IODINE LIPIDS FORTIFICATION RESEARCH

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1. INTRODUCTION

Insufficiency of iodine represents a nutritional problem that severely affects the health of the entire population. The deficit of iodine is an especially actual problem for Moldova as in fine it negatively affects not only the public health but also the entire social-economic development of the country. It is conditioned by the reduced levels of iodine in the country's natural geographic environment – soil, water, air, plants [1].

Iodine is an essential oligo – element , its content in human organism varies from 15 to 23 mg, it is indispensable for the synthesis of thyroidal hormones (thyroxine – 65%, tri-iodinetrionine – 59%), which of primordial importance for the cellular metabolism, especially for the cerebral and bone tissues [2]. Deficit of iodine leads to the disturbances in the functioning of thyroid gland, delays in physical and psychic development, etc.

The small content of thyroidal hormons in blood (hypothyroidism) leads to affections of brain, to the development of other harmful processes known as iodine deficit diseases. So it is considered that the deficiency of iodine first of all leads to the negative affections of intellect. Respectively, widely spread iodine deficiency can affect not only the health but also the intellectual resources of nation [3].

Major measures of prophylaxis of iodine deficit diseases consist in the iodination of salt and other foodstuffs, including sunflower oil. For the moment the consumption of iodinated salt is very low, only 32% of families consume adequately iodinated salt, thus not satisfying the needs of organism fully [4]. Besides these, there are certain categories of population (children, etc.) that consume less salt.

Sunflower oil is a very common product in Moldova, so the production and consumption of oil enriched with iodine (40 - 50 μg/day), equivalent to the quantity of iodine received with the salt, would allow to reduce the iodine deficiency.

The objective of this work consists in the elaboration of sunflower oil iodination and evaluation of its quality indicators (physical-chemical properties).

2. MATERIALS AND METHODS

2.1 Preparation of iodinated oil

On purposes of these investigations we used double refined and deodorized sunflower oil of local production. In order to obtain iodinated oil per one liter of product we added 1g of iodine (I_2) in crystals of type „ХЧ". After the establishment of equilibrium the oil was further investigated. The iodinated oil had an intensive brown color due to the presence of free iodine. The obtained oil (A) with a total content of iodine of 1mg/ml was diluted in the proportion of 1:100 and so was obtained the product (B) with content of iodine 10μg /ml . From the product (B) by dilution (1:500) was prepared the sample (C) with content of iodine not exceeding 2 μg/ml i.e. much lower than recommended daily rate. The iodinated oils with different content of iodine (A,B,C) served as objects of research for this theses. All measurements have been done in conformity with the norms STAS – 1129 – 93 [5].

2.2 Acidity indices (AI) and free fat acids (FFA)

The acidity of oil is determined depending on the acidity index or depending on the content of free fat acids expressed in terms of a single fat acid, oleic acid [6]. The acidity index is determined by the quantity of KOH required for the neutralization of one gram of oil.

A sample of oil with known weight is titrated with a solution of KOH with known normality, initially dissolved in ethanol before the phenolphthalein point.

2.3. Saponification index (SI)

The saponification index measures the quantity of base used for the saponification of an exact quantity of oil initially solubilized in ethanol. This is an index of average molecular mass of fat acids and it implies the hydrolysis of each ester liaison that joins the fat acids with the molecules of glycerin [6]. The analyzed samples are warmed up in order to accelerate the reaction of hydrolysis.

2.4 Peroxyde index (HI)

The peroxyde index is defined as a number of milli-equivalents of peroxyde per kilo of fat substance. In order to measure the peroxide index of oil the sample was solubilized in a mixture of acetic acid and chloroform with addition of excess KI solution, the molecular iodine was titrated with solution of $Na_2S_2O_3$ in the presence of starch as color indicator.

2.5. The iodine index (value) (II)

The iodine index is frequently used in order to classify the oils depending on the domain of use and in order to control the hydrogenation process. The iodine index represents the quantity of iodine (in grams) absorbed by the fat substance. The obtained results reflect the degree of unsaturation of oil if the following conditions are satisfied:

- Absence of light;
- Excess of halogen;
- Good control of reaction time.

The analysis of iodine was performed by titration with sodium thiosulfate after extraction in ethanol by indirect method [8].

2.6. Determination of mass share of water and volatile substances

This method is based on the drying of oil samples at the temperature of 100 - 105ºC.

