— STANDARDIZATION, CERTIFICATION, QUALITY, AND SAFETY —

UDC 663.8:628.19
DOI 10.12737/1563

THE IMPACT OF PRIORITY WATER CONTAMINANTS ON THE STABILITY OF THE MAIN COMPONENTS OF NECTARS

T. A. Krasnova and I. V. Timoshchuk

Kemerovo Institute of Food Science and Technology,
bul'v. Stroitelei 47, Kemerovo, 650056 Russia
phone:/Fax: 8 (3842)-39-00-61, e-mail: ecolog1528@yandex.ru

(Received February 19, 2013; Accepted in revised form August 01, 2013)

Abstract: This paper presents the results of a study on the impact of organic impurities contained in water (phenol, chlorophenol, chloroform, formaldehyde, and acetaldehyde) on the stability of nectar components: sucrose, citric acid, vitamins A and C, and B group vitamins.

A reduction in the concentrations of the main components of nectars and priority contaminants, except for chloroform, has been established.

The mechanism of interaction of sucrose, citric acid, and vitamins contained in nectars with phenol, chlorophenol, chloroform, formaldehyde, and acetaldehyde has been substantiated theoretically.

Key words: nectar, sugar, citric acid, vitamins, water, phenol, chlorophenol, chloroform, formaldehyde, acetaldehyde.

INTRODUCTION

At present, nectars, as opposed to juices, are becoming popular soft drinks with the Russian public in terms of price affordability. Having a variety of flavors, nectars are not only a pleasant way of refreshment and thirst quenching but also a source of vitamins and other essential nutrients. In accordance with GOST R 51398-99 and the AIJN Code of Practice (European Association of the Industry of Juices and Nectars), nectars are defined as drinks obtained by the addition of water and sugar to fruit juice, concentrated fruit juice, or puree from edible parts of fresh fruits. Citric or ascorbic acid may be added. The minimum fruit juice content in nectars should be 25–50%, depending on the type of berries or fruits.

Presently, water from the central water supply system is predominantly used in the production of nectars. The quality of such water determines the consumer appeal of finished soft drinks: flavor, taste, color stability, etc.

Kemerovo oblast forms a large territorial production unit within the Russian Federation. Hence, in addition to natural organic substances, water supply sources contain anthropogenic organic impurities from industrial wastewater. According to the Kemerovo Oblast Sanitary and Epidemiological Center, in 2011, 30.5% of water samples from the Kuzbass central water supply system did not comply with the hygienic standards in terms of sanitary and chemical indices, including 33.9% of water samples from surface water bodies and 29.8% from underground water bodies. The phenol concentration constantly exceeds the MAC values in many Kuzbass surface and underground water bodies. According to the State Environmental Protection Committee for Kemerovo Oblast, random samples taken from the Tom' River during snowmelt show phenol concentrations exceeding 30 MAC [1]. In natural waters, the content of humic substances responsible for the formation of organic halogen compounds is 10–50 mg/dm^3 [2].

Water treatment plants act as barriers against organic substances only to a slight extent; moreover, water treatment yields more dangerous toxic agents than the initial substances. The application of chlorine for decontamination during water treatment results in the formation of such by-products as chlorophenol and chloroform; in the same way, the application of ozone results in the formation of formaldehyde and acetaldehyde [3–5]. As a result of experimental studies, we have found out a two- to five-times exceedance of the MAC values of the above organic impurities in random water samples taken in spring and summer. When concentrations of these contaminants in water exceed the MAC values, they exert toxic, allergenic, mutagenic, and carcinogenic effects on humans [6–9]. In addition to their toxic effect, the organic impurities found in water can interact with the main components of soft drinks, degrading their quality. Thus, studies on the impact of priority organic contaminants periodically present in water on the quality of nectars during their production and storage are relevant and timely.

In this work, we will study the impact of priority organic contaminants periodically present in water (phenol, chlorophenol, chloroform, formaldehyde, and acetaldehyde) on the quality attributes of nectars (the contents of sucrose, citric acid, vitamins A and C, and B group vitamins) during their production and storage.

OBJECTS AND METHODS OF RESEARCH

The objects of research were water solutions containing organic contaminants (chloroform, phenol, chlorophenol, formaldehyde, and acetaldehyde) with added sucrose and citric acid. The sucrose concentration in the test samples was taken at 110 mg/kg according to GOST R 53396-09. The citric acid concentration was taken at 5 mg/l according to the Fruit Juice Regulations. For a reliable assessment of the impact of organic impurities on the stability of the nectar components, the concentration of organic contaminants in the systems under investigation was taken at 10 MAC values; sucrose and citric acid water solutions without any harmful impurities were used as reference standards. The sucrose content in the samples was measured using refractometry; the content of citric acid, phenol, formaldehyde, chlorophenol, and acetaldehyde was measured using molecular absorption spectroscopy; and the chloroform content was measured using gas–liquid partition chromatography.

Given the volatility of some organic contaminants and the duration of the study of nectar components stability after selection of the next sample for the analysis, the source samples were stored in sealed vessels in a dark place.

The objects of research also included nectars (apple, blackcurrant, raspberry, sea-buckthorn, and chokeberry) made with water without organic impurities and with water containing phenol, chlorophenol, chloroform, formaldehyde, and acetaldehyde. Changes in the color intensity of nectars during their production and storage were studied using molecular absorption spectroscopy; the vitamin content was measured using capillary electrophoresis [10, 11].

Changes in all indicators were observed until reaching a constant concentration of the test components in drinks and solutions.

RESULTS AND DISCUSSION

Sucrose ($C_{12}H_{22}O_{11}$) is one of the main components of nectars. Considering chemical properties of sucrose and the organic contaminants under investigation, there is a probability that their chemical interaction will occur.

It has been established that all organic contaminants except for chloroform interact with sucrose, as follows from the chemical equations (Fig. 1). The reaction of sucrose and formaldehyde was the most active, while the reaction of sucrose and chlorophenol was the least active (Table 1).

Table 1. Variation in the sucrose content in the samples under investigation during storage, %

Number of days of storage	Water solution without organic impurities	Water solution containing chloroform	Water solution containing phenol	Water solution containing chlorophenol	Water solution containing formaldehyde	Water solution containing acetaldehyde
1	100	100	100	100	100	100
3	100	100	85	90	61	85
6	100	100	82	85	55	74
8	100	100	71	83	40	63
14	100	100	66	70	35	56
20	100	100	65	68	30	56

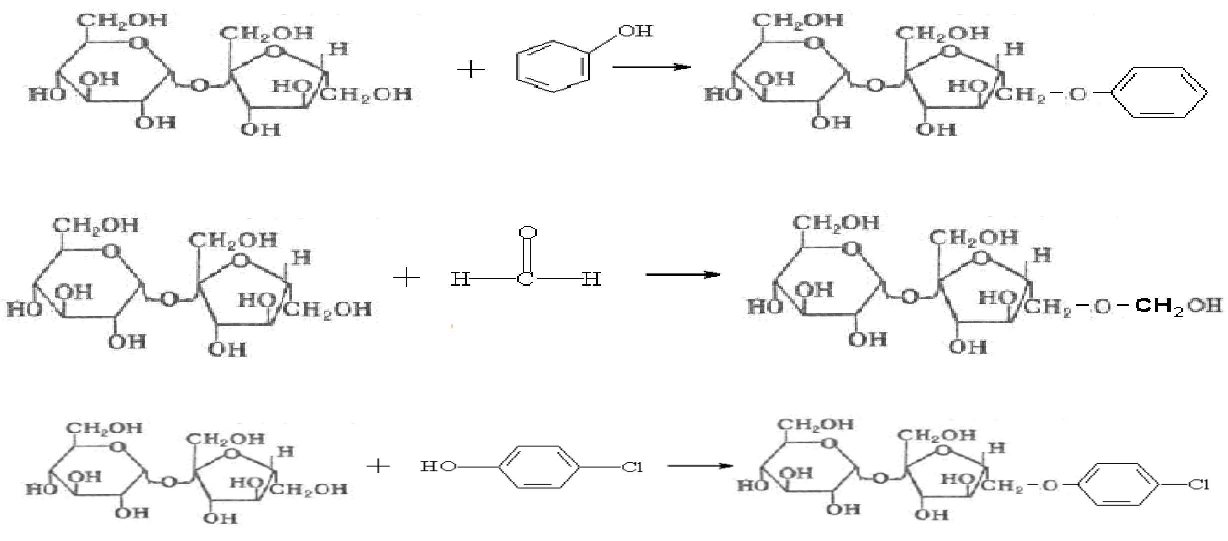


Fig. 1. Chemical reaction of contaminants and sucrose.

