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THE COMPOSITION STUDY OF TERPENOIDMALEIC ADDUCTS

The work contains studies of the chemical composition of adducts on the basis of terpenoids and maleic anhydride to provide controlled synthesis on the basis of their secondary products with specified performance characteristics.

The determination of the qualitative and quantitative composition of the mixtures of resin acids of pine turpentine and rosin by their methyl esters was performed with GLC analysis; the components of pine resin, rosin, turpentine, adducts was performed with NMR spectroscopy, functional groups in the original terpenoid resins and products of their interaction with oxygen-containing compounds (maleopimaric acid) and terpenoidmaleic adducts by the method of IR spectroscopy.

Good convergence of the results obtained by NMR spectroscopy and GLC analysis on the composition of pine resin, gum rosin and turpentine confirms their authenticity.

Using the obtained experimental and calculated data the composition of terpenoidmaleic adducts was set. When obtaining resin terpenoidmaleic adducts, the composition of turpentine solution of resin varied in the range from 30/70 to 70/30 wt %, the calculated amount of maleic anhydride to link all resin acids with conjugated double bonds and terpene hydrocarbons varied from 57.7 to 38.3 wt %. It is shown that when modification of turpentine composition from 30/70 to 70/30 wt % with maleic anhydride increases, there is a significant change in the compositions of obtained terpenoidmaleic adducts of rosin.

When comparing experimental data and theoretical calculations regularity is established in the change of composition of terpenoidmaleic of rosin adducts obtained from various turpentine: content of maleopimaric acid naturally increases with the increase of resin acids and the content of terpenoidmaleic adducts decreases. It is shown that terpenoidmaleic adducts are multicomponent systems composed of maleopimaric acid, terpinolene adducts, and of resin acids, which do not react with maleic anhydride. By varying the composition of the turpentine and the amount of maleic anhydride, adducts with different content components can be obtained, and hence, regulating their specifications. The efficiency of using the methods of NMR and IR spectroscopy to study the composition terpenoidmaleic adducts is demonstrated.

Key words: analysis, anhydride adduct, rosin, rosin acid, modification, synthesis, turpentine, range, terpenoid, chromatography.

Introduction. Terpenoid-maleic adducts (technical name – TDMA) obtained through the interaction of terpenoids with maleic anhydride (MA) and products on their basis (compound ethers, imides and salts of heavy metals) can be used in electrical engineering, paint and coating, general rubber, pulp and paper industry and other industries [1].

TDMA represent complex multicomponent mixtures the contents of which is determined by the type of raw materials and conditions of their production [2–4]. The use of gas-liquid chromatography (GLC) as applied to TDMA till present time was limited only by the identification of separate methyl ethers of terpene-maleic adducts (TMA) [4], methyl ethers of rosin-terpenoid-maleic adducts (RTMA) and methyl ethers of rosin-maleic adduct (RMA) [5, 6]. The diadducts also contained in RTMA and TMA prevented from the identification of the chemical composition of adducts.

The technologies for RTMA processing from turpentine developed earlier [7–9] can be applied on any rosin-turpentine plant of the CIS countries. However the synthesis of the secondary products using

them requires the necessary level of knowledge in the sphere of the chemical composition of adducts.

That's why the goal of this research lies in the analysis using NMR and IR spectroscopy methods of the group composition of TDMA: RTMA, RMA and TMA.

Main part. Determination of the qualitative and quantitative composition of the mixtures of resin acids (RA) of pine resin and rosin through their methyl ethers were performed using GLC method according to methodology [10] on LKhM-8MD chromatograph. The column (2×3 mm) was filled with chromosorb G (60–80 mesh) and impregnated with polyethyleneglycolphthalate (5%). Column temperature 200°C, gas bearer – nitrogen (0.45 GA on the input), hydrogen consumption – NMT 20 ml/min.

The qualitative and quantitative composition of turpentine oil was determined according to the methodology provided in the work [11]. In order to determine the functional groups in the initial terpenoid resins and products of their interaction with oxygen-containing compounds (maleopimaric acid (MPA) and TMA the IR spectroscopy analysis

was applied. IR spectrums of the studied samples were recorded using FT-IR NEXUS spectrophotometer with Fourier transform in the range of frequencies of 500–4,000 cm^{-1} . The studied materials were analyzed in the form of the firm tablets pressed in potassium bromide. Identification and analysis of IR spectrums were carried out using the methodology provided in the sources [12–14].

