Elena Aleksandrovna Butina et al /J. Pharm. Sci. & Res. Vol. 10(1), 2018, 65-69

ISSN:0975-1459
Journal of Pharmaceutical Sciences and Research
www.jpsr.pharmainfo.in

Features of vegetable oils' distillates obtained by Russian oil processing enterprises

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Abstract.

The work is dedicated to the study of the chemical composition and physicochemical parameters of vegetable oils' distillates obtained by large Russian oil processing enterprises. The estimation of of vegetable oils' distillates as a promising secondary resource for deep technological processing for obtaining natural fatty acids and valuable microingredients is provided. The results of research of the distillates obtained by foreign enterprises, the results of own experimental research, and the description of the test methods are presented in a brief overview. Based on the analysis of the obtained results, it is concluded that the distillates of vegetable oils obtained by the majority of large Russian oil processing enterprises can be considered as a promising raw material for obtaining high-tech innovative products – concentrates of purified fatty acids, as well as concentrates of natural phytosterols and tocopherols.

Keywords: vegetable oils' distillates (VOD), secondary resources, phytosterols, tocopherols, fatty acids, distillation refining.

INTRODUCTION

The VOD are the main cost-effective raw material for the industrial production of natural fatty acids, phytosterols and natural antioxidants – tocopherols [1-6].

The VOD are the secondary resources of the oil and fat industry obtained as byproducts during the deodorization and distillation (physical) refining [7].

The availability and prospects of this type of raw material in Russia are determined by the perspective plan presented in the forecast of long-term socio-economic development of the Russian Federation up to 2030, construction of new and reconstruction of the existing processing capacities are expected, which in 2030 will ensure an increase in the level production of vegetable oils 1.6 times compared to the level of 2011.

According to various literary data, the composition of VOD includes free fatty acids (from 30 to 85%), tocopherols (from 1 to 8%), phytosterols (from 2 to 15%), ethers of phytosterols (up to 15%), acylglycerols (up to 20%), and various organic and inorganic substances, including antinutrient ones (up to 10%) [3-9].

Wide limits of variation of the content of components in VOD are explained by the peculiarities of the initial composition of processed vegetable oils, technological distillation modes, and also by the specifics of the analytical control methods used [10-12].

For example, according to the data of [13], the phytosterols in unrefined corn oil average 850 mg%; in the rapeseed - 820 mg%; sunflower - 430 mg%, and in soy - 350 mg%. After refining, including the removal of phospholipids and other hydrophilic substances, pigments and free fatty acids, the content of phytosterols on average decreases by 15-25%.

Considering the prospect of using the distillation of vegetable oils as a raw material for the isolation of valuable substances, the attention of researchers is directed to the study of their composition and features [5, 6, 14].

According to the data presented in the paper [14], the main mass of VOD is represented by a lipid fraction (the content of crude fat is from 83.1 to 98.4%, moisture - from 1.8 to 0.9%, ash - from 0.06 to 0.9%). It is established that the composition of VOD includes energy-valuable (triglycerides and fatty acids), biologically active substances (vitamins A and E), and plastic-regulative substances, such as phytosterols.

In the Russian Federation, the processing of distillation of vegetable oils with the allocation of phytosterols and tocopherols as an independent commodity production is not available.

The VOD obtained at Russian oil and fat enterprises are mainly used as technical raw materials for the isolation of fatty acids, which are used in soap or paint and varnish production. A small proportion of VOD is used in the production of feed for farm animals [15].

Such use of the VOD does not correspond to the actual principles of resource saving and deep processing of food raw materials, as well as tendencies of world practice of vegetable oils' processing.

It should be noted that recently there has been a tendency of increasing the share of export of domestic VOD to foreign countries, mainly to China. As a rule, the cost of VOD is determined by the content of tocopherols in them and is calculated from the ratio of $220 per 1% of tocopherols. Abroad such a large company as Kargil is one of the processors of VOD with the isolation of phytosterols, tocopherols and fatty acids as a commodity product.

The advantages of the VOD of the Russian vegetable oils is, firstly, the absence of risks associated with the use of genetically modified raw materials, and, secondly, the prevalence of the total amount of produced VOD, are of sunflower oils' distillation that differ in the composition of sterols, tocopherols and fatty acids from the most widely used abroad VOD of soybean oils' distillation [16].

In order to assess the prospects of using the VOD obtained by Russian oil processing enterprises as raw materials for obtaining valuable natural substances such as fatty acids, tocopherols and phytosterols, comparative studies of their chemical composition and physical and chemical indices were conducted.