The chemical reaction of organic impurities and sucrose is verified empirically by the respective reduction of phenol, chlorophenol, formaldehyde, and acetaldehyde in the presence of sucrose (Fig. 2).

Citric acid ($C_6H_8O_7 \cdot H_2O$) is often used as an acidity regulator in the production of nectars since it has a milder flavor compared to other edible acids and does not irritate the mucosae of the gastrointestinal tract.

There is a probability of interaction between citric acid and organic components. During the interaction, the content of citric acid may decrease, whereas its overconsumption may grow. Since citric acid is an expensive component, its wastage is undesirable. Therefore, it is appropriate to study the impact of organic impurities (phenol, chlorophenol, chloroform, formaldehyde, and acetaldehyde) on the stability of citric acid in the water used for nectar production.

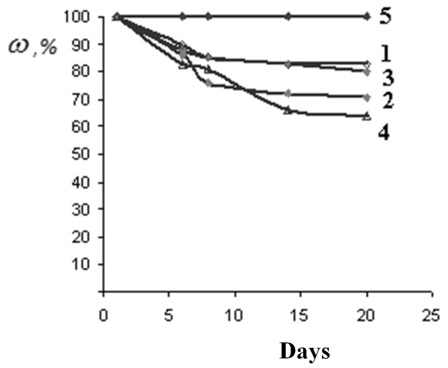


Fig. 2. Variations in (1) acetaldehyde, (2) phenol, (3) formaldehyde, (4) chlorophenol, and (5) chloroform contents in water containing sucrose over time.

The experimental data suggest that the citric acid content decreases in the presence of all of the organic contaminants except for chloroform (Table 2).

Table 2. Variation in the citric acid content in the samples under investigation during storage, %

Number of storage days	Water solution without organic impurities	Water solution containing chloroform	Water solution containing phenol	Water solution containing chlorophenol	Water solution containing formaldehyde	Water solution containing acetaldehyde
1	100	100	100	100	100	100
6	100	100	81	100	90	98
8	100	100	75	100	76	95
12	100	100	63	93	60	87
18	100	100	53	83	54	83
20	100	100	53	63	53	70

Chemical reactions between citric acid and priority water contaminants are given in Fig. 3.

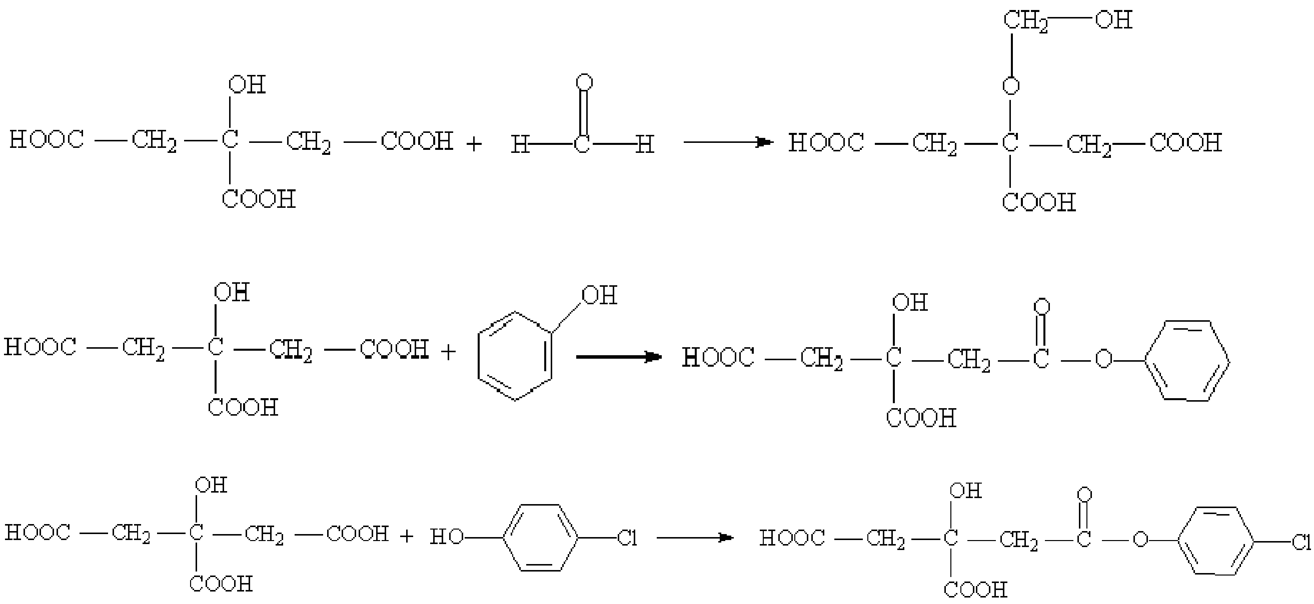


Fig. 3. Chemical reaction between the contaminants and citric acid.

The chemical reaction of organic impurities and citric acid is verified empirically by the respective reduction of phenol, chlorophenol, formaldehyde, and acetaldehyde in water containing citric acid over time, as is shown in Fig. 4.

Berries and fruits used in nectars contain substances that determine their color. The colors of all berries and fruits are largely determined by coloring substances, such as flavonoids (anthocyanins) and carotenoids. Flavonoids produce red, blue, and purple pigmentation in fruits, while carotenoids produce yellow-to-orange colors. The content of the components that provide fruits and berries with colors is given in Table 3. It appeared appropriate to study the impact of organic contaminants on the color stability of nectars.

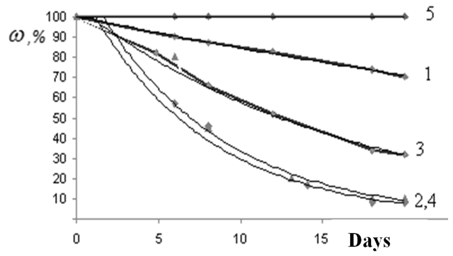


Fig. 4. Variations in (1) acetaldehyde, (2) phenol, (3) formaldehyde, (4) chlorophenol, and (5) chloroform contents in water containing citric acid over time.

Berries and fruits used in nectars contain substances that determine their color. The colors of all berries and fruits are largely determined by coloring substances, such as flavonoids (anthocyanins) and carotenoids. Flavonoids produce red, blue, and purple pigmentation in fruits, while carotenoids produce yellow-to-orange colors. The content of the components that provide fruits and berries with colors is given in Table 3. It appeared appropriate to study the impact of organic contaminants on the color stability of nectars.

Table 3. Content of components providing berries and fruits with color, mg/100 g

Substance	Flavonoids (anthocyanins, catechines, leucoanthocyanins), mg	Carotene (provitamin A), mg
Sea-buckthorn	800—1.000	11
Chokeberry	250–600	0.5
Raspberry	600—1.300	1
Apple	300–600	1.1–15

No variation in the color intensity in nectars produced from all sorts of berries in the presence of chloroform was detected during the entire research period (Figs. 5–8).

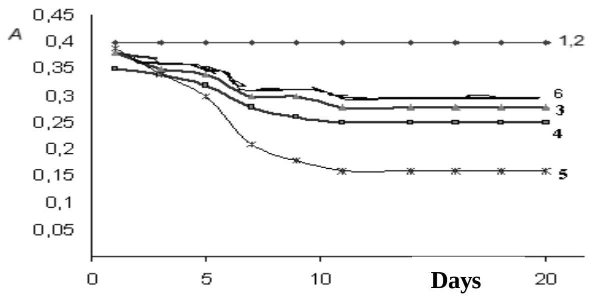


Fig. 5. Variations in the color of apple nectar over time made with (1) water without organic impurities and with water solutions containing (2) chloroform, (3) formaldehyde, (4) phenol, (5) chlorophenol, and (6) acetaldehyde.

The least color fading occurs in raspberry nectar in the presence of chlorophenol and in apple, chokeberry, and sea-buckthorn nectars in the presence of acetaldehyde; the most color fading occurs in raspberry nectar in the presence of formaldehyde; in sea-buckthorn and chokeberry nectars in the presence of phenol; and in apple nectar in the presence chlorophenol.

