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REVIEW

Maleated rosin-derived advanced materials: preparation, properties and application

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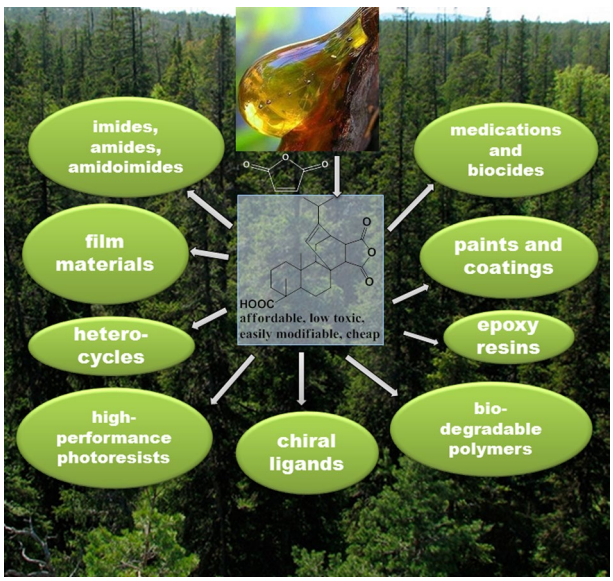
Abstract

The review is devoted to current trends in the development of the chemistry of tricyclic diterpenoids, in particular maleated derivatives of resin acids of the abietane series. Among the derivatives of plant terpenes, maleopimaric acid has become a popular molecule in recent years and is attracting growing interest. In this review, the chemical properties of maleopimaric acid (MPA) and its methyl ester (MMP) was studied, data on the methods of synthesis of imides, amides, and amidoimides of acid are systematized. Oxidation reactions and ozonolysis with the participation of monomethyl ether MPA are presented. Synthesis of monomers and polymers based on MPA is described. The expediency of using the most interesting developments with the use of MPA in pharmacology, in the chemistry of macromolecular compounds, photolithography, stereochemistry, etc. is considered.

Graphical abstract



Keywords Diterpenoids · Resin · Maleopimaric acid · Amides · Imides · Polymers

Introduction

The search, development of new approaches to the synthesis and study of the pharmacological, physicochemical properties of derivatives of polycarbocyclic compounds

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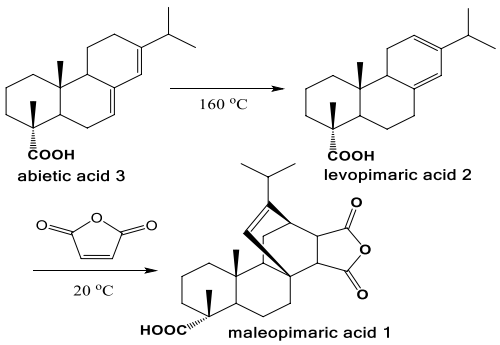
generated from plant raw materials is an important area of research in modern organic chemistry. Maleopimaric acid **1** (MPA) is a readily available compound obtained from levopimaric acid **2** and maleic anhydride by the Diels–Alder reaction [1] (Scheme 1). MPA is widely used in the technology of paints and varnishes and polymeric materials [2] and is considered as a promising starting material for the synthesis of biologically active compounds [3–5] and chiral ligands [6].

Resin acids, about ten of them are known in total, belong mainly to two structural types, pimaranic and abietanic, the ratio of which in natural sources is very different [7–10].

Abietic acid **3** is the most common resin acid and is found in all types of rosin. Levopimaric acid **2** was first found in French rosin [11]. Pimaric, isopimaric, etc. acids do not contain conjugated double bonds and therefore are resistant to heating in air. Acids with conjugated double bonds (levopimaric, abietic, etc.) are rapidly oxidized in air and easily isomerized into each other [12–14]. At elevated temperatures, they are in a state of mobile equilibrium, which is continuously shifting toward the formation of levopimaric acid. This is the basis for the possibility of synthesizing maleopimaric acid **1** on an industrial scale.

Among nitrogen-containing derivatives of maleopimaric acid, amides, imides, amidoimides with a complex of valuable properties, including biologically active ones, have been described.

To date, many methods have been proposed for modifying MPA with aliphatic, aromatic, and heterocyclic amines at the anhydride and carboxyl groups. The methods described in the literature for condensation of MPA with amines do not allow achieving complete conversion of MPA. Known catalytic systems and reaction conditions do not always provide high yields of target molecules. The main direction of the review is the analysis and generalization of materials that offer solutions to these problems, as well as the most interesting publications and promising areas of MPA chemistry.



Scheme 1 Isolation MPA from rosin

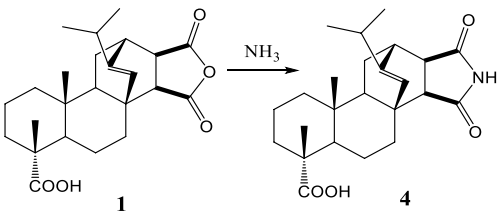
Methods of preparation and properties of maleopimaric acid imides

Known methods for the preparation of MPA imides are divided into two groups: the first method is direct melting with various amines [15–17], the second method is the condensation with amines in various high-boiling solvents [18–21]. The main disadvantages of these methods are the duration of the process, limitations on the nature of amino compound, low conversion of MPA and low product yields.

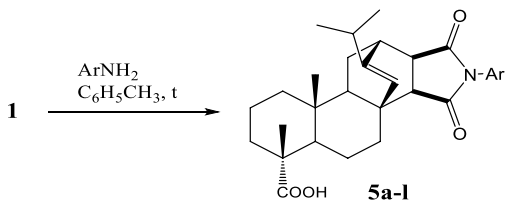
The interaction of MPA with a twofold excess of liquid ammonia gave the simplest maleopimarimide **4** in 35% yield (Scheme 2). In order to simplify the technology, it is proposed to use maleopimaric acid in the form of a reaction mass obtained by the interaction of rosin and maleic anhydride in a turpentine media [22].

The development of an efficient approach to the synthesis of MPA N-arylimides without isolation of maleopimaric acid from rosin was reported (Scheme 3) [23, 24].

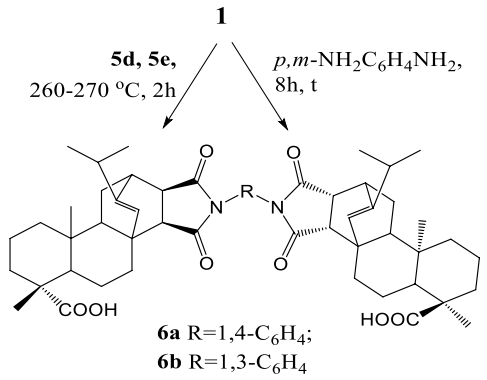
Imides **5a-l** were obtained in 51–71% yields (with respect to the adduct of rosin with maleic anhydride) or 60–99% (with respect to maleopimaric acid contained in the adduct of rosin with maleic anhydride). The duration of the reaction depends on the type of substituent in the aromatic ring and increases in the series R = OH (4 h) < CH_3 (6 h) < Br (10 h) < H (16 h). Diimide diacid **6a** was isolated in 46% yield upon refluxing MPA with p-aminoimide in dichlorobenzene for 3–8 h (Scheme 4). Upon fusion of MPA with **5d** for 2 h at 260–270 °C, the product yield was 37%. Diacid



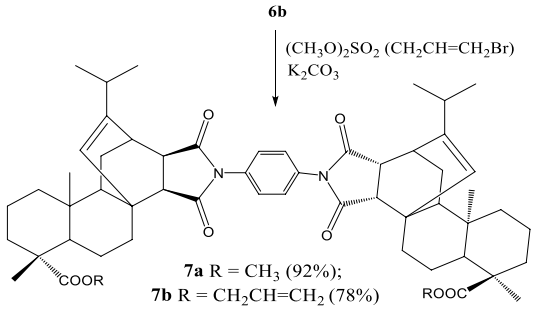
Scheme 2 Preparation of MPA imide **4**



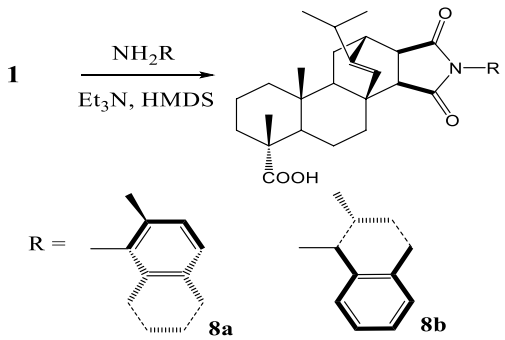
Scheme 3 Efficient synthesis of MPA N-arylimides



Scheme 4 Interaction MPA with arylimides or phenylenediamines



Scheme 5 Synthesis of MPA dimethyl and diallyl ethers

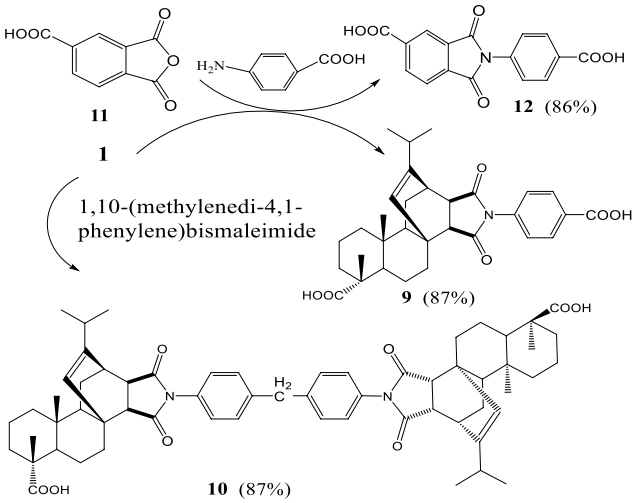


Scheme 6 Preparation of MPA N-arylimide atropisomers

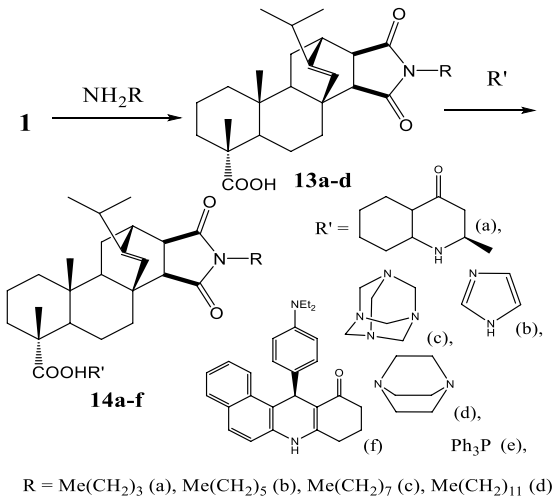
diimides were obtained in higher yields upon the interaction of MPA with phenylenediamines (**6a**—68% and **6b**—48%).

Dimethyl and diallyl ethers **7a, 7b** were obtained from **6a** by treatment with dimethyl sulfate or allyl bromide (Scheme 5).