In order to carry out the qualitative and quantitative determination of the composition of pine resin, rosin, turpentine oil, RTMA, RMA and TMA components the method of NMR-spectroscopy was applied. The record of spectrums ^1H and ^{13}C during NMR was performed using AVANCE-500 spectrometer (Germany) (500 MHz for nuclei of ^1H and 126 MHz – for ^{13}C in 5 ml standard ampoules) [15]. Homogeneous solutions of terpenoid products (50 mg) in 0.5 ml deuterated solvent (CDCl_3) were prepared. Chemical shifts of the signals of protons of compounds were determined by chloroform signal (CHCl_3 , $\delta = 7.27$ ppm) that was present as an impurity in the deuterated solution. Chemical shifts of ^{13}C of carbon atoms of the compounds were measured in relation to the solvent signal ($\delta = 77.7$ ppm). Allocation of signals was performed using DEPT method. Spectrums were recorded in the “qualitative” mode. In order to identify signals in the spectrums of terpenoid products NMR spectrums of solutions (^1H , ^{13}C and DEPT) in CDCl_3 of the following RAs were recorded: abietic (1), neoabietic (2), palustric (3), levopimaric (4), maleopimaric (5), dehydroabietic (6), isopimaric (7) and pimaric (8).

The chemical shifts (δ , ppm) of the signals used for the quantitative analysis in the spectrums of ^1H NMR and ^{13}C NMR RA (solutions of CDCl_3) and the spectrums themselves are provided in the works [16–22]. RA and MPA were separated using the standard methods by the staff of the Institute of Physical Organic Chemistry of the National Acad-

emy of Sciences of Belarus and Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus.

In order to synthesize TDMA pine resin, pine oleoresin and gum turpentine were used. Tables 1 and 2 contain the compositions of the base mixtures of rosin acids of pine resin and rosin according to the data of GLC analysis and NMR spectroscopy.

The analysis of the data provided in Tables 1 and 2 demonstrates the good reproducibility of the obtained results in respect to the composition of pine resin, pine oleoresin and turpentine oil determined by NMR and GLC methods thus confirming their soundness.

According to Table 1 the quantity of RAs with conjugated double bonds in pine resin is 72.0–73.5%. The quantity of RAs with conjugated double bonds in rosin is 76.2–76.3%.

During the synthesis of RMA the quantity of MA introduced in the reaction of rosin modification was determined based on the supposition that 1 gram-mol of RA with conjugated double bonds reacted with 1 gram-mol of MA.

After the receipt of RTMA the quantity of MA introduced in the reaction of turpentine modification was determined based on the supposition that 1 gram-mol of RA with conjugated double bonds and 1 gram-mol of terpene carbons of turpentine oil reacted with 2 grams-mol of MA.

For the production of RTMA turpentines were used in ratio RA 30–70%, turpentine oil 70–30%. Various compositions of turpentine were obtained according to the methodology provided in the work [23].

During the synthesis of TMA it was assumed that the quality of MA introduced in the reaction of turpentine oil modification was determined by the fact that 1 gram-mol of terpene hydrocarbon reacted with 1 gram-mol of MA.

Table 1

Composition of the mixtures of resin acids of pine resin and rosin according to the data of GLC analysis and NMR spectroscopy

Acid	Composition of the mixtures of resin acids, %	
	Pine resin	Pine oleoresin
	GLC analysis*/ NMR spectroscopy**	GLC analysis*/ NMR spectroscopy**
Levopimaric, palustric	47.0/47.0	27.5/26.3
Abietic	13.2/13.0	34.0/33.7
Neoabietic	13.3/12.0	14.8/16.2
Pimaric	10.0/8.0	7.5/9.3
Sandaracopimaric	1.6/–	1.5/–
Isopimaric	6.5/8.0	5.2/5.7
Dehydroabietic	5.7/6.0	6.1/2.9
Dihydroabietic	0.3/–	1.2/–
Resin acids with unknown composition	2.4/6.0	2.2/4.9

* Data on the contents of methyl ethers of resin acids.