MATERIALS AND METHODS

As the objects of the study, samples of VOD obtained from different manufacturers and provided by Yuzniy Polyus, LLC, Kropotkin, Russia, were used.

The acid value of the VOD was determined according to GOST R 50457; peroxide ~~number~~ value - according to GOST R 51487; anisidinous value - according to GOST 31756; content of unsaponifiable substances - according to GOST 5479; and saponification value - according to GOST 5478.

The fatty acid composition of the VOD was determined according to GOST 31663 using a hardware-software system based on the Crystal 5000 gas chromatograph (Chromatek,

Russia). The samples were prepared in accordance with GOST 31665.

The content and composition of phytosterols were determined using the Crystal 5000 XMS gas chromatography-mass spectrometer (Chromatek, Russia). Standard samples were used for quantitative determination of phytosterols, as well as phytosterols isolated from vegetable oil using digitonin according to GOST 31979.

The content of tocopherols was determined according to GOST EN 12822 using the Agilent 1260 Infinity liquid chromatograph (Agilent Technology, USA).

The color of the VOD was determined in accordance with DIN 6162-2014 on the Lovibond PFX995 tintometer (Great Britain).

Spectral analysis in the IR region was carried out using a Cary 630 infrared spectrometer (Agilent Technologies, USA).

The content of nitrogen-containing substances was determined by the Kjeldal method according to the adapted procedure presented in GOST 31762.

The results were evaluated using modern methods of static reliability calculation using Statistica, Microsoft Office Excel, and Mathcad.

The studies were carried out on the equipment of the CCU "Research Center for Food and Chemical Technologies", "Kuban State Technological University".

RESULTS

The average results of studies of the chemical composition of the VOD samples are presented in Table 1.

The analysis of the data presented shows that the investigated samples of VOD by the content of fatty acids can be divided into two groups: high (from 58 to 86%) and low (about 30%) content of free fatty acids. The average content of free fatty acids of the majority (more than 65%) of VOD is 70%.

All samples are characterized by the high saponification values, which define the quantity of substances interacting with alkali in the process of alkaline hydrolysis.

The average value of the " content of unsaponifiable substances" for most samples is 14%, with an average phytosterols content of 4% and tocopherols of 2%.

The obtained data are consistent with the data of scientific literature on the composition of VOD, according to which the content of free fatty acids in the VOD is from 30 to 85%, tocopherols - from 1 to 8%, phytosterols and their ethers - from 2 to 15%, acylglycerols - up to 20%, and various substances, including anti-nutrient organic and inorganic ones - up to 10% [3. 4].

Among the samples studied, the essential differences of the analyzed parameters are characteristic for sample HE10. This sample of VOD is characterized by high content of dark colored compounds, primary and secondary oxidation products with low content of unsaponifiable substances, phytosterols and tocopherols and sufficiently low content of free fatty acids. Taking this into account, VOD with such indicators should not be considered as raw material for obtaining the desired products: fatty acids and (or) monoacylglycerols, a concentrate of phytosterols and tocopherols.

In order to identify the substances that determine the dark brown color of the VOD, the experiments were carried out on "exhaustive adsorption" by mixing the VOD with adsorbent (BASF F-160 bleaching earth) in 1:1 ratio and successive exhaust fraction elutions with a nonpolar (hexane) and polar (ethanol 96%) solvent.

The hexane fraction was characterized by a light yellow color. The ethanol fraction was of dark brown color.

Each fraction after removal of the solvent under vacuum was analyzed by chromatography-mass spectrometry.

The chromatogram of the relevant ethanol fraction showed pronounced peaks that were absent from the hexane fraction chromatogram. Mass-detection and recognition of substances using the NIST library allowed the identification of substances contained in the ethanol fraction in the prevailing quantities. The list of detected substances and their brief characteristics are presented in Table 2.

Structural formulas for the substances found are shown in Figure 1.

