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D. A. Medvedev, PhD (BSTU); **O. I. Lazovskaya**, engineer (BSTU);
V. N. Leontiev, PhD (Chemistry), assistant professor (BSTU)

CHEMICAL PROCESSES CAUSING SPOILAGE OF OIL AND FAT PRODUCTS

Article is devoted to the problem of spoilage of oil and fat products in the course of their production, transportation and storage which is caused by the hydrolytic and oxidative processes leading to deterioration of organoleptic properties of fat and oil products and decrease in their nutrition value. Chemical basics of hydrolysis of triacylglycerols are considered in detail. The mechanisms of an acid and base catalysis of hydrolysis of acyl bonds are presented. The mechanisms of lipid peroxidation, antioxidant action of ascorbic acid and α-tocopherol are shown. Influence of natural vegetable emulsifiers and antioxidant vitamins on quality of margarine and spreads during storage is shown.

Introduction. The main problem of production, transportation and storage of oils and fats is their spoilage, which is caused by hydrolytic and oxidative processes [1]. These processes deteriorate the organoleptic properties of fat and oil production, decreasing its nutritional and biological value.

Main part. All fats and oils are composed of triacylglycerols and related substances (phospholipids, sterols, tocopherols, free fatty acids and others) [2]. Triacylglycerols of fats mostly contain saturated fatty acids, while triacylglycerols of oils contain unsaturated. Unsaturated acids in oils preferably form ether bonds with hydroxyl groups of C_1 and C_3 atoms, while unsaturated acids in fats of C_2 and C_3 atoms. The degree of unsaturation of fatty acids in fats is less than that in oils.

When the triacylglycerols are decomposed hydrolytically, at first 1,2- and 2,3-diacylglycerols are formed, then monoacylglycerols and eventually fatty acids and glycerol are formed (Fig. 1).

