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STUDY OF THE EFFECT OF VARIOUS FACTORS ON THE SYNTHESIS OF VINYL ESTERS OF WINE ACIDS

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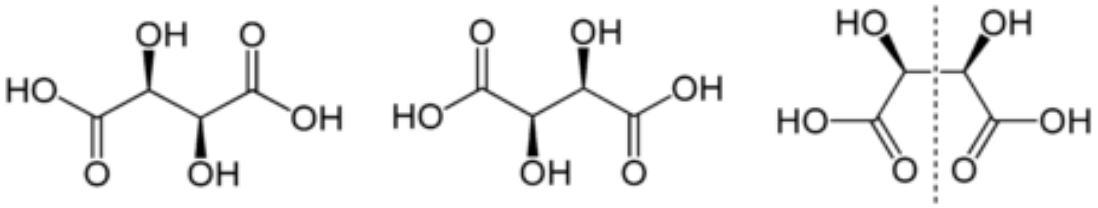
Abstract: Fruit acids and their vinyl derivatives are widely used as biologically active substances in agriculture, medicine and industry. Adding a vinyl group to the acid molecule to increase its reactive active centers, thereby further increasing its biological activity, is one of the urgent tasks. Potassium-sodium salt of tartaric acid $NaKC_4H_4O_6 \cdot 4H_2O$ is used in chemical analysis and radio technology under the name of segnet salt. In this paper, complicated vinyl esters of dibasic carboxylic acids, including wine acid, are synthesized in a homogeneous solution of the solvent dimethylformamide in the presence of zinc acetate and $AlCl_3$-$6H_2O$ catalysts, along with a description of the spectra of the end products.

Keywords: Vinyl esters, wine acids, esterification, vinyl ester synthesis, catalysts, reaction conditions, temperature effect, solvent effect, reaction kinetics, selectivity, yield optimization, mechanism of ester formation, organic synthesis.

Introduction. Wine acid is a typical natural substance. It is abundant in the tart liquids of many foods, including grape juice. The effect of mineral acids on the acidic potassium salt (tartar) produced during the fermentation of grape juice results in the production of D-tartaric acid [1-3].

There are 3 stereoisomeric forms of tartaric acid: D-(-)-enantiomer (a), L-(+)-enantiomer (b) and meso-form (c) (mesovinic acid). **(Figure 1)**:



a b c

Figure 1. Spatial structure of wine acid

Vinylization reactions of wine acid in the presence of acetylene were studied. DMFA solvent-catalyst system was used in this reaction. The DMFA solvent-catalyst system is a catalytic system prepared by mixing Zn $(CH_3COO)_2$ salt in a dimethylformamide solvent medium as a catalyst and 10% $AlCl_3$ as a co-catalyst relative to zinc acetate mass [4-6].

Materials and methods.

The vinylization reaction proceeds in the following mechanism (**Figure 2**.):

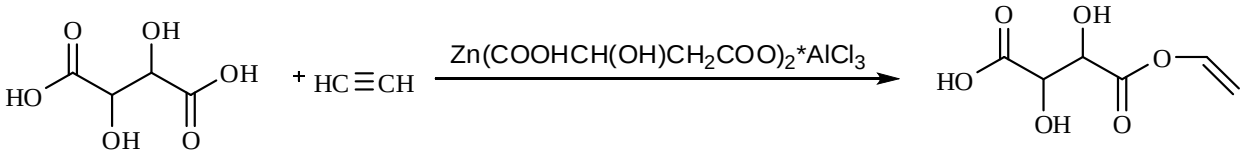


Figure 2. Synthesis of wine acid monovinyl ether

When a reagent is present, the acid's monovinyl ether combines with acetylene to create divinyl ether.[7] (**Figure 3**.).

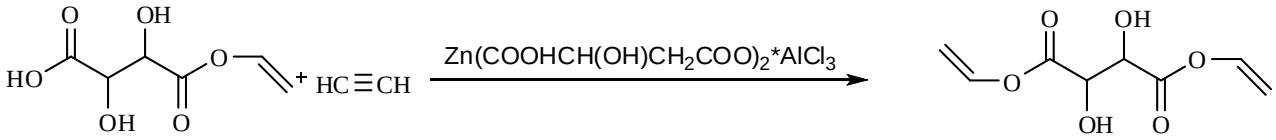


Figure 3. Synthesis of wine acid divinyl ester

Following is the conclusion of the process. In the beginning, π complex is created when the zinc acetate catalyst interacts with acetylene in a DMFA medium. (**Figure 4**).

