DEPENDENCE OF THE POLARITY AND SURFACE ACTIVITY OF PHOSPHOLIPID MOLECULES ON THE COMPOSITION AND SPATIAL STRUCTURE OF THEIR MOLECULES

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Abstract. The problems of the Arctic economy are especially relevant today and require an urgent solution. The main factor in solving these problems is a human being, a person (individual) whose health is the key to his full-fledged creative work. Preventive methods of combating diseases, an integral part of which is the creation of food products with dietary, therapeutic and preventive properties, should be of the greatest importance in programs to improve and maintain a healthy lifestyle of the population. Products manufactured by the fat and oil industry make up a significant part of the traditional diet of the Russian population. The authors have investigated and proved that the lower value of the dipole moments of phospholipids derived from oils of modern types of sunflower justifies the lower hydration of oils, and, therefore, the need to select a hydrating agent, taking into account its polarizing ability. The findings will make it possible to contribute to protection of the health of a person living in extreme conditions.

1. Introduction
Arctic peoples have a unique food culture based on the experience of their ancestors and the desire to maintain health in extreme conditions, and products containing high-quality phospholipids are an integral part of the diet here.

Vegetable oils are a complex mixture of triacylglycerols of high molecular weight and related substances of various compositions and properties. A special place among the latter is occupied by phospholipids, which have high biological activity and play a decisive role in the normalization of the activity of the human body.

Nowadays, the issues of nutrition and creation of rationally balanced food products are being emphasized. This is due to the changing pace of modern life, the presence of a significant number of semi-finished products, products with long storage life in the consumer market, followed by a decrease in the content of physiologically valuable food functional ingredients in the diet. However, in modern conditions, a trend of healthy lifestyle is steadily forming, a part of which is a balanced diet. However, in modern conditions, the trend of a healthy lifestyle is steadily forming, balanced nutrition being its integral part.

Full-fledged healthy food products, which are complex systems, are not only a source of physiologically functional ingredients imported into the human body, but also perform protective functions. The problem of creating healthy food products is currently being widely resolved by incorporating into the formulation a complex of substances with pronounced biologically active
properties that can have a favourable effect on one or several physiological functions, as well as metabolic processes in the human body as a whole. This group of biologically active substances includes lecithins obtained from various vegetable oils (sunflower, soybean, rapeseed and corn oils) [1].

Phospholipids are natural metabolites, that affect the activity of enzymes, stimulate the synthesis of prostaglandins, promote better use of protein and fat in tissues, prevent their excessive accumulation and exhibit other mediator properties. Phospholipids not only regulate the energy supply of cells and their need for oxygen, but also facilitate the transfer of information between them. Certain groups of phospholipids exhibit selective activity and are successfully used as active components of medical drugs that normalize the functions of the liver, gastrointestinal tract, cardiovascular and immune systems [1]. The lack of phospholipids in the diet is one of the reasons for the decrease of the body’s resistance to adverse environmental influences and viral infection.

Taking into consideration the wide range of positive effects of phospholipids on the body, they are successfully used in many countries as a base or an active component of food products and medicines. The main agricultural oilseed crop in Russia is sunflower and it is quite rich in phospholipids. In the Russian Federation there are many oil extraction plants that receive vegetable oils, while until now such a valuable product as phospholipids has been considered as a by-product. The reason of that is the lack of effective technologies to obtain high quality phospholipids and preserve their natural biological properties. It is known that the chemical structural features of phospholipids have a decisive effect on the stability of the system «phospholipids – triacylglycerols – water» [1, 2].

2. Results and discussion

The aim of our work was to reveal the regularities of the effect of the chemical composition on the polarity and polarizability of phospholipids, to establish the dependence of the significance of each metal in reducing the dipole moments, to assess the main characteristics of the interphase layer of the «phospholipids – triacylglycerol» system at the border with water.

Unrefined sunflower oils are obtained in laboratory conditions by pressing under conditions close to industrial ones.

The main physicochemical indicators of unrefined oils are shown in Table 1. The tables 1-7 shows samples: «А» – «Peredovik», «B» – «Perdovik uluchshenny (improved)», «C» – «Donskoy-60», «D» – «Yubileyniy-60», «E» – «Berezanskiy». As it can be seen, in terms of the physical and chemical indicators of modern sunflower seed oils differ from seed oil of the «A» variety by higher peroxide numbers, a high mass fraction of non-hydratable phospholipids, unsaponifiable lipids, waxes and ashes, which indicates a higher metal content in the oils of the seeds under investigation.