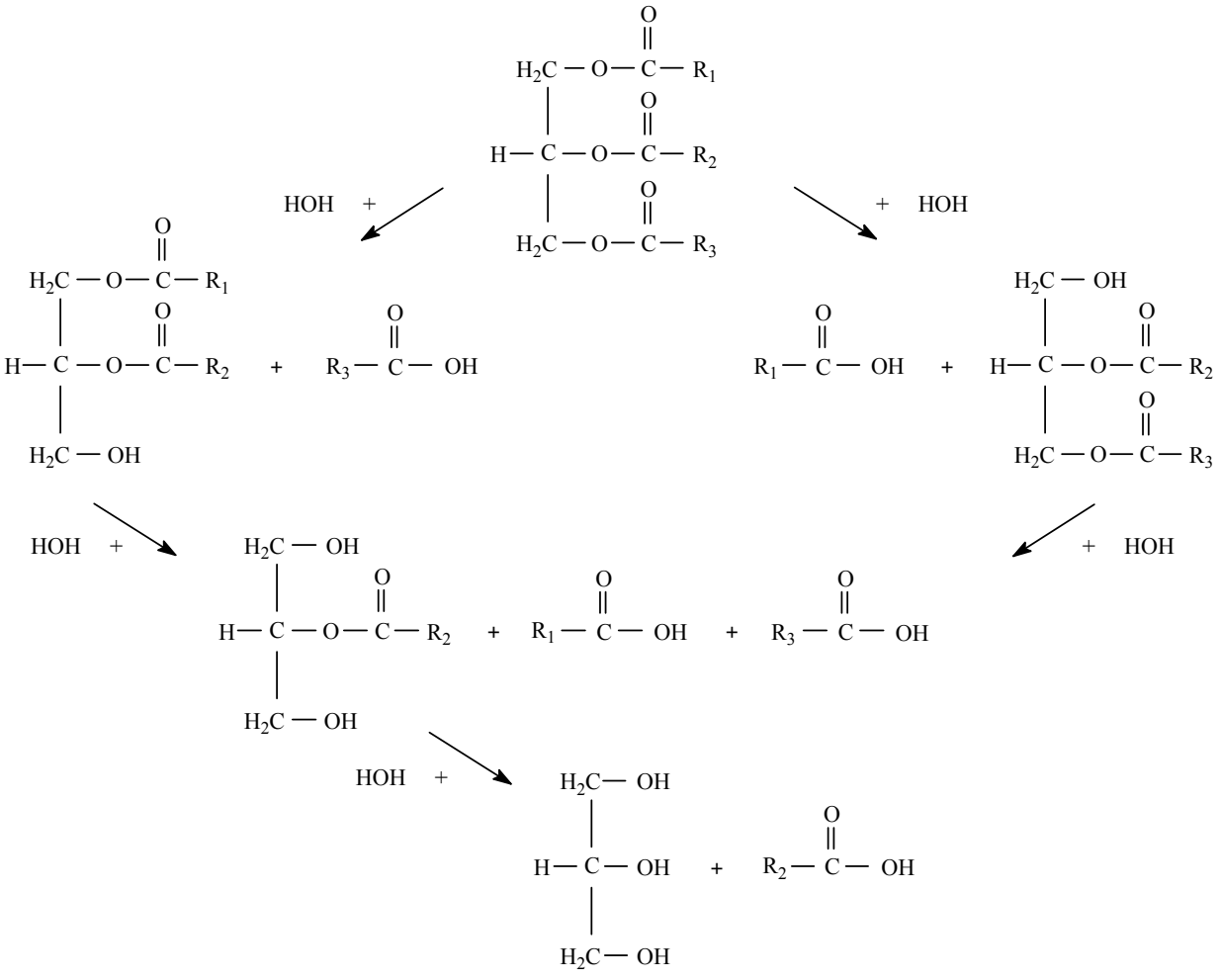

Fig. 1. The hydrolysis of triacylglycerols

Enzymatic hydrolysis of triacylglycerols can occur under the action of plants lipases: the cells of the seeds are destructed in the process of cold-pressed of oil.

However, its impact is negligible, and this type of hydrolysis arises in case of the oil processing technology disruption. The greatest impact to spoilage of oil is made by enzymatic hydrolysis of triacylglycerols under the action of lipases (phospholipases) of microorganisms.

This hydrolysis occurs when the technical regulations and sanitary and hygienic norms of production are disrupted, and also during the transportation and storage of fat and oil products.

Non-enzymatic hydrolysis of triacylglycerols may occur under acidic or basic catalysis, the speed of the process depends on the product temperature and moisture content (humidity). Hydrolysis under the action of bases is called saponification of fats. This hydrolytic cleavage of acyl bonds proceeds as a bimolecular reaction under acidic mechanism $A_{AC}2$ (Fig. 2), and under basic mechanism $B_{AC}2$ (Fig. 3) [3].

Fatty acids formed during the triacylglycerols hydrolysis alter the acidity of the product. Acids with high molecular weight practically do not change the organoleptic properties of fats and oils, and some acids with low molecular weight, such as oileic, pentanoic, hexanoic (caproic) acids, add to fat and oil products unpleasant taste and odour. However, the specific content of these acids with low molecular weight in natural triacylglycerols is low; therefore, to detect the hydrolytic cleavage is possible only through the determination of acid index [4].

Enzymatic oxidation of lipids goes under the action of lipoxygenase of microorganisms with the formation of hydroperoxides.

Non-enzymatic oxidation (autoxidation) of lipids occurs as a radical process, which is initiated by an active forms of oxygen, such as singlet and atomic oxygen, hydroxyl or hydroperoxide radicals, superoxide anion radical (Fig. 4) [5].

