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Features of the main components of vegetable oils' distillates

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Abstract

The work is devoted to the identification and research of the chemical composition of the main components of vegetable oils' distillates (VOD) obtained by large Russian oil processing enterprises during the deodorizing process combined with distillation removing of free fatty acids (FFA). The features of fatty acids' composition are presented as the main component of distillation refining. Another important component is the fraction of unsaponifiable substances, the content of which averages 15%. The composition of the unsaponifiable fraction is presented, which includes tocopherols, phytosterols and various minor components. The phytosterols, tocopherols and minor components have been identified, among which the nitrogen-containing substances, hydrocarbons and oxidation products have been detected. These components have different degrees of volatility, determine the dark color of the VOD and have a negative impact on the efficiency of the processes of splitting the VOD into components. Based on the analysis of the obtained results, it has been concluded that for efficient processing of distillation VOD in order to obtain purified fatty acids and concentrates of the valuable substances' unsaponifiable fraction, it is necessary to preliminarily remove the undesirable minor components.

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

INTRODUCTION

The VOD produced by processing of oil-bearing crops, being the basic ones for the Russian agro-industrial complex, such as sunflower, soybean and rapeseed, in addition to fatty acids, contain significant amounts of natural biologically active substances, such as essential fatty acids, tocopherols (including vitamin E), calciferols (including vitamin D) and phytosterols [1, 2].

The main purpose of the vegetable oils' distillation refining is to remove free fatty acids and odorizing substances. Taking into account that a number of concomitant substances of vegetable oils constituting the unsaponifiable fraction have similar volatility with fatty acids, the obtained VOD contain aliphatic alcohols, tocopherols, phytosterols, as well as a number of other compounds along with fatty acids and odorizing substances. Such compounds contain substances characteristic for the lipid complex of initial oil seeds, as well as products of various adverse reactions that occur under the technological influences.

In a number of countries, the VOD obtained from distillation refining are used as the main raw material for the production of natural fatty acids and concentrate of the valuable substances' unsaponifiable fraction such as phytosterols and tocopherols [3, 4].

In the Russian Federation, the volume of VOD performed by enterprises of the fat-and-oil complex is about 7,000 tons per year [5]. However, the obtained VOD of distillation refining are mainly used for technical or fodder purposes and are not subjected to deep technological processing [1, 6].

According to the literature data, the VOD contain an average of 60% of free fatty acids; 6% of tocopherols; 5% of phytosterols; 2.5% of phytosterol esters and about 10% of various including anti-nutrient organic and inorganic substances [7-9]. The latter group includes a variety of unidentified substances, including thermal degradation products and oxidative degradation of lipids and concomitant substances present in the raw vegetable oils [8]. The presence of these substances in the VOD significantly complicates the process of their processing with the purpose of allocating individual components in the form of independent products.

Considering the prospect of using the VOD as raw material for the allocation of valuable substances, the identification of constituent components is actual.

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 fatty acid composition of the heavy ends of vegetable oils' distillation refining 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 of unsaponifiable substances was determined according to GOST 5479.

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.

Identification of the substances included in the unsaponifiable fraction was carried out using the Crystal 5000 XMS gas chromatography-mass spectrometer (Chromatek, Russia) and the NIST library.

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

The results were evaluated using modern methods of static reliability calculation using Statistica ~~6.0~~, Microsoft Office Excel ~~2007~~, 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

Fatty acids are the main components (more than 60%) of the test samples of the VOD.

The results of determining the fatty acid composition of the test samples are shown in Table 1.

It is shown that the quantitative and qualitative composition of the prevailing fatty acids corresponds to the fatty acids' composition of the feedstock. Thus, a comparative analysis shows that the majority of the VOD test samples are obtained during distillation refining of the linoleic type oils, with a high probability of sunflower oil. At the same time, a large number of minor acids that are absent in vegetable oils are present in the fatty acid composition of the VOD.

This indicates a possible course of oxidative and thermal transformations of lipids and accompanying substances during distillation refining.

