [44].

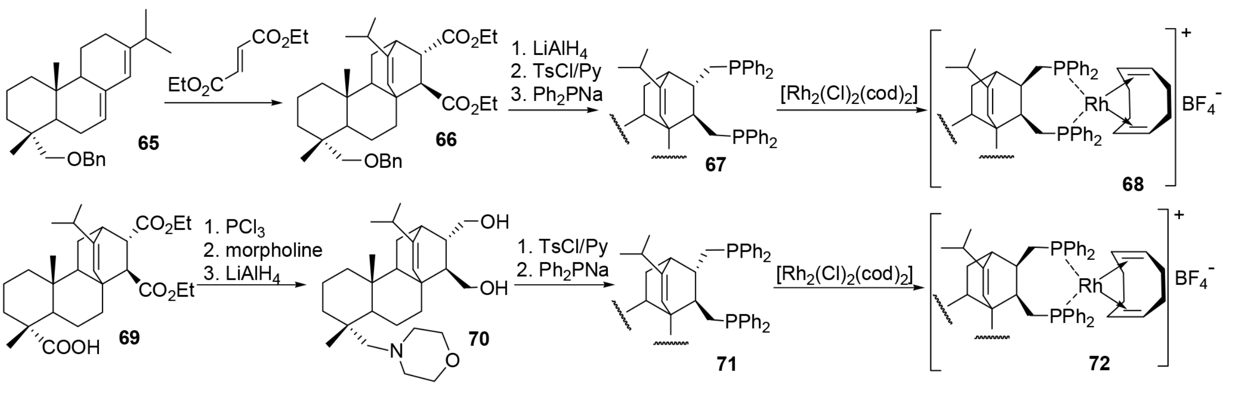


Asymmetric synthesis has been one of the most important topics in organic chemistry over the past decades and terpenoid substances prepared from rosin are very accessible optical pure compounds that make them useful starting synthone for synthesis of chiral ligands.

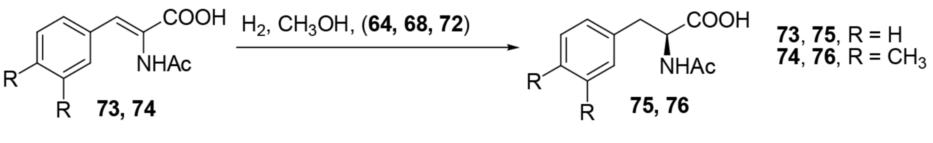
Chiral bisphosphinic ligand **63, 67, 71** were synthesized from MPA [45]. Reduction of MPA methyl ester **37** with $LiAlH_4$ and protection of 1,4-diol moiety gave benzylidenedihydroxy derivative **59**. Formation of benzylic ether and deprotection led to the diol **60** that was treated with phosphine chlorides to give 1,4-bisphosphineoxides **61, 62**. Treatment of diol with *p*-toluenesulfochloride gave ditosylate that on reaction with sodium diphenylphosphide afforded bisphosphine **63**. Reaction of bisphosphine with di-**μ**-chloro-bis-(1,5-cyclodiene)dirhodium and $NaBF_4$ in CH_2Cl_2 yields the cation Rh(I)-complexes **64**.



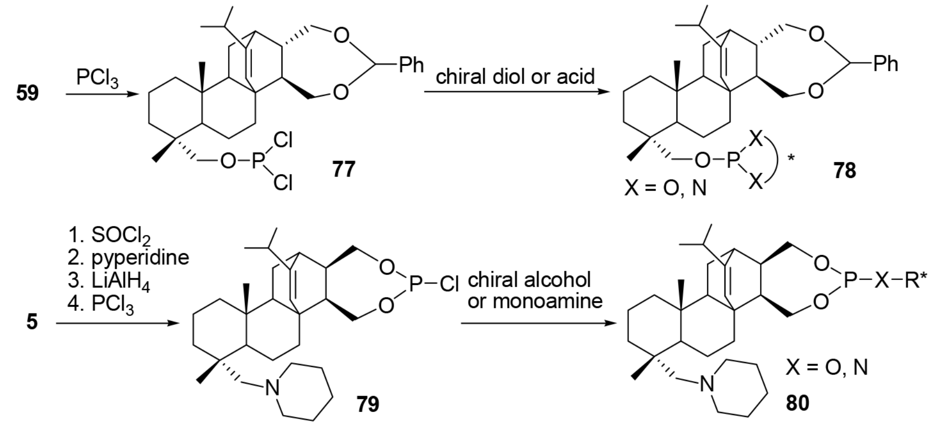
The ligands **67, 71** and their Rh(I)-complexes **68, 72** were prepared from benzylic ether of abiethynol **66** and diethyl fumaropimarate **69** in a similar manner [45].