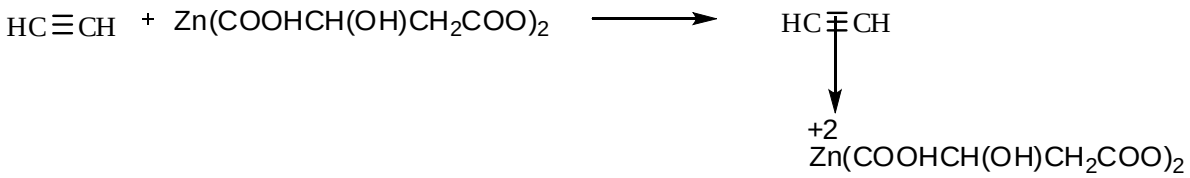


Figure 4. π-complex formation

To break down the acetic acid anion and the complex, one acetylene p-bond is severed from the resulting δ complex. [8] (**Figure 5**).

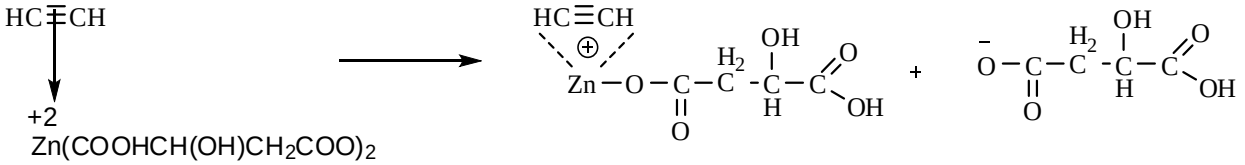


Figure 5. δ -complex formation

Due to tartaric acid's carbonyl group's strong negative charge value, oxygen in the solvent's surroundings has a minor negative charge. (**Figure 6**).

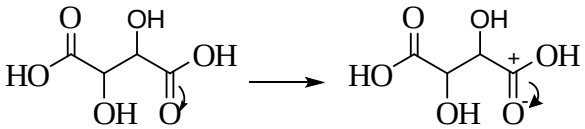


Figure 6. Charge of atoms of wine acid molecule

Vinyl acetorux's cation combines with the acid anion to create a compound. (**Figure 7**).

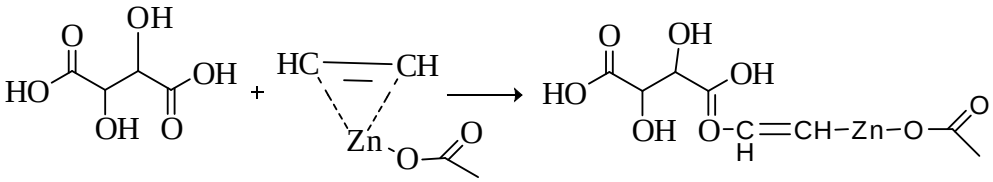


Figure 7. Formation of vinyl acetorux complex of wine acid

Results and discussion.

The monovinyl ester of dioxyacarboxylic acid is created by the elimination of the tartaric acid molecule that results. [9] (**Figure 8)**.

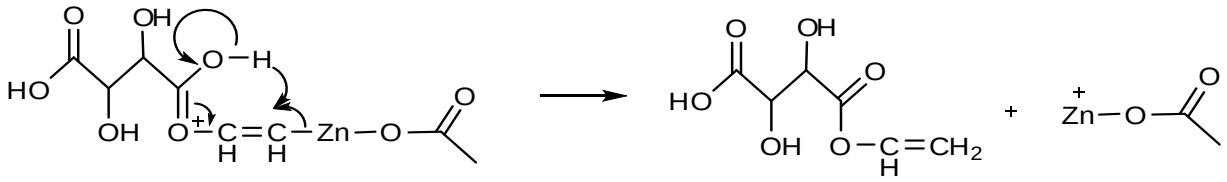


Figure 8. β-elimination of the complex

In the same manner, the second carboxyl group is vinylized to form the divinyl ester of wine acid. The process, of course, occurs through the formation of acetorux complexes of acid monovinyl ester.