It is obvious that chemical properties of the coloring substances and organic contaminants predetermined the possibility of their interaction, as is shown by the example of carotenoids (Fig. 9).

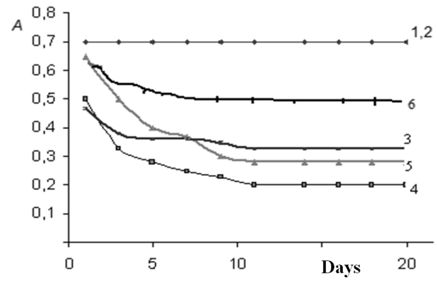


Fig. 6. Variations in the color of chokeberry nectar made with (1) water without organic impurities and with water solutions containing (2) chloroform, (3) formaldehyde, (4) phenol, (5) chlorophenol, and (6) acetaldehyde.

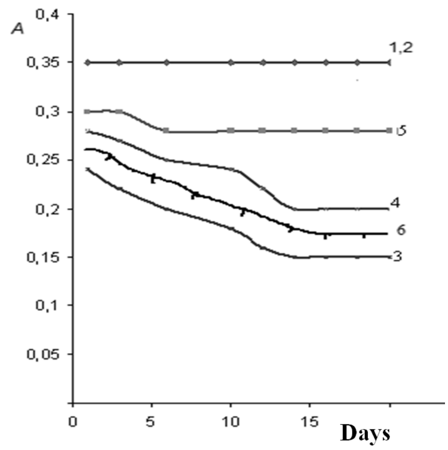


Fig. 7. Variations in the color of raspberry nectar made with (1) water without organic impurities and with water solutions containing (2) chloroform, (3) formaldehyde, (4) phenol, (5) chlorophenol, and (6) acetaldehyde.

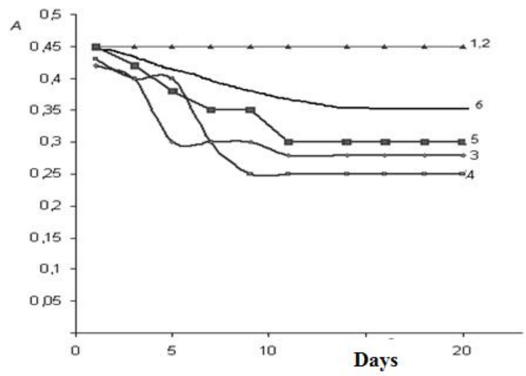


Fig. 8. Variations in the color of sea-buckthorn nectar made with (1) water without organic impurities and with water solutions containing (2) chloroform, (3) formaldehyde, (4) phenol, (5) chlorophenol, and (6) acetaldehyde.

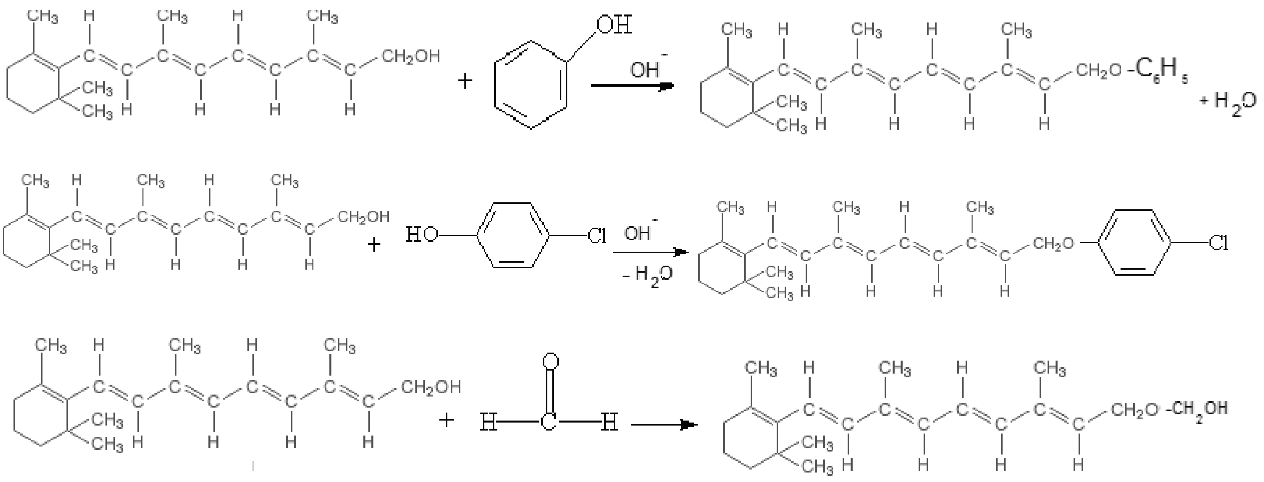


Fig. 9. Chemical reaction of carotenoids and priority contaminants contained in water.

Vitamins contained in nectars are organic compounds of different chemical nature, which can lead to their interaction with organic impurities contained in water. The content of individual vitamins in the nectar samples under investigation is shown in Table 4.

Table 4. Vitamin content in the nectar samples under investigation, mg/100 g

Vitamins, mg/100 g	Apple	Black-currant	Rasp-berry	Choke-berry	Sea-buckthorn
C	33.2	26.6	21.5	22.1	54.7
B_3	0.03	0.02	0.009	0.055	0.06
B_6	-	0.04	-	-	0.065
B_9	-	-	0.037	0.062	-
B_5	-	-	0.009	0.023	-
B_2	0.03	-	-	0.0021	-
B_1	-	-	-	0.05	0.05

Over the research period, the vitamin B_2 reduction in apple nectar was 80% in the presence of formaldehyde in water, 75% in the presence of chlorophenol, 65% in the presence of acetaldehyde, and 60% in the presence of phenol . The vitamin B_3 reduction was 40% in the presence of phenol, 47% in the presence of formaldehyde, 33% in the presence of chlorophenol, and 27% in the presence of acetaldehyde. The vitamin C reduction was 50% in the presence of phenol, 44% in the presence of formaldehyde, 35% in the presence of chlorophenol,; and 25% in the presence of acetaldehyde (Fig. 10).

In blackcurrant nectar, vitamin B_3 was reduced by 45% in the presence of acetaldehyde in water, by 40% in the presence of phenol, by 30% in the presence of chlorophenol, and by 25% in the presence of formaldehyde. Vitamin B_6 was decomposed almost by 100% due to its small initial concentration in the presence of phenol and acetaldehyde, by 95% in the presence of formaldehyde, ; and by 90 % in the presence of chlorophenol. Vitamin C was reduced by 38% in the presence of chlorophenol, by 30% in the presence of phenol, by 25% in the presence of formaldehyde, and by 20% in the presence of acetaldehyde (Fig. 11).

In raspberry nectar, vitamin B_3 was reduced by 40% in the presence of acetaldehyde in water, by 30% in the presence of formaldehyde and phenol, and by 20% in the presence of chlorophenol, . Vitamin C was reduced by 40% in the presence of chlorophenol, by 35% in the presence of phenol, by 30% in the presence of formaldehyde, and by 25% in the presence of acetaldehyde. Vitamin B_5 was reduced by 40% in the presence of phenol, by 35% in the presence of acetaldehyde, and by 35% in the presence of formaldehyde and chlorophenol. Vitamin B_9 in the presence of all water contaminants was reduced by 20–28% (Fig. 12).

In chokeberry nectar, the vitamin B_3 content was reduced by 35% in the presence of phenol and formaldehyde, by 40% in the presence of phenol, by 55% in the presence of chlorophenol, and by 65% in the presence of acetaldehyde. Vitamin B_9 was decomposed by 40% in the presence of phenol, by 50% in the presence of formaldehyde, and by 60% in the presence of chlorophenol and acetaldehyde. Vitamin B_5 was reduced by 25% in the presence of acetaldehyde, by 58% in the presence of formaldehyde, by 70% in the presence of phenol, and by 80% in the presence of chlorophenol (Fig. 13).

In sea-buckthorn nectar, vitamin B_1 was reduced by 60% in the presence of formaldehyde in water, by 45% in the presence of phenol, by 40% in the presence of acetaldehyde, and by 35% in the presence of chlorophenol. Vitamin B_3 was reduced by 95% in the presence of chlorophenol, by 90% in the presence of formaldehyde, by 87% in the presence of acetaldehyde, and by 50% in the presence of phenol. Vitamin C was reduced by 60% in the presence of acetaldehyde, by 55% in the presence of formaldehyde, by 44% in the presence of chlorophenol, and by 34% in the presence of phenol (Fig. 14).