The rhodium complexes **64, 68, 72** were used as catalysts for hydrogenation of substituted cinnamic acids **73, 74**. It was found application of these catalysts provided hydrogenation to give amino acids **75, 76** with up to 100% yield and 66% *ee* [45].

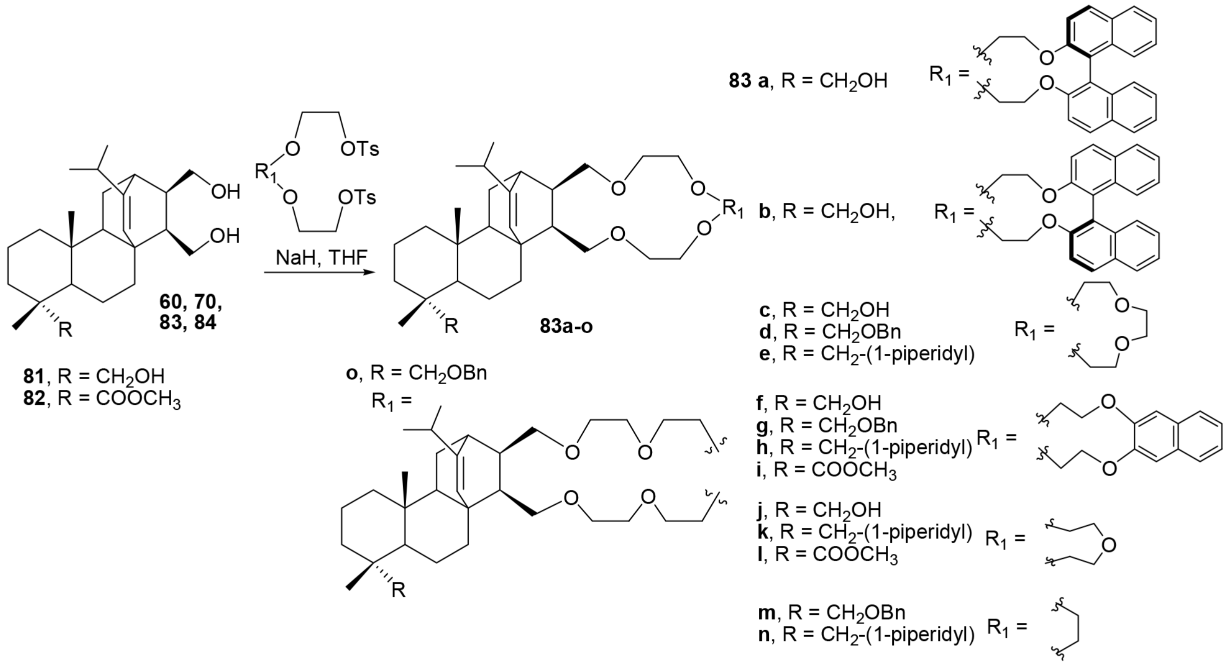


Two chiral phosphorus derivatizing agents **77** and **79** were synthesized from MPA and it was established these derivatives are well suited for the ^{31}P NMR-based determination of enantiomeric excess of chiral alcohols and amines in solutions [46].