N-arylimides of MPA were successfully separated into diastereomeric atropisomers **8a** and **8b**, stable at room temperature (Scheme 6) [25, 26]. Compound **8a** exhibited higher cytotoxicity compared to fluorouracil. It was also revealed that the cytotoxicity of the R-configuration is higher than that of S.



Scheme 7 Synthesis of rosin-derived imide-diacids

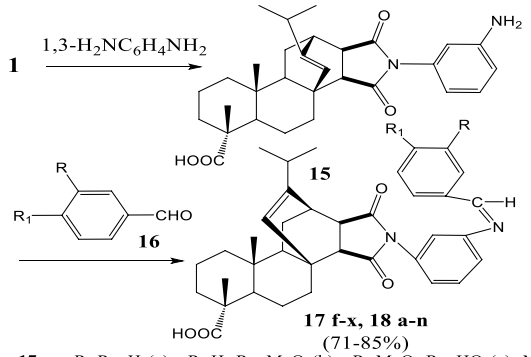


Scheme 8 Preparation of rosin-based organic salts

As epoxy hardeners, diacid imide MPA **9** and diimide **10** in DMF at 160 °C in an argon atmosphere for 4 h were obtained (Scheme 7) [27, 28]. Rosin-based diacid imides have a significantly higher glass transition temperature, elastic modulus, and better dynamic-mechanical properties than diacid imide **12** obtained from trimellitic acid anhydride **11**.

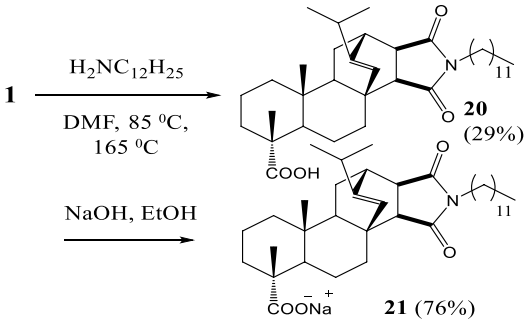
Yuvchenko et al. [16, 17, 29] obtained MPA N–H-alkylimides **13a-d** by the interaction of primary aliphatic amines with MPA in melt or in solution, and salts **14a-f** with amines and triphenylphosphine were synthesized (yields higher than 94%) [30] (Scheme 8).

Since the rate of formation of maleopimarimides in solution decreased with an increase in the length of the alkyl radical in amines, the reaction of MPA with dodecyl and

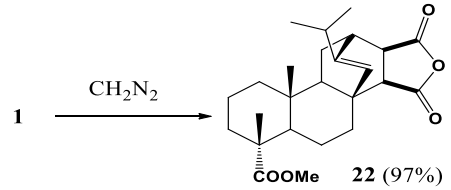


17a-x: R=R_1=H (a); R=H, R_1=MeO (b); R=MeO, R_1=HO (c), MeO (d), MeC(O)O (e), EtC(O)O (f), PrC(O)O (g), $Me_2CHC(O)O$ (h), BuC(O)O (i), $Me_2CHCH_2(O)O$ (j), $Me(CH_2)_6C(O)O$ (k), $Me(CH_2)_8C(O)O$ (l), $Me(CH_2)_{16}C(O)O$ (m), H_2C=C(Me) C(O)O (n), $C_6H_5CH(Me)CH_2C(O)O$ (o), $C_6H_5C(O)O$ (p), 2,4-$Cl_2C_6H_3C(O)O$ (q), 4-$BrC_6H_4C(O)O$ (r), 3-$O_2NC_6H_4C(O)O$ (s), MeOC(O)O (t), EtOC(O)O (u), 1-AdC(O)O (v), o-$HCB_{10}H_{10}C(O)O$ (w), m-$HCB_{10}H_{10}C(O)O$ (x); **18a-n**: R_1=EtO, R_1=HO (a), MeO (b), MeC(O)O (c), EtC(O)O (d), PrC(O)O (e), $Me_2CHC(O)$ O (f), BuC(O)O (g), $Me_2CHCH_2C(O)O$ (h), 4-$MeC_6H_4C(O)O$ (i), MeOC(O)O (j), EtOC(O)O (k), 1-AdC(O)O (l), o-$HCB_{10}H_{10}C(O)O$ (m), m-$HCB_{10}H_{10}C(O)O$ (n).

Scheme 9 Synthesis of aromatic azomethinesbased on MPA



Scheme 10 Synthesis of MPA derivativeas bio-based surfactant



Scheme 11 Generation of MMP

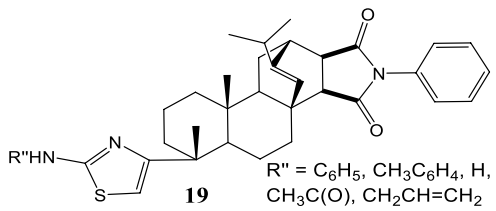


Fig. 1 Structure of N-maleopimarimides **19**

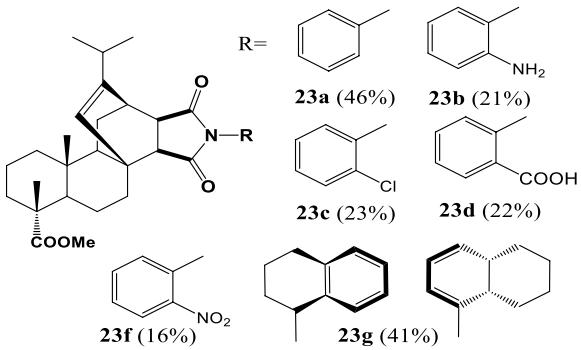


Fig. 2 Structures of methyl N-maleopimarimides **23**

octadecylamines was carried out in the melt. The yields of imides reached 99% and the reaction time was reduced by 4 times.

Azomethines **17f-x**, **18a-n** were synthesized by condensation of substituted benzaldehydes **16** with 3-aminophenylene-N-imide of MPA **15** (MeOH-DMF, 1:1, 3–4 h.) [31]. Maleopimarimide **15** was obtained by condensation of MPA with 3-phenylenediamine (toluene, 6 h.) (Scheme 9).

The possibility of obtaining azomethines using 4-aminophenylene-N-maleopimarimide was also shown [32]. 2-Aminothiazole derivatives of MPA have been synthesized **19** as potential antioxidants (Fig. 1) [33].

Sodium N-dodecylmaleimidepimarcarboxylate **21** was prepared as a surfactant (Scheme 10) [34].

Worm-like annular, filamentous, and ordinary micelles with a diameter of 100–200 nm in an anisotropic homogeneous phase were formed without any additives [35].

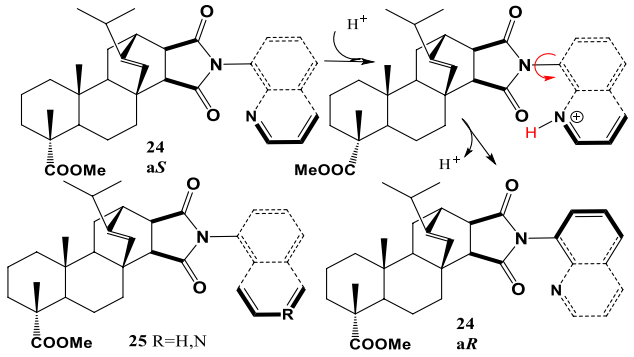
Methods of preparation and properties of methyl maleopimarate imides

Methyl ester **22** is one of the available derivatives of MPA, is obtained in good yield by treating MPA with diazomethane in diethyl ether (Scheme 11) [1].

Since MMP has a higher cytotoxic activity than MPA [36] the synthesis of imides MMP and the study of their biological activity are of great interest.

Studies of the inhibitory activity and cytotoxicity of maleopimarimide-substitutedphenylalanine show significant cytotoxicity against MGC-803 and Hct-116 cells (IC_{50} = 9.85 ± 1.24 and 8.47 ± 0.95 μM, respectively) [37].

The atropisomerism and kinetic data of N-arylimides MMP **23a-g** were studied (Fig. 2) [38]. The compounds **23a-f** with lower steric effects do not exhibit



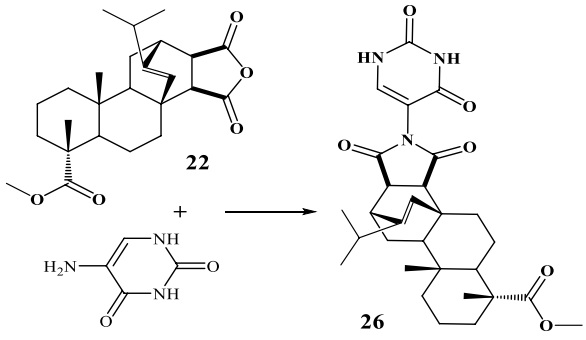
Scheme 12 Protonation-controlled axial chirality in MPA imides

Table 1 MMP-aminouracil condensation conditions

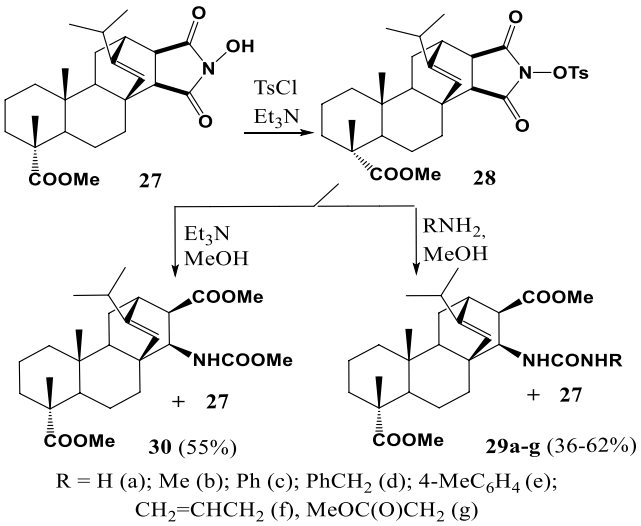
№	Excess of 5-aminouracil	Solvent	Yields of 26, t °C, time	
			160 °C[a],60 min	Ultrasound, 120ºC, 30 min
1	×1	–	13% (210 °C)	–**
2	×2	–	22% (210 °C)	–**
3	×2	DMFa	–[b]	–**
4	×1,2	DMSO	38%	48%
5	×1,5	DMSO	58%	76%
6	×2	DMSO	69%	88%
7	×4	DMSO	70%	90%

[a]The temperature of the oil bath is 160 ºC

[b]Initial substances remain unchanged



Scheme 13 Condensation MMP with 5-aminouracil



Scheme 14 Synthesis of ureidoesters from MMP imide

atropisomerism, whereas compounds **23 g** undergo a slow *cis–trans* transition when dissolved in $CDCl_3$ at room temperature.

A new class of atropisomericarylimides MMP **24, 25** with limited rotation around the $C(_{SP}{}^2)$–N bond was obtained and analyzed (Scheme 12) [39].