The fraction of unsaponifiable substances (about 15%) is another important component of the VOD. In order to study the chemical composition of the unsaponifiable fraction, its separation and identification of the components were carried out by the method of gas chromatography-mass spectrometry.

Table 2 shows the composition of the substances of unsaponifiable fractions isolated from typical samples of the VOD.

As can be seen from the data presented, the VOD contain a wide range of organic substances of various nature. At the same time, the unsaponifiable fraction contains hydrocarbons, aliphatic and alicyclic alcohols, aldehydes, terpenes, phytosterols, tocopherols and their derivatives.

The presence of nitrogen-containing substances in the unsaponifiable fraction (serial number 29 and 36) is of interest.

The mass spectra and structural formulas of these compounds are shown in Figure 1.

Table 1 - Fatty acid composition

Name of fatty acid	Fatty acids composition, % to the sum of fatty acids:					
	HE1	HE2	HE5	HE8	HE12	Sunflower oil
$C_{4:0}$ Butyric acid	<0.1	-	-	<0.1	-	-
$C_{6:0}$ Hexanoic acid	<0.1	-	-	<0.1	<0.1	-
$C_{8:0}$ Decanoic acid	<0.1	-	<0.1	-	-	
$C_{10:0}$ Decatonic acid	<0.1	0.1	<0.1	<0.1	0.1	-
$C_{10:1}$ Decenoic acid	<0.1	0.1	0.1	<0.1	<0.1	-
$C_{11:0}$ Hendecanoic acid	<0.1	-	<0.1	-	-	
$C_{12:0}$ Lauric acid	<0.1	0.3	<0.1	-	-	-
$C_{13:0}$ Tridecanoic acid	<0.1	0.1	0.1	<0.1	0.1	
$C_{14:0}$ Myristic acid	0.1	0.1	0.2	0.1	0.1	0.1
$C_{14:1}$ Myristoleic acid	<0.1	0.1	0.2	<0.1	0.2	-
$C_{15:0}$ Pentadecanoic acid	<0.1	<0.1	<0.1	<0.1	<0.1	-
$C_{15:1}$ Pentadecenic acid	0.1	<0.1	0.1	-	0.1	-
$C_{16:0}$ Palmitic acid	9.4	9.1	11.5	8.6	11.4	6.1
$C_{16:1}$ Palmitoleic acid	0.1	0.1	0.1	0.1	0.1	0.1
$C_{17:0}$ Margaric acid	0.1	0.1	0.1	0.1	0.2	-
$C_{17:1}$ Heptadecenoic acid	<0.1	0.7	<0.1	<0.1	<0.1	-
$C_{18:0}$ Stearic acid	4.4	3.7	3.0	4.2	4.3	3.0
$C_{18:1\,t}$ Elaidic acid	0.1	0.1	2.0	0.1	0.3	-
$C_{18:1}$ Oleic acid	25.5	22.1	31.6	24.9	29.3	30.3
$C_{18:2t}$ Linoleic acid	0.2	<0.1	0.1	<0.1	0.2	-
$C_{18:2}$ **Linoleic acid**	54.7	60.7	49.0	59.1	48.4	59.2
$C_{18:3}$ Linolenoic acid	0.7	0.3	0.2	0.3	0.4	<0.1
$C_{20:0}$ Arachic acid	0.5	0.4	0.3	0.4	0.7	0.2
$C_{20:1}$ Eicosenic acid	0.2	0.2	0.2	0.2	0.2	0.1
$C_{21:0}$ Geneicosenic acid	<0.1	<0.1	<0.1	<0.1	0.1	-
$C_{20:2}$ Eicosadienoic acid	<0.1	-	-	<0.1	-	
$C_{20:3}$ Eicosatrienoic acid	0.2	0.1	0.1	0.1	0.3	-
$C_{20:4}$ Arachidonic acid	1.8	0.1	<0.1	<0.1	<0.1	-
$C_{22:0}$ Behenic acid	0.9	0.6	0.6	0.8	1.7	0.7
$C_{22:1}$ Erucic acid	-	<0.1	<0.1	-	-	<0.1
$C_{22:2}$ Docosadienoic acid	0.2	0.2	0.1	0.2	0.6	-
$C_{22:3}$ Docosatrienoic acid	-	-	-	-	-	-
$C_{22:6}$ Docosahexaenoic acid	0.1	0.1	0.1	<0.1	0.1	
$C_{23:0}$ Tricosanoic acid	0.1	0.1	<0.1	0.3	<0.1	-
$C_{24:0}$ Lignoceric acid	0.4	0.5	0.2	0.4	1.0	0.2
$C_{24:1}$ Nervonic acid	0.1	<0.1	0.1	0.1	0.1	-
Note: hereinafter HE1, HE2, ..., HEi is the designation of the analyzed samples of VOD						