Note: * Means a chiral group

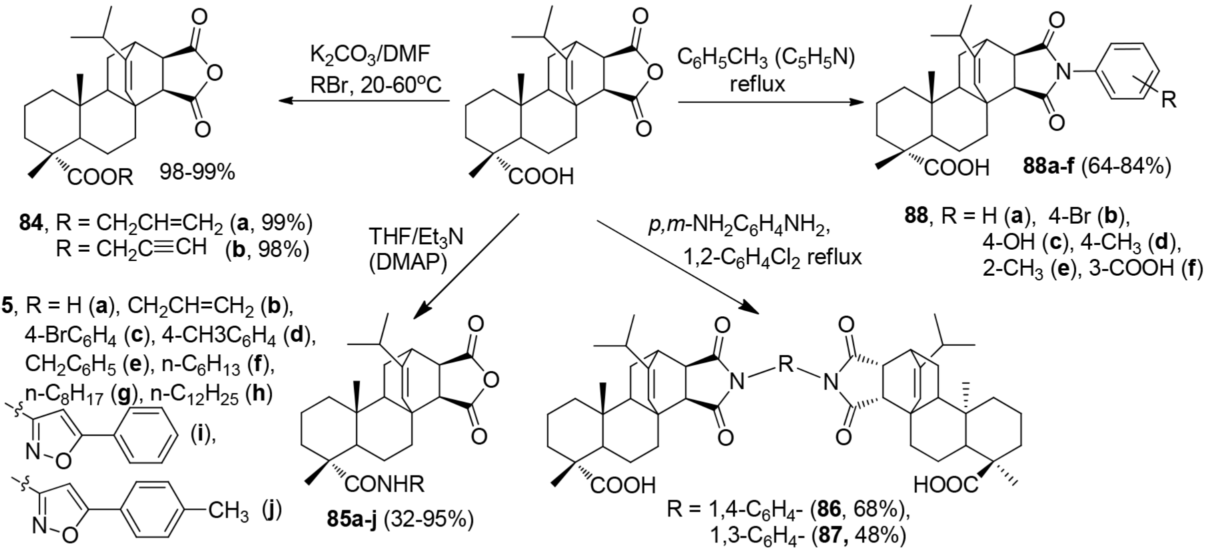
A series of chiral crown ethers **83a–o** including 28-crown-8, 22-crown-6, 20-crown-6, 17-crown-5 and 14-crown-3 bearing hydroxyl side group derivatives comprising of binaphthyl, naphthalene and rosin acid moieties in the crown ring was prepared based on MPA [47, 48].



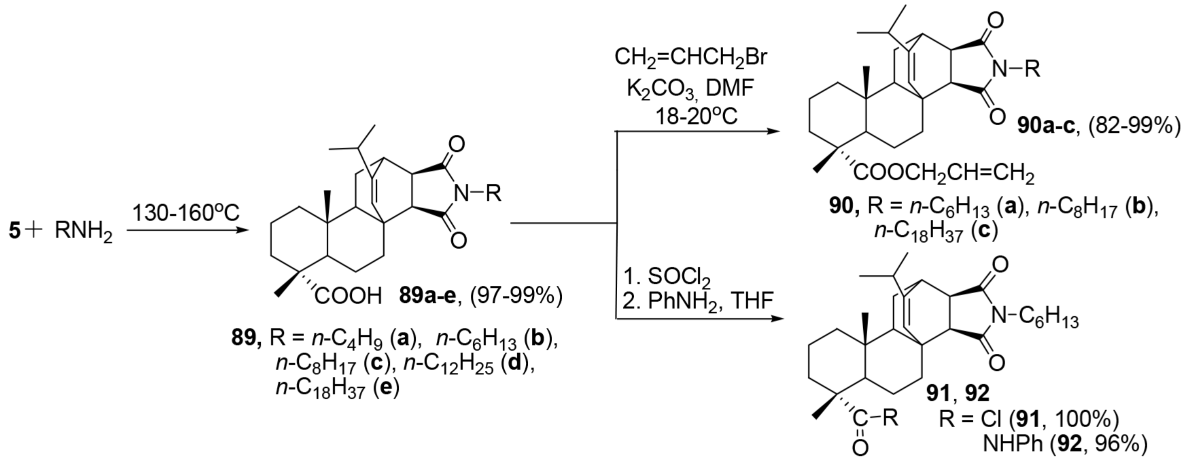
These receptors **83a–o** showed strong affinity and different complementarity for various amine salts, and exhibited excellent enantiodiscriminating abilities towards protonated primary amines and amino acid methyl ester salt isomers in chiral recognition [48].