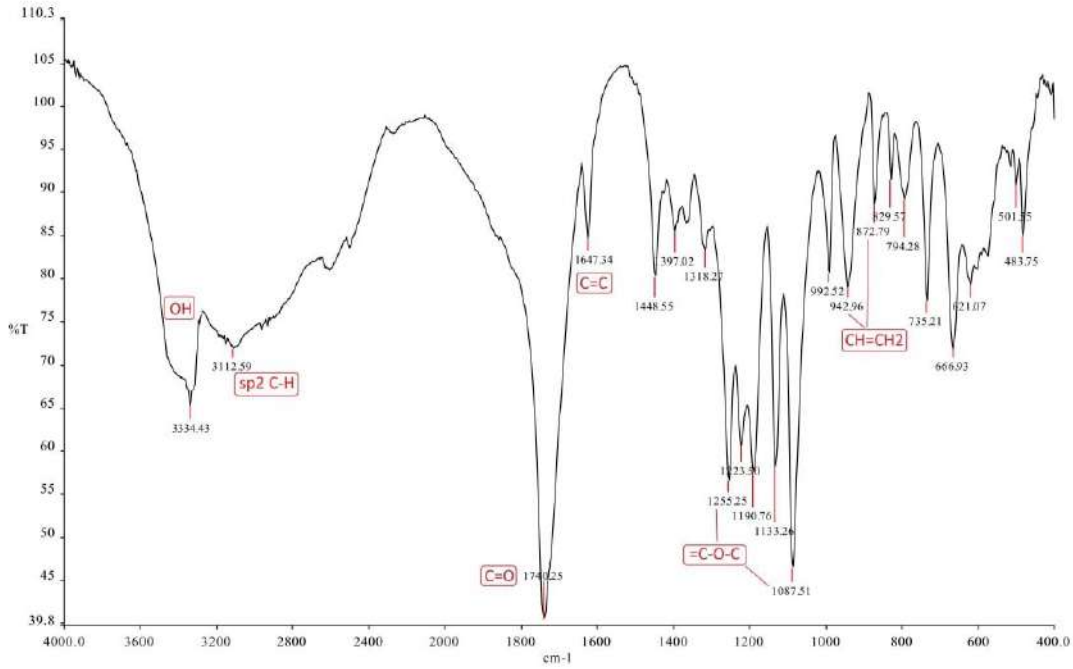


Figure 9. Wine acid monovinyl ether IR spectrum

In the IR-spectrum of monovinyl ester of tartaric acid (Fig. 9), absorption lines typical of the C=O group were observed in the region of 1740.25 cm^{-1}. In the area of 1255.25 cm^{-1}, the valence vibrations characteristic of the C-O-C group appeared, in the

area of 1243.67 cm^{-1} the valence vibration of the C-OH group, in the area of 942.96 cm^{-1} the deformation vibration characteristic of the $=CH_2$ group, 1397.02 cm^{-1} area shows valence vibrations specific to the =CH group, -OH group in the 3334.43 cm^{-1} area, and vinyl group ($-CH = CH_2$) in the 1647.34 cm^{-1} area.

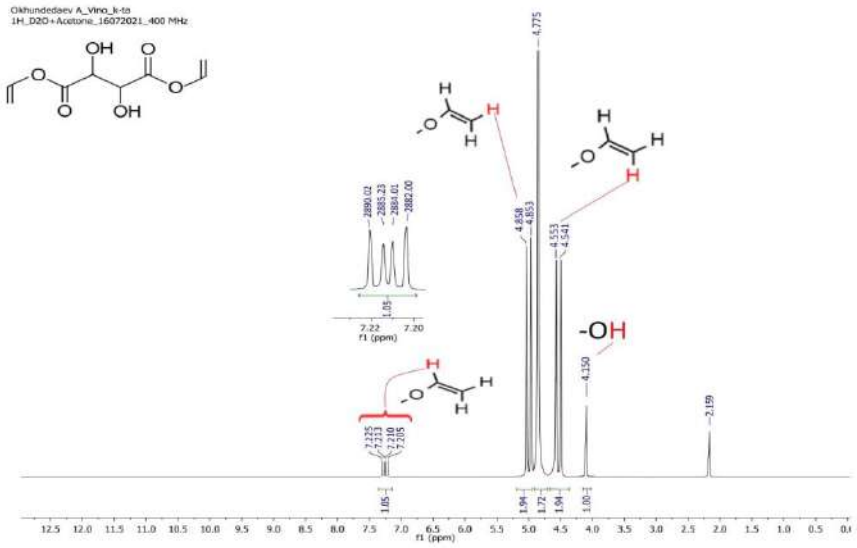


Figure 9. Tartaric acid divinyl ether ^{1}H-NMR spectrum

^{1}H-NMR spectrum of tartaric acid divinyl ester (Fig.9), the doubletdoublet signal of two protons (CH_2 =) in the vinyl group (CH_2=CH-) is 4.54 – 4.85 m.u. areas,and the quartet signal of one proton atom (=CH) was observed in the 7.20-7.22 area. Triplet signals of proton atoms in divinyl ether containing methylene groups (CH_2) are 2.16 m.u. observed in the fields.