The mass is considered constant if its reduction between two weighing procedures doesn't exceed 0,0005g.

3. RESULTS AND DISCUSSIONS

The use of iodinated sunflower oil is an accessible and low cost method. The particular advantage of this method consists in the liposolubility of iodine that facilitates its incorporation in oil. However, it is a very complex phenomenon associated with modifications of physical-chemical properties of the finite product as thereafter discussed in the present work.

Addition of iodine and positioning of double bonds takes place according to a mechanism that implies the formation of a halonium-type ion in result of bimolecular nucleophilic substitution [6].

Addition of iodine is a slow process and depends on the position of double bond in the chain of the acid. In order to saturate the double bonds an excess of iodine is required, as a rule, of 100%. Besides these, the reaction must be activated. The activation of double bond is a result of displacement of a pair of electrons of the π bond to one of the non-saturated atoms of carbon.

The same process is observed in the molecules of iodine:

$$I : I \leftrightarrow I^{+}.....I^{-}$$

It is supposed that the saturation of double bonds is a two-staged process [10].

On the first stage the cation of iodine interacts with the unsaturated fat acid in the position of double bond. Addition takes place with formation of a covalent bond C : I based on the pair of electrons of π bond. This stage is very slow.

On the second stage the less active anion of iodine very quickly is bound to the cation established due to the addition of iodine cation to the unsaturated acid fat. In this manner, to each double bond one molecule of iodine is added, while the substitution of hydrogen in methyl groups of the fat acid doesn't take place.

The speed of double bond saturation in the molecules of fat acids depends very much in their number and position in molecule.

The double bonds in the vicinity of the carboxylic group are more or less inactivated. This affects the experimentally determined iodine index, whose values depend on the positions of isomers of oleic acid, varying considerably depending on the position of double bond in relation to the carboxylic group [9].

The unsaturated fat acids present in oil contain double bonds in the positions – 9 = 10 – şi -11 = 12 – (linoleic acid). From here one may conclude that addition of iodine in these positions is possible in the given conditions. Addition is possible if the iodine is fully bound in the types of clathrate as indicated below (fig.1).

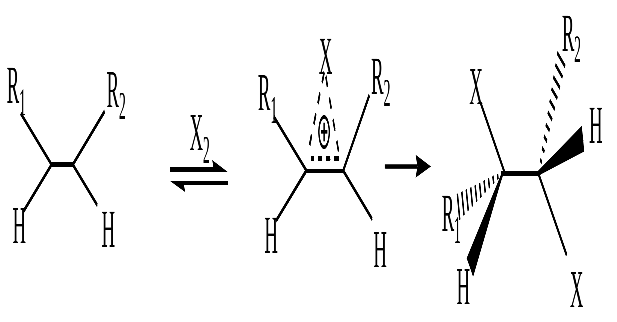

Figure 1. Bounding of molecular iodine with triglycerides

Experimentally it was determined that the iodine index decreases gradually depending on the quantity of iodine added (fig.2).

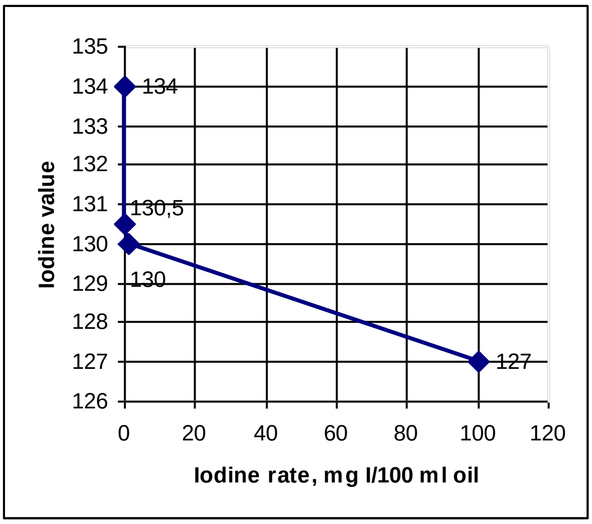

Figure 2. Evolution of iodine value of oil depending on the quantity of iodine added

The saponification index of iodinated oil doesn't vary considerably compared to the reference sample (fig.3).

This fact demonstrates that the molecular mass of triglyceride doesn't vary during the process of oil iodination.