To conclude this section it is worth noting that apart from individual MPA derivatives the esters of RMA with polyols (ethylene glycol, glycerol, pentaerythritol etc.) as well as RMA imides are widely used in industry for production of alkyd and epoxy resins, printing inks, polymers and copolymers, sizing agents for paper making [3, 4].

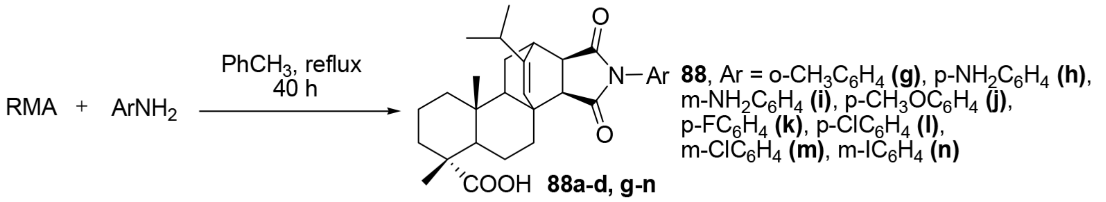
2. Researches on diterpenoids at The Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus. The new preparative methods for synthesis of MPA unsaturated esters **84a, b**, amides **85a–j**, imides **88a–f** and diimido diacids **86, 87** were developed by reaction of MPA with allyl-, propargyl bromide, aliphatic and aromatic amines [49–52].



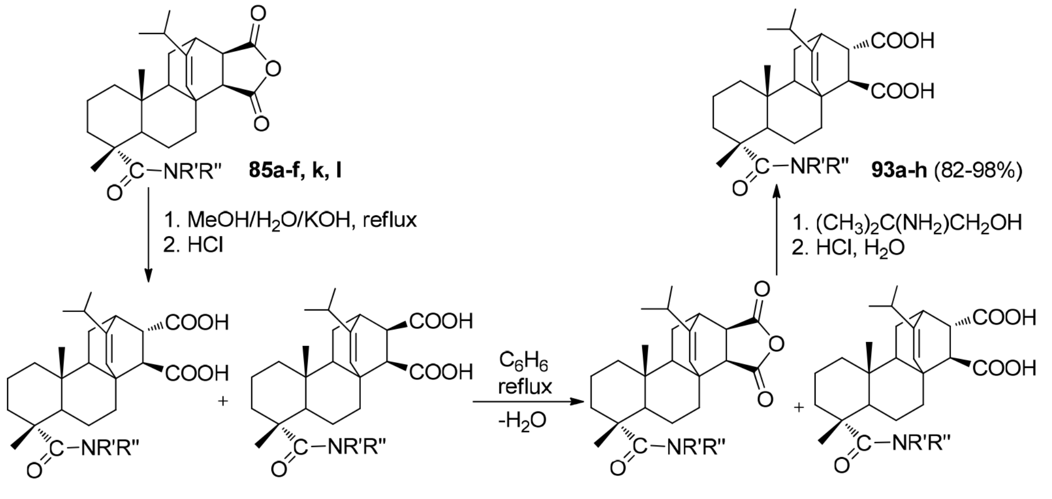
The synthesis of previously unknown MPA N-alkylimides **89a–e**, including long-chain dodecyl- and octadecylimides **89d, e** by reaction of primary aliphatic amines with MPA in the melt was developed. The method eliminates the use of organic solvents, allows application as a starting compound MPA and acetic acid solvate, significantly reduces reaction time [53]. Imido amide **92** was prepared by reaction of imide **89b** with thionyl chloride followed by reaction with aniline.



The MPA N-arylimides synthesis directly from RMA without isolation of individual MPA was developed based on treatment of RMA with primary aromatic amines in toluene (refluxing) to form exclusively N-arylimides **88a–e**, **g–n** in preparative yields (60–99% based on MPA contained in the RMA) [51].