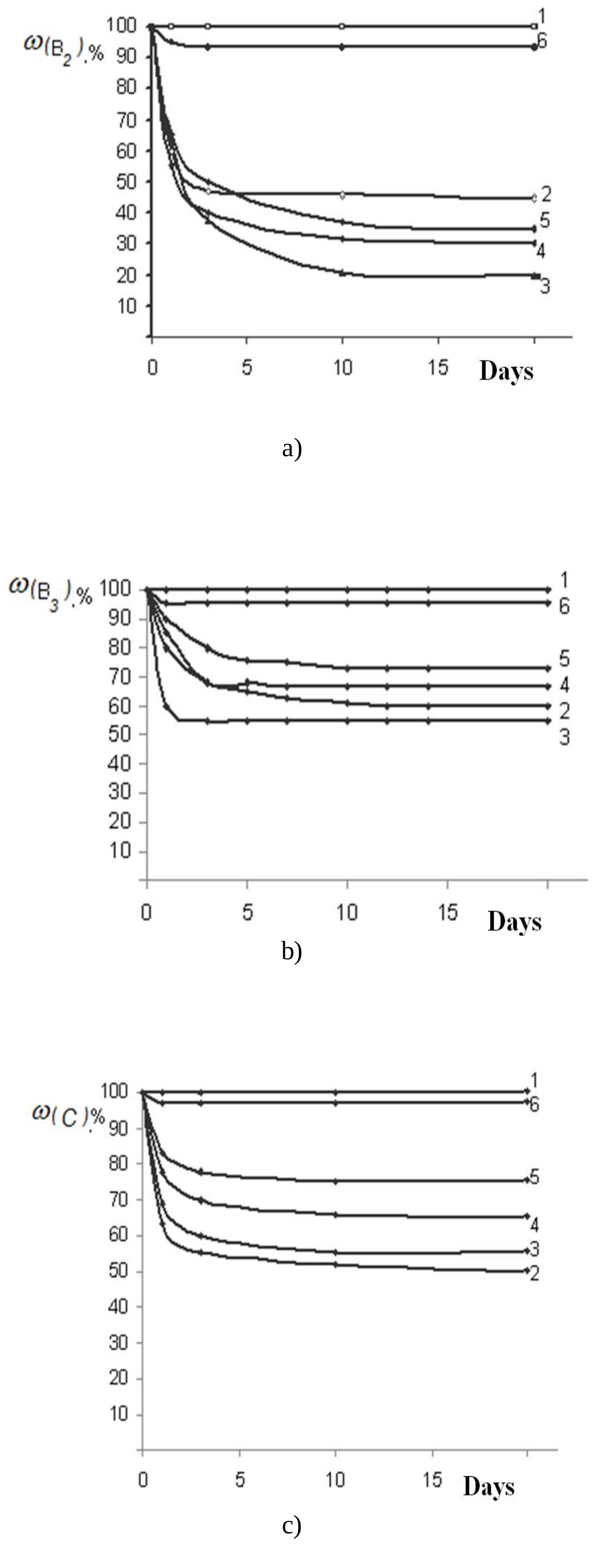


Fig. 10. Vitamins B_2, B_3, and C contents in apple nectar made with (1) water without organic impurities and with water solutions containing (2) phenol, (3) formaldehyde, (4) chlorophenol, (5) acetaldehyde, and (6) chloroform.

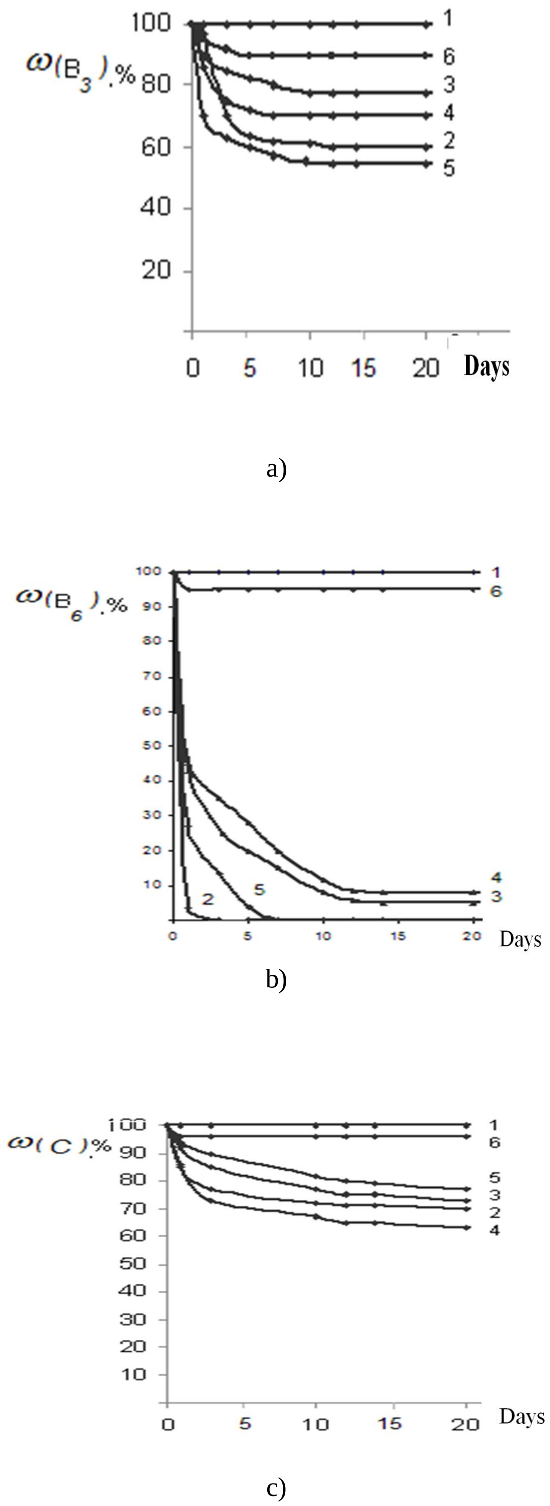


Fig. 11. Vitamins B_3, B_6, and C content in blackcurrant nectar made with (1) water without organic impurities and with water solutions containing (2) phenol, (3) formaldehyde, (4) chlorophenol, (5) acetaldehyde, and (6) chloroform.

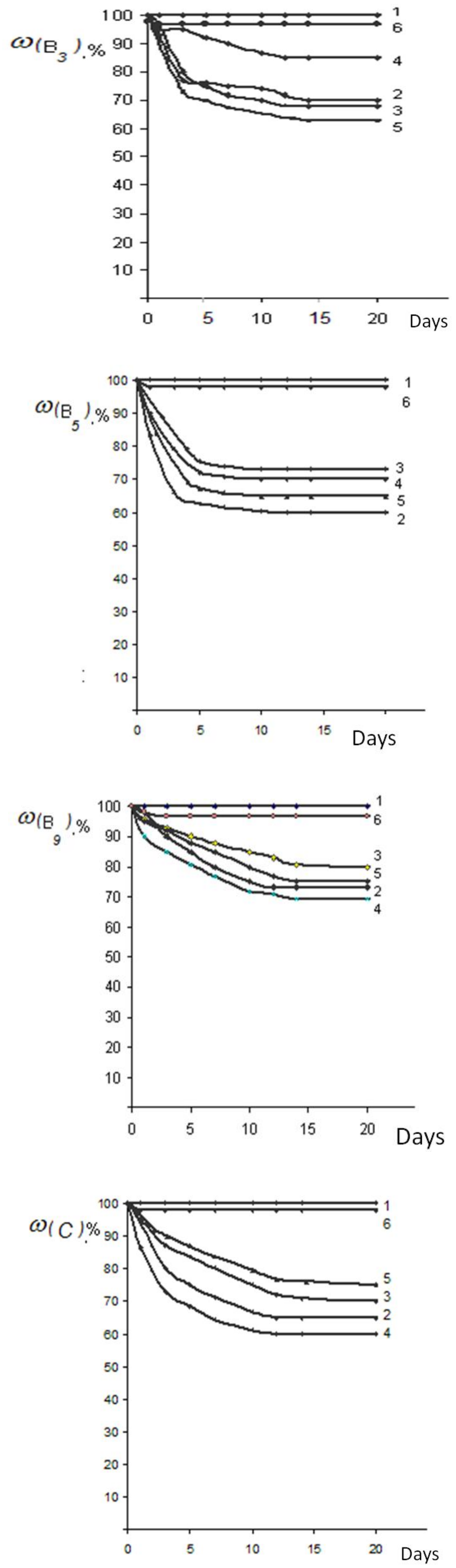


Fig. 12. Vitamins B_3, B_5, B_9, and C content in raspberry nectar made with (1) water without organic impurities and with water solutions containing (2) phenol, (3) formaldehyde, (4) chlorophenol, (5) acetaldehyde, and (6) chloroform.