** Data on the contents of RAs determined by NMR method.

Table 2

Composition of gum turpentine according to the data of GLC analysis and NMR spectroscopy

Terpene	GLC analysis	NMR spectroscopy
α -Pinene	51.0	49.7
β -Pinene	2.4	2.4
Δ^3 -Carene	34.0	32.7
Camphene	0.6	0.9
Dipentene	4.0	4.3
Terpinolene	3.8	4.4
γ -Terpinene	–	0.4
β - Phellandrene	–	0.9
Myrcene	–	1.5
<i>n</i> -Cymene	–	0.4
β - Caryophyllene	–	0.3
Components of non-established structure	4.2	2.1

The synthesis of adducts was carried in three-necked flask with a mixer, backflow condenser and thermometer. The flask was loaded with the estimated amounts of turpentine (rosin or turpentine) and MA. The flask was placed in the thermostat. The mixer and thermostat electric heating were switched on. The process of interaction of the components (turpentine, rosin, turpentine oil with MA) was carried out at the temperature of $(190 \pm 2)^\circ\text{C}$. The synthesis of adducts was controlled according to the residual contents of MA: the reaction was considered to be complete after the contents of MA that failed to react of not more than 2 wt % [24]. After the completion of adduct synthesis the backflow condenser was exchanged for the direct one and the unreacted turpentine oil and MA were distilled out in vacuum ($P = 20$ mmHg, $T = (190 \pm 2)^\circ\text{C}$, $\tau = 30$ min). The obtained TDMA is a solid glass-like substance of light yellow color.

In IR spectrums of RMA, TMA, RTMA_{30/70–70/30} the characteristic absorption bands of C=O bonds of the cyclic anhydrous groups with maximum at 1,780 and 1,860 cm^{-1} and absorption band C=O of carboxyl group with maximum at 1,690 cm^{-1} were seen that are also present in IR spectrums of pine oleoresin and turpentine oils. It can be assumed that in the line of RTMA_{30/70–70/30} the intensiveness of the absorption of C=O bond of acids (1,690 cm^{-1}) is increased due to the increase in the contents of RAs in the base turpentine. At the same time the intensiveness of absorption bands of C=O of anhydrous groups has almost no changes (maximum 1,780 and 1,860 cm^{-1}) thus additionally confirming the fact that the product is representing both adducts of MA (maleopimaric acid) and adducts of monoterpene hydrocarbons.

Using the obtained experimental and calculation data and the data of the works [16–22] the composition of TDMA (TMA, RTMA, RMA) was established.

Table 3 contains the compositions of TMA, RTMA and RMA determined by NMR-method. Table 4 contains the conditions for the receipt and established compositions of TMA, RTMA and RMA. As it can be seen from the data provided in Tables 3 and 4 at the moment of the receipt of RTMA the composition of the turpentinic solution of gum varied in the range of 30/70 and 70/30%, and the calculated quantity of the MA introduced to bind all RAs with conjugated double bonds and terpene hydrocarbons varied from 57.7 to 38.3 wt %. From the data contained in Table 3 it can be seen that upon the increase of the depth of turpentine modification from 30/70 to 70/30 wt % of MA the significant alteration of the composition of the obtained RTMA can be viewed. Thus, the contents of MPA increases correspondingly from 24.3 to 51.9 wt %. The contents of TMA reduce from 70 to 30 wt %. The increase of the general content of resin acids from 5.7 to 18.1 wt % is observed. Including the increase of the contents of dehydroabietic acid from 2.0 to 3.7 wt %, isopimaric acid from 1.2 to 6.2 wt % and pimaric acid from 1.4 to 7.4 wt %. At the same time the contents of RAs of non-established composition is about 0.8–1.1 wt %.

Variation of MA contents in RTMA was determined by the composition of the used turpentine (from 30/70 to 70/30 wt %).

During the comparison of experimental data (Table 3) with the data obtained by the means of theoretical calculation (Table 4) it can be seen that there is similar dependency in the alteration of the composition of RTMA produced from different turpentines. So, in all cases the contents of MPA grow together with the growth of RAs and the contents of TMA are decreasing.

The data on the change of turpentine components in the process of its modification by MA were determined by the method of NMR spectroscopy.