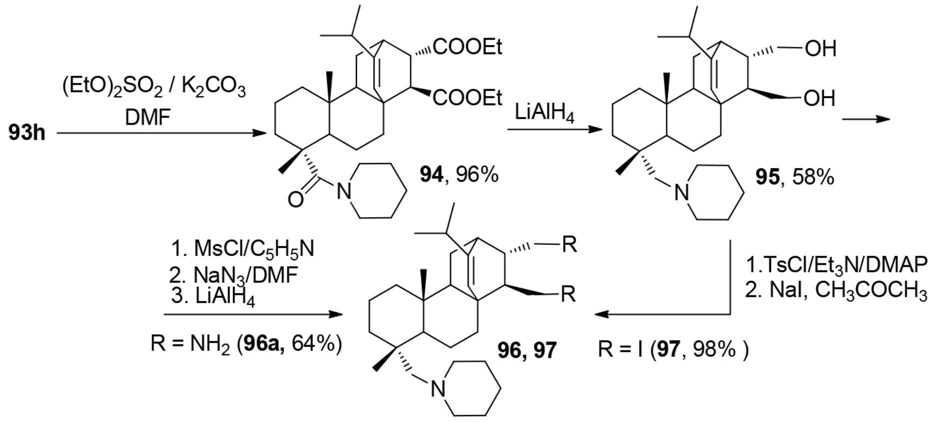
We elaborated the method of fumaropimaric acid monoamides **93a–h** synthesis containing *trans*-1,2-dicarboxylic fragment by alkali hydrolysis of anhydride group in MPA amides **85a–f, k, l** and subsequent isomerization of *cis*-1,2-dicarboxylic acid. The monoamides **93a–h** were isolated from the reaction mixture by conversion into water-soluble ammonium salts [54].



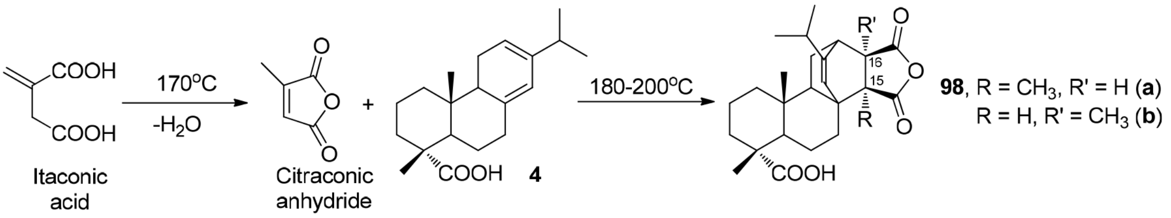
85, NR'R'' = NHPh (**k**), NC_5H_{10} (**l**)

93a-h, NR'R'' = NH_2 (**a**), $NH(CH_2)_5CH_3$ (**b**), $NHCH_2CH{=}CH_2$ (**c**), NHPh (**d**), $NHCH_2Ph$ (**e**), NH-(*p*)-$C_6H_4CH_3$ (**f**), NH-(*p*)-C_6H_4Br (**g**), NC_5H_{10} (**h**)

Esterification and subsequent reduction of amide **93h** afforded diol **95** that was converted into diamine **96** and diiodide **97** by conventional methods.



