



# Synthesis of Vinyl Esters of Fruit Acids under High Pressure

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## Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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## ABSTRACT

This article describes a method for the synthesis of vinyl esters from fruit acids: malic, tartaric, citric and acetylene, as well as the results of a spectrophotometric analysis of the obtained compounds. Process conditions, product yields, and physicochemical properties of the resulting vinyl esters are given. The homogeneous catalytic reaction of vinylation of malic, tartaric and citric acids with acetylene has been studied and the formation of the corresponding vinyl esters has been proven. The mechanisms of vinylation reactions in the presence of acetylene are proposed. In the synthesis of vinyl ethers, the effect of pressure, temperature, and reaction time on the product yield was established.

**Keywords:** Dimethylformamide; malic acid; tartaric acid; citric acid; acetylene; vinyl ether.

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## 1. INTRODUCTION

An analysis of the literature on new trends in the chemistry of acetylene compounds, ethynylation [1-3] and vinylation reactions [4-6], process conditions and patterns arising from them [7-10], practical and theoretical concepts shows that acetylene is a primary or secondary raw material for the thermal processing of hydrocarbons and carbon [11,12]. Acetylene is also obtained from calcium carbide. For example, in China, 15 million tons of calcium carbide per year is produced to produce acetylene [13-15].

It should be noted that, despite the fact that vinyl esters of carboxylic acids are used in many areas, the literature mainly contains information on the synthesis of vinyl ester from acetic acid [16,17]. Information on the synthesis of other series of acids, for example, vinyl esters of fruit acids, is practically not given. In addition, there are relatively few sources on the use of vinyl substitution and reactions based on malic, citric, and tartaric acids in the synthesis of vinyl esters.

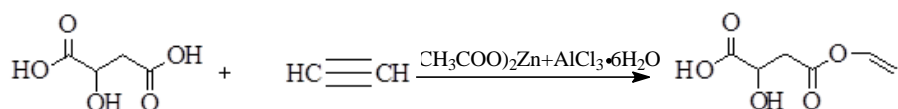
## 2. MATERIALS AND METHODS

The synthesized compounds were subjected to column chromatography. Column chromatography was performed on neutral alumina (Brockmann activity II), Silicagel L 40/60 or Merck Kieselgel 60 sorbents. diethyl ether, ethanol and acetone. Solvents used in chromatography are purified and absoluteized by standard methods.

Spectrophotometric analyzes of the synthesized substances were carried out in the laboratories of the Institute of Chemistry of Plant Substances and Bioorganic Chemistry of the Academy of Sciences of Ukraine and the Center for Advanced Technologies of the Ministry of Innovative Development.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the compounds were obtained in  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  solvents on BK-AP3 and Unity-400plus instruments manufactured by Varian. Also, FT-IR was performed on Nicolet iS50 spectrometers manufactured by Thermo Fisher Scientific.

Vinylation reaction with acetylene in DMF and DMSO in the presence of malic acid catalyst and its mechanism. In this case, complex mono- and divinyl esters of malic acid are formed according to the following scheme:



## 3. THE RESULTS OBTAINED AND THEIR DISCUSSION

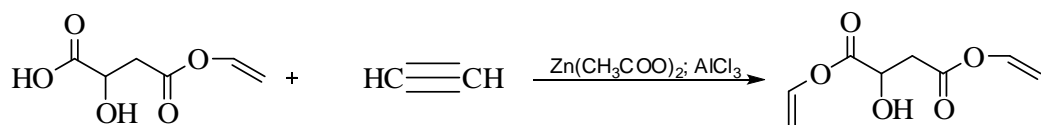
The vinylation reaction in the presence of acetylene was carried out according to the same procedure for all substrates: malic, citric, and tartaric acids. A high-pressure reactor with semi-automatic temperature control "RCG Reactor" (volume 1.6 l) was used.