Table 3

Composition of rosin-terpenoid-maleic adducts determined using NMR method

Sample	Composition, wt %						
	Maleopimaric acid	Adduct of terpene hydrocarbons with maleic anhydride	General contents of resin acids	Resin acids			
				Dehydroabietic acid	Isopimaric acid	Pimaric acid	Resin acids of non-established composition
TMA	–	97.0	–	–	–	–	–
RTMA _{30/70}	24.3	70.0	5.7	2.0	1.2	1.4	1.1
RTMA _{40/60}	33.6	60.0	6.4	2.4	1.4	1.6	1.0
RTMA _{50/50}	40.4	50.0	9.6	3.5	2.2	3.0	0.9
RTMA _{60/40}	45.6	40.0	14.4	2.9	4.7	5.8	1.0
RTMA _{70/30}	51.9	30.0	18.1	3.7	6.2	7.4	0.8
RMA	80.0	–	20.0	–	–	–	–

Table 4

Production conditions and established composition of TDMA adducts

Raw materials	Reaction conditions			Distilled f or the time of reaction, wt %	Produced, wt %	Output, %	Product name	Calculated group composition, wt %			High-boiling unsaponifiable matter*	MA**
	Quantity of MA, wt %	T, °C	τ, h					MPA	TMA	RA		
Turpentine oil	72.0	170 ± 2	12.0	25.8	146.2	85.0	TMA	–	97.0	–	2.0	1.0
Turpentine _{30/70}	57.7	190 ± 2	9.0	18.9	138.8	88.0	RTMR _{30/70}	21.1	73.1	5.8	Traces	Traces
Turpentine _{40/60}	52.8	190 ± 2	9.0	15.3	137.5	89.0	RTMR _{40/60}	28.2	63.9	7.9	Traces	Traces
Turpentine _{50/50}	48.0	190 ± 2	9.0	14.8	133.2	90.0	RTMR _{50/50}	36.6	53.5	9.9	Traces	Traces
Turpentine _{60/40}	43.1	190 ± 2	9.0	11.7	131.4	91.8	RTMR _{60/40}	44.4	43.5	12.1	Traces	Traces
Turpentine _{70/30}	38.3	190 ± 2	9.0	9.7	128.6	93.0	RTMR _{70/30}	52.6	33.0	14.4	Traces	Traces
Free fatty acids	25.0	190 ± 5	6.0	1.2	123.8	99.0	RMA	78.0	–	22.0	Traces	Traces

* Reaction was considered to be finished where the reaction mixture contained NMT 2.0 wt % of free unbound MA. The residues of unreacted turpentine oil and MA were distilled for 30 min at the temperature of (190 ± 2)°C and in vacuum $P = 20$ mmHg

** Contents of free unbound MA were determined according to the methodology provided in the work [24].

Fig. 1 and 2 contain full spectrums of ^1H NMR and ^{13}C NMR RTMA_{60/40}. The chemical shifts (δ , ppm) of signals used for qualitative analysis in spectrums ^1H NMR and ^{13}C NMR of resin acids and maleopimaric acid (solutions in CDCl_3) were provided in the works [16, 22].

Fig. 3 demonstrates the kinetics of the alteration of the contents of the group composition of RTMA in the process of turpentine modification (composition of 60/40 wt %) MA without the distillation of the residues of turpentine oil and MA. As it can be seen from the data on Fig. 3 upon the increase of the depth of turpentine oil modification by MA the reduction of the contents of the latter from 30 to 1 wt % within 9–10 h takes place. These data are well confirmed by the results of tests provided in the work [3].

Terpene hydrocarbons of turpentine oil react with MA with formation of adducts and their maximum quantity is 34–37 wt % (during 7–8 h). By the end of the process of RTMA formation

their contents is 38 wt %. At the same time the contents of terpene hydrocarbons of turpentine oil reduces from 28 to 0 wt %. The general contents of RAs reduce from 40 to 11 wt % during the process of turpentine modification. The reduction of the contents of RAs of turpentine is based on the fact that RA with conjugated double bonds contained in turpentine (levopimaric, palustric, neoabietic, abietic) fully reacts with MA with the formation of MPA within 4–6 h. At the same time the contents of RAs with conjugated double bonds reduces from 29 to 0 wt % during this time (4–6 h). The contents of RA (dehydroabietic, isopimaric, pimaric acids and RA of non-established composition) remains almost on the same level and by the end of the process corresponds to 10–11 wt %. In the process of turpentine modification the sharp increase of MPA contents during 4–6 hours equal to 32–41 wt % is observed.

