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L - (-) - Spectroscopic Analysis of Menthol Compounds Formed with Certain Dicarboxylic Acids

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Annotation

Natural compounds isolated from plants have a high biological activity, and terpenoids and their derivatives occupy a special place among such compounds.
The healing properties of herbs are determined by their chemical composition, i.e. the presence of alkaloids, flavonoids, vitamins, carbohydrates and other substances. One such plant is the Menthapiperita plant, the monoterpene-menthol substance is the basis of the essential oil extracted from the surface of the plant. Peppermint oil is extracted from the leaves and other surface parts of the plant, and its composition consists of 50% menthol, 9% acetic acid and valeric acid menthol esters.
This paper provides information on some physicochemical properties of compounds of monoterpenoid menthol formed with some dicarboxylic acids. The results of the analysis of the chemical structure of the obtained compounds based on the *results obtained by IR, Mass and Raman spectroscopy were presented.*

Keywords: menthol, essential oils, Raman spectroscopy, eluent, detector.

Introduction

Menthol occurs naturally in the form of a colorless crystal or powder [1]. The antispasmodic nature of mint depends on the amount of menthol it contains [2]. Menthol affects bile flow [3], reduces pain in the esophagus [4], which facilitates digestion [5], and also has antibacterial properties [6]. In addition, mint is also a rich source of polyphenolic compounds and therefore has strong antioxidant properties [7]

Menthol ($C_{10}H_{20}O$) is a crystalline substance, transparent or white, solid at room temperature and soluble at slightly higher temperatures. There are several isomers of menthol, some are menthol fragrant, while some are odorless. Menthol is a (-) menthol with a strong aromatic odor in nature, and its formal name is (1R, 2S, 5R) -2-isopropyl-5-methylcyclohexanol. Other isomers are called isomenthol, neomenthol, neoisomenthol [8]. Menthol and its derivatives are now used widely in medicine, perfumery and food industry. Menthol cools the skin when rubbed into the skin, so it is used as a sedative for headaches, it also has antiseptic properties, which is used for inflammation of the mucous membranes of the nose and throat and is included in painkillers and ointments [9-11].

(-) menthol is included in the composition of strong cooling and refreshing agents, the properties of the (+) isomer are similar but differ in bitter taste and low sensitivity. The cooling effect is four times greater than that of the (-) menthol (+) isomer [12].

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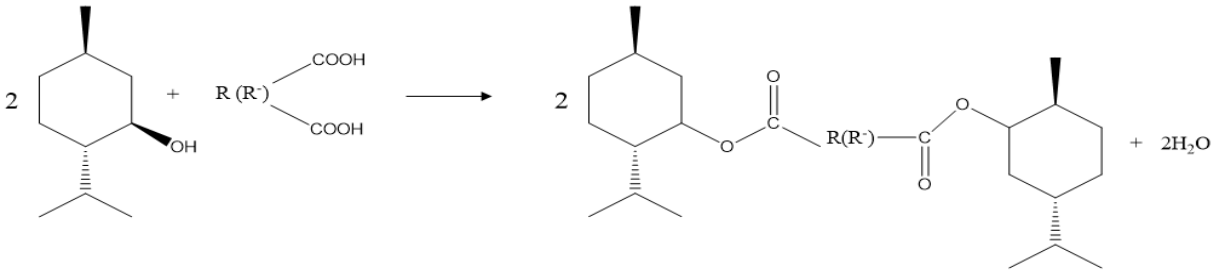
The aim of this work is to synthesize derivatives of menthol with some dicarboxylic acids, to study their physicochemical properties and spectral properties.

In the study, derivatives of menthol with some dicarboxylic acids were obtained based on a method known in the literature [13-14].

DISCUSSION OF RESULTS

The synthesis of new derivatives of menthol with dibasic carbonic acids was carried out with the following reaction scheme:



R -CH_2^*
R- - CH=CH^*

In the IR spectrum of newly synthesized menthol derivatives with dicarboxylic acids, the valence oscillations of the C = O group of carbonyl groups are observed in the range of 1730-1710 cm^{-1}, while the valence oscillations of the menthol -OH groups are observed in the range of 3500-3250 cm^{-1}, which is explained by the extinction of the corresponding oscillation frequency.

The physicochemical quantities of the obtained esters were determined, their structure was confirmed by comparing the IR spectra with the spectra of the original substances. The results are presented in Table 1.