A small increase in the index of saponification for the oil containing 100 mgI_2/100 ml oil (sample A) can be explained by the possible chemical interaction between iodine and hydroxide.

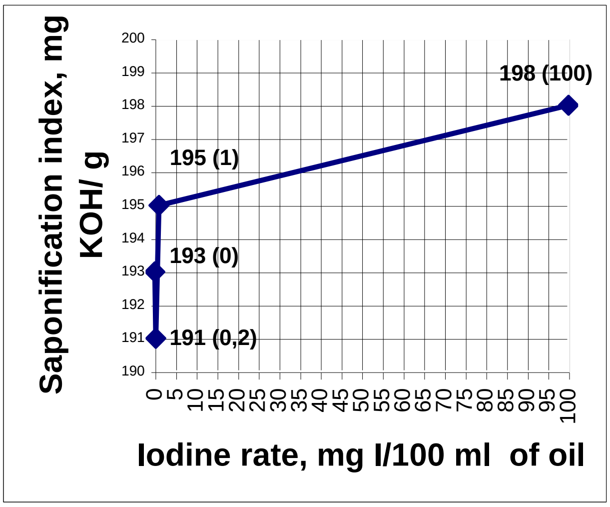

Figure 3. Variation of saponification index of the iodinated oil

It was determined that the content of free fat acids in the iodinated oil increases for both samples A and B in line with the increase of quantity of iodine added. This fact can be explained by the consumption of certain quantities of KOH for interaction with iodine. The only sample in which the AGL index was exceeded was the sample A that contains 100 mg I_2/100 ml oil. For iodinated oil containing 0,2 mg I_2/100 ml (sample C) the AGL index doesn't vary compared to the reference sample.

Variation of peroxide index of iodinated oil is represented on the figure 4.

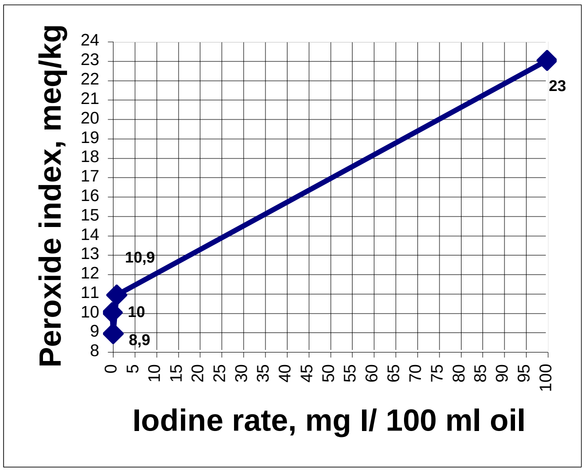

Figure 4. Variation of peroxide index of the iodinated oil

It was determined that the peroxide index doesn't vary significantly for oils with small concentration of iodine (samples B and C) compared to the reference sample while for the oil with high content of iodine 100 mg/ 100ml (sample A) it far exceeds the maximum admissible value.

This can be explained by the presence of free iodine in the iodinated oil - sample A. The infrared spectrums of iodinated oil samples, compared to the natural oil, demonstrate that there are no essential changes in the structure of oil (samples B and C). In the infrared region of electromagnetic spectrum the iodinated oil, similar to the natural one, absorbs the irradiation energy of two specific wave lengths 3,45 and 5,73μn. A band of intense absorption is observed between the 1724 nm and 2300 nm in the close infrared region. Vibrations of characteristic groups of oil lead to the increase of optical density of samples at specific wave lengths.

In the region of middle infrared spectrum absorption is observed at wave length of 5,73 μn and is associated with the vibration of carbonylic group of ester bond of triglycerides. At 3,45 µn absorption is associated with the vibration of C-H bond of the chains of fat acids.

4. CONCLUSIONS

This work demonstrates the possibility of iodination of sunflower oil; iodine doesn't affect the main physical-chemical indices of sunflower oil. Formation of chemical bonds in the process of iodine addition in the position of double bonds of fat acids assures a high stability of resulting compounds (samples B, C). For this reason the use of iodinated oil for the production of highly accessible foodstuffs (margarine, mayonnaise) represents a particular interest.

A small quantity of iodinated oil in foodstuffs doesn't affect the organoleptical and physical-chemical properties of finite products. Use of these products in combination with iodinated salt would allow to prevent the deficit of iodine and the associated incidence of iodine deficiency diseases.

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