By the end of the process of RTMA formation the contents of MPA equals 42 wt %.

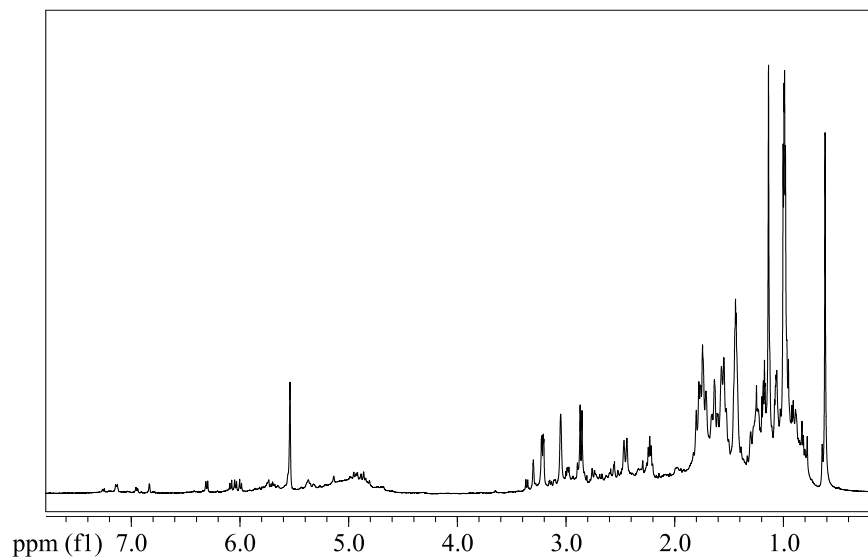


Fig. 1. Spectrum ^1H NMR solution in CDCl_3 of adduct $\text{RTMA}_{60/40}$

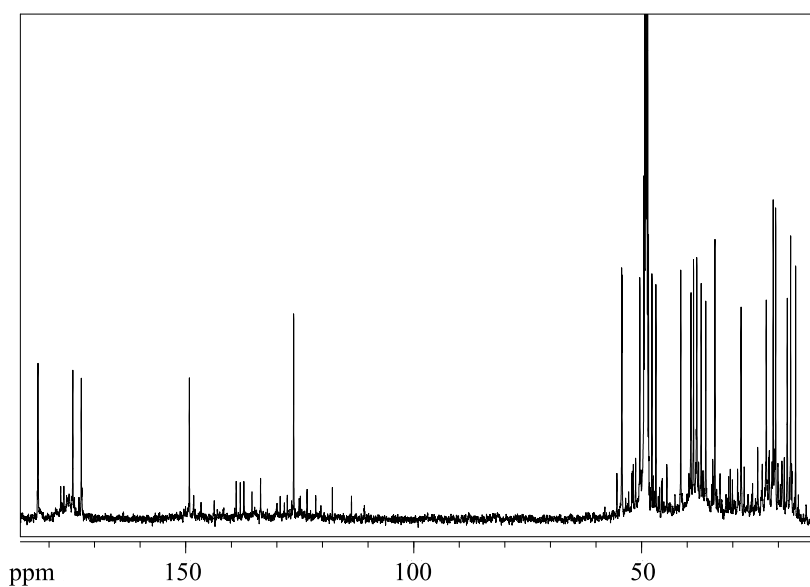


Fig. 2. Spectrum of ^{13}C NMR solution in CDCl_3 of adduct $\text{RTMA}_{60/40}$