The IR spectrum of the ester does not show the frequency of vibration -OH in the range of 3245 cm^{-1}, which in turn showed the formation of a complex of ester of dicarboxylic acid with the hydroxyl group of menthol (Table 1).

Table 1

Results of physicochemical constants of new derivatives of menthol with some dibasic carbonic acids

№	Substances	Brutto formula and appearance M.M.	$T._{liquid}$· ^0C	R_f^* (system)	Solubility	IK spectrum sm^{-1}	percentage%
1.	Menthol (M)	$C_{10}H_{20}O$ Whitecrystal	42±2	0,3	Ethanol, Acetone Dioxane, Pyridine	2869-2953(CH_2)29	84,6

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		156				27(CH_3) 3245(OH)	
2	Dimentol-oxalate	$C_{22}H_{38}O_4$ 366	103±2	0,35	Hexane, Ethyl acetate Chloroform Benzene, ethanol	1712(CO), 2956(CH_3)	85,2
3	Mentholmalonate	$C_{13}H_{22}O_4$ 242	98±2	0,4	Ethanol, Acetone Chloroform, benzene	1718(CO)2937(CH_3) 3350(OH)	87,9
4	Mentholmaleinate	$C_{14}H_{22}O_4$ 254	95±2	0,35	Hexane, Ethyl acetate Chloroform, Benzene ethanol	3063 (OH); 1712-1729 -(CO), 2954(CH_3)	80,2
5	Dimentolsuccinate	$C_{24}H_{42}O_4$ 394	110±2	0,5	Hexane, Ethyl acetate Chloroform, Benzene, ethanol	2957-2869 (CH_2), 1712-1728 -(CO)	81,6
6	Dimentolglutarate	$C_{25}H_{44}O_4$ 408	100±2	0,6	Hexane, Ethyl acetate Chloroform, Benzene, ethanol	1698(CO),2954-2351(CH_2)	84,5

In the field of oscillation of functional groups in the range of 1726 cm^{-1}, the observation of valence oscillations of the group -C = O (carbonyl) proves once again the formation of an ether bond based on the literature.

The IR spectrum of menthol, the IR spectrum of mentholmaleinate ester and the IR spectrum of dimentoluccinate ester are shown in Figure 1 below.

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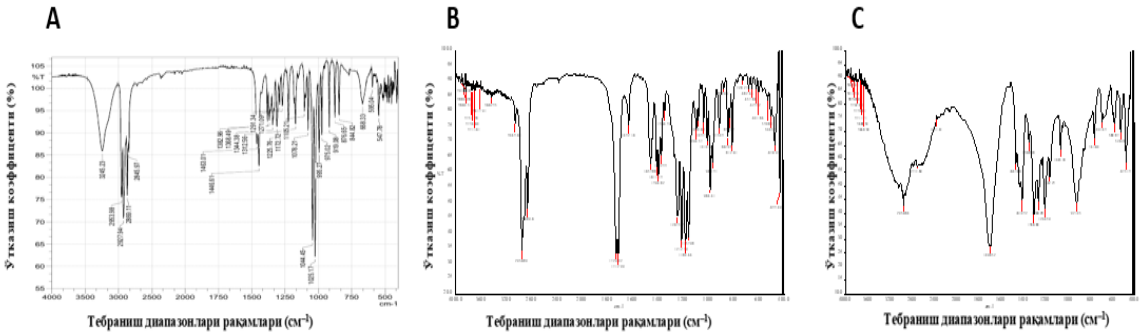

Figure 1. A) IR spectrum of menthol; V) IR spectrum of mentholmaleinate ester; C) IR spectrum of dimentoluccinate ester;

In order to determine the chemical structure of new derivatives of menthol with dibasic carbonic acids, its mass spectrometric analysis was performed. The results obtained show that the product formed as a result of a chemical reaction between menthol and maleic acid was formed as a result of the reaction of mentholmaleinate, a hydroxyl group containing menthol, and a carboxyl group of dicarboxylic acid. Theoretically, two menthols had to be combined into one carbonic acid.

However, mass-spectral analysis showed that they reacted in a 1: 1 ratio. The molecular mass of the resulting substance should be 253.0. The mass-spectral analysis observed during the experiments shows that in addition to the main molecular ion m / z 253 [M-H] in the spectrum, there is also a maleic acid ion in the molecular fragment m / z 115 mentholmaleinate molecule (Figure 2).

Figure 2 below shows the mass spectrum of mentholmaleinate.