Effective method [40] for the synthesis of methyl maleopimarimides using 5-aminouracil under ultrasound exposure (with a frequency of 22 Hz) in DMSO has been developed (Table 1, Scheme 13).

Lossen's rearrangement of p-toluenesulfonate of N-hydroxymaleopimaric acid **28** in the presence of amines in methanol led to the formation of the corresponding ureidoesters **29**, **30** with high regio- and stereoselectivity (Scheme 14) [41].

Treatment of the obtained ureidoesters **29** with bromine led to the product **31**, and with phosphoryl chloride gave cyclic amidines by intramolecular cyclization **32**. Dioxoimidazolidines **33** were obtained by the reaction of ureidoesters with glyoxal in an acidic medium, and treatment with sodium ethylate led to compounds of the naphtho [1,2-n] quinosaline series **34** (Scheme 15) [41].

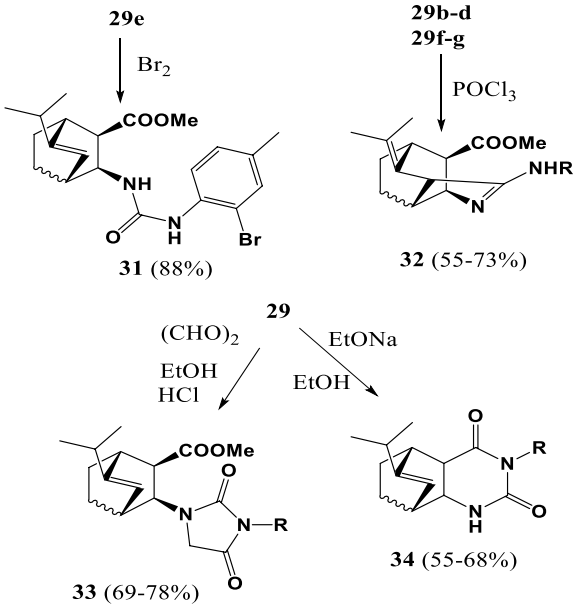
Then **32** was converted to phenacyl derivative **35** (Scheme 16) [42].

The MMP-aspartic acid condensation product **36** was reacted with thionyl chloride in benzene, resulting in an anhydride **37**. Then **37** reacted with a twofold excess of $Ph_3P=CH_2$ (Scheme 17), to form an isomeric mixture of products **38a-d** [43].

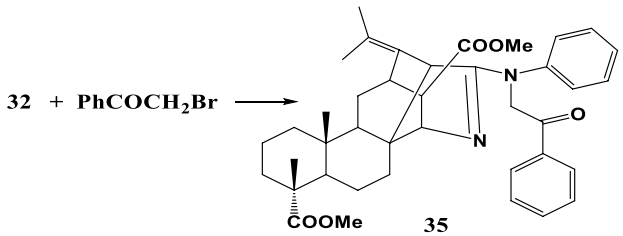
An efficient method of condensation of MMP with amino acids under ultrasound exposure in DMSO was proposed (Scheme 18) [36, 40].

The resulting N-maleopimarimide-substituted amino acids were used to conjugate the diterpene block with important pharmacaphoric and functional groups: chloro-, bromomethyl ketones **41, 42** [44, 45], sulfide **43** [44], allenoates **44** [46–49], 1,2,3- triazoles **45** [49, 50], methanofullerenes **46** [51] and cyclopentenofullerenes **47** [52] C_{60} [53–55], adamantane derivatives **48** [56] (Schemes 19, 20).

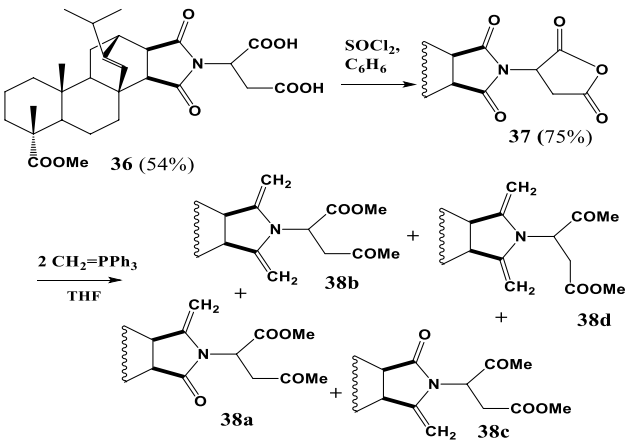
The use of ultrasound made it possible to synthesize maleopimarimides even in the case of poorly soluble amines,



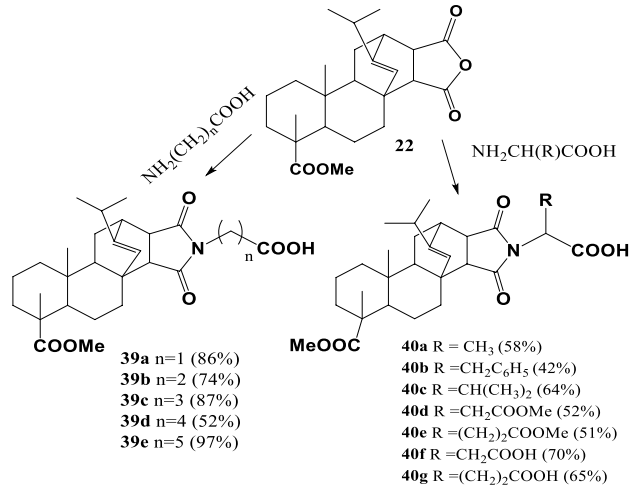
Scheme 15 Reactivity of MMP-based ureidoesters



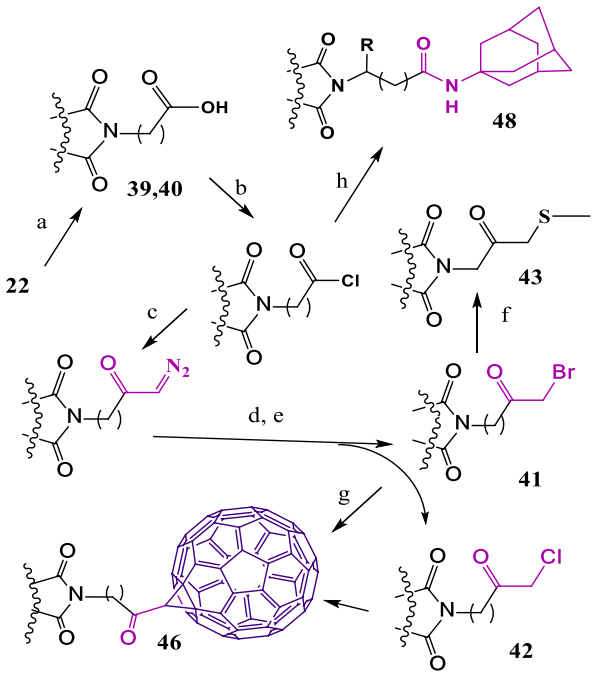
Scheme 16 Preparation of phenacyl derivative with diterpene fragment



Scheme 17 Chemical properties of MMP imide dicarboxylic acid



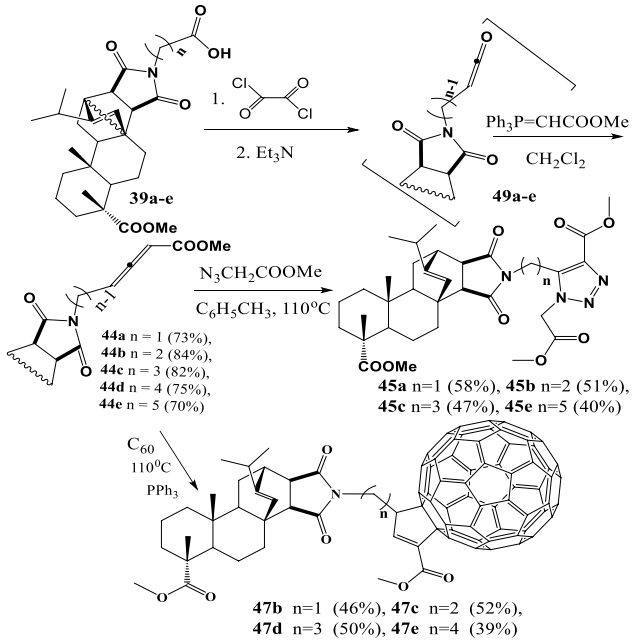
Scheme 18 Efficient interaction between MMP and amino acids



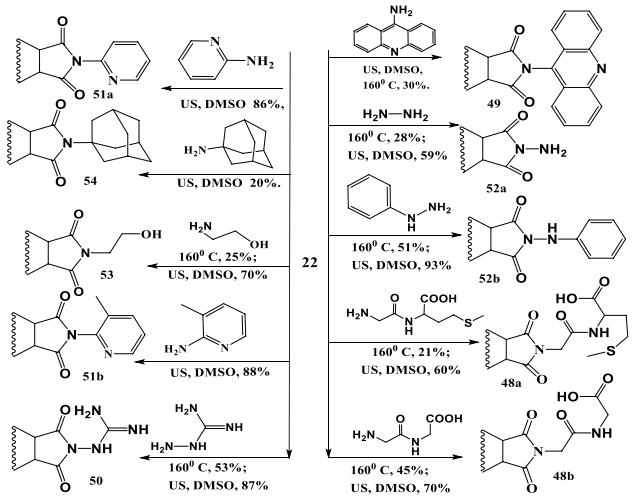
a: US, DMSO. b: 1. $C_2Cl_2O_2$, CH_2Cl_2. c: CH_2N_2, CH_2Cl_2. d: HBr, CH_2Cl_2. e: HCl, CH_2Cl_2. f: $(CH_3)_2S$, acetone. g: C_{60}, DBU, $C_6H_5CH_3$. h: amantadine, Et_3N, CH_2Cl_2

Scheme 19 Synthetic route for the preparation of some MMP derivatives

significantly reduced the reaction time and increased the yield of target products [57]. A number of new maleopimarimides [36, 58] with fragments of: peptide **48a, b**; aminoacridine **49**, aminoguanidine **50**, aminopyridines **51a, b**; hydrazines **52a, b**; ethanolamine **53**, amantadine **54** have been obtained (Scheme 21).