Synthesis of vinyl esters of malic acid. First, the reaction mixture was prepared in a 500 ml round bottom flask. To do this, 250 ml of dimethyl sulfoxide is poured into the flask. 13.4 g (0.10 mol) of malic acid (1-hydroxy-1,2-ethanedicarboxylic acid) are dissolved in it. Then, 10% (1.34 g) zinc salt of malic acid is added to the solution with respect to the mass of added malic acid and, with respect to the mass of added zinc salt of malic acid, it is mixed with 10% (0.134 g) Lewis acids:  $\text{AlCl}_3$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .

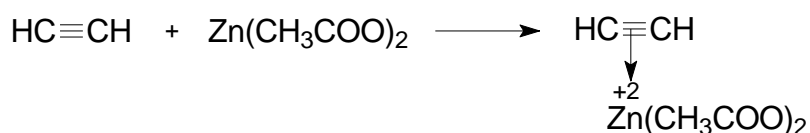
The prepared reaction mixture is poured into the reactor, the reactor is hermetically sealed, and air is removed from the reactor using nitrogen gas. The temperature is then gradually raised to  $60^\circ\text{C}$ . After reaching a temperature of  $60^\circ\text{C}$ , acetylene is introduced into the reactor through a cylinder under a pressure of 4 atm. The supply of acetylene is continued until the reactor pressure gauge shows a pressure of 4 atm. Then the acetylene cock supplied to the reactor is closed, and gaseous nitrogen is supplied from the second fitting through a nitrogen cylinder until the pressure inside the reactor reaches 14 atm. Start the stirrer and bring the heating up to  $120\text{-}130^\circ\text{C}$ . In this case, the pressure inside the reactor rises to 15-16 atm under the influence of temperature. In this case, the process is carried out for 2-8 hours until the pressure in the reactor decreases and remains unchanged.

Then the process is stopped, the reactor is cooled and the reaction mixture is removed. The reaction mixture was filtered and extracted twice with ethyl acetate. The extract is dried over potassium carbonate and the solvent is distilled off. The residual product is separated into fractions by distillation under vacuum.

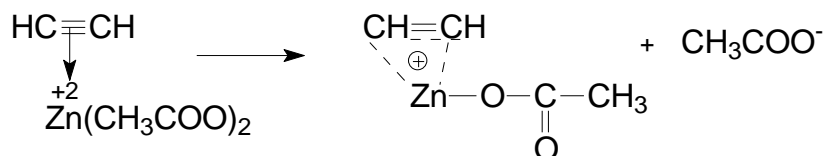
The resulting monovinyl ester of malic acid reacts with acetylene in the presence of a catalyst to form a divinyl ester.



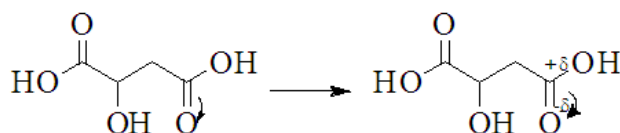
The reaction mechanism is as follows. Initially, the zinc acetate catalyst reacts with acetylene in DMSO to form a  $\pi$ -complex.



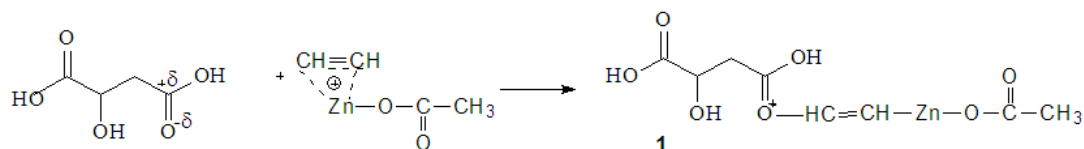
From the formed  $\pi$ -complex, one  $\pi$ -bond of acetylene is broken, then the complex and the acetic acid anion are separated.