| Indicators                        | «А» | «B» | «C» | «D» | «E» |
|----------------------------------|-----|-----|-----|-----|-----|
| Acid index, mg KOH/g             | 1.85| 1.96| 2.37| 2.45| 2.52|
| Peroxide number, 1/2 mM O2/kg    | 3.17| 4.21| 4.76| 4.86| 5.16|
| Mass fraction, % of:             |     |     |     |     |     |
| Phospholipids among them:        | 0.68| 0.72| 0.77| 0.80| 0.75|
| non-hydratable phospholipids     | 0.15| 0.23| 0.29| 0.34| 0.36|
| unsaponifiable lipids            | 0.62| 0.67| 0.76| 0.82| 0.95|
| ashes                            | 0.03| 0.10| 0.11| 0.13| 0.17|
| waxy substances                  | 0.05| 0.07| 0.08| 0.09| 0.12|
| brown pigments                   | 0.08| 0.05| 0.05| 0.05| 0.06|
| Hydratability, %                 | 78  | 68  | 61  | 58  | 52  |

The presented data show that the phospholipids of the oils under examination and seed oils of the «А» variety are identical in group composition, however, the phospholipids of the oils of the seeds of
modern sunflower types contain more phosphatidylserines, phosphatidic and polyphosphatidic acids with a lower content of phosphatidylcholines and phosphatidylethanol-amines.

As a result of the analysis of the group composition of phospholipids isolated by dialysis from the control samples of unrefined sunflower oils, as well as the group content of hydrated and non-hydrated fractions by thin layer chromatography, 6 groups of phospholipids were identified. The quantitative composition of phospholipids was determined by the mass fraction of phosphorus in individual spots by the method [3-6].

Resulting from comparing the group composition of the hydrated and non-hydrated phospholipid fractions, it can be concluded that the ratio of the groups of two phospholipid fractions of modern-type seed oils is basically similar to the ratio of the phospholipid fractions of oils of the house-brand «A».

Thus, in the composition of the non-hydrated fraction, there are no phosphatidyl-cholines; on the contrary, the mass fraction of phosphatidic and polyphosphatidic acids significantly exceeds these indicators for the hydrated fraction. This pattern is observed both for phospholipids of modern types of sunflower seeds and for phospholipids of the control variety. It should be noted that the content of phosphatidylserines, phosphatidic and polyphosphatidic acids in the non-hydratable fraction of phospholipids of modern types of sunflower seeds is higher than in the non-hydratable fraction of the control variety.

The predominance of non-hydratable phospholipids in unrefined seed oils of modern sunflower types is, whereas, determined primarily by the high mass fraction of phosphatidic and polyphosphatidic acids, as well as phosphatidylserines.

The efficiency of the hydration process depends, first of all, on the ability of certain groups of phospholipids to participate in the formation of mixed surface layers «phospholipids – triacylglycerols» at the edge of water.

Phospholipids are amorphous substances, they are freely soluble in aliphatic and aromatic hydrocarbons and their halogen-derivatives. Individual groups of phospholipids differ in solubility in different solvents, for example, phosphatidylcholines and phosphatidic acids are readily soluble in methyl and ethyl alcohols, phosphatidylethanolamines are slightly soluble, and phosphatidylserines are practically insoluble. The difference in solubility is largely due to the structure of aliphatic chains of phospholipids, temperature fluctuations, moisture content in solvents; the solubility of phospholipids is also affected by the oxidative polarization of non-saturated aliphatic chains.

Phospholipid molecules are characterized by the presence of non-polar (hydrophobic) and polar (hydrophilic) regions, which determines their behavior in aqueous solutions. Depending on the concentration, phospholipid molecules form various ordered structural elements: at low concentrations spherical micelles are formed, in which the polar parts of the molecules form the outer layer, and the non-polar parts form the inner layer.

At an increased concentration, micelles are grouped into long cylinders; with a further increase in concentration, a specific type of liquid crystal structure is formed – lamellar (layered) one, consisting of bimolecular layers of lipids separated by water layers [7-10]. In aqueous solutions, phospholipids exhibit surface-active properties. Of all phospholipid groups, phosphatidylcholines have the highest surface activity. By the value of surface activity (in descending order), phospholipids form a following series: phosphatidylycholines - phosphatidylethanolamines - phosphatidylserines - phosphatidylinositol - phosphatidic acids. In low-polar and non-polar solvents, phospholipids form associates and micelles of various orders. In such solvents, the polar groups of phospholipids are directed towards the inside of the micelle, and the non-polar groups are directed towards the outside [11, 12].

The most important properties of phospholipids that determine their behavior at individual stages of processing oilseeds and vegetable oils, include polarity and polarizability. Polarity is one of the fundamental characteristics of substances and causes a sharp difference in the physicochemical properties of polar and non-polar ones. The dipole moment of a complex molecule can be represented as a vector sum of the moments belonging to individual bonds. The presence of a dipole moment in
phospholipids is determined by the electronic effects of active groups of phospholipids, such as - P = 0, - P-OH, - NH2, - M (CH3)3, etc. [13-16]. Considering the importance of this characteristic for the choice of the method of hydration of the investigated oils, we have determined the dipole moments of individual groups of hydrated and non-hydrated phospholipids (see Table 2).

