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Abstract

Full Text

Chemistry

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ON THE RELATION BETWEEN UNSATURATION AND THE RATE OF AUTOOXIDATION OF MIXTURES OF TRIGLYCERIDES OF NATURAL FATS

(Presented by Academician B. A. Kazanskii, 12 XI 1960)

It is believed that the rate of autooxidation of natural fats—if the influence of oxidation inhibitors and activators is excluded—is the greater, the higher the unsaturation of the mixture of fat triglycerides, expressed by the value of the iodine number ⁽¹⁾. Such an assessment of the tendency of fats toward oxidation is based chiefly on comparison of the rapid oxidizability of vegetable fats with a high iodine number (drying oils) with the relative inertness toward oxidation of solid animal fats with low iodine numbers.

Since the dependence of the rate of autooxidation on the degree of unsaturation of natural mixtures of triglycerides has not been studied in detail for fats of a single type, the present work investigated the relation between the intensity of oxidation and the iodine number in various samples of natural fat having a triglyceride composition of one and the same type. Mixtures of triglycerides of pork fat were chosen as the object of study, because in this fat the content of the unsaponifiable fraction is very small (not more than 0.3%) and the fat triglycerides are practically not protected from oxidation by the presence of inhibitors.

Samples of pork fat were obtained by rapid isolation from tissue at 60° in a nitrogen atmosphere; in them the iodine number JN , according to Rosenmund and Kuhnenn ⁽²⁾, and the thiocyanogen number RN were determined, the average molecular weight of the triglycerides referred to one double bond was calculated by the formula

$$M_m/\Delta = \frac{J_2 \times 100}{JN}$$

where M_m is the average molecular weight, Δ is the number of double bonds; and the triglyceride composition was determined using the known Kaufmann equations according to the method previously developed by us ⁽³⁾. The results of these determinations are summarized in Table 1.

Fig. 1. Rate of autoxidation of a mixture of lard triglycerides

Figure 1: Fig. 1. Rate of autoxidation of a mixture of lard triglycerides

Fig. 2. Intensity of oxygen absorption by lard samples with different iodine numbers: 1 –30.1; 2 –32.4; 3 –55.4; 4 –65.8

Figure 2: Fig. 2. Intensity of oxygen absorption by lard samples with different iodine numbers: 1 –30.1; 2 –32.4; 3 –55.4; 4 –65.8

Table 1

Sample No.	Iodine number	Thiocyanogen number	M_m/Δ	saturated acids, %	oleic acids, %	linoleic acids, %
1	30.10	29.90	842.5	65.38	34.36	0.26
2	32.40	31.80	783.0	63.16	36.15	0.69
3	34.52	33.20	735.3	60.50	38.18	1.55
4	42.90	38.40	591.6	55.50	39.40	5.20
5	46.20	44.10	549.4	48.50	49.30	2.20
6	53.40	49.00	475.3	43.26	50.82	6.23
7	56.20	34.80	451.6	60.32	15.47	24.54
8	64.00	45.30	396.6	47.54	31.00	21.60
9	70.40	58.30	360.5	32.48	53.74	13.68

The obtained fat samples with different iodine numbers were quickly and simultaneously poured, in layers of equal thickness, into completely identical Petri dishes and left standing in air at 20° under illumination by diffuse sunlight. Every 12 hours, samples were taken to observe the appearance, among the autoxidation products, of low-molecular acids by means of the reaction with neutral red according to Schoenberg's method⁽⁴⁾. This reaction was checked by a highly sensitive test for the appearance of physiologically distinguishable signs of deep oxidation. As a rule, the results of these tests for the depth of oxidative changes agree well.

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The results of the autoxidation experiments performed are shown in Fig. 1, from which it is evident that, contrary to the usual notions, the rate of appearance of signs of deep oxidative change, i.e. the rate of the autoxidation process of the mixture of lard triglycerides, decreases with increasing iodine number. On comparing the obtained results with the data of Table 1, it is also evident that the intensity of oxidation of the mixture of lard triglycerides is directly

proportional to the value of the average molecular weight of the triglycerides referred to one double bond, i.e. to the value M_m/Δ .

In order to confirm this conclusion, experiments were carried out to determine the intensity of oxygen absorption by lard samples with different iodine numbers. For these experiments, the method described by us previously⁽⁵⁾ was used, which makes it possible to conduct autoxidation at a constant oxygen content in the gas phase. The experiments were carried out at 60° and under weak illumination by diffuse sunlight for 24 hours. The results of experiments with fat samples having iodine numbers 30.10; 32.40; 55.40; and 65.80, expressed in moles of absorbed oxygen per M_m/Δ of fat, are shown as curves in Fig. 2.

From a comparison of the curves in Fig. 2 it is clearly seen that the molar absorption of oxygen referred to one double bond (and, consequently, also the intensity of the autoxidation process) decreases with increasing iodine number of the fat. It follows from this that the depth of oxidative changes depends—

depends not on the number of double bonds per unit weight, i.e., not on the magnitude of the iodine value JN , but on the intramolecular distribution of double bonds in the triglycerides of the fat.

The results obtained show that such a distribution of unsaturated bonds, at least for lard, apparently corresponds to the principle of uniform distribution of residues of unsaturated acids, and in particular of oleic acid, in the triglycerides forming the fat. This principle deserves attention alongside the already known⁶ and discussed principles of ordered (equal) and probable (random) distribution of fatty-acid residues in triglycerides of natural fats.

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Note: Figure translations are in progress. See original paper for figures.

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