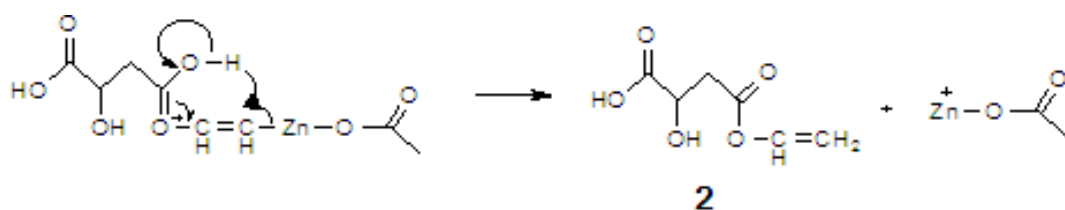
Due to the high value of the negative charge of oxygen in the carbonyl group of malic acid, oxygen in the solvent medium is partially negatively charged.



The acid anion interacts with the vinylacetorux cation to form complex 1.



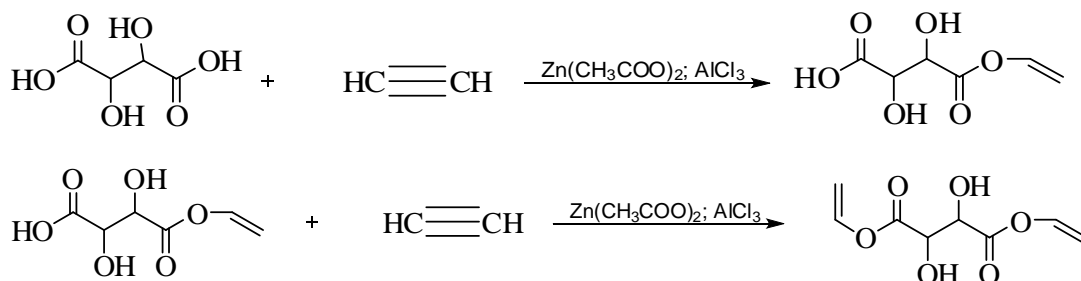
The resulting compound of monovinyl ester of malic acid with acetorux undergoes  $\beta$ -elimination with the formation of monovinyl ester of malic acid 2.



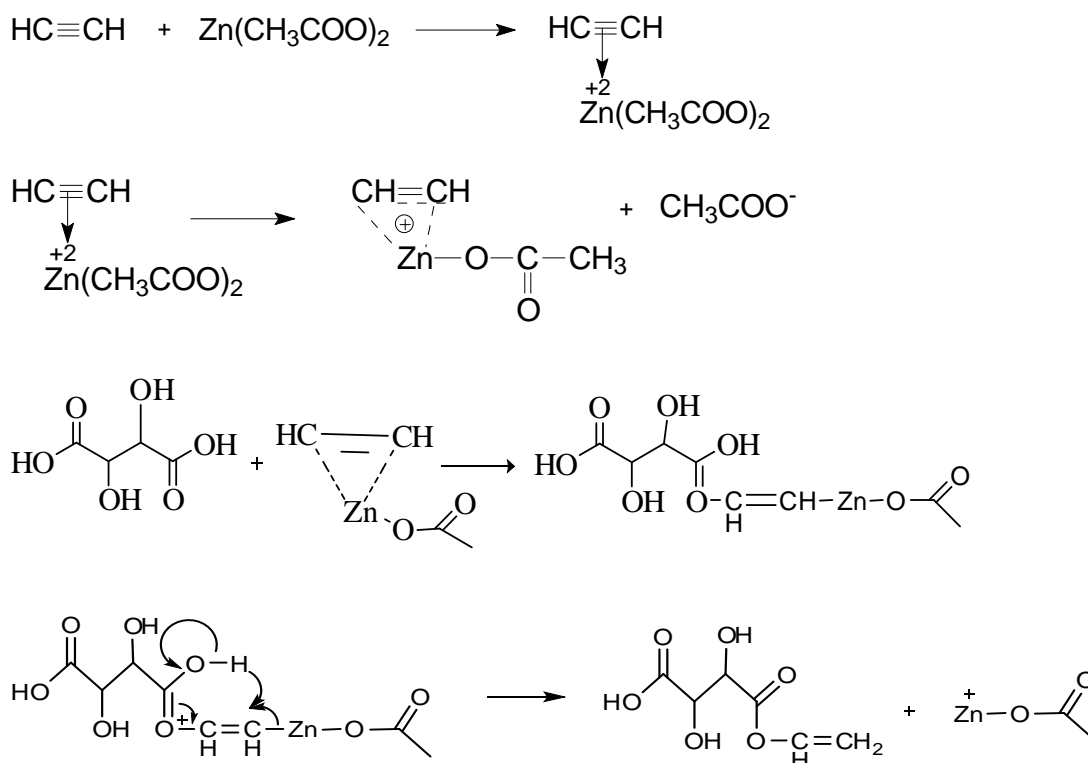
Yield of the obtained products: malic acid monovinyl ester (1-hydroxy-1,2-ethanedicarboxylic acid) - 65.0% (10.4 g),  $T_{melt} = 97-98\text{ }^{\circ}\text{C}$  (10.1325 kPa; 76.0 mmHg), divinyl ester of malic acid (1-hydroxy-1,2-ethanedicarboxylic acid) - 31.0% (5.766 g),  $T_{bp} = 93-94\text{ }^{\circ}\text{C}$  (10.1325 kPa; 76.0 mmHg).