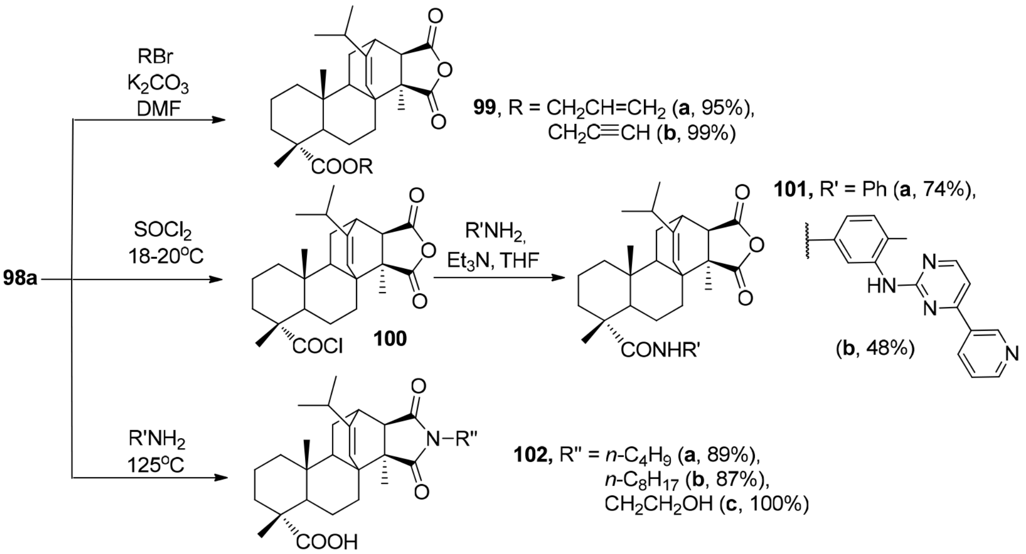
With a goal of citraconopimaric acid (CPA) synthesis the reaction of citraconic anhydride, formed *in situ* from readily available itaconic acid (produced industrially by the fermentation of carbohydrates) on heating above the melting point (172 °C), and rosin has been studied. It was established that the heating of mixture of rosin and itaconic acid at 180–200 °C for 8–12 h leads to the reaction of citraconic anhydride with levopimaric acid and to the formation of complex mixture containing isomeric citraconopimaric acids **98a, b** and unreacted resin acids (IR, ^1H NMR data). IR-spectra of the mixture contain characteristic bands of anhydride cycle at 1850, 1785 cm^{-1}. The crystallization of the reaction product from CCl_4 at 18–20 °C gives precipitate of solvate CPA with CCl_4, and its thermal decomposition at 130 °C gives CPA as a mixture of two isomers **98a, b** at ratio ~1:0.36. CPA isomers differ in the arrangement of the methyl group in the anhydride cycle only and have almost the same chromatographic mobility in different systems. By partial crystallization of mixture of isomers **98a** and **98b** from benzene the isomer **98a** was separated in 36% yield (based on mixture of isomers **98a, b**) [55].



98, R = CH_3, R' = H (**a**)
R = H, R' = CH_3 (**b**)

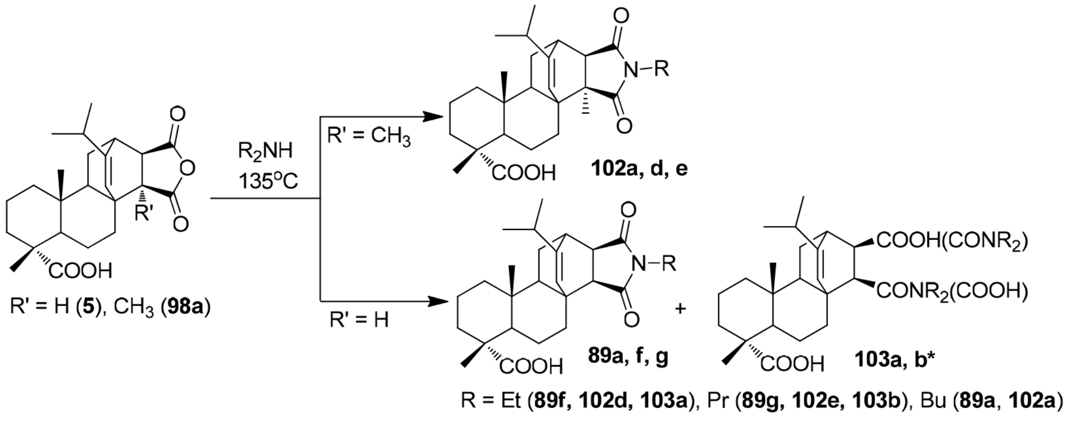
The full assignments of peaks in ^1H and ^{13}C NMR spectra were performed by two-dimensional NMR spectroscopy, and it was confirmed that the compound **98a** is the adduct of citraconic anhydride and levopimaric acid (citraconopimaric acid) and a close structural analog of MPA, containing methyl in the α-position of the anhydride group [56].