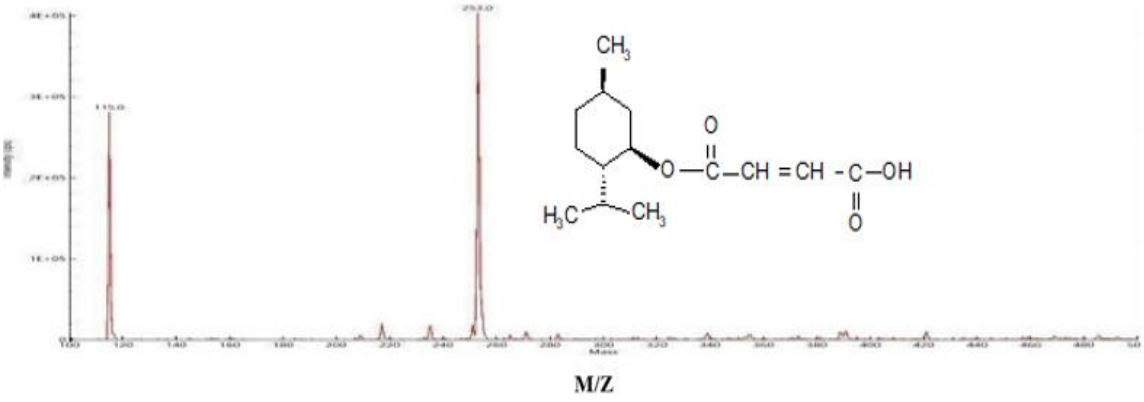

Figure 2. Mass spectrum of mentholmaleinate

Also, in the analysis of the mass spectrum of the reaction product obtained with menthol and amber acid, the basic quasimolecular ion m / z 417.0 [M-H] - corresponds. This molecular mass

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corresponds to a theoretically calculated dimentoluccinate compound (Fig. 3). This means that menthol reacts with amber acid in a 1: 2 mole ratio.

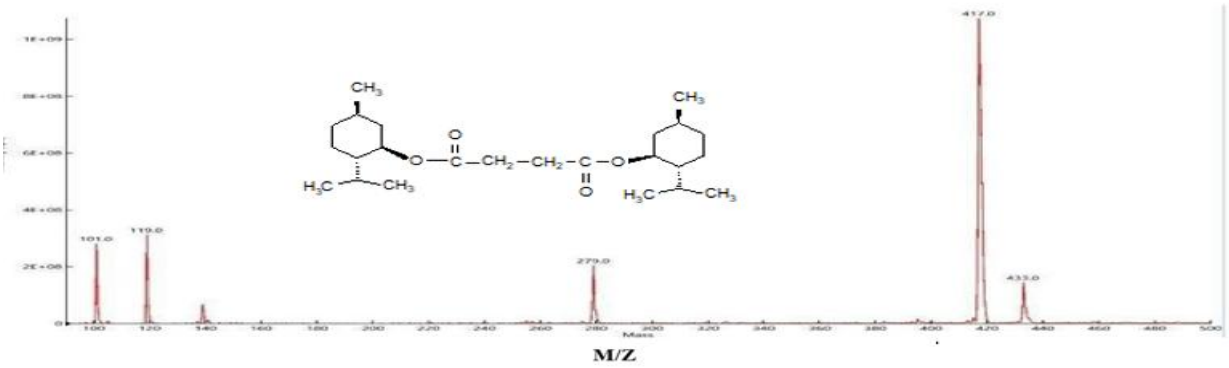
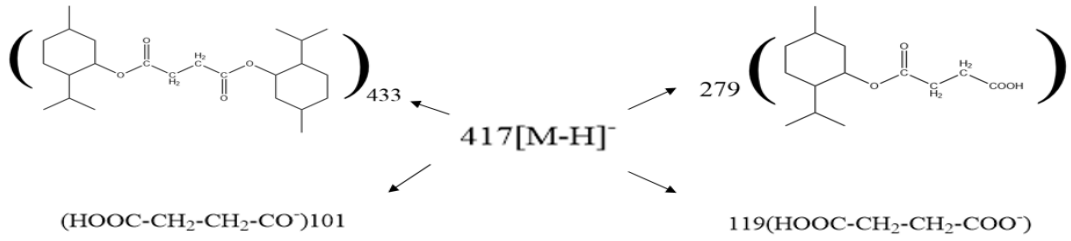


Figure 3. Mass spectrum of dimentoluccinate

In mass spectrometric analysis, in addition to the main quasimolecular ion m / z 417.0 [M-H], several molecular fragment ions correspond to the m / z 119.0 of the amber acid particle in the dimentolsuccinate molecule and the m / z 279.0 to the menthol succinite ion.