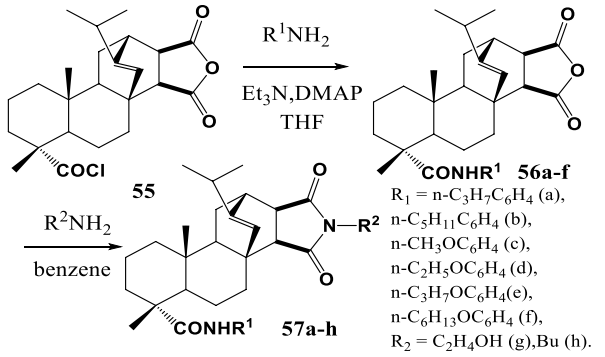
Scheme 20 Synthetic route for the preparation of some MMP derivatives



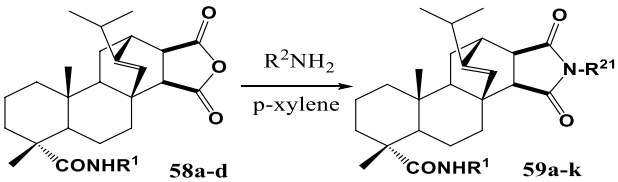
Scheme 21 MMP-amine condensation products

Synthesis and properties of MPA amides

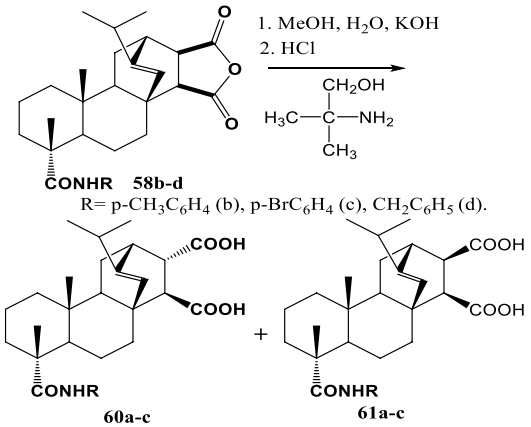
Syntheses of alkyl-, alkoxyphenylamides **56a-f** and imidoamides **57a-h** have been proposed through the maleopimaric acid chloride **55** [59]. Compounds **56a-f** and **57a-h** (Scheme 22) are capable of forming stable chiral liquid crystal compositions and can be used in various electro-optical systems for displaying and converting information, in particular, in displays with a matrix addressing system [59].



Scheme 22 Synthesis of MPA alkyl-, alkoxy(phenyl)imidoamides



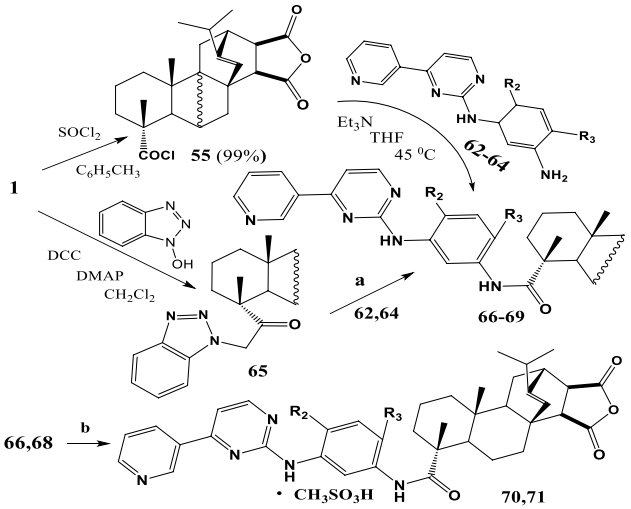
Scheme 23 Synthesis of MPA N-aryl(aralkyl)imidoamides



Scheme 24 Preparation of trans-1,2-dicarboxylic acids from MPA amides

The synthesis of MPA N-aryl (aralkyl) imidoamides **59a-k** was carried out by the reaction of the corresponding aromatic MPA amides with amines by refluxing in p-xylene (Scheme 23) [24, 60].

Boiling of MPA amides **58b-d** in an aqueous-methanol solution of KOH for 2 h led to monoamides of *trans*-fumaropimaric acid **60a-c** in 82–98% yields with an impurity of *cis*-isomers **61a-c**, which were separated (Scheme 24) [61, 62].



a: DMAP, CH_2Cl_2, 25°C; b: CH_3SO_3H; R_2 = Me, R_3 = H (**62**); R_2 = H, R_3 =Me (**63**), $R_2 = R_3$ = H (**64**); R_3 = H, R_2 = Me (**65, 66**); R_2 = H, R_3 = Me (**67**); $R_2 = R_3$ = H (**68, 71**); R_2 = Me, R_3 = H (**69**).

Scheme 25 Synthetic process for amides and methanesulfonates containingpyrimidin, pyridine, diamine and aryl groups

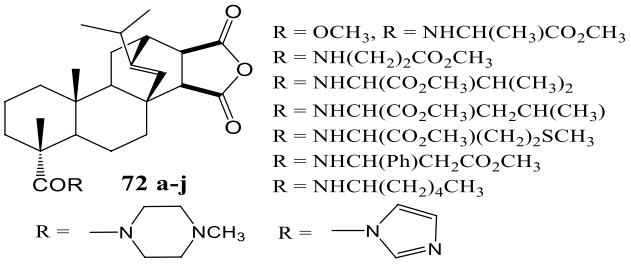
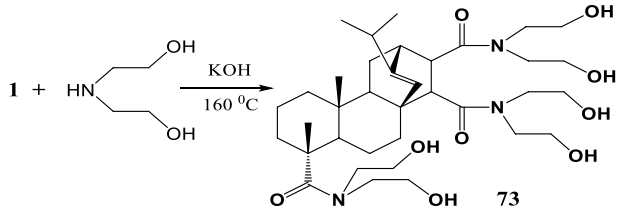


Fig. 3 Structure of some biologically active MPA amides **72**

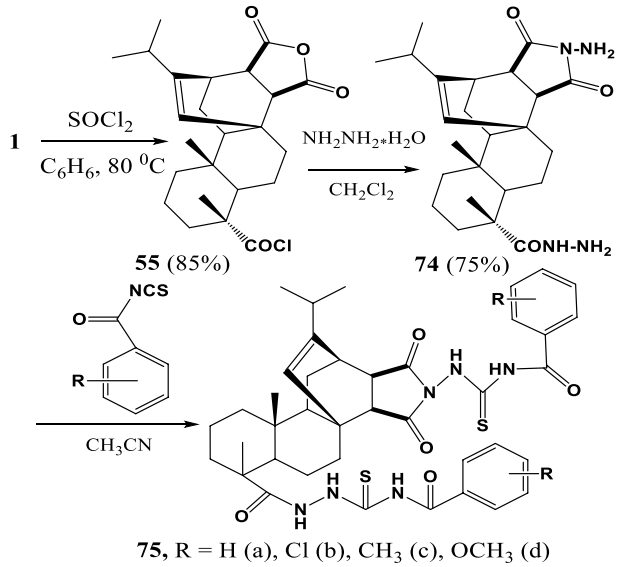
The acylation of diamines **62–64** with **55** and benzotriazolylmaleopimarate **65** at a temperature of 20–65 ºC gave N- [3- (pimiridin-2-yl) aryl] amides MPA **66–69**. Biologically active methanesulfonates **70, 71** were obtained from MPA N-arylamides **66, 68** (Scheme 25) [63].

New bioactive MPA amides **72** containing fragments of methyl esters of amino acids, aliphatic amines, imidazole, and N-methylpiperazine were synthesized (Fig. 3). The compounds act bi-directionally as anti-inflammatory and anti-ulcer agents and have no negative effects on the body [64].

Maleopimaric acid N-diethanolamide **73** was synthesized from maleopimaric acid and diethanolamine according to Scheme 26 [65]. Having better viscosity and stabilization indicators compared to a commercial dispersant—a condensate of sulfated naphthalene and formaldehyde, compound **73** can be used as a dispersant and a viscosity depressor in a water-coal suspension.



Scheme 26 Rosin-based amide as a dispersant for coal-water slurry



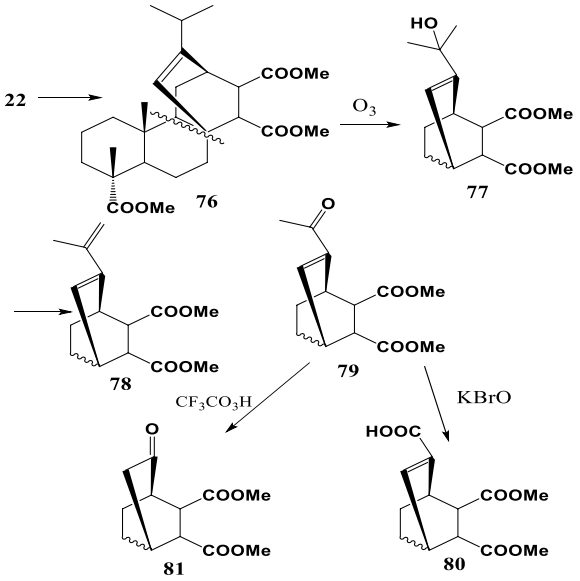
Scheme 27 Bioactive MPA derivatives modified with thiosemicarbazide fragments

Compounds **75a-d** exhibiting fungicidal and herbicidal activities and containing two thiosemicarbazidefragments were obtained (Scheme 27) [66].

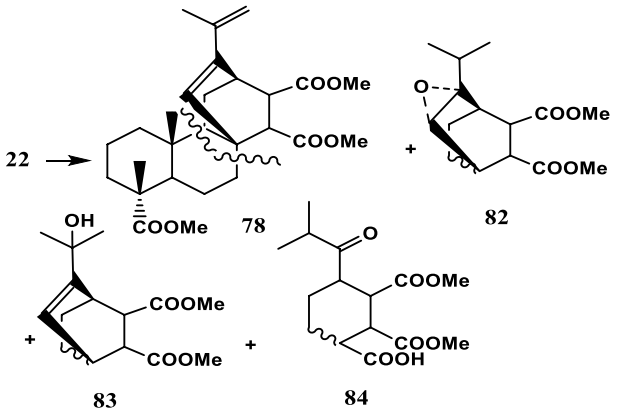
Oxidation reactions and ozonolysis of MMP

The first modifications of MMP **22** are associated with the study of the ozonolysis of trimethyl ether **76** [67, 68], when the inertness of the double bond with regard to ozone was shown (Scheme 28). Ozone attack on the isopropyl group resulted in oxyether **77**. This is followed by dehydration to diene **78** and ozonolysis to ketoester **79**. Oxidation of ketone with KBrO led to acid **80**, and with CF_3CO_3H to ketoester **81** [67, 68].

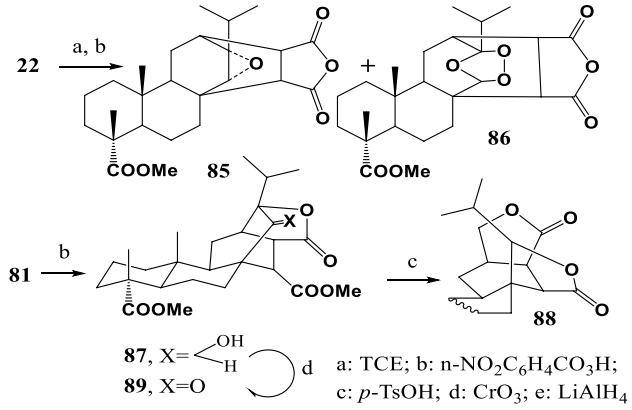
However, experiments [64, 69] show the possibility of the reaction proceeding at the olefin fragment. Ozonolysis of MMP followed by treatment with Me_2S yielded diene **78** (10%), epoxide **82** (19%), alcohol **83** (18%), and keto acid **84** (32%) (Scheme 29). Ozonolysis of MMP in the CH_2Cl_2—MeOH system at 0 °C increased the yield of keto acid **84** [64].