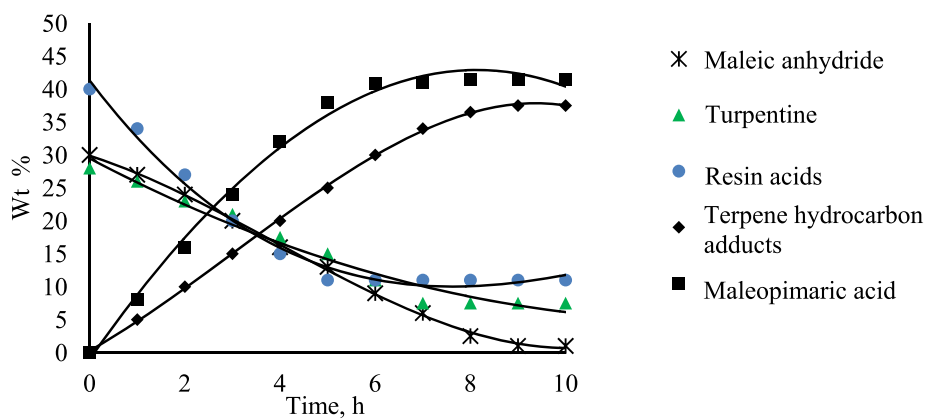


Fig. 3. Kinetics of changes in the content of components terpentina 60/40 in the process of modifying MA