Synthesis of vinyl esters of tartaric acid. 15.0 g (0.1 mol) tartaric acid (1,2-dihydroxy-1,2-ethanedicarboxylic acid), 1.5 g zinc tartrate (10% w/w based on acid), 0.15 g Lewis acid (10% by weight relative to the weight of zinc tartrate) and injected into the reactor (4 atm). acetylene, 10 atm. nitrogen and heated to  $130\text{ }^{\circ}\text{C}$ .

Tartaric acid vinylation reaction mechanism:



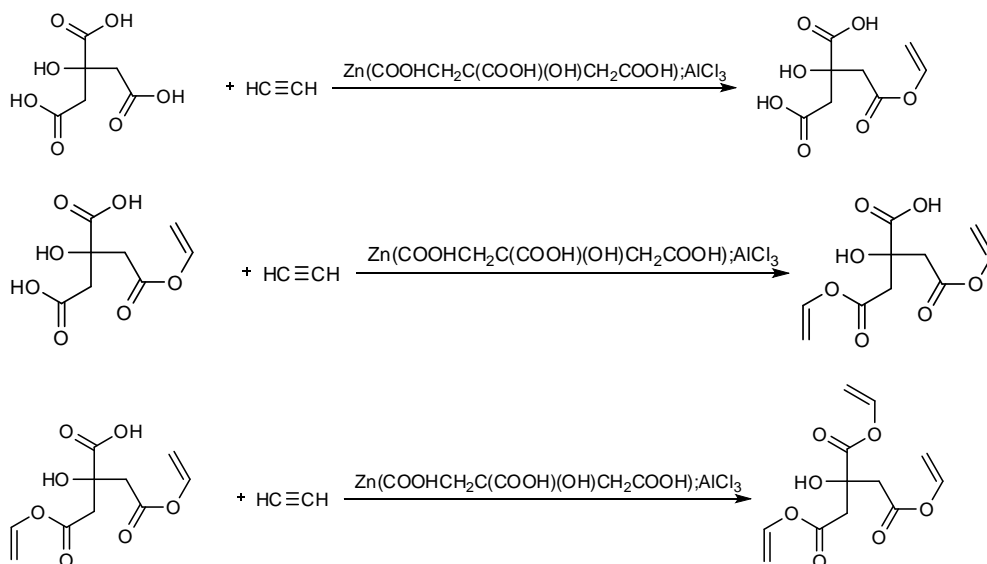
Reaction mechanisms.