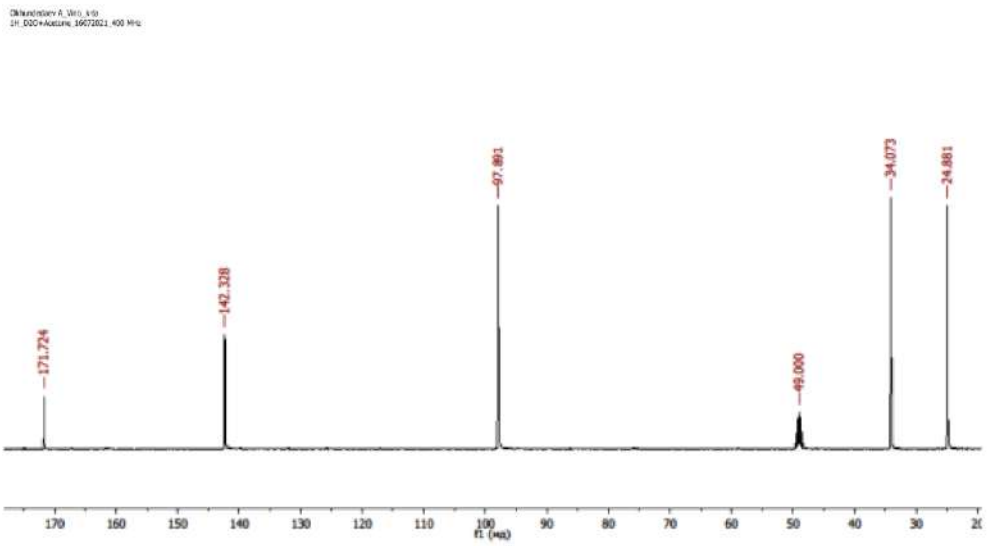


Figure 10. Tartaric acid divinyl ether ^{13}C - NMR spectrum

^{13}C-spectrum of tartaric acid divinyl ester (Fig.10), the signal of carbon atoms in the vinyl group (CH_2 = CH-) is 97.89 and 142.32 m.u. was seen at.

The resulting preparations are named as follows:

1. WA MVE - wine acid monovinyl ether.
2. WA DVE - wine acid divinyl ether.

Experimental trials were conducted in the "Krasnodar" winter wheat field in order to determine the effect of new drugs against yellow rust. The test plots were treated with a motor sprayer with a 0.005% working solution of the drugs 3 times (25.03, 03.04 and 10.04) during the spinning and spinning phases of wheat [10].

The first experimental tests were carried out at the initial appearance of the disease and 7-10 days before the onset of high temperature, during the transition of fungi to the conservation stage (teliostadia). The extent of plant damage was assessed by the scale of Peterson et al., as well as the guidelines for registration tests of fungicides in agriculture [11]. With the aid of Ebot's algorithm, biological efficiency is determined as a percentage.[12,13,14]:

$$A = \frac{K - B}{K} \cdot 100$$

Here: A-biological performance, %;

K - in the controlled region is the ultimate degree of crop harm. (uncultivated area);

B- in the experimental region represents the ultimate degree of crop harm.

The research revealed that the medications (WA MVE and WA DVE) were successful in preventing yellow corrosion. (shown in the table 1).

Table 1. Dynamics of the "Krasnodar" wheat yellow rust disease and the biochemical efficacy of fungicides

№	Experiment options	Repeatability	Damage ratio on the set dates, %						
			25.03	3.04	B.S, %	10.04	B.S, %	17.04	B.S, %
1	WA MVE	3 times	1.0	0.5	84.4	1.5	88.1	0.8	90.2
2	WA DVE		1.0	0.6	80.6	1.8	82.4	1.0	85.6
3	Control (unprocessed)		–	1.0	3.2	–	8.2	–	12.6

Three applications of the drug made it possible to achieve the highest efficiency compared to untreated areas. At the same time, the maximum damage level of the cultivated areas not treated with the drug was higher than 12.6, and when using the drug, the damage level was reduced to 0-0.8 or the disease was eliminated up to 90%.

These new compounds are recommended for extensive research as fungicides against yellow rust (Puccinia striiformis) in cereals.

Conclusion. In addition, chapter describes the use of newly synthesized vinyl ethers as fungicides in agriculture. According to the results of the experiment, it turns out that all the obtained substances had positive effects in the fight against the yellow rust disease. This indicates that the application of this research work to industry and agriculture is promising.

The technology of homogeneous-catalytic synthesis of vinyl esters of malic, citric and tartaric acids was proposed and their effect on agricultural crops was studied. These substances have been found to have a positive effect in the fight against the yellow rust disease of wheat.

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CONTENTS

TECHNICAL SCIENCES: COTTON, TEXTILE AND LIGHT INDUSTRY

TECHNICAL SCIENCES: AGRICULTURE AND FOOD TECHNOLOGIES

CHEMICAL SCIENCES

TECHNICAL SCIENCES: MECHANICS AND MECHANICAL ENGINEERING