Table 1 - Features of VOD of Russian manufacturers

Sample cypher	Acid value, mg KOH/g	Peroxide, value meq/kg	Saponification, value mg KOH/g	Anisidine, value cond. units	Color number, mg I_2 / Lovibond	content of unsaponifiable substances,%	content of phytosterols,%	content of tocopherols, %
HE 1	150.2	2.3-8.4.	185	73.2	93 / 5.4R 46.0Y	13.3	6.2	2.00
HE 2	150.3	8.6	176	48.5	100 / 5.9R 51.0Y	13.2	4.5	1.5
HE 3	150.7	3.5	198.7	119.1	41 / 2.9R 19.0Y	18.2	5.5	1.7
HE 4	49.3	2.6	186.9	170.8	Above 500	17.8	3.0	0.7
HE 5	116.8	2.9	209.6	66.6	58 / 4.3R 23.6Y	14.2	4.7	1.9
HE 6	121.7	3.7	194.9	39.2	28 / 4.1R 15.6Y	12.5	5.0	2.3
HE 7	158.7	5.4	198	79.3	65 / 4.2R 26.0Y	15.0	4.1	1.6
HE 8	161.6	4.2	202	75.7	42 / 3.2R 16.0Y	-	-	-
HE 9	172.0	3.2	204	74.6	32 / 2.4R 15.0Y	15.0	4.8	2.0
HE 10	63.7	15.7	227.8	208.5	Above 500	3.3	0.5	0.1
HE 11	155.7	6.1	193.0	137.1	220 / 13.9R 70.5Y	13.6	3.7	0.7
HE 12	139.3	1.2	184.6	116.5	14 / 1.1R 6.8Y	25.4	6.5	3.8

Table 2 - Composition of substances predominantly contained in the ethanol extract (in descending order)

Item No.	Substance name	Chemical formula	Molecular mass, Da	Substance class	CAS No.
1	9,12-Octadecadenoic acid (Z,Z)-, 2-hydroxy-1-(hydroxymetil) ethyl ester	$C_{21}H_{38}O_4$	354.52	Mono-glycerides	3443-82-1
2	Hexadecanoic acid, 2-hydroxy-1-(hydroxymetil) ethyl ester	$C_{19}H_{38}O_4$	330.50	Mono-glycerides	23470-00-0
3	12-Hydroxy-16,17-dimethylpregn-4-ene-1, 20-dione	$C_{23}H_{34}O_3$	358.51	Steroids	-
4	Kauran-18-al, 17-(acetiloxe)-, (4 beta)-SS1	$C_{22}H_{34}O_3$	346.51	Acids	22910-60-7
5	Limonen-6-ol,pivalate	$C_{15}H_{24}O_2$	236.35	Monoterpenes	-

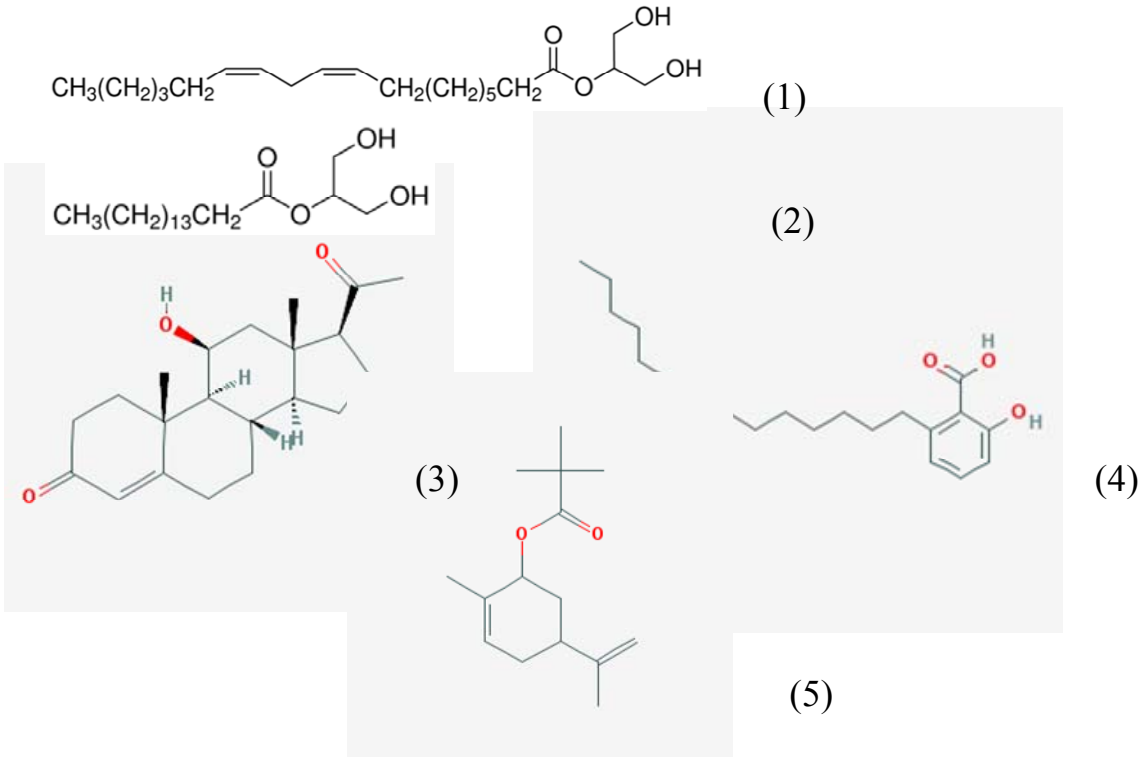

Figure 1 – Structural formulas of the compounds shown in Table 2

The analysis of the data presented shows that substances predominantly contained in the ethanol extract are polar but their presence does not explain the dark color of the heavy ends.