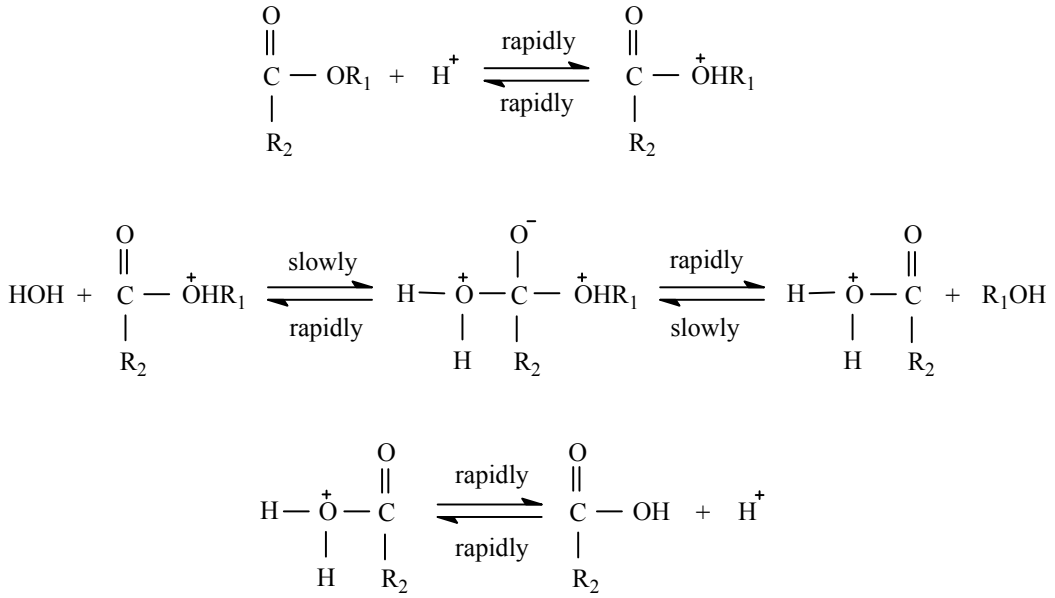

Fig. 2. The mechanism of hydrolysis of ester bonds during acidic catalysis

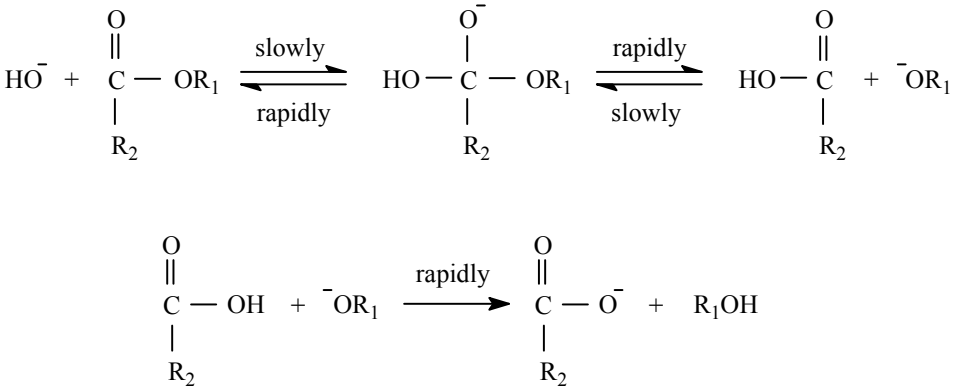

Fig. 3. The mechanism of hydrolysis of ester bonds during basic catalysis

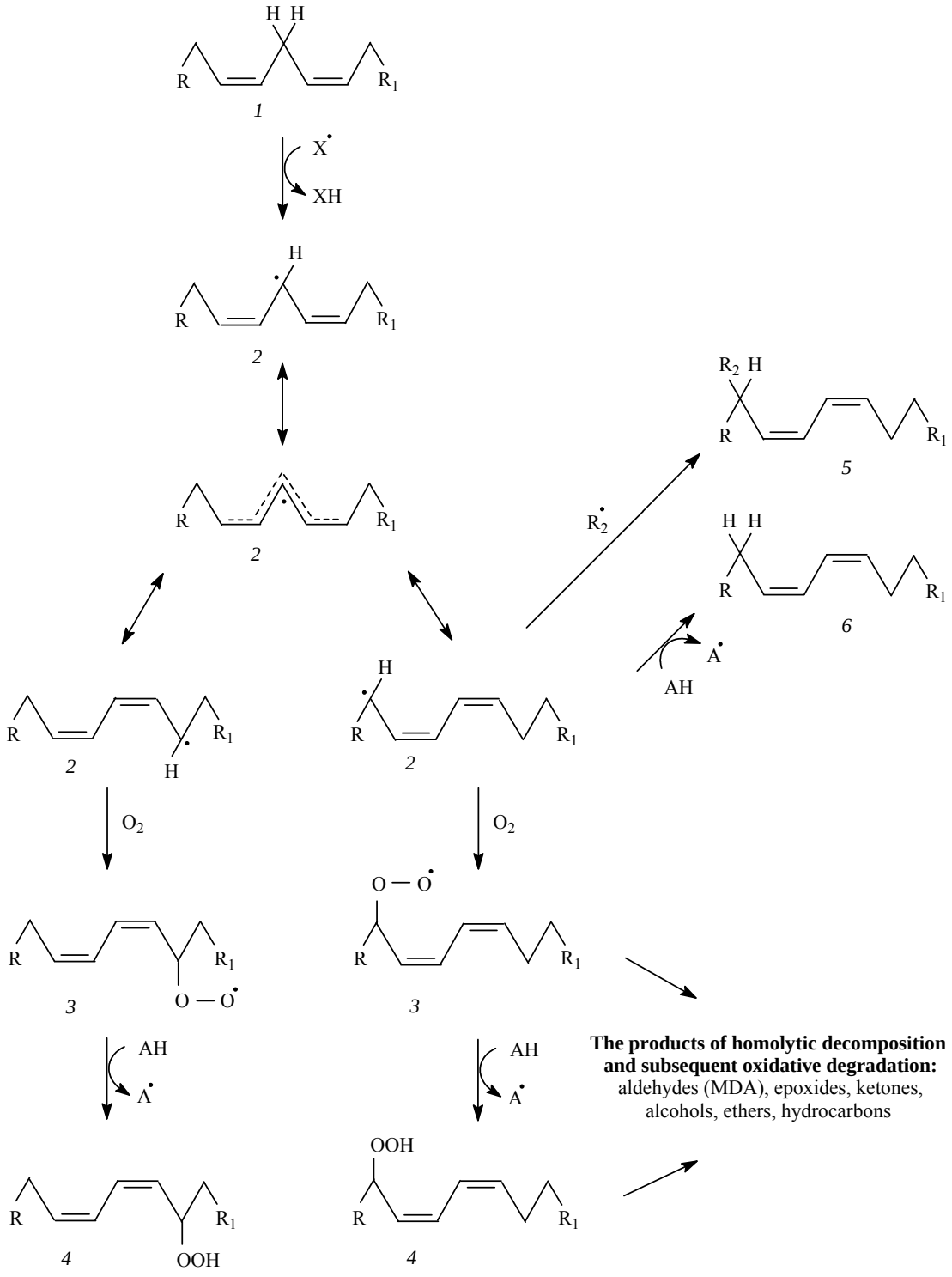

Fig. 4. The scheme of lipid peroxidation:
1 – polyunsaturated fatty acid; *2* – pentadienyl radical; *3* – peroxyl radical;
4 – hydroperoxide; *5, 6* – conjugates of dienes

The number of peroxides and hydroperoxides is characterized by peroxide index, which is determined in fat and oil products in accordance with GOST (national standard) [6]. The final oxygen-containing product of oxidative destruction of fatty acids is malonic dialdehyde (MDA), the content of which is determined by the reaction with thiobarbituric acid [7].

In fat and oil products lipid peroxidation occurs at the boundary of phase separation at the expenses of active forms of oxygen or developing microbiota formed in the aqueous environment. Therefore, to prevent free radical reactions leading to oxidative damage of fat and oil products, it is necessary to use water- and oil-soluble inhibitors.

Water-soluble ascorbic acid and oil-soluble α-tocopherol can serve as such inhibitors.