Yield of the obtained products: monovinyl ester of tartaric acid (1,2-dihydroxy-1,2-ethanedicarboxylic acid) - 62.0 % (10.912 g),  $T_{melt} = 103-105\text{ }^{\circ}\text{C}$  (10.1325 kPa; 76.0 mmHg) , divinyl ester of tartaric acid (1,2-dihydroxy-1,2-ethanedicarboxylic acid) - 28.0% (5.656 g),  $bp = 99-100\text{ }^{\circ}\text{C}$  (10.1325 kPa; 76.0 mmHg).

Synthesis of vinyl esters of citric acid. 19.2 g (0.1 mol) citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid), 1.92 g zinc citrate (10% by weight based on acid weight), 0.192 g Lewis acid (10% by weight relative to the mass of zinc citrate) and the reactor is injected with 4 atm of acetylene, 10 atm. nitrogen and heated to  $130\text{ }^{\circ}\text{C}$ .

The mechanism of the reaction of vinylation citric acid:



Yield of the obtained products: monovinyl ester of citric acid (2-Hydroxy-1,2,3-propane tricarboxylic acid) - 57.0 % (12.426 g), Tmelt = 120-123 °C (10.1325 kPa; 76.0 mmHg), divinyl ester of citric acid (2-Hydroxy-1,2,3-propanetricarboxylic acid) - 25.0 % (6.1 g), Tmelt = 115-117 °C (10.1325 kPa; 76.0 mmHg), trivinyl ester of citric acid (2-Hydroxy-1,2,3-propane tricarboxylic acid) - 11.0% (2.97 g), Tmelt = 105-106 °C (10.1325 kPa; 76.0 mmHg).

The structure of the synthesized complex mono-, di- and trivinyl ethers was proved by IR-, <sup>1</sup>H-, <sup>13</sup>C-NMR and chromato-mass spectrometry, and some physical constants were determined.

Monovinyl ester of malic acid. Yield: 65%. White crystalline solid, m.p. 97-98 °C. IR, cm<sup>-1</sup>: 3106.1 (OH), 2930 (CH<sub>2</sub>), 1735.8 (-C=O), 1693.04 (-CH=CH<sub>2</sub>), 1386 (CH<sub>2</sub>), 1296.18 (C-OH), 1072.7 (C-O-C), 1112 (CH-OH). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 7.44 (1H, dd, J= 14.8, 7.8 Hz, CH=), 5.12 (1H, dd, J=14.8, 2.3 Hz, =CH<sub>2</sub>), 5.0 (1H, dd, J= 7.8, 2.3 Hz, =CH<sub>2</sub>), 2.34-2.39 (4H, 2.36 (t, J= 7.4 Hz, -CH<sub>2</sub>), 2.37 (t, J=7.4 Hz, -CH<sub>2</sub>), 1.81 (2H, m, J=7.4 Hz) <sup>13</sup>C-NMR (400 MHz, CD<sub>3</sub>OD, δ, ppm): 176.0 (-COO-), 174.0 (-COOH), 141.4 (CH=), 97.0 (=CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 20.0 (CH<sub>2</sub>).

Divinyl ester of malic acid. Yield: 31 %. Colorless liquid. bp=93-94 °C/, IR, cm<sup>-1</sup>: 3334.43 (OH), 2928-2868 (CH<sub>2</sub>), 1740.25 (-C=O), 1647.34 (-

CH=CH<sub>2</sub>), 1087.51 (C-O-C), 1094 (CH-OH). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 7.44 (2H, dd, J= 14.8, 7.8 Hz), 5.12 (2H, dd, J=14.8, 2.3 Hz), 5.0 (2H, dd, J= 7.8, 2.3 Hz), 2.38 (4H, t, J=7.4 Hz), 1.82 (2H, q, J=7.4 Hz). <sup>13</sup>C-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 171.0 (-COO-), 141.0 (CH=), 98.5 (=CH<sub>2</sub>), 34.7 (CH<sub>2</sub>), 20.1 (CH<sub>2</sub>).