It is known that at the influence on vegetable oils of high temperatures (250-290°C) even under reduced pressure, partial decomposition of triacylglycerols occurs, accompanied by the formation of volatile low-molecular substances, including acrolein, free fatty acids, ketenes and a number of unsaponifiable substances, including hydrocarbons.

Unsaturated fatty acids can react in an aldol condensation reaction, which results in substances of different molecular weight, characterized by a brown color.

Ketenes, having high reactivity, are capable of polymerization with the formation of a number of substances with different molecular masses.

It is also known that, under the influence of high temperatures, oxidation reactions are catalyzed, accompanied by the formation of primary and secondary oxidation products.

As can be seen from the data presented in Table 1, for the majority of investigated ~~heavy end~~ VOD samples, the anisidine value is fairly high, on the average, from 40 to 80 cond. units. Taking into account that the anisidine values characterize the content of carbonyl compounds, their importance correlates with the content of aldehydes and ketones in the VOD.

The aldehydes and ketones formed during the oxidation of vegetable oils of the linoleic type are not the colored compounds. This is confirmed by the absence of clear correlation between the anisidine value and the chromaticity of the samples studied.

However, it should be noted that individual aldehydes are able to enter into the aminocarbonyl reaction, which causes the development of the so-called carbonylamine browning. As a result, compounds with imine bonds C = N are formed. Imines readily undergo an addition and polymerization reaction to form macromolecular brown products.

Given this, the content of nitrogen in the VOD samples was determined. Nitrogen was determined by the Kjeldahl method on a semi-automatic unit.

It was found that the nitrogen content in the samples was from 0 to 0.12%.

Thus, it can be concluded that the better the initial oil is prepared for physical refining, the lower the residual content of phospholipids is, as one of the main source of nitrogen-containing substances in vegetable oils, and the lower the content of brown pigments in the VOD is.

This is confirmed, for example, by sample HE12 obtained by distillation refining of sunflower oil, previously subjected to enzymatic degumming, providing the maximum

removal of phospholipids. Taking this into account, the low chromaticity of VOD with a high anisidine value can be explained by the absence of nitrogen-containing compounds, and, consequently, the impossibility of the carbonylamine browning reaction.

The formulated conclusion is consistent with the results of the studies presented in the scientific literature.

For example, in [17] the results of investigations of chromatographic separation of VOD into fractions of different polarity are presented, using petroleum ether, ethyl acetate and ethanol. The fractions obtained were analyzed by the IR Fourier spectrometry and TLC.

As a result of the distillation of the solvents, three fractions were obtained, the yield of which was: 88.3% - the first; 9.7% - the second, and 0.8% - the third. The mass fraction of the adsorbed residue, respectively, was 1.2% of the weight of the VOD. Each fraction was analyzed by the IR Fourier spectrometry and TLC.

It has been found that the first fraction (88%) is predominantly a mixture of nonpolar or weakly polar substances, such as esters of sterols and fatty acids, as well as acylglycerols. The second fraction (10%) includes medium polar substances, such as polyalcohol or carbohydrates with long groups of carbon chains. The third fraction (1%) includes polar substances the chemical composition of which, along with carbonyl and hydroxy groups, includes the amino groups and nitrile groups, which determines the dark brown color of this fraction.

As a result of reproducing the experiment with the samples of the HE1 and HE2 VOD, similar results were obtained.

Infrared (IR) Fourier spectroscopy methods were also used to study the composition of the VOD.

Figure 2 shows the IR spectra obtained for individual samples of VOD.

Analysis of the presented spectra shows that for all samples a characteristic intense absorption band at a wavelength of 1,707 cm^{-1} is observed, which refers to the vibrations of the C = O group in dimers of carboxylic acids. This band also coincides with the absorption band on the IR spectrum of oleic acid, while in the region of a wavelength of 1,740 cm^{-1} there is one more absorption band of medium intensity, which can be attributed to the stretching vibrations of the C = O group in esters.