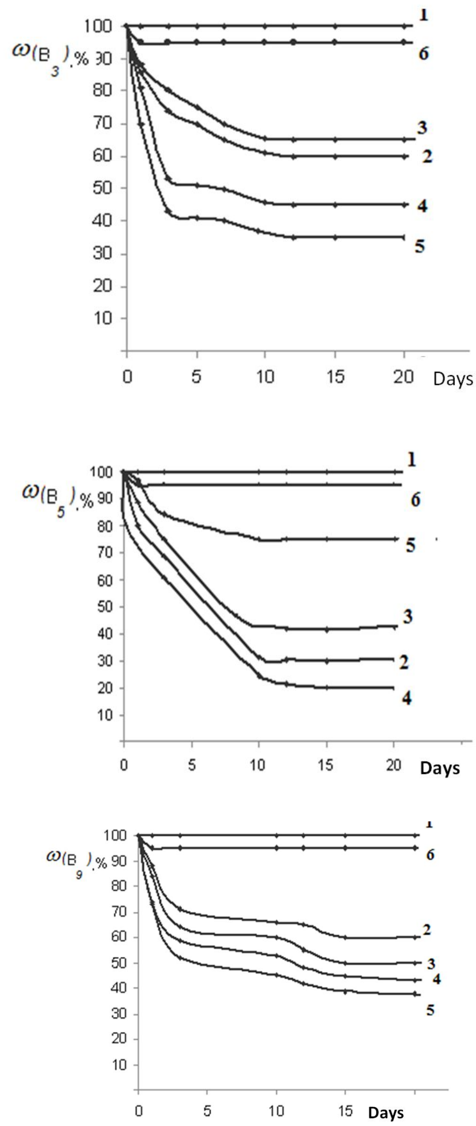
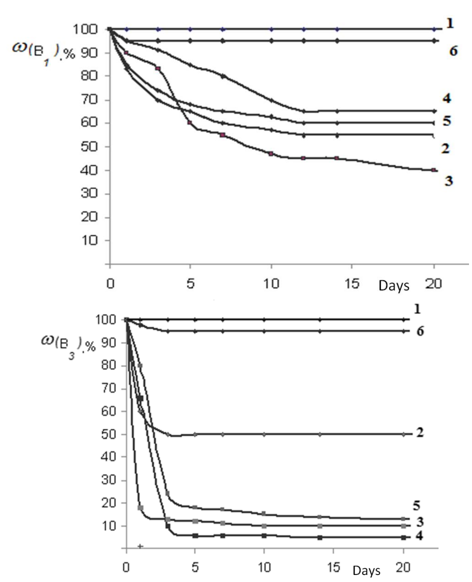


Fig. 13. Vitamins B_3, B_5, B_9 contents in chokeberry nectar made with (1) water without organic impurities and with water solutions containing (2) phenol, (3) formaldehyde, (4) chlorophenol, (5) acetaldehyde, and (6) chloroform.



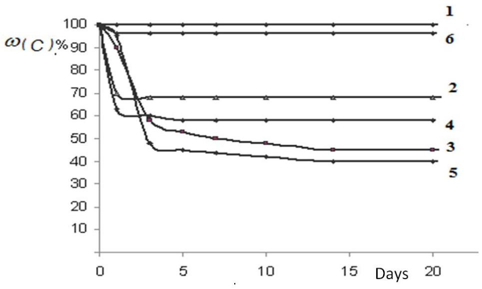


Fig. 14. Vitamins B_1, B_3, C content in sea-buckthorn nectar made with (1) water without organic impurities and with water solutions containing (2) phenol, (3) formaldehyde, (4) chlorophenol, (5) acetaldehyde, and (6) chloroform.

Variation in the vitamin content in nectars in the presence of chloroform was not shown over the entire period of research. The chemical reaction of priority contaminants (phenol, formaldehyde, acetaldehyde, and chlorophenol) contained in the water used for the production of nectars and vitamins is verified by the following chemical equations (Figs. 15–21):

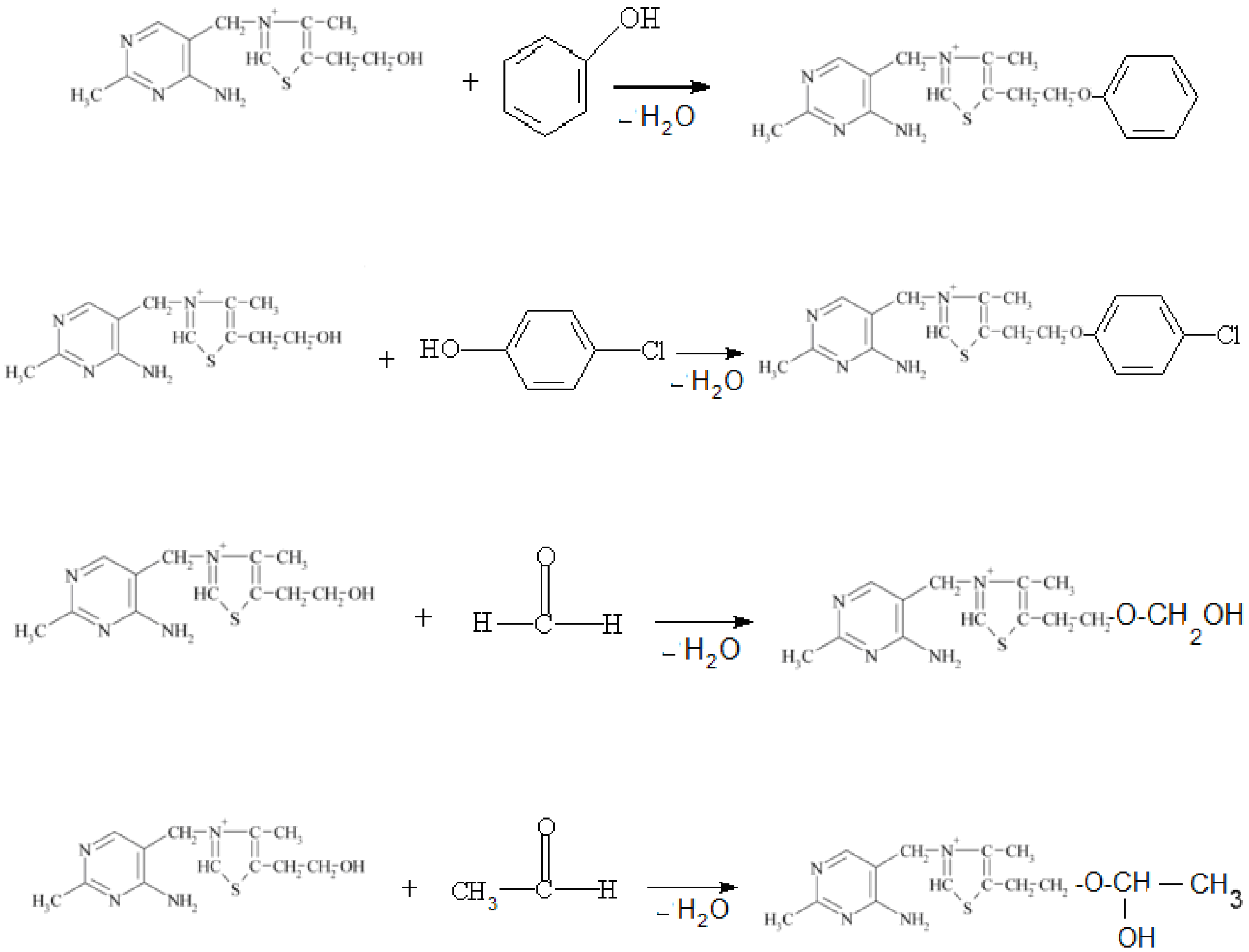
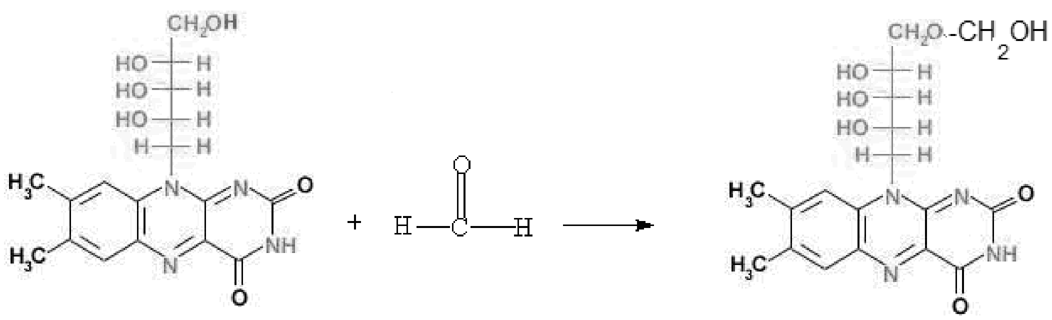


Fig. 15. Chemical reaction of vitamin B_1 and priority contaminants contained in water.