In order to more accurately determine the chemical structure of new derivatives of menthol with dibasic carbonic acids, its raman-spectrometric analysis was performed. The results show that the product formed as a result of a chemical reaction between menthol and maleic acid was formed by the reaction of mentholmaleinate, a hydroxyl group containing menthol, and a carboxyl group of dicarboxylic acid (Fig. 4).

Deformation and valence oscillations of functional groups with dipole moment 0 can be seen in Raman spectroscopy. The observation of valence oscillations in the field of oscillation of functional groups in the range of 2867 cm^{-1} (–C = O) 1659 cm^{-1} (SOON) once again proves the formation of an ether bond based on the literature.

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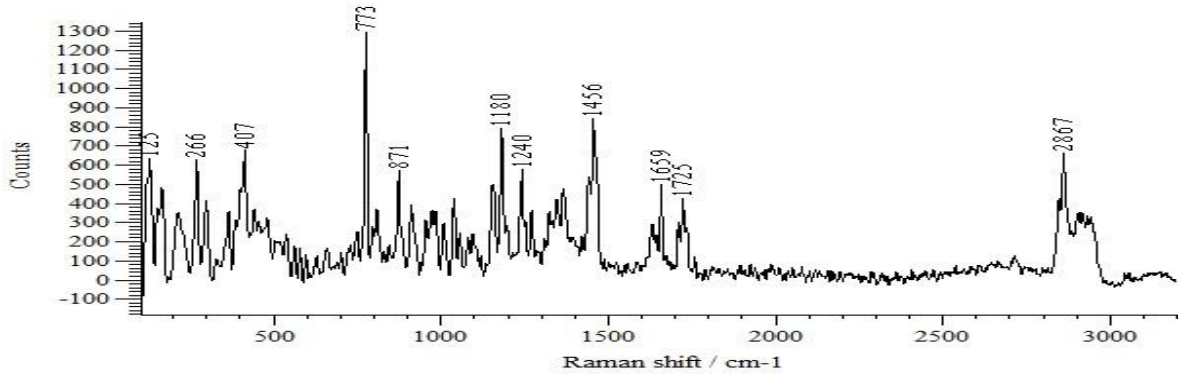

Figure 4. Raman spectroscopy of mentholmaleinate ester

Raman spectroscopy of dimentolsuccinate proves that the formation of an ether bond based on the observation of deformation vibrations of 1343 cm^{-1} (CH_2CH_3) in the field of functional group oscillations in the range of 2867 cm^{-1} (–C = O).

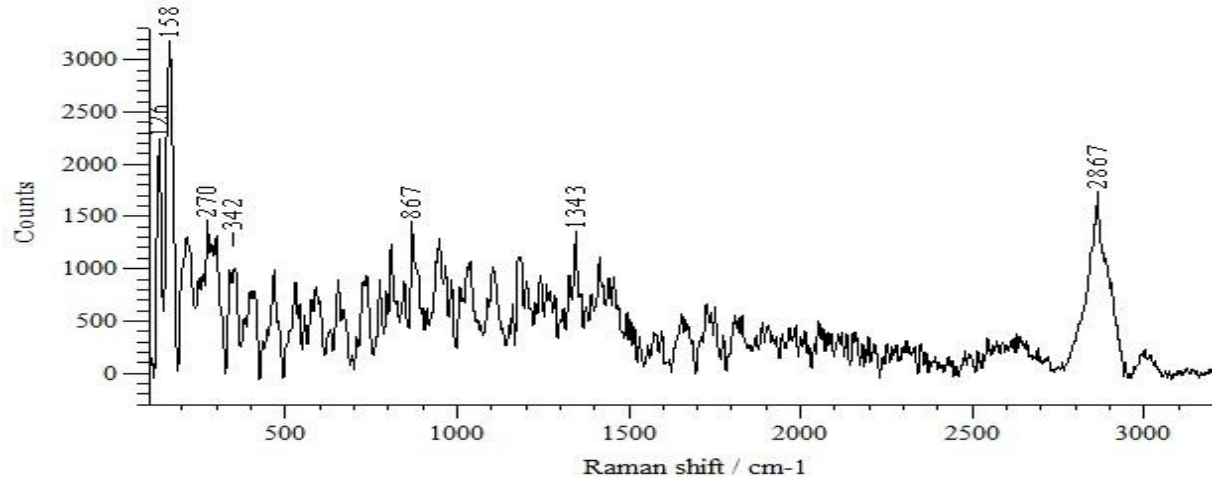

Figure 5 Raman spectroscopy of dimentolsuccinate

From the results obtained, it can be concluded that, depending on the chemical properties of acids, it is possible to determine their ability to react with menthol.