Fig. 5 shows the mechanism of autoxidation of ascorbic acid (Asc).

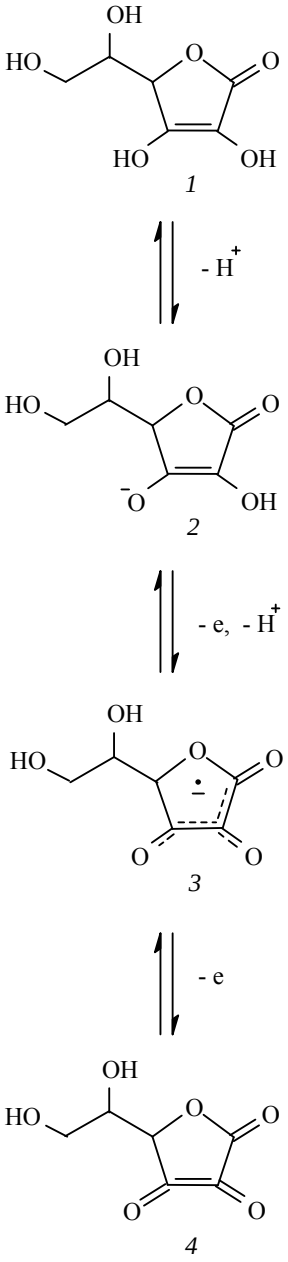

Fig. 5. The mechanism
of antioxidation action of Asc:
1 – Asc; *2*– anion Asc; *3* – anion-radical Asc;
4 – dehydroascorbic acid

Mobile hydrogen atoms of hydroxyl groups of the lactone ring of ascorbic acid (1) provide antioxidant properties of this vitamin. In addition, the anion-radical (3), which is formed in the course of autoxidation, may also serve as effective "trap" of free radicals [8].

The antioxidant properties of α-tocopherol (1) are provided by a phenolic hydroxyl group at the expense of quite stable α-tocopheryl radical formation (2), as well as by stabilization the structure in the form of tocopherolequinone (4) (Fig. 6) [9].

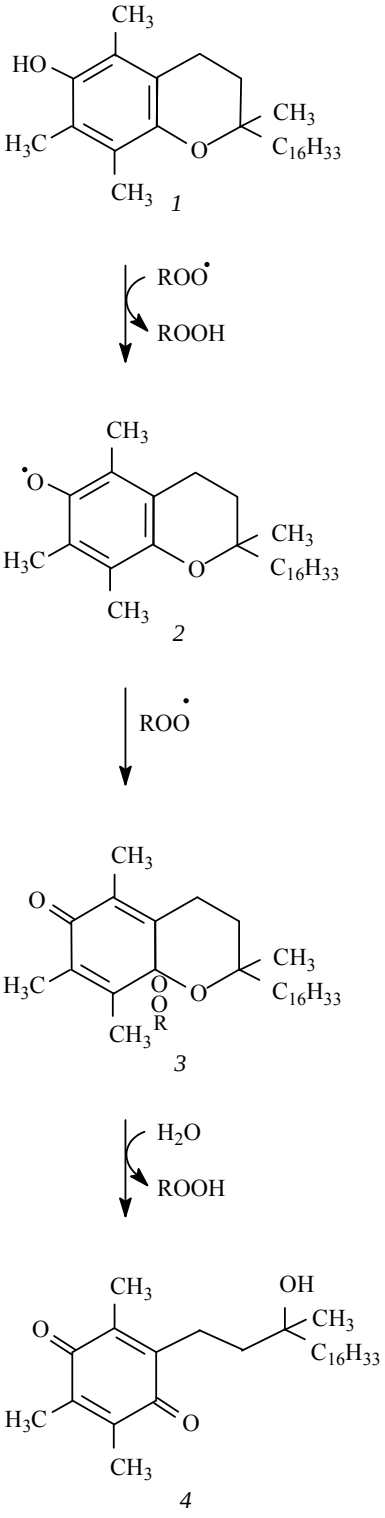

Fig. 6. The mechanism
of antioxidation action of α-tocopherol:
1 – α-tocopherol; *2* – α-tocopheryl radical;
3 – tocopherolperoxide;
4 – tocopherolequinone

The important components stabilizing emulsion systems in fat and oil products are emulsifiers. Lecithin and dimodan (DIMODAN® HP 85-S6) are the most often used emulsifiers.