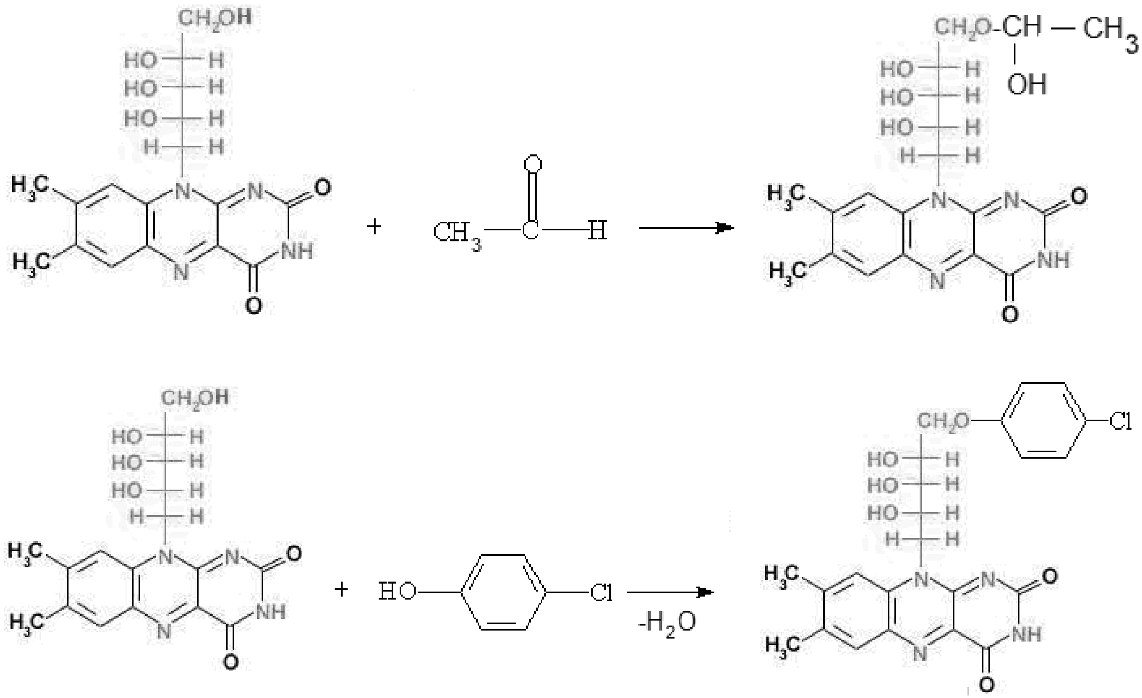


Fig. 16. Chemical reaction of vitamin B_2 and priority contaminants contained in water.

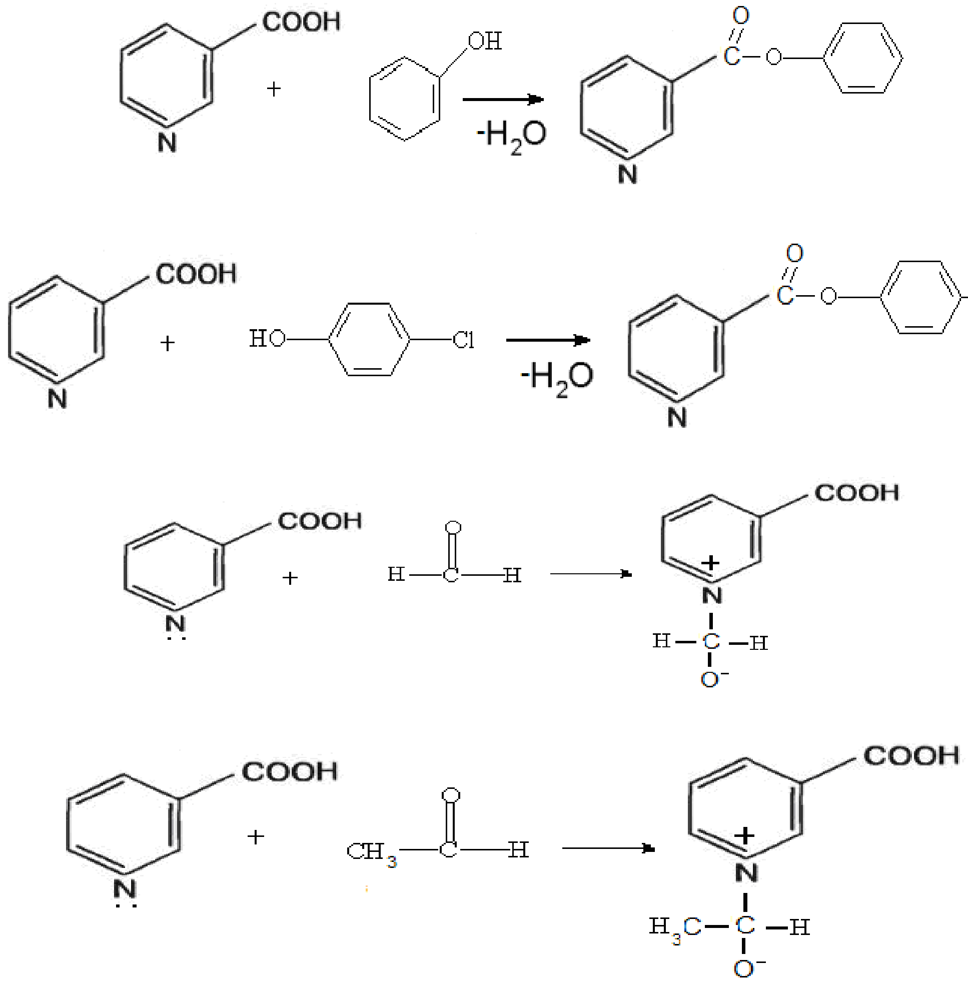


Fig. 17. Chemical reaction of vitamin B_3 and priority contaminants contained in water.