EXPERIMENTAL PART

Carbonic acids have the same properties as monobasic carbonic acids, reacting with alcohols to form esters. This is called the etherification reaction.

Menthol exhibits secondary alcohol properties, and in the next phase of the study, new derivatives of menthol with dicarboxylic acids were synthesized based on the literature.

Knowing the chemical properties of the starting materials, a new derivative of menthol with dicarboxylic acids was synthesized. Menthol (2-isopropyl 5-methylcyclohexanol) was synthesized with dicarboxylic acids (oxalate, malon, malein, amber, glutaric acid) in a 2: 1 ratio, in the presence of a catalyst (H_2SO_4).

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To do this, 500 ml of the flask was filled with 80 ml of oxylene solution by adding crystals of menthol and dicarboxylic acids obtained in equal amounts. A Din-Stark and a return refrigerator were installed at the mouth of the tube. Heated for 12 hours . From the separated mixture, the solvent was expelled in the rotor evaporator, the remaining residue was dried and the pure substance was obtained by recrystallization. The yield of menthol esters obtained with dicarboxylic acids was 80-85%.

IR-Fure spectra were recorded in the absorption range 4000–400 cm^{-1} using an IR-Fure spectrophotometer ("Perkin-Elmer Spectrum IR" -10.6.1; USA). The spectra were determined at a tolerance value of> 4 cm^{-1}. The test specimens were pressed in the form of KBr (Merck, Germany) tablets in a spectrally pure state under vacuum conditions (0.1–0.05 mm Hg) to adsorb moisture.

Highly effective liquid chromatography Mass spectrometry analysis was performed under the following conditions:

A) Scan mode Q-1; B) Carrier gas flow 80 ml/min; C) The temperature of the desolvation process in the chamber is 250^{o}C; D) Gas flow through the sprayer-100; E) Electric field voltage 70 V F) solvent acetonitrile: water.

The InViaRaman spectrometer is manufactured in Renishaw, UK. The InViaRaman spectrometer is designed for basic research and systematic studies of a typical nature, including taking fingerprints of molecules, as well as monitoring changes in the structure of molecular bonds (e.g., changes in state, stress, and strains). It has its own specific dimensions - better than 0.5 cm-1 in the visible range, good signal-to-noise ratio, the ability to work from 1 cm-1 in the acoustic part of the spectrum. Reproduction is better than 0.1 cm-1.

The following were used as a source of excitation:

- Cobalt CW 532nm DPSS laser, wavelength 532 nm and the standard detector of the Renishaw CCD camera as a diffraction grating and recording device with a rated power of 100 mWatt, a circuit of 1800 lines/mm

- Spectral stabilized laser module laser with a wavelength of 785 nm 785 nm. and a standard detector of the Renishaw CCD camera as a nominal power and recording device with a power of 100 mWatt using a diffraction grating with a circuit of 1200 lines/mm.

During the measurements, the laser beams were focused on a point 10 mm in diameter on the sample surface. The irradiance on the surface of the sample varied depending on the value of the output signal on the detector. An X50 lens was used to direct the excited light and collect the scattered light. The exposure time was 10 s and the measurements were made in an extended mode, which allows measurements to be made in the desired wavelength range.

CONCLUSION

1. For the first time, derivatives of menthol with some dicarboxylic acids were synthesized
2. Some physical and chemical properties of the obtained compounds were studied, their chemical structure was studied by IR spectroscopy.

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3. The structure of the obtained compounds was determined using mass spectrometric analysis.
4. . The structure of the obtained compounds was determined using raman spectrometric analysis
5. For the first time, derivatives of menthol with some dicarboxylic acids were synthesized. the chemical structure of the synthesized substances was analyzed using raman spectroscopy. From the results obtained, it can be concluded that, depending on the chemical properties of acids, it is possible to determine their ability to react with menthol.

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