As an additional emulsifier with a good buffer capacity caused by weak acidic properties, as well as with antioxidant properties, we have proposed a finely dispersed licorice root [1].

Licorice root contains a variety of biologically active substances such as mono-, oligo-, and polysaccharides, organic acids, essential oils, triterpenoids (glycyrrhizinic acid), resins, steroids (β-sitosterol), phenol carbonic acids and their derivatives, coumarins, tannins, flavonoids (liquiritin, isoliquiritin, liquiritoside, quercetin and others), high aliphatic hydrocarbons and alcohols, higher fatty acids, alkaloids.

At simultaneous use of different emulsifiers and biologically active substances of licorice root the resistance to hydrolysis of triacylglycerols of margarines increased. That was demonstrated on samples from Gomel fat and oil plant. The results demonstrating the dynamics of triacylglycerols hydrolysis during storage of margarine samples are presented in Table 1.

Considering the results presented in Table 1, the greatest inhibiting effect has a composition containing dimodan and finely dispersed licorice root.

For evaluation of antioxidant action of vitamins during the storage of fat and oil products, the analysis of pilot lots of spreads produced at Gomel fat and oil plant was conducted.

The peroxide index as a criterion of oxidative damage was determined in accordance with GOST [6]. The values of peroxide index in samples spread during storage are presented in Table 2.

As can be seen from the obtained results, after 60 d of storage the peroxide index in the control was (12.9 ± 0.2), in the sample with vitamin C was (9.2 ± 0.3), and in the sample with vitamins A, E and C was (8.3 ± 0.3) mmol of active oxygen/kg.

It is experimentally shown that the combined use of water-soluble and fat-soluble antioxidants more effectively "inhibit" peroxidative processes in fat and oil products.

Thus, licorice saponins, as well as water- and fat-soluble antioxidant vitamins, increase the shelf life of fat and oil products, making them a functional food.

Table 1

The accumulation of fatty acids in margarine samples with different emulsifiers

Time storage, d	Margarine acidity, °K		
	Margarine sample with dimodan and lecithin	Margarine sample with dimodan, lecithin and licorice saponins	Margarine sample with dimodan and licorice saponins
3.3	1.54	2.63	1.71
4.5	2.80	3.55	2.11
5.9	3.95	4.10	2.62
6.9	4.70	4.40	2.95
8.1	5.53	4.71	3.20
9.6	6.15	5.09	3.40
11.0	6.74	5.56	3.63

Table 2

The accumulation of hydroperoxides in spreads

Time storage, d	Peroxide index, mmol of active oxygen/kg		
	Spread sample (control)	Spread sample with vitamin C	Spread sample with vitamins A, E and C
0	1.2 ± 0.5	0.6 ± 0.4	0.6 ± 0.3
15	4.7 ± 0.2	3.9 ± 0.1	3.3 ± 0.2
30	8.6 ± 0.3	6.2 ± 0.3	5.3 ± 0.1
45	10.4 ± 0.3	8.5 ± 0.2	7.8 ± 0.1
60	12.9 ± 0.2	9.2 ± 0.3	8.3 ± 0.3

Conclusion. The presented in the article theoretical foundations of hydrolytic and oxidative processes leading to spoilage of fat and oil products, as well as mechanisms of antioxidant action of ascorbic acid and α-tocopherol formed the basis of the studies performed at Gomel fat and oil plant. The results demonstrate the ability to protect margarines and spreads from adverse chemical reactions.

In addition, the adding of vitamins and plant materials to the recipe of margarines and spreads transforms them into functional food increasing their role in modern dietology.

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