Monovinyl ester of tartaric acid. Yield: 62 %. White crystalline solid, m.p. 103-105 °C. IR, cm<sup>-1</sup>: 3334.43 (OH), 2930 (CH<sub>2</sub>), 1740.25 (-C=O), 1647.34 (-CH=CH<sub>2</sub>), 1386 (CH<sub>2</sub>), 1318.27 (C-OH), 1087.51 (C-O-C), 1112 (CH-OH). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 7.44 (1H, dd, J= 14.8, 7.8 Hz, CH=), 5.12 (1H, dd, J=14.8, 2.3 Hz, =CH<sub>2</sub>), 5.0 (1H, dd, J= 7.8, 2.3 Hz, =CH<sub>2</sub>), 2.34-2.39 (4H, 2.36 (t, J= 7.4 Hz, -CH<sub>2</sub>), 2.37 (t, J=7.4 Hz, -CH<sub>2</sub>), 1.81 (2H, m, J=7.4 Hz) <sup>13</sup>C-NMR (400 MHz, CD<sub>3</sub>OD, δ, ppm): 176.0 (-COO-), 174.0 (-COOH), 141.4 (CH=), 97.0 (=CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 20.0 (CH<sub>2</sub>).

Divinyl ester of tartaric acid. yield: 28 %. Colorless liquid. bp=99-100 °C/, IR, cm<sup>-1</sup>: 2928-2868 (CH<sub>2</sub>), 1722 (-C=O), 1667-1644 (-CH=CH<sub>2</sub>), 1254 (C-O-C), 1094 (CH-OH). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 7.44 (2H, dd, J= 14.8, 7.8 Hz), 5.12 (2H, dd, J=14.8, 2.3 Hz), 5.0 (2H, dd, J= 7.8, 2.3 Hz), 2.38 (4H, t, J=7.4 Hz), 1.82 (2H, q, J=7.4 Hz). <sup>13</sup>C-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 171.0 (-COO-), 141.0 (CH=), 98.5 (=CH<sub>2</sub>), 34.7 (CH<sub>2</sub>), 20.1 (CH<sub>2</sub>).

**Table 1. Some physical constants of synthesized vinyl ethers and their yield**

No.	Name vinyl ether	Formula	Molecular weight, g/mol	T bale °C/(10.1 kPa; 76.0 mmHg)	T <sub>mel.</sub> °C	$n_D^{20}$	$d_4^{20}$ g/sm <sup>3</sup>	Yield, %
1	Monovinyl ester of malic acid.	C <sub>6</sub> H <sub>8</sub> O <sub>5</sub>	160,124	-	97-98			65,0
2	Divinyl ester of malic acid.	C <sub>8</sub> H <sub>10</sub> O <sub>5</sub>	186,161	93-94	-	1,472	1,196	31,0
3	Monovinyl ester of tartaric acid.	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	176,123	-	103-105			62,0
4	Divinyl ester of tartaric acid.	C <sub>8</sub> H <sub>10</sub> O <sub>6</sub>	202,160	99-100	-	1,499	1,316	28,0
5	Monovinyl ester of citric acid.	C <sub>8</sub> H <sub>10</sub> O <sub>7</sub>	218,159	-	120-123			57,0
6	Divinyl ester of citric acid.	C <sub>10</sub> H <sub>12</sub> O <sub>7</sub>	244,197	-	115-117			25,0
7	Trivinyl ester of citric acid.	C <sub>12</sub> H <sub>14</sub> O <sub>7</sub>	270,235	105-106	-	1,490	1,228	11,0