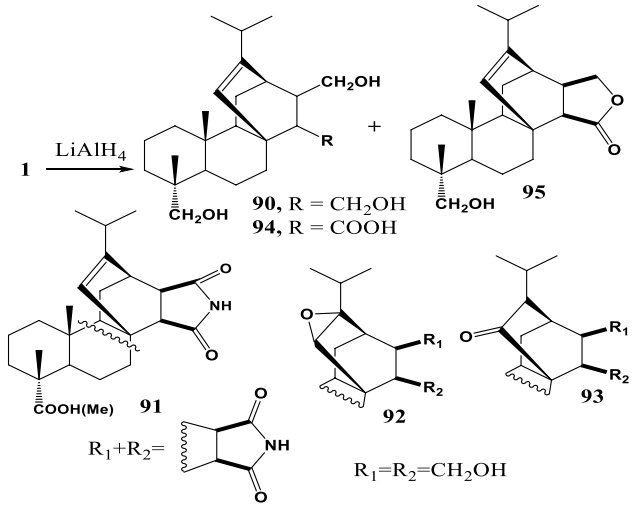
Scheme 28 The action of ozone on the trimethyl ester of MPA



Scheme 29 Ozonolysis products of MMP



Scheme 30 Ozonolysis of MMP and ketoester



Scheme 31 Reduction of MPA and oxidation of triol and imide products

Described ozonolysis of MMP in the presence of TCE, leading to epoxide **85** in 20% yield and stable ozonide **86** in 7% yield [65]. Compound **81** is oxidized under these conditions to oxylactone **87**, the structure of which was confirmed by transformation into dilactone **88** and oxidation into ketolactone **89** (Scheme 30).

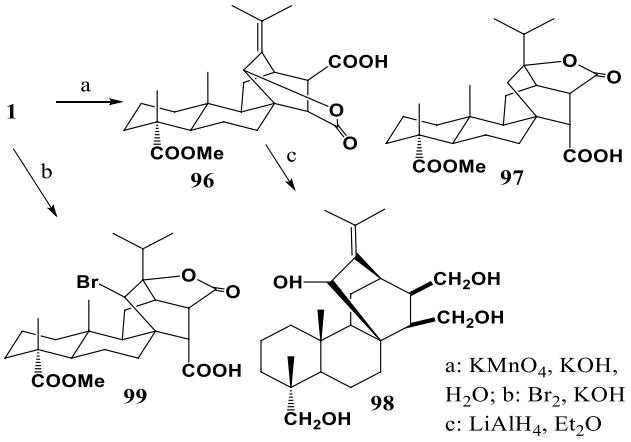
Triol **90** and imide **91** were oxidized to epoxides **92** and ketones **93**. Triol **90**, dioxy acid **94** and oxylactone **95** were formed by the reduction of MPA with $LiAlH_4$ (Scheme 31) [70].

Selective oxidation of MPA with an excess of $KMnO_4$ in an alkaline medium was carried out [1]. The yield of lactone **96** exceeds 90%. Upon oxidation with less than two equivalents of $KMnO_4$, lactone **99** was obtained in 10% yield. Reduction of lactone **96** led to tetraol **98**. The reaction of MPA with bromine in an alkaline medium gave bromlactone **99** (Scheme 32).

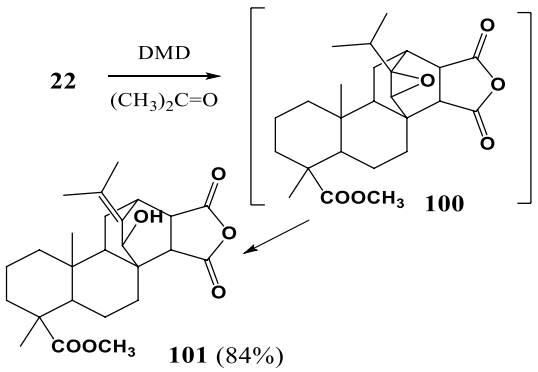
Regioselective oxidation of the double bond of MMP with dimethyldioxirane (DMD) led to 13(15)-ene-14S-hydroxy derivative **101** (Scheme 33) [71].

MPA in the synthesis of monomers and polymers

Polymers obtained on the basis of MPA have high thermal stability [72, 73], show good mechanical properties. These compounds have great prospects for use for various purposes, as evidenced by the progressive interest of chemists in research in this direction. The biochemical part of this subject can also be noted, for example, it is reported about new reliable antimicrobial agents **102, 103** obtained from resin acid, which are effective against a wide range of bacteria and do not cause significant hemolysis of red blood cells in a



Scheme 32 Selective oxidation and bromination of MPA



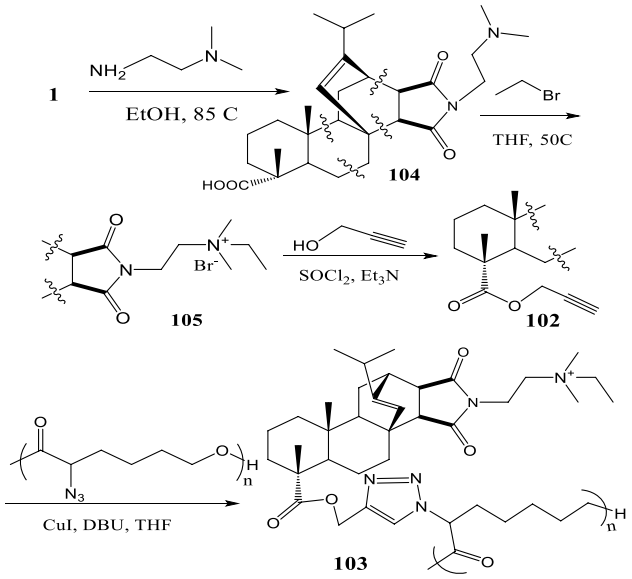
Scheme 33 Regioselective oxidation of MMP with dimethyldioxirane

wide concentration range [74, 75]. The reaction of ethyl bromide with imide **104** leads to the quaternary ammonium salt **105** (Scheme 34). Further, esterification of the latter with propargylalcohol gives **102**. Compound **103** was obtained by the action of azide-substituted poly(Ɛ-caprolactone) in the presence of a catalytic amount of CuI/DBU [74, 75].

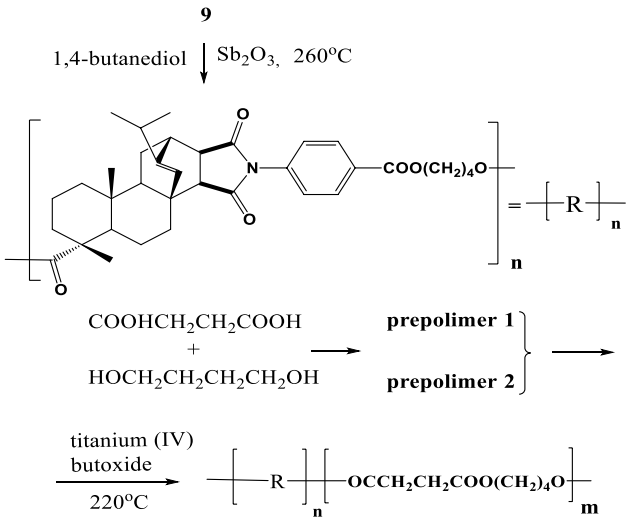
Antifungal [76, 77], antimicrobial [78–81] activities of the MPA ammonium salts were also investigated. The potential application of quaternary ammonium derivatives of MPA as corrosion inhibitors [82], dispersants for magnetite nanoparticles [83, 84] and as inhibitors of protein aggregation processes [85–87].

In the work [88] maleopimarimide segments were introduced into the polymer product (Scheme 35). As the amount of diterpene in the molecule increased, the melting point, crystallization temperature and degree of crystallinity gradually decreased, while the impact strength and stretching increased.

Allyl imides were obtained with the subsequent synthesis of allyl ethers (Scheme 36) [89]. Imides **13b,c,e** can



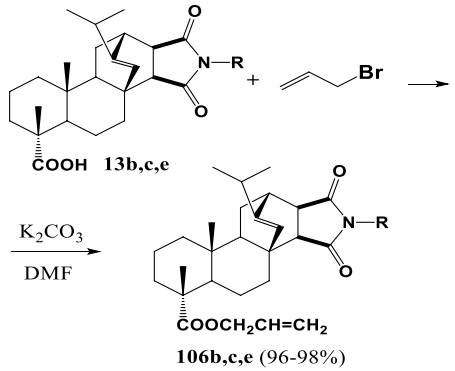
Scheme 34 Rosin-derived polymer product as antimicrobial agent



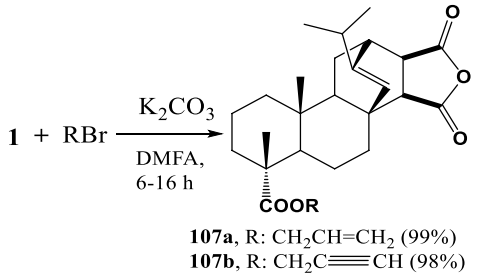
Scheme 35 Polymer synthesis of poly(butylene succinate) modified with MPA imide

be used as components of adhesive materials, allyl ethers **106b,c,e** are of interest as new monomers for the functionalization of olefin copolymers and mixtures thereof. Octadecylmaleopimarimide **13e** is of interest as a surfactant for thin films.

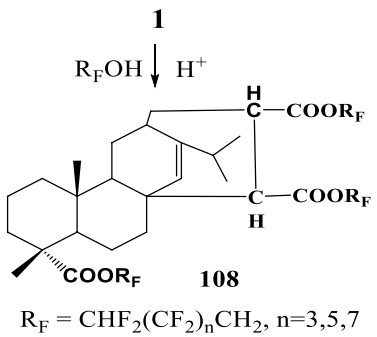
Since MPA contains both anhydride and carboxyl groups, the selective esterification of the carboxyl group with alcohols is difficult. Allyl bromide and propargyl bromide reacted regioselectivelywithcarboxyl group of MPA upon treatment with K_2CO_3 in DMF to form **107** (Scheme 37) [90]. Compound **107a** was also synthesized in 62% yield using oxalyl chloride and allyl alcohol in THF [91].