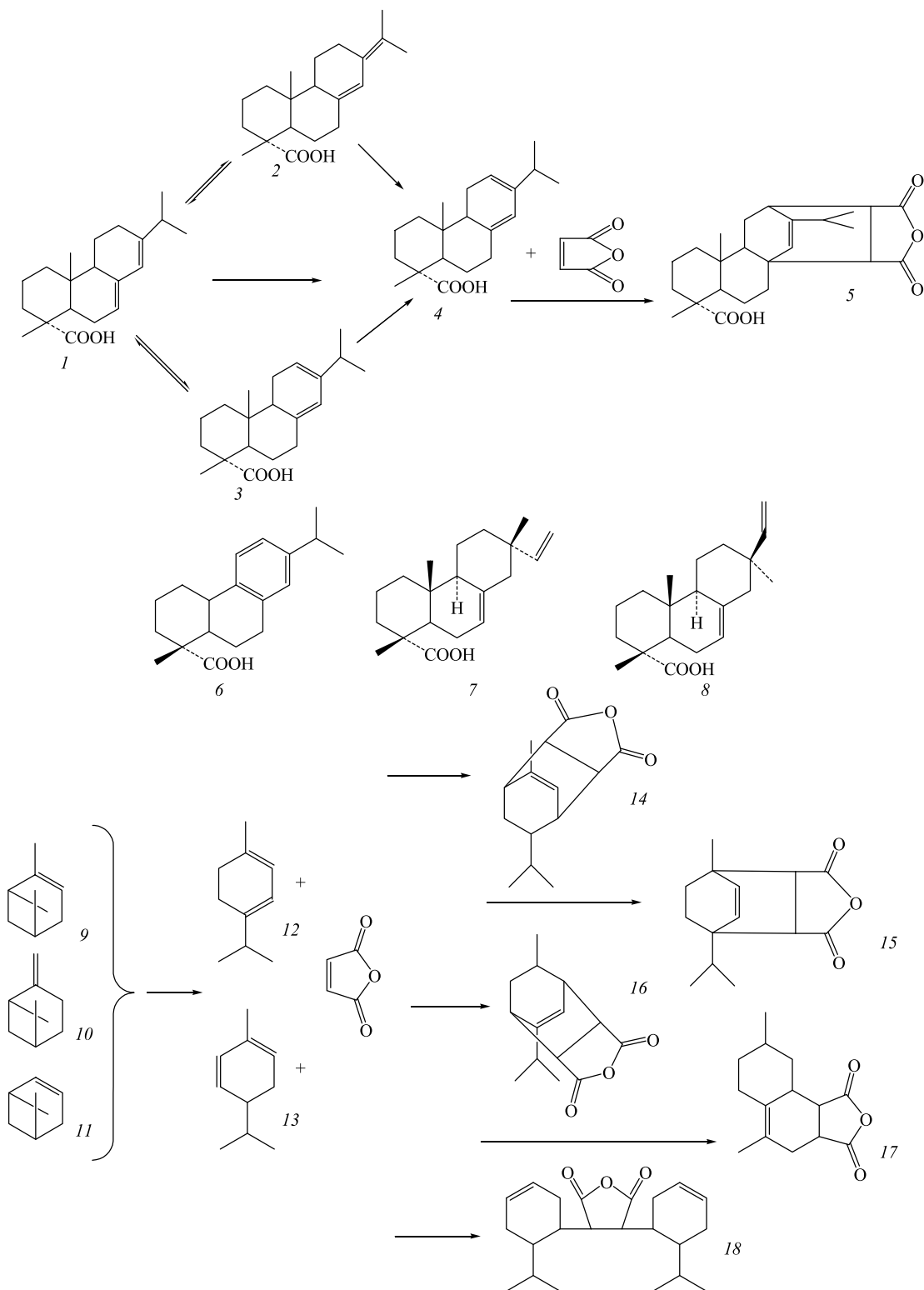


Fig. 4. Scheme of production of rosin-terpene-maleic adducts:

- 1 – abietic acid; 2 – neoabietic acid; 3 – palustric acid;
 4 – levopimaric acid; 5 – maleopimaric acid; 6 – dehydroabietic acid;
 7 – isopimaric acid; 8 – pimaric acid; 9 – α -pinene; 10 – β -pinene; 11 – Δ^3 -carene;
 12 – α -terpinene; 13 – α -phellandrene; 14 – monoadduct of α -phellandrene;
 15 – monoadduct of α -terpinene; 16 – monoadduct of 2,4-*n*-mentadiene;
 17 – monoadduct of 3,8(9)-*n*-mentadiene; 18 – diadduct

Using the obtained experimental and calculated data and the data of the works [16–22] the composition of TDMA (TMA, RTMA, RMA) was established.

Thus, the optimal duration of turpentine modification (composition 60/40 wt %) of MA equals to 8–10 h (Fig. 3).

According to the present literature [1, 3, 4] and experimental data the reaction of diene synthesis of resin acids and terpene hydrocarbons probably follows the scheme described in Fig. 4.

The reaction starts at the temperature of 50–60°C. The most chemically reactive levopimaric acid (4) reacts with MA until its full transformation into MPA (5). At the temperatures from 150 to 200°C in the presence of MA isomerization of double bonds can be seen in abietic (1), neoabietic (2) and palustric (3) acids with formation of levopimaric acid (4) that reacts with MA [2]. Thus, all the components with conjugated double bonds undergo a reaction. Dehydroabietic (6), isopimaric (7) and pimaric (8) acids due to the peculiarities of their chemical structure do not enter into the reaction of diene synthesis with MA. Terpene hydrocarbons start to react with MA at the temperature about 70–80°C. At the same time first of all such monoterpene hydrocarbons like α -phellandrene (13) with conjugated double bonds enter into reaction. Taking into account that the reactions of interaction of terpene hydrocarbons of turpentine oil (turpentine) with MA are not studied to the end we can suppose that bicyclic terpene hydrocarbons like α -pinene (9), β -pinene (10) and Δ^3 -carene (11)

at the temperature of 150°C and higher can isomerize into monoterpene hydrocarbons (reaction with bicycle opening) like α -terpinene (12) and α -phellandrene (13) that are probably enter into reaction with MA forming TMA mix. TMA mix according to the data provided in the work [4] allegedly consists of: monoadduct of α -phellandrene (14), monoadduct of α -terpinene (15), monoadduct of 2,4-*n*-mentadiene (16), monoadduct of 3,8(9)-*n*-mentadiene (17) and diadduct (18). We must add that the process of the interaction of terpene part of turpentine with MA requires additional research.

Conclusion. As it can be seen from the studies mentioned above, RTMA represent multicomponent systems containing different quantities of MPA, TMA and resin acids that have not entered into reaction with MA. Varying the composition of turpentine and quantity of the introduced MA we can get RTMA with different contents of components.

So, varying the contents of turpentine from 30/70 to 70/30 wt % and introducing in Diels-Alder reaction of MA in the quantities from 57.7 to 38.3 wt % we see the increase of MPA acid contents from 24.3 to 51.9 wt %, RAs not reacting with MA from 5.7 to 18.1 wt % and reduction of TMA contents from 70 to 30 wt %. The ability of the efficient use of NMR and IR spectroscopy methods for the study of TDMA composition was demonstrated. The data of theoretical calculation of RTMA composition correlate with the data obtained during the use of NMR spectroscopy method.

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