Reaction of CPA **98a** with allyl- or propargylbromide in the presence of K_2CO_3 afforded unsaturated esters **99a, b** [49]. The treatment of CPA **98a** with thionyl chloride gave the acid chloride **100**, and its reaction with aniline and N-(2-methyl-5-aminophenyl)-4-(pyrid-3-yl)pyrimidine-2-amine led to the formation of anilide **101a** and heterocyclic amide **101b** [57].



The N-alkylimides **102a–c** were synthesized by reaction of CPA with secondary *n*-butylamine, *n*-octylamine, ethanolamine at 125°C [58]. The treatment of CPA N-(2-hydroxyethyl)imide **102c** with dimethylsulfate in the presence of K_2CO_3 gave methyl ester of CPA N-(2-hydroxyethyl)imide (yield 73%).

Reactions of CPA and MPA with secondary aliphatic amines (diethyl-. dipropyl-, dibutylamine) were investigated for the first time [59]. Formation of CPA N-substituted imides instead of expected amido acids was found. In contrast to CPA reaction of MPA gives the only product in reaction with dibutylamine, but in reactions with diethyl- and dipropylamines amido acids **103a, b** were formed together with MPA N-ethyl(propyl)imide.



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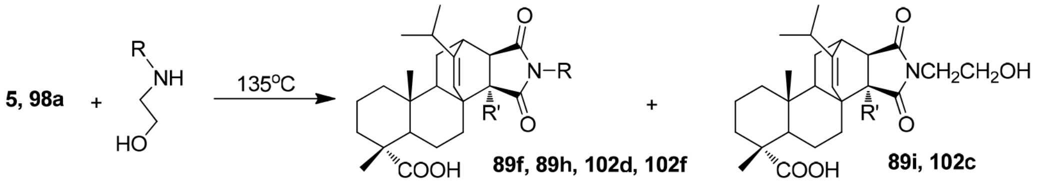
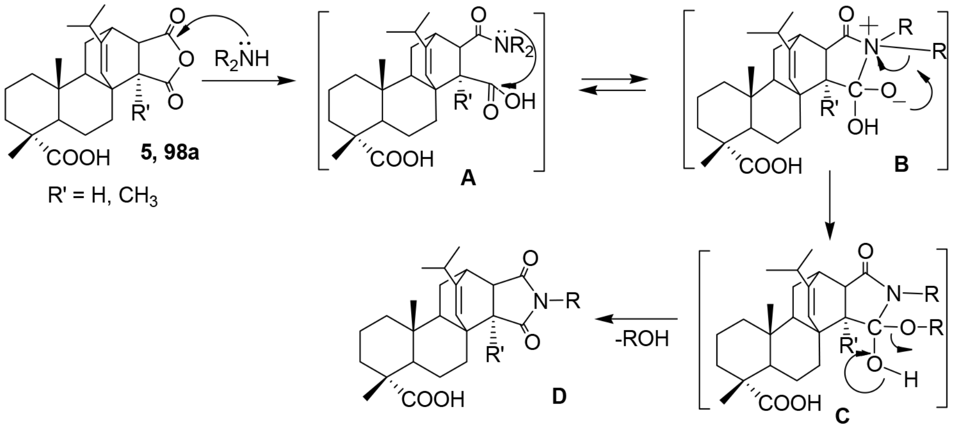
* Exact location of the amide group in compounds **103 a, b** is not defined.

The treatment of MPA and CPA with unsymmetrical methyl(ethyl)-2-hydroxyethylamines leads to formation of two imides: N-methyl(ethyl)- and N-(2-hydroxyethyl)imides of MPA and CPA (in molar ratio 1:(0.78–1.63)) [59].



R' = H (**89f, 89h, 89i**), R = Me (**89h**)
R' = Me (**102c, 102d, 102f**), R = Me (**102f**)

The mechanism of this reaction presumably involves the formation of the intermediate amic acid **(A)** that undergoes intramolecular cyclization to form the cyclic intermediate **(B)**, which is stabilized by the migration of the alkyl group **(C)**, followed by elimination of alcohol and formation of the cyclic N-alkylimid **(D)**. In the case of the reaction MPA, CPA with unsymmetrical secondary amines the formation of two imides, presumably, the result of migration of various alkyl groups in the intermediate **(B)**. The mechanism of this reaction is likely close to the mechanism of N-substituted imides formation in reaction of cyclic anhydrides with primary amines.