Scheme 36 Synthesis of allyl ethers from MPA imides



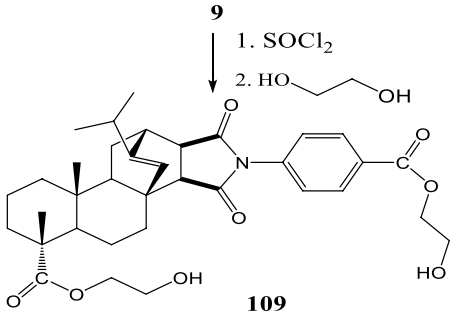
Scheme 37 Preparation of rosin-based monomers



Scheme 38 Esterification of MPA with *α*,*α*,*ω*-trihydroperfluoroalkanols

The reaction of esterification of the maleopimaric adduct with *α*,*α*,*ω*-trihydroperfluoroalkanols under catalysis with concentrated sulfuric acid at 150–220 °C led to new three substituted polyfluoroalkyl ethers **118** in 55–70% yields (Scheme 38) [92, 93].

A chain extender based on MPA **109** was synthesized and introduced. The polyurethane polymer with the shape memory effect at 100% deformation reshapes to 96% in 3 min at room temperature (Scheme 39) [19].



Scheme 39 Synthesis of rosin-based shape memory polyurethanes

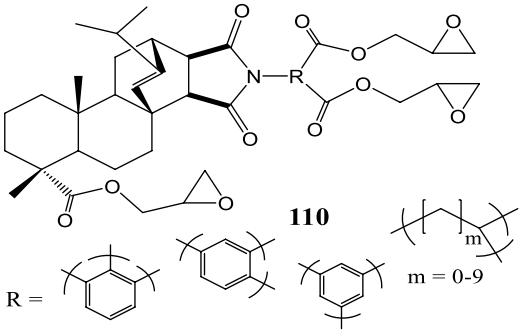


Fig. 4 Structure of epoxy resins **110**

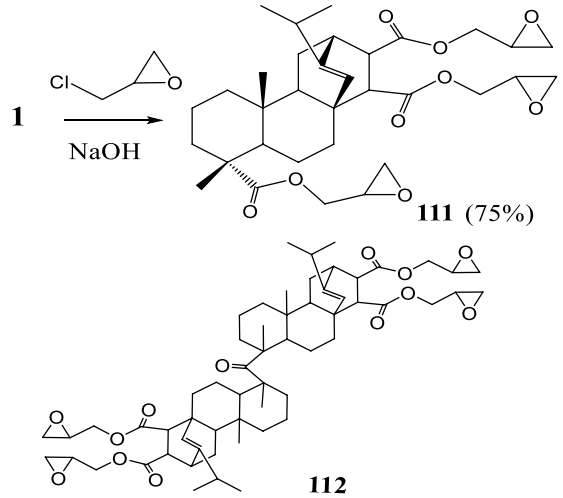
A method was proposed for the preparation of new epoxy resins **110**, which are of interest as a hardener for polyester powder paints with a high glass transition temperature (~ 153.8 °C), a high storativity at room temperature (~ 2.4 hPa), and good thermal stability (Fig. 4) [19, 94].

To obtain bionanocomposites, an epoxy resin based on MPA **111** [95, 96] was synthesized as well as polyurethane based on castor oil and carbon nanotubes (Scheme 40). The impact strength of such a film is 15 kg/cm higher than that of a pure resin system; the cell survival rate for 48 and 72 h exceeds 90%, which indicates excellent biocompatibility. The synthesis of tetraglycidyl dimaleopimaryl ketone **112** has also been reported [97].

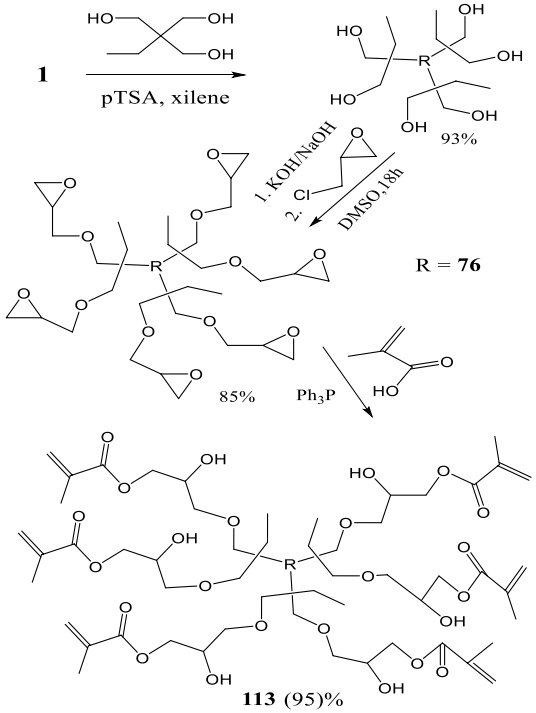
The epoxyacrylate derivative of MPA **113** (EEW = 199.68 g/eq.) is suitable for use as a resin cross-linked with styrene, methacrylated eugenol or methacrylated guaiacol and can be prepared according to scheme 41 [98] via maleopimaric acid triester, trimethylolpropane and epoxy derivative [99].

Diterpenoidethylene glycol acrylate **114** has been proposed as combinatorial cross-linking agents [100], a selective stationary phase in HPLC [101] and to increase the thermal stability of styrene-acrylate copolymers [102] (Scheme 42).

Polymer **115a** was proposed as a base for two-component polyurethane water-dispersion coatings and paints [103].



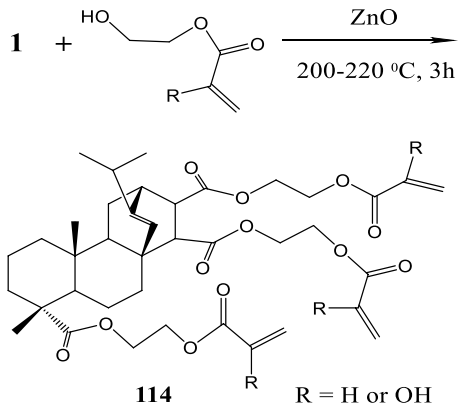
Scheme 40 Preparation of triglycidyl and tetraglycidyl derivatives of MPA



Scheme 41 Production process for epoxy acrylate derivative of MPA

The inclusion of a diterpene moiety improved such material properties as strength, gloss, hardness, water resistance and alcohol resistance [104]. The synthesis, modification and properties of nonisocyanate polyurethane coatings based on MPA **115b** were also studied (Fig. 5) [105].

The authors [106] compared the rosin-modified phenolic resin with an environmentally friendly, phenol-free resin **116**, which exhibited superior carrier properties in terms of gloss, yellowing, usability and storage stability (Scheme 43).



Scheme 42 Synthesis of ethylene glycol acrylate based on MPA

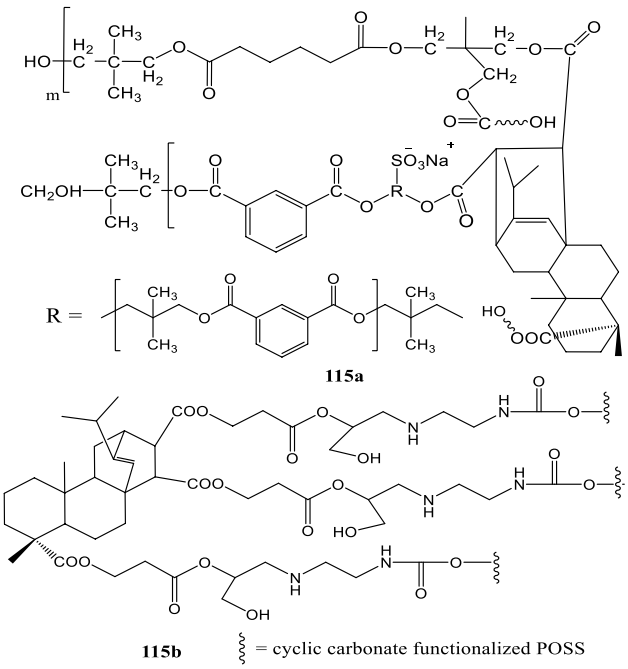
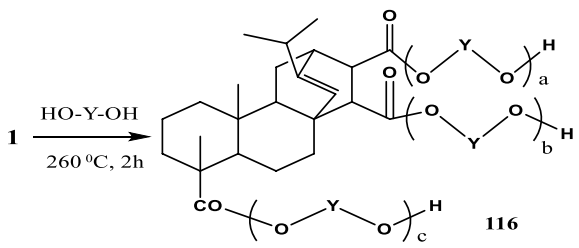
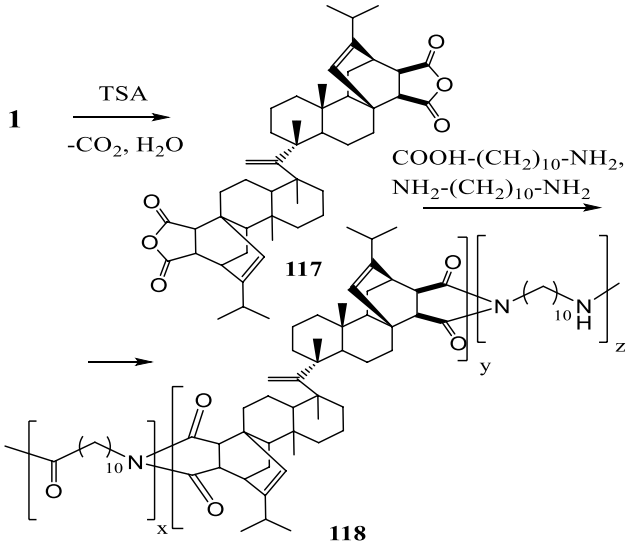


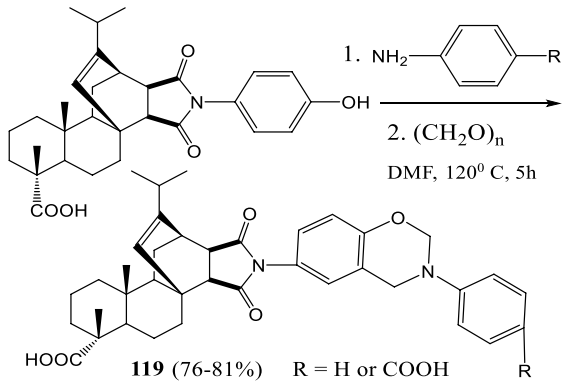
Fig. 5 Structures of MPA-based polyester polyol dispersion for waterborne polyurethane **115**



Scheme 43 Esterification of polyphthalate and MPA



Scheme 44 Diterpenoid polyamide-imide copolymer synthesis



Scheme 45 Cyclization of MPA imidophenol to benzoxazine monomer

Dianhydride MPA **117** was obtained by boiling MPA with methyl sulfonic acid in toluene under nitrogen. Further, a polyamide-imide copolymer **118** was obtained, which can be used as a structural plastic and also as film materials (Scheme 44) [107].

Benzoxazines are a special type of aminophenol formaldehyde resins and high temperature polymer binders [108]. Diterpene benzoxazine monomer **119** was obtained via imidophenol (88% yield) using aniline or 4-aminobenzoic acid (Scheme 45) [109, 110].

Tetraglycyl epoxy ester resins **120a,b** with high strength and high chemical resistance to solvents were investigated (Fig. 6) [111].