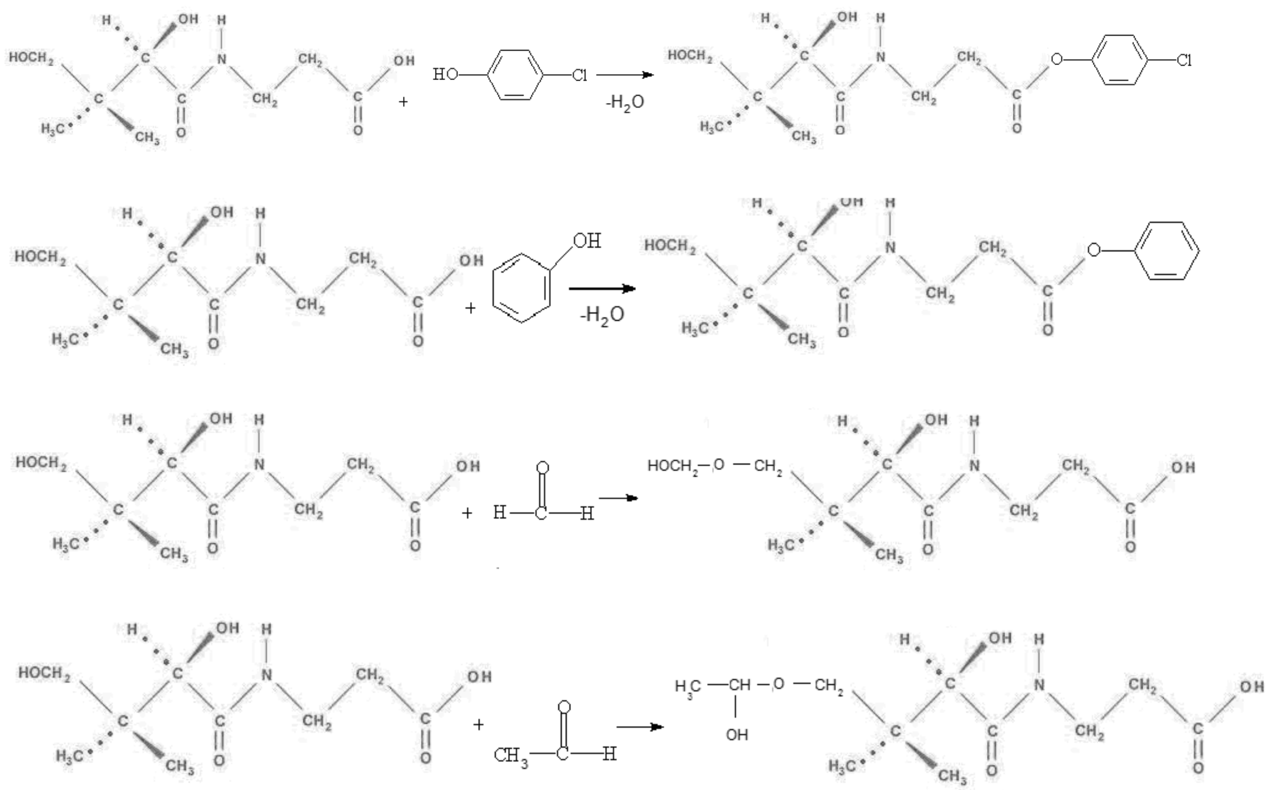
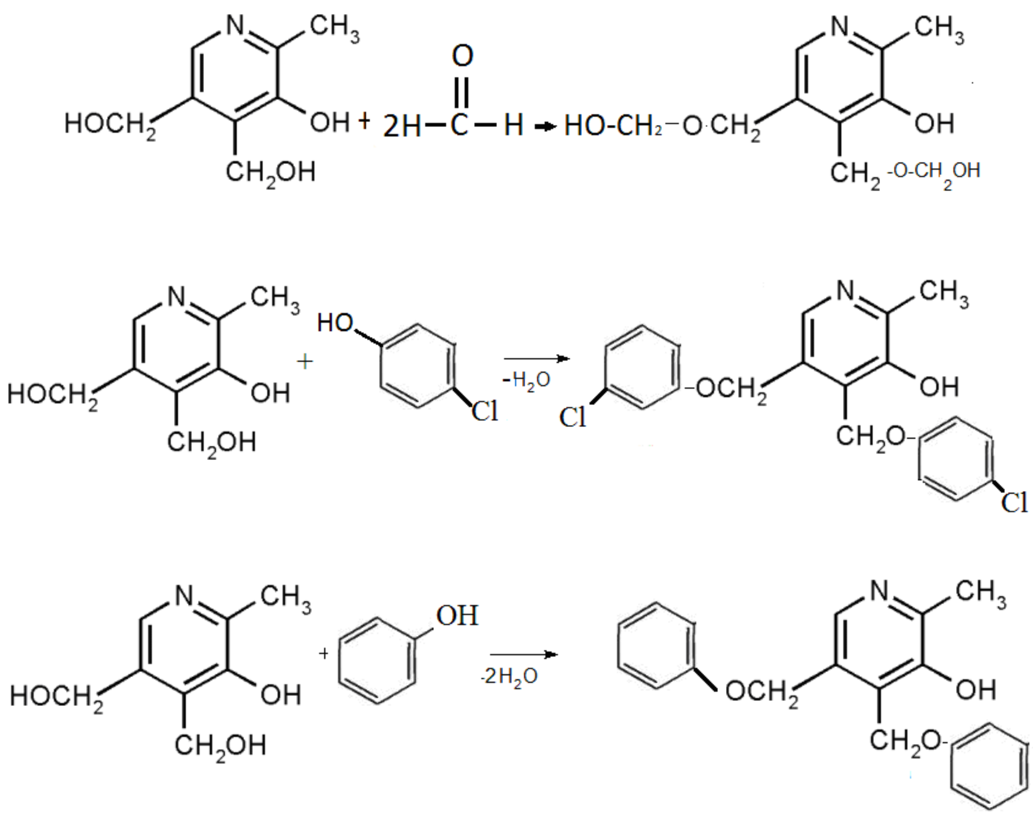


Fig. 18. Chemical reaction of vitamin B_5 and priority contaminants contained in water.



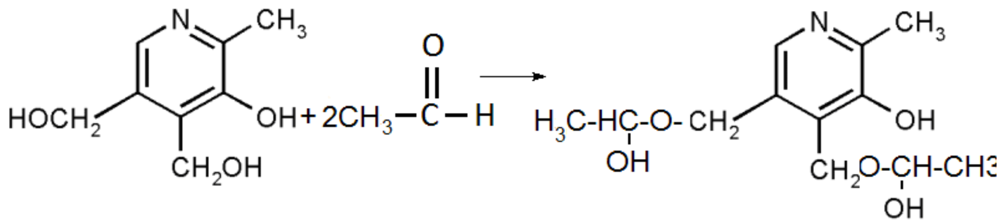


Fig. 19. Chemical reaction of vitamin B_6 and priority contaminants contained in water.

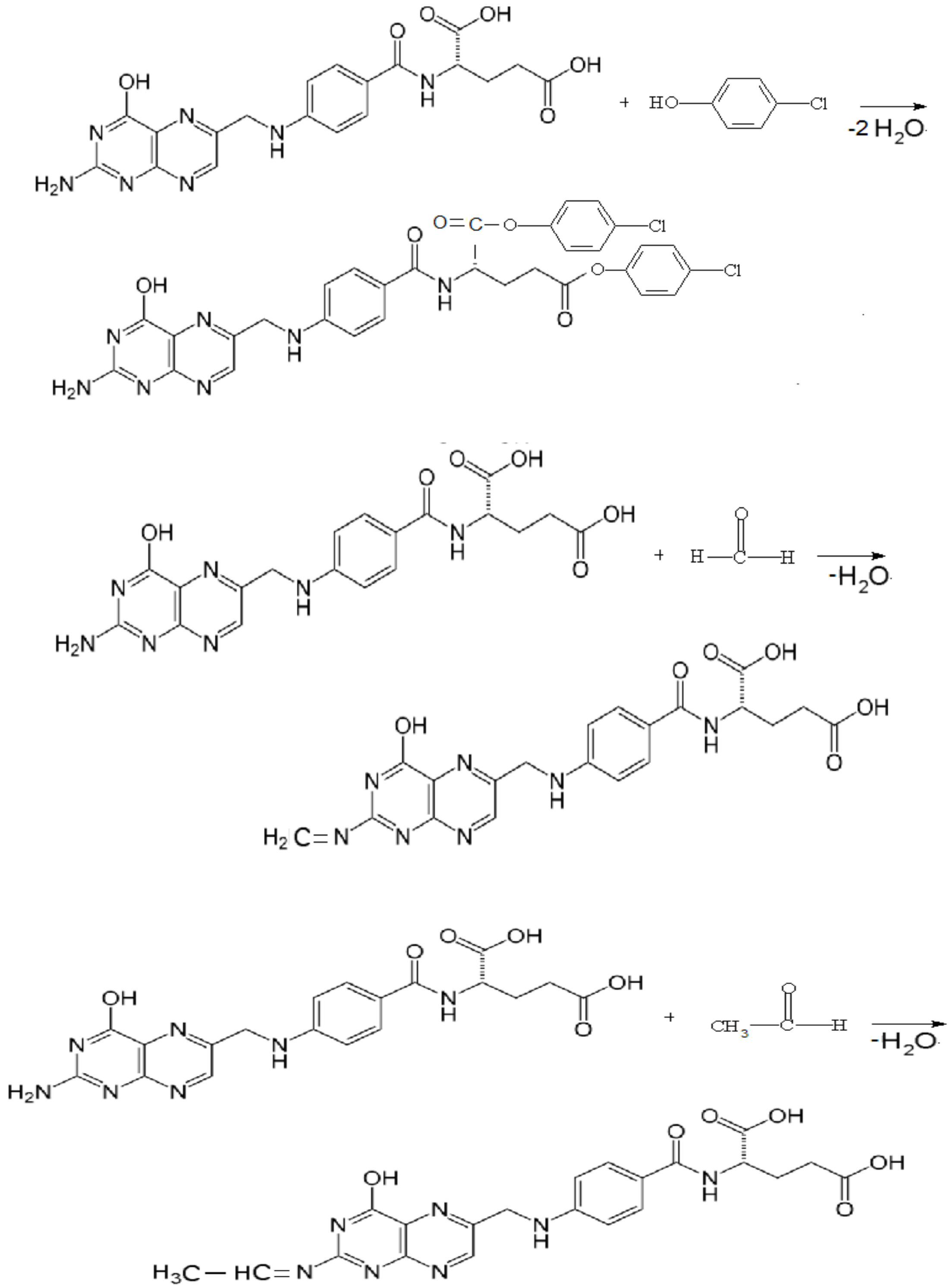


Fig. 20. Chemical reaction of vitamin B_9 and priority contaminants contained in water.