### Table 2. Dipole moments of phospholipid molecules.

| Phospholipid group     | Hydrated Dipole moment, C·m·10⁻³⁰ | Non-hydrated Dipole moment, C·m·10⁻³⁰ |
|------------------------|------------------------------------|--------------------------------------|
|                        | «A» Modern varieties               | «A» Modern varieties               |
| Phosphatidylethanolamines | 24.84 24.26-24.96                  | 17.71 16.18-16.74                  |
| Phosphatidylserines     | 22.62 21.45-21.57                  | 15.65 13.23-14.21                  |
| Phosphatidylinositol    | 20.95 20.75-20.89                  | 13.58 11.85-12.51                  |
| Phosphatidic acids      | 19.68 17.58-19.44                  | 12.25 10.38-11.11                  |
|                        |                                    |                                      |

Table 3 shows the values of the dipole moments of individual groups of phospholipids separated from oils of various modern types of sunflower seeds.

### Table 3. Dipole moments of non-hydrated molecules phospholipids.

| Phospholipid group     | Dipole moment, Debye |
|------------------------|----------------------|
|                        | «A» «B» «C» «D» «E» |
| Phosphatidylethanolamines | 5.36 5.07 5.00 4.95 4.90 |
| Phosphatidylserines     | 4.74 4.10 4.05 3.99 3.90 |
| Phosphatidylinositol    | 4.30 3.19 3.40 3.30 3.20 |
| Phosphatidic acids      | 3.71 3.36 3.29 3.20 3.10 |

As it can be seen from the data presented, the dipole moments of individual groups of hydrated phospholipids of oils of modern types of sunflower seeds have much in common with the dipole moments of individual groups of hydrated phospholipids of the «A» variety (control variety). It should be noted that the value of the dipole moments of individual groups of non-hydratable phospholipids obtained from seed oils of modern types of sunflower, slightly lower than the value of the dipole moments of corresponding groups of seed oils phospholipids of the control variety.

We suggest that this fact is associated with the different qualitative and quantitative composition of the metals of phospholipids under examination, since it is known that metals of different valences affect the magnitude of the dipole moments to different extents. For example, phosphatidylethanolamines, which form compounds with monovalent metals, are polar to a greater degree than phosphatidylserines, phosphatidylinositol and phosphatidic acids, which form compounds with bivalent and trivalent metals. In addition, phospholipids with a higher metal content have a lower polarity. We have determined the dipole moments of phospholipids separated from oils of four types of sunflower seeds (tables 4-7).

### Table 4. Influence of metal content on dipole moments non-hydratable phosphatidylethanolamines.

| Phosphatidylethanolamines of the following varieties: | Dipole moment, D | Metal content, % |
|------------------------------------------------------|------------------|------------------|
|                                                      | Potassium        | Sodium           |
| «A»                                                  | 5.36             | 1.310            | 0.890            |
| «B»                                                  | 5.07             | 1.280            | 0.937            |
| «C»                                                  | 5.00             | 1.215            | 1.005            |
| «D»                                                  | 4.95             | 1.010            | 1.235            |
| «E»                                                  | 4.90             | 0.968            | 1.275            |
Table 5. Influence of metal content on dipole moments non-hydratable phosphatidylserines.

| Phosphatidylserines of the following varieties | Dipole moment, D | Metal content, % |
|---------------------------------------------|------------------|------------------|
|                                             | Calcium          | Magnesium        | Ferrum | Copper |
| «A»                                         | 4.74             | 0.630            | 0.915  | 0.069  | 0.080 |
| «B»                                         | 4.10             | 0.964            | 1.263  | 0.106  | 0.091 |
| «C»                                         | 4.05             | 0.939            | 1.297  | 0.125  | 0.108 |
| «D»                                         | 3.99             | 0.930            | 1.305  | 0.131  | 0.124 |
| «E»                                         | 3.90             | 0.920            | 1.315  | 0.148  | 0.135 |

The obtained data made it possible to determine the significance of each metal in reducing the dipole moment, i.e. polarity of non-hydrated phospholipids, and hence their hydration. It was found that the content of sodium and potassium ions has little or no effect on the value of the dipole moments, this effect is not so significant for magnesium and calcium ions, at the same time, even a slight increase in the iron and copper ions content leads to a significant decrease in the value of the dipole moments of individual groups of non-hydratable phospholipids.