A trivinyl derivative of MPA **121** (Scheme 46) was synthesized and proposed as an alternative to some petroleum-based monomers [112]. It is considered as hard monomers for copolymerization with acrylic epoxidized soybean oil

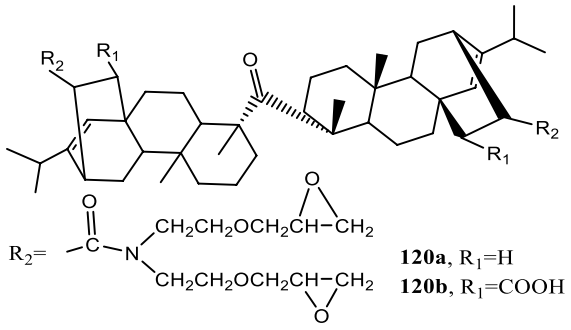
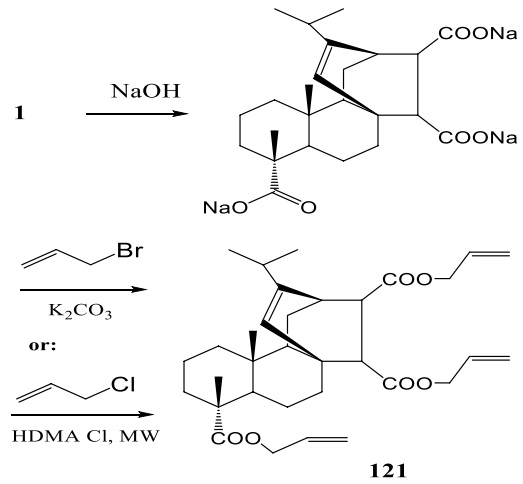
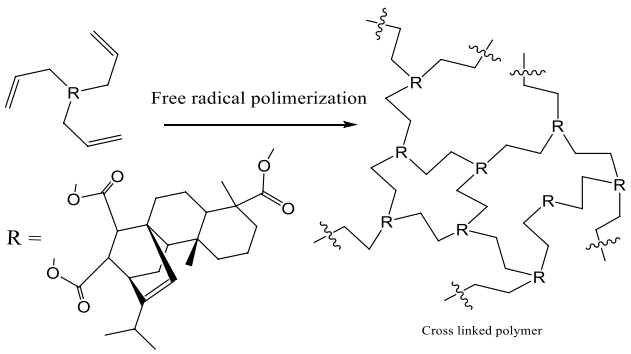


Fig. 6 Structures of tetraglycyl epoxy ester resins **120**



Scheme 46 Production of trivinyl derivative of MPA

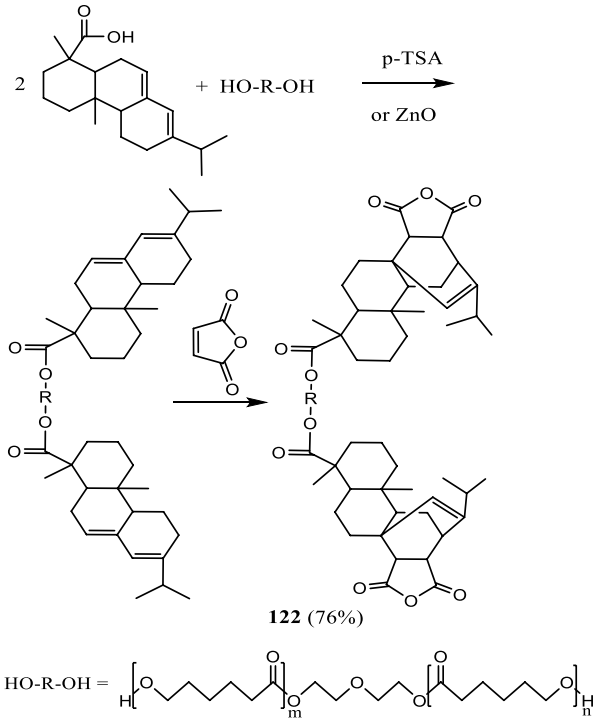


Scheme 47 Polymerization of tri-allylmaleopimarate

having improved glass transition temperature, tensile modulus, and curing modulus.

Further, a mechanism for the polymerization of tri-allylmaleopimarate was proposed (Scheme 47) [113].

The use of rosin-based polycaprolactones with flexible dianhydride part **122**, obtained according to scheme 48 [114]—as a bio-based curing agent for epoxy resins.



Scheme 48 Synthesis of rosin-polycaprolactone anhydride curing agent

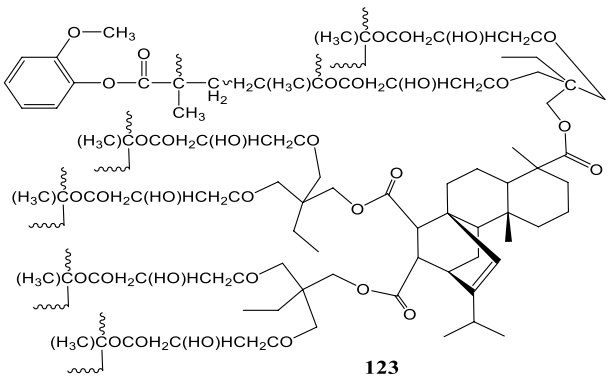
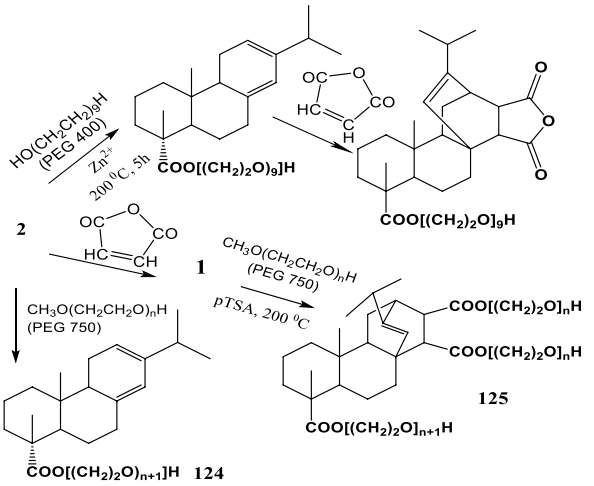


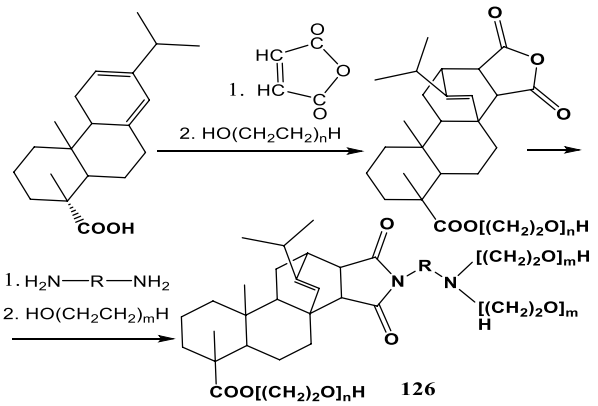
Fig. 7 Structure of vinyl ester resin **123**

By creating a biofunctional vinyl ester resin **123**, an excellent alternative to styrene has been proposed [98]. The obtained samples showed better thermal stability and mechanical strength and better chemical and corrosion resistance and had comparable characteristics compared to oil based materials (Fig. 7).

Diterpenoid polyethylene glycol ethers (PEGs) have been investigated as microencapsulated materials for long-term drug delivery [115, 116]. Two approaches have been shown for the synthesis of oligomers **124,125** (Scheme 49). Compounds of this type can also be used as dental films for the



Scheme 49 Route of synthesis of PEGylated rosin derivatives



Scheme 50 Synthesis of PEGylated MPA imides

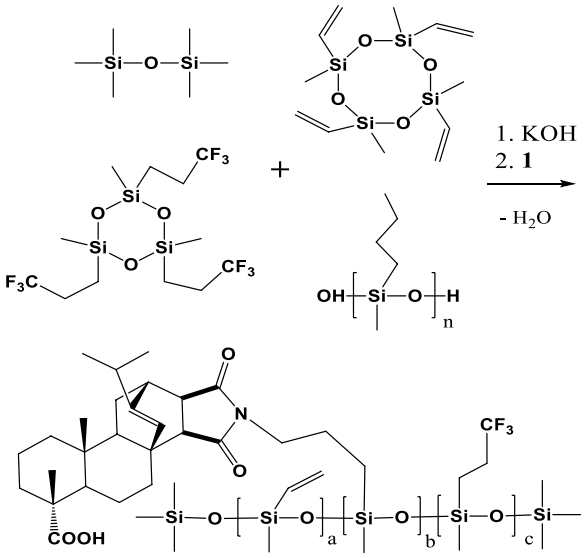
treatment of periodontitis [117] and as anticorrosive materials for carbon steel [118].

Obtained by esterification of rosin with different molecular weights of polyethylene glycol (PEG 400, 600, 1000, 2000) (Scheme 50), surfactant derivatives of MPA**126** were proposed as oil sludge dispersants [119, 120].

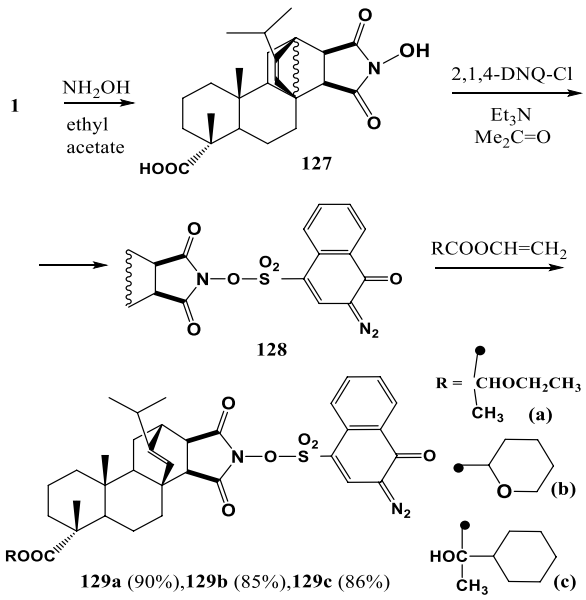
The introduction of MPA into a fluorosilicone rubber according to Scheme 51 can enhance its microphase separation, ultimate tensile strength, and heat resistance [121].