Ways of practical use of MPA and CPA derivatives. The effect of the MPA allyl ester **84a** was studied on rheological properties in modifying of low density polyethylene (LDPE) with itaconic acid in the presence of free radical initiators. It was found that ester **84a** additive in an amount of 1 wt. % of the reaction system decreases the efficiency of grafting only in 13% with more than 2 times the viscosity of the grafted product is reduced. The MPA ester **84a** may be used as a viscosity regulator during reactive extrusion of functionalized polyethylene with the desired rheological performance as well as in the preparation of coextruded multilayer polymeric products. Adhesive was developed based on ethylene-vinyl acetate copolymer (CEVA) with the addition of the MPA allyl ester **84a**, including CEVA, fumaric acid, an organic peroxide, a stabilizer and 0.01–1.0% of allyl ester **84a**. Adhesive bond strength with polar substrate of polyamide-6 for developed adhesive reaches 4.9 kN/m, which is 91% higher than that for similar adhesive compounds [60].

The MPA N-hexylimide **89b** is the effective adhesive additive to LDPE in the preparation of composite materials to wood at a concentration of 3%. The application of imide **89b** retains strength, highly elastic and rheological properties of the polymer composition, simultaneously the adhesive strength of the LDPE to the wood increases to 3.6 MPa, which is 1.6–1.8 times greater in comparison with samples of pure LDPE [61].

It was found that the nitrogen-containing MPA derivatives (aromatic amides **85a–c, f,** imide **89e** etc.) have twisting power and can be used as effective additives to nematic LC-materials [62].

A fungicidal composition comprising a salt of MPA N-hexylimide and 8-hydroxyquinoline was designed to protect the cellulose-containing materials [63].

Films of the compounds **5, 84a, b, 98a, 99a, b** prepared by thermal vacuum deposition method (TVD) are sensitive to UV radiation (3.6–7.1 J/cm^2) and of practical interest for the production of photomasks for wet etching topology in transparent conductive layers of indium tin oxide (ITO) [49].

To conclude this short review, since the last decades there has been a trend towards the development of methods for the use of renewable raw materials instead of fossil in the manufacture of industrial products. As it is evident from the review, it is possible to obtain a great number of based on rosin substances with diverse structures and properties for various applications, and these works constitute important part of the green chemistry development.

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Информация об авторах

Бей Максим Петрович – канд. хим. наук, ст. науч. сотрудник, Институт химии новых материалов НАН Беларуси (ул. Ф. Скорины, 36, 220141, Минск, Республика Беларусь). E-mail: beymaksim@gmail.com.

Ювченко Анатолий Петрович – канд. хим. наук, ст. науч. сотрудник, зам. директора по науч. работе, Институт химии новых материалов НАН Беларуси (ул. Ф. Скорины, 36, 220141, Минск, Республика Беларусь). E-mail: mixa@ichnm.basnet.by.

Сокол Ольга Валерьевна – мл. науч. сотрудник, Институт химии новых материалов НАН Беларуси, (ул. Ф. Скорины, 36, 220141, Минск, Республика Беларусь). E-mail: sokal.volha@gmail.com.

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Information about the authors

Bei Maksim Petrovich – Ph.D. (Chemistry), Senior Researcher, Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus (36 Skorina Str., 220141, Minsk, Republic of Belarus). E-mail: beymaksim@gmail.com.

Yuvchenko Anatolij Petrovich – Ph.D. (Chemistry), Senior Researcher, Deputy Director, Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus (36 Skorina Str., 220141, Minsk, Republic of Belarus). E-mail: mixa@ichnm.basnet.by.

Sokol Olga Valer’evna – Junior Researcher, Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus (36 Skorina Str., 220141, Minsk, Republic of Belarus). E-mail: sokal.volha@gmail.com.

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