Table 6. Effect of metal content on dipole moments non-hydratable phosphatidylinositol.

| Phosphatidylinositol of the following varieties | Dipole moment, D | Metal content, % |
|------------------------------------------------|------------------|------------------|
|                                                | Potassium        | Sodium           | Calcium | Magnesium | Ferrum | Copper |
| «A»                                            | 4.30             | 0.450            | 0.348   | 0.585     | 0.597  | 0.025  | 0.070  |
| «B»                                            | 3.59             | 0.361            | 0.525   | 0.825     | 0.714  | 0.041  | 0.079  |
| «C»                                            | 3.40             | 0.350            | 0.548   | 0.815     | 0.815  | 0.050  | 0.084  |
| «D»                                            | 3.30             | 0.335            | 0.557   | 0.810     | 0.847  | 0.065  | 0.091  |
| «E»                                            | 3.20             | 0.320            | 0.595   | 0.800     | 0.869  | 0.078  | 0.101  |

Table 7. Effect of metal content on dipole moments non-hydratable phosphatidic acids.

| Phosphatidic acids of the following varieties | Dipole moment, D | Metal content, % |
|---------------------------------------------|------------------|------------------|
|                                             | Potassium        | Sodium           | Calcium | Magnesium | Ferrum | Copper |
| «A»                                         | 3.71             | 0.002            | 0.150   | 0.495     | 0.881  | 0.010  | 0.002  |
| «B»                                         | 3.36             | 0.001            | 0.210   | 0.763     | 1.442  | 0.020  | 0.004  |
| «C»                                         | 3.29             | 0.001            | 0.232   | 0.775     | 1.453  | 0.031  | 0.007  |
| «D»                                         | 3.20             | 0.001            | 0.240   | 0.791     | 1.480  | 0.043  | 0.009  |
| «E»                                         | 3.10             | 0.001            | 0.249   | 0.805     | 1.497  | 0.050  | 0.011  |

Thus, the lower value of the dipole moments of phospholipids obtained from oils of modern types of sunflower, justifies lower hydration of these oils, and, therefore, the need to select a hydrating agent, taking into account its polarizing ability.

The stage that bounds hydration of phospholipids is diffusion of phospholipids from the oil phase to the «oil – water» interface or on the surface of the aqueous phase. The efficiency of this stage is largely determined by the surface activity of phospholipid molecules at the interface, as well as the structure of the interfacial layer. In order to elucidate the laws governing the mass exchanging process, we have studied some features of the formation of the interphase layer at the interface «oil–water» in the presence of various groups of hydratable and non-hydratable phospholipids in the oil phase [4, 5]. For this, we determined the interfacial tension at the interface: phospholipids solution in a simulated system «oil – water», at various mass fractions of phospholipids and temperatures of 20.45 and 60 °C.

The data obtained were interpreted using the Shishkovsky equation, which makes it possible to estimate the surface activity of the SAS (surfactant) under examination and the properties of the interphase layer.

In analyzing the values of maximum Gibbs adsorption for the system «phospholipids – oil» at the water interface, it has been found that for sunflower seeds of modern types, hydrated phospholipids have a higher value of maximum Gibbs adsorption compared to the corresponding groups of non-hydrated phospholipids. This indicates a higher surface activity of hydrated phospholipids and a closer packing of the molecules of these phospholipids at the oil-water interface. It should be noted.
that for modern types of sunflower the difference in the values of Gibbs adsorption is more significant, which is due to the increase in the amount of metals in seed oils of modern types of sunflower.

3. Conclusion

Thus, it may be concluded that non-hydratable phospholipids of oils of modern types of sunflower seeds, which are complex compounds with metal ions, unsaponifiable lipids and have a lower polarity and surface activity compared to the control variety, and special conditions of hydration are required for their removal.

According to the findings of the WHO (World Health Organization), the simplest and most effective solution to the problem of anthropogenic impacts on human beings is the creation of a healthy diet system. Implementation of such programs is one of the priorities of Russian state policy.

These studies prove that the efficiency of the hydration process depends primarily on the ability of certain groups of phospholipids to participate in the formation of mixed surface layers «phospholipids – triacylglycerols» at the border with water.

These studies prove that the effectiveness of the hydration process depends primarily on the ability of certain groups of phospholipids to participate in the formation of mixed surface layers of «phospholipids – triacylglycerin» at the oil-water interface.

The research undertaken has made it possible to reveal the dependence of the polarity and surface activity of phospholipids on the chemical composition and structure of their molecules. It has been demonstrated that phospholipids of sunflower seed oils of modern types have a lower polarity and surface activity, which is explained by a higher content of complex compounds with metal ions, unsaponifiable lipids in their composition. Correlation dependences of the influence of metal ions on the value of the dipole moments of molecules of individual groups of non-hydratable phospholipids, – phosphatidylethanolamines, phosphatidylserines, phosphatidylinositol, and phosphatidic acids, – were established.

The quality of products, due to modern research having been undertaken by many scientists, is improving, which has a beneficial effect on human health and an increase in the duration of an active, healthy life, considering the peculiarities of the Arctic climate as well.

4. References

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