A comparative analysis of the spectra of different samples shows that the intensity of the absorption bands depends on the composition of the VOD components therein. Thus, the maximum intensity of the absorption bands at 1,707 cm^{-1} is manifested in the spectra of the HE2, HE6, HE12 samples, in which the acid value is 151.2, respectively; 121.7 and 139.3 mg KOH/g. At the same time, the intensity of the band at 1,707 cm^{-1} in the spectrum of HE4 sample is much smaller, which is probably due to the low acid value of this sample, which is 49.3 mgKOH/g.

On the contrary, the intensity of the absorption band at 1,740 cm^{-1} of the spectrum of the HE4 sample is significantly higher than the intensity of the same band in the spectra of the HE2, HE6 and HE12 samples. This allows us to conclude that in this sample the content of esters is higher than in others. The difference in the intensity of the absorption band is also observed at 1,160 cm^{-1}, which can be attributed to the stretching C-O vibrations in ketals and acetals. The highest intensity of this band is observed in the spectra of the HE4 sample. This is consistent with the highest anisidine value of this sample.

On the whole, the results obtained show that the VOD obtained by the majority of large Russian oil processing enterprises can be considered as a promising raw material for obtaining high-tech innovative products – concentrates of purified fatty acids, as well as concentrates of natural phytosterols and tocopherols.

Analysis of the data obtained also indicates the advisability of developing technical documentation for VOD used as raw materials for obtaining the above-mentioned target products, where the requirements ensuring economic efficiency of their processing will be regulated.

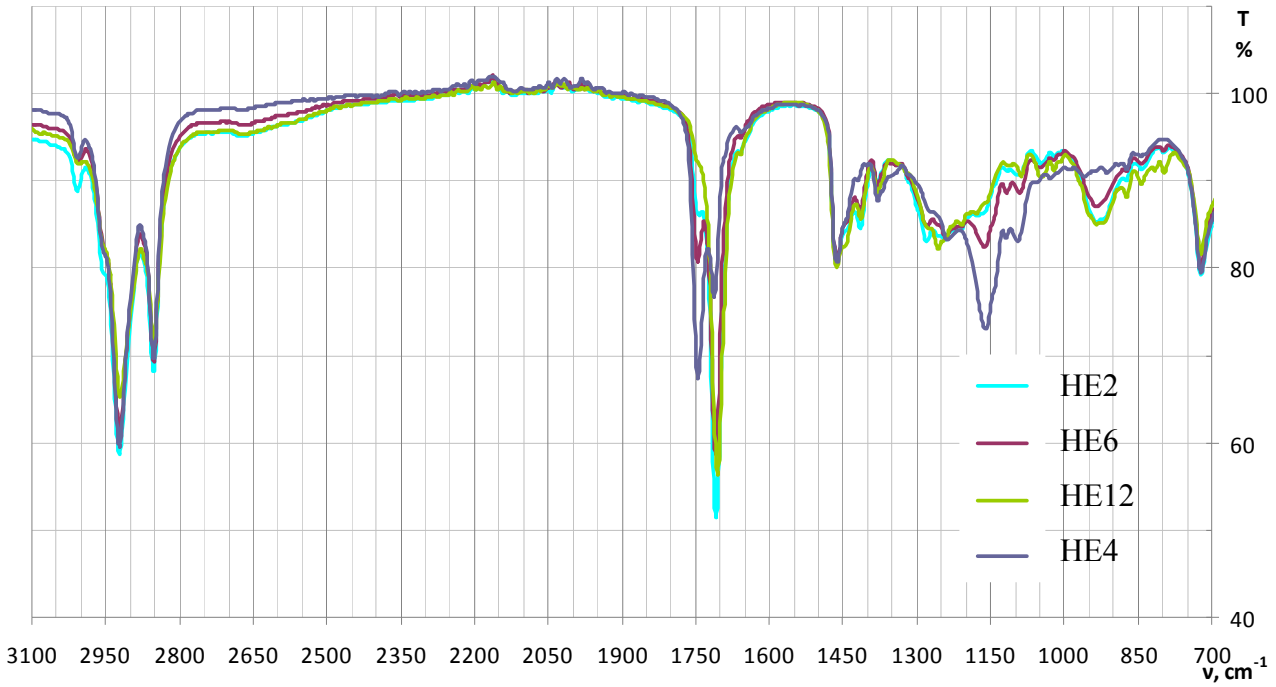

Figure 2. IR spectra of VOD samples

ACKNOWLEDGMENTS

The work was financially supported by the Ministry of Education and Science of the Russian Federation in the framework of the implementation of Contract No. 03.G25.31.0262 dated April 28, 2017, for the implementation of a comprehensive project for the creation of high-tech production (RF Government Decree No. 218 dated 09.04.2010).

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