Monovinyl ester of citric acid. yield: 57%. White crystalline solid, m.p. 120-123 oC. IR, cm<sup>-1</sup>: 3295.91 (OH), 2930 (CH<sub>2</sub>), 1758.6 (-C=O), 1643.3 (-CH=CH<sub>2</sub>), 1386 (CH<sub>2</sub>), 1292.72 (C-OH), 1217.57 (C-O-C), 1112 (CH-OH). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 7.44 (1H, dd, J= 14.8, 7.8 Hz, CH=), 5.12 (1H, dd, J=14.8, 2.3 Hz, =CH<sub>2</sub>), 5.0 (1H, dd, J= 7.8, 2.3 Hz, =CH<sub>2</sub>), 2.34-2.39 (4H, 2.36 (t, J= 7.4 Hz, -CH<sub>2</sub>), 2.37 (t, J=7.4 Hz, -CH<sub>2</sub>), 1.81 (2H, m, J=7.4 Hz) <sup>13</sup>C-NMR (400 MHz, CD<sub>3</sub>OD, δ, ppm): 176.0 (-COO-), 174.0 (-COOH), 141.4 (CH=), 97.0 (=CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 20.0 (CH<sub>2</sub>).

Divinyl ester of citric acid. yield: 25%. White crystalline solid, m.p. 115-117 oC. IR, cm<sup>-1</sup>: 3439 (OH), 2930 (CH<sub>2</sub>), 1722 (-C=O), 1652 (-CH=CH<sub>2</sub>), 1386 (CH<sub>2</sub>), 1254 (C-OH), 1206 (C-O-C), 1112 (CHOH). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 7.44 (1H, dd, J= 14.8, 7.8 Hz, CH=), 5.12 (1H, dd, J=14.8, 2.3 Hz, =CH<sub>2</sub>), 5.0 (1H, dd, J= 7.8, 2.3 Hz, =CH<sub>2</sub>), 2.34-2.39 (4H, 2.36 (t, J= 7.4 Hz, -CH<sub>2</sub>), 2.37 (t, J=7.4 Hz, -CH<sub>2</sub>), 1.81 (2H, m, J=7.4 Hz) <sup>13</sup>C-NMR (400 MHz, CD<sub>3</sub>OD, δ, ppm): 176.0 (-COO-), 174.0 (-COOH), 141.4 (CH=), 97.0 (=CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 20.0 (CH<sub>2</sub>).

Trivinyl ester of citric acid. yield: 11 %. Colorless liquid. b.p. OH). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 7.44 (2H, dd, J= 14.8, 7.8 Hz), 5.12 (2H, dd, J=14.8, 2.3 Hz), 5.0 (2H, dd, J= 7.8, 2.3 Hz), 2.38 (4H, t, J=7.4 Hz), 1.82 (2H, q, J=7.4 Hz). <sup>13</sup>C-NMR (400 MHz, CD<sub>3</sub>OD, δ, m.s.): 171.0 (-COO-), 141.0 (CH=), 98.5 (=CH<sub>2</sub>), 34.7 (CH<sub>2</sub>), 20.1 (CH<sub>2</sub>).

Some physical constants of the synthesized vinyl esters of carboxylic acids were studied (Table 1).

## 4. CONCLUSIONS

In the synthesis of vinyl esters of hydroxy acids, the main starting materials are the corresponding fruit acids and acetylene.

The scientific significance of the research results lies in the systematic study of the reaction of vinylation of some hydroxy acids with acetylene, the synthesis of their vinyl esters as a result of the reaction of malic, citric and tartaric acids with acetylene at high pressure, as well as the interpretation of the role of intermediate compounds during the process with a change in the potential energy of the products. The practical significance of the research results lies in the fact that a method for the synthesis of vinyl

esters of individual fruit acids by the method of homogeneous catalytic vinylation at high pressure was developed, the optimal conditions for the occurrence of individual processes were found, and the synthesized compounds were recommended as fungicides against yellow rust (*Puccinia striiformis*) of grain in agriculture. economy.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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