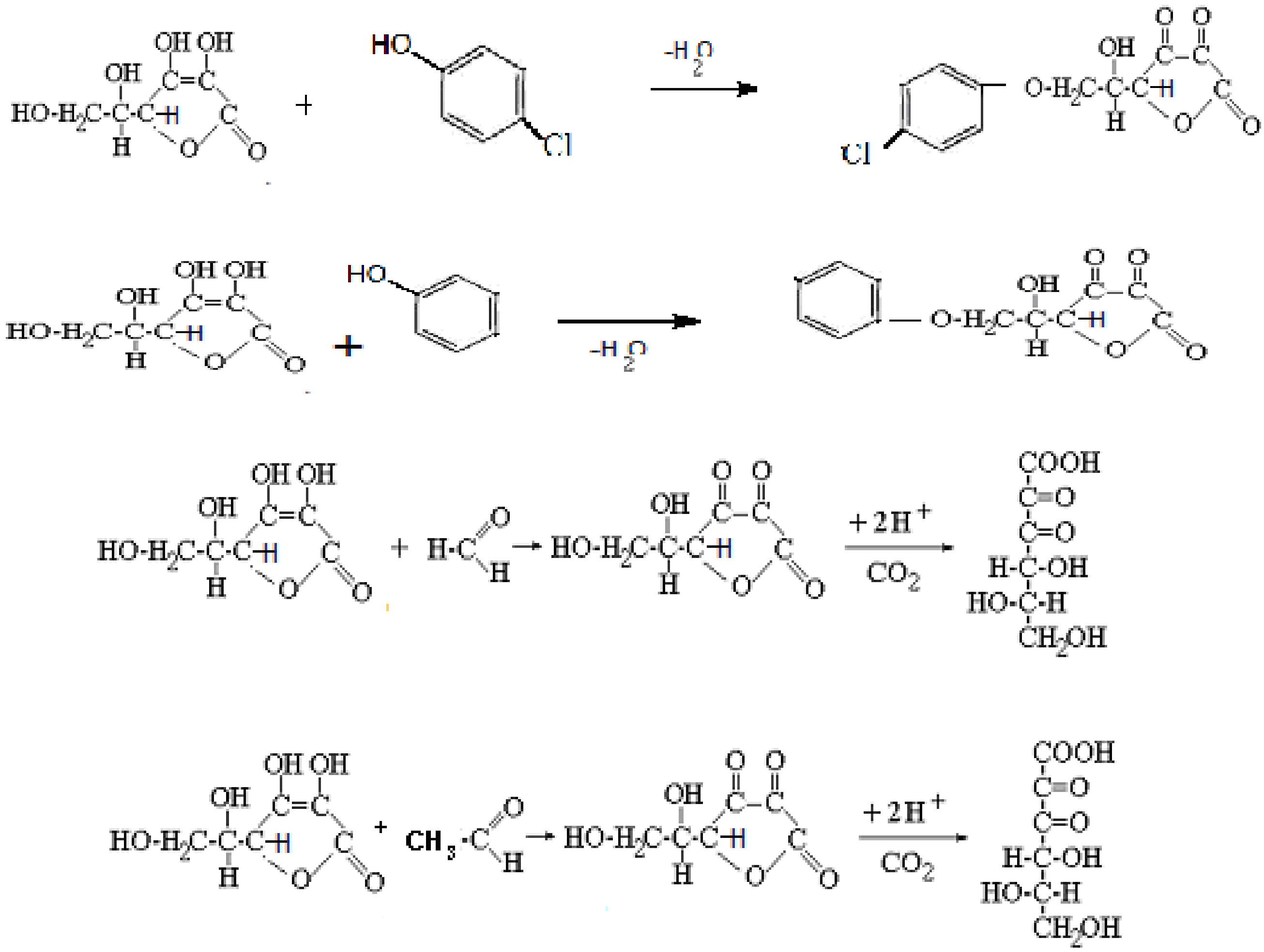


Fig. 21. Chemical reaction of vitamin C and priority contaminants contained in water.

The study of the changes in the organic contaminant concentrations has shown that a relation can be traced between the reduction of the vitamin concentrations and their molecular weights and the molecular weights of the priority water contaminants.

The research results show that formaldehyde, acetaldehyde, chlorophenol, and phenol have a considerable impact on the color stability and preservation of nectar components, such as sugar, citric acid, ascorbic acid (vitamin C), provitamin A (carotene), and B group vitamins by interacting with them and degrading the quality attributes of nectars. Therefore, the water used in nectar production must undergo additional decontamination to remove organic impurities using, for instance, adsorption on activate carbon.

REFERENCES

1. Materialy k gosudarstvennomu dokladu "O sostoyanii I okhrane okruzhayushchei sredy Kemerovskoi oblasti v 2011" (Materials to the State Report “On Environmental Condition and Protection in Kemerovo Region in 2011). http://gosdoklad.kuzbasseco.ru/2011/

2. Nikoladze, G.I., *Podgotovka vody dlya pit'evogo i promyshlennogo vodosnabzheniya* (Water Treatment for Potable and Industrial Water Supply), Moscow: Vysshaya Shkola, 1984.

3. Slavinskaya, G.V., Vliyanie khlorirovaniya na kachestvo pit'evoi vody (Impact of water chlorination on the quality of drinking water), *Khimiya i tekhnologiya vody (Water chemistry and technology)*, 1991, vol. 12, no. 11, pp. 1013–1022.

4. Sato, T., Yamamori, H., and Matsuda, H., Estimation of safety of ozonation and chlorination of a water purification plant, *Water Science and Technology*, 1992, vol. 26, no. 9, pp. 2385–2388.

5. Warming to ozone, *Water and Waste Treatment*, 1992, no. 4, pp. 12–16.

6. Neale, P., Antony, A., and Bartkow, M., Bioanalytical assessment of the formation of disinfection byproducts in a drinking water treatment plant. *Environmental Science and Technol*ogy, 2012, vol. 46, no. 18, pp. 10317–10325.

7. Itoh, S., Gordon, B., and Callan, P., Regulations and perspectives on disinfection by-products: importance of estimating overall toxicity, *Journal of Water Supply: Research and Technology–Aqua*, 2011, vol. 60, no. 5, pp. 261–274.

8. Jeong, C., Wagner, E., and Siebert, V., Occurrence and toxicity of disinfection byproducts in European drinking water in relation with the HIWATE epidemiology study, *Environmental Science and Technology*, 2012, vol. 46, no. 21, pp. 12120–12128.

9. Grushko, Y.M., *Vrednye organicheskie soedineniya v promyshlennykh stochnykh vodakh: Spravochnik* (Harmful organic compounds in industrial wastewaters: Reference Book), Leningrad: Khimiya, 1982.

10. Zhao, D., Lu, M., and Cai, Z., Separation and determination of vitamins and essential amino acids in health drinks by CE-LIF with simultaneous derivatization, *Electrophoresis*, 2012, vol. 33, pp. 2424–2432.

11. Dziomba, S., Kowalski, P., and Baczek, T., Field-amplified sample stacking-sweeping of vitamins B determination in capillary electrophoresis. *Journal of Chromatography,* 2012, vol. 1267, pp. 224–230.