MPA in the synthesis of photoresists

The reaction of MPA with hydroxylamine gave N-hydroxymaleopimarimide **127**, which was esterified with 2,1,4-DNQ-Cl to obtain N-hydroxymaleopimarimide sulfonate **128** (Scheme 52) [18]. The 2,1,4-DNQ group is easily photolyzed under light irradiation at 365 nm. Thus, new single-component glasses of molecular composition **129a-c**



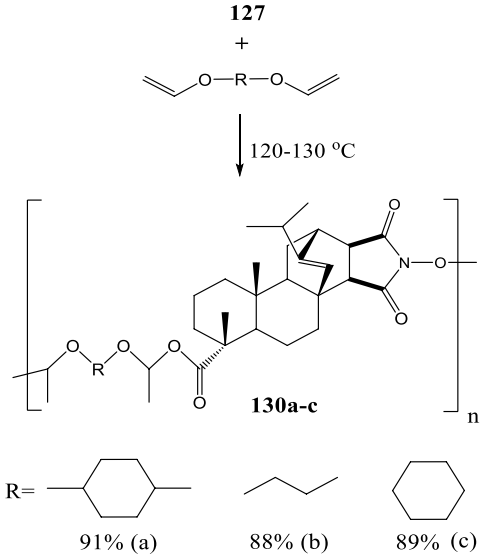
Scheme 51 Preparation of fluorosilicone resin based on maleopimarimide



Scheme 52 Synthetic pathway to i-line molecular glass photoresists

were obtained with good yields, which showed great potential as high-performance photoresists [18].

The polyaddition reaction of N-hydroxymaleopimarimide **127** with divinyl ethers made it possible to obtain new acetoester polymers **130a-c** according to Scheme 53 [122]. The ester bond in the polymer chain can be hydrolyzed in the presence of a strong acid with mild heating. The obtained polymer films have excellent UV light transmission (above 230 nm) and great potential for use as high-performance photoresists in lithography technology.



Scheme 53 Preparation of ester acetal polymers

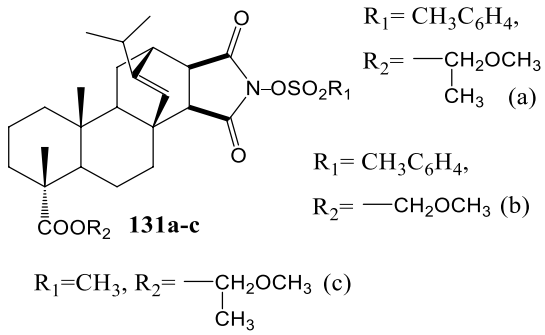
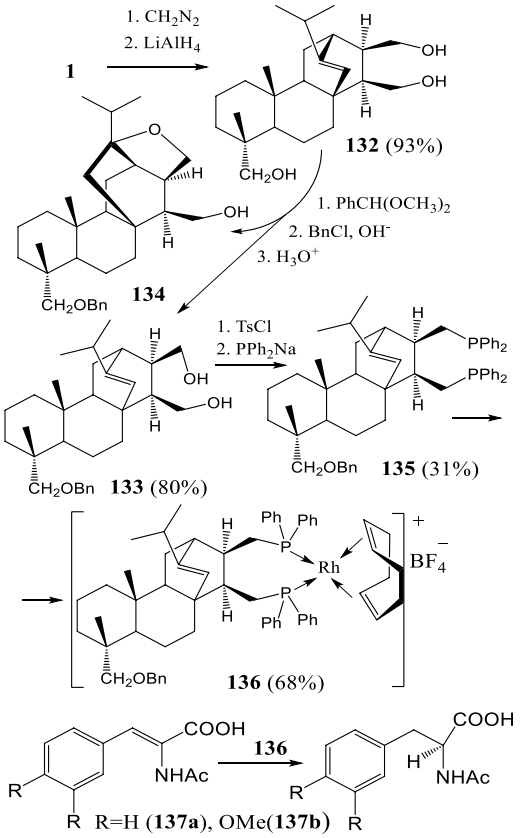


Fig. 8 Structures of sulfonate derivatives of MPA imides **131**

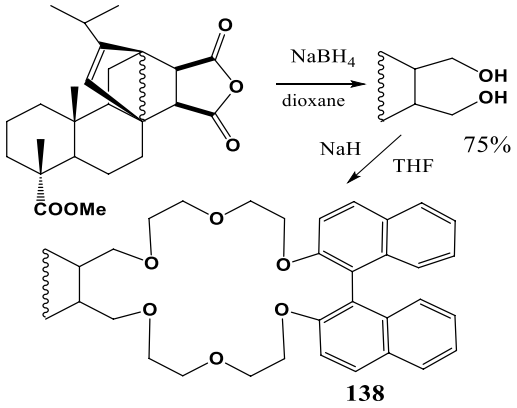
Sulfonate derivatives of N-hydroxymaleopimarimides **131a-c**, promising as photoacid generators of a new type, were obtained (Fig. 8) [123]. Sulfonate compounds have good solubility in typical organic solvents and high thermal stability, transparency within 193 nm, and can be used as polyalkylene glycol (PaGs) photoresists.

MPA in the synthesis of chiral ligands

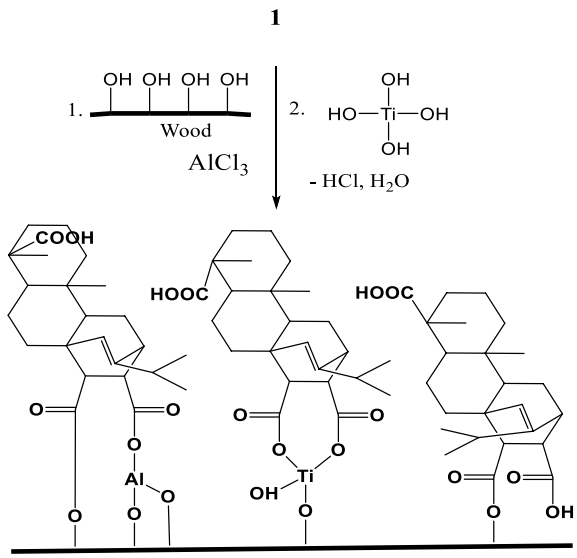
Phosphorus-containing ligands and chiral complexes of rhodium (I) were synthesized for enantioselective reactions [124]. MPA **1** was converted to triol **132** (Scheme 54). Further protection and benzylation resulted in the desired diol **133** in 40% yield and the tetrahydrofuran derivative **134** in 50% yield. And the use of a weaker acid, pyridinium p-toluenesulfonate, increased the diol **133** yield to 80%. Next, the diol **133** was converted to the chiral ligand of bisphosphine **135** via ditosylate. The asymmetric hydrogenation of (Z)-N-acetylaminocinnamic acid and its derivative with the



Scheme 54 Synthesis of new chiral phosphorous-containing ligands from MPA



Scheme 55 Preparation of rosin-based binaphthyl-appended 22-crown-6 ether



Scheme 56 A simple fabrication of superhydrophobic wood surface based on MPA

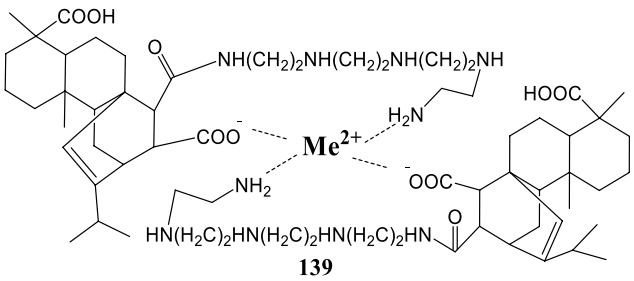


Fig. 9 Structure of rosin-derived nano-micelles **139**

catalytic amount of the obtained cationic complex Rh (I) **136** led to **137a** in 27% optical yield and **137b**- 37% [124].

The synthesis of chiral alcohols and phosphorus derivatives based on MPA was reported. Their use in ^{31}P-NMR analysis for the determination of the enantiomeric excess of alcohols and amines was proposed [125].

Also the synthesis of crown ether **138** according to Scheme 55 was reported [126]. The MMP derivative is capable of recognizing the enantiomers of amines.

Some rosin-modified materials

A simple method for making rosin-modified superhydrophobic wood surfaces by impregnation has recently been reported (Scheme 56) [127].

Similar materials based on rosin and starch were also obtained [128].

Based on the results of the absorption experiments, it was shown that nano-micelles **139** obtained from MPA and tetraethylenepentamine in aqueous solution have an outstanding ability to absorb metal (Fig. 9). Moreover, the adsorption of metal ions did not depend on pH, and the materials had a higher affinity for Ni (II) than for Cu (II) and Cd (II) [129].

The interaction of microcrystalline cellulose with maleopimaric acid chloride gave ether, which is promising as thermoplastic materials, hot melt adhesives,

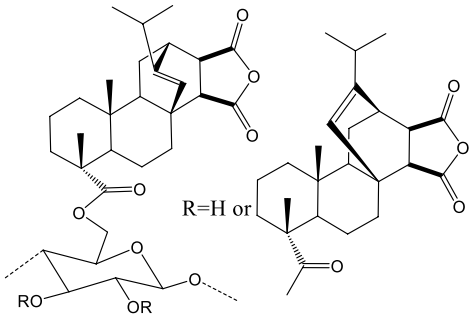


Fig. 10 Structure of cellulose ether based on MPA

superhydrophobizing agents for paper, or as biodegradable polymers (Fig. 10) [130].

Conclusion

Analysis of literature data indicates that maleopimaric acid and its monomethyl ether have unique properties and attract many researchers from all over the world to create affordable and valuable materials based on them. A wide range of biological activity of diterpenoid derivatives is associated with the structural features of maleopimaric acid, namely the similarity of the structure of the A, B and C rings with the structure of steroid hormones.

To date, mainly aromatic and heterocyclic amides, aliphatic and aromatic imides of MPA have been obtained. The target products are obtained both from the individually isolated MPA in the reaction with amines, and from the resin or rosin by the reaction of diene synthesis with N-substituted maleimides. Various high-boiling solvents have been proposed to accelerate the process (glacial acetic acid, toluene, xylene, DMF, dichlorobenzene, etc.). An efficient method was developed for the synthesis of imides MMP upon condensation with amino acids and various amines under ultrasonic action in a DMSO medium [40, 57]. The method made it possible to increase the yields of target products, shorten the reaction time by an order of magnitude, and synthesize maleopimarimides even in the case of poorly soluble amines by dispersing adducts. Diacid diimides were obtained in the reaction of diamines with a twofold excess of MPA [23, 27].

The chemistry of diterpenoids has developed greatly in recent years [131]. The interest in these compounds is due to their availability, low cost, low toxicity, and easy modifiability. To date, data have been obtained on the most probable fields of application of MPA derivatives in medicine, etc., including in the form of polymer systems. These compounds can be successfully used as biodegradable polymers, high-performance photoresists and chiral ligands, engineering plastics, film materials, curing agents, absorbents, thermoplastic materials, hot melt adhesives, surfactants, paints and coatings, superhydrophobizators and sealing agents for paper, photoacid generators of a new type, corrosion inhibitors, dispersants for magnetite nanoparticles (Fe_3O_4), inhibitors of protein aggregation processes, as microencapsulated materials for drug delivery, etc.

Thus, maleopimaric acid and substances based on it can be confidently considered excellent objects of innovative research, and the expansion the scope of application of these compounds in the synthesis of various materials with valuable properties is of interest both from a scientific point of view and from a practical point of view.

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