Table 2 - The composition of the substances of unsaponifiable fraction of the VOD.

Item No.	Substance name	Substance class	CAS No.	Note:
1	6,10,14-Trimethyl-pentadecane-2-ol	High molecular weight saturated alcohol	69729-17-5	
2	Neofitadiene	Alken with two conjugated double bonds	504-96-1	
3	3,7,11,15-Tetramethyl-2-hexadecene-1-ol	High molecular weight unsaturated alcohol	102608-53-7	
4	6-Pentadecene-1-ol	High molecular weight unsaturated alcohol	77899-11-7	
5	1,6,10,14-Hexadecatetraen-3-ol	High molecular weight unsaturated alcohol	1113-21-9	
6	17-Norkaur-15-ene	Cyclic double bond compound	3564-54-3	
7	α-Tocopheryl acetate	Tocopherol	58-95-7	
8	Trachylobane	Limit cyclic compound	5282-35-9	
9	Atis-15-ene	Cyclic double bond compound	5975-29-1	
10	Kaur-15-ene	Cyclic double bond compound, diterpen	5947-50-2	Gibberellin phytohormone
11	Squalene	Hydrocarbon	111-02-4	
12	11,14-Eikosadienoic acid methyl ester	Fatty acid methyl ester	2463-02-7	
13	Octadecane	Alcan	55282-12-7	
14	Cyclopentane Ethanol	Cyclic dihydric alcohol	485-42-7	
15	Hibaen	Cyclic double bond compound	2359-73-1	
16	Eikozan	Alcan	1560-84-5	Isomer
17	Ergost-5-en-3-ol oleate and acetate	Esters of phytosterols	2458-53-9	
18	γ -Sitosterol	Phytosterol	83-47-6	
19	Campesterol	Phytosterol	474-62-4	
20	9,17-octadecadienal	unsaturated aldehyde	56554-35-9	
21	Stigmasterol	Phytosterol	83-48-7	
22	7,11,15-Trimethyl-3-methylhexadeca-1,6,10,14-tetraene	unsaturated hydrocarbon	70901-63-2	
23	Atis-16-ene	Cyclic double bond compound	5975-29-1	
24	Kaur-16-ene	Cyclic double bond compound, diterpen	562-28-7	
25	6,9-Pentadecadiene-1-ol	Unsaturated alcohol	77899-11-7	
26	Octadecane	Saturated hydrocarbon	55282-12-7	Isomer
27	Pregn-16-en-20-one	Cyclic compound with a keto- and ester group	7/2/2601	Hormone
28	Ergosta-5,22-dien-3-ol	Cyclic compound with ester group, phytosterol derivative	2458-53-9	
29	2- (3,7-Dimethyl-octa-2,6-dienylidene) -4,8-dimethyl-non-3,7-dienetryl	Amino group containing nitrile	absent	Nitrogen-containing compound
30	Stigmast-5-ene-3-ol oleate	Sterol and oleic acid ester	absent	
31	Dihydrosmilagenin 26-tosylate	A p-toluenesulfonic acid ester of a cyclic alcohol with an ether group as part of one of the cycles	absent	
32	Heptadecane	Saturated hydrocarbon	54833-48-6	Isomer
33	9,19-Cycloergost-24 (28) -ene-3-ole acetate	Double bond cyclic ether, a derivative of phytosterols	10376-42-8	There are three-five- and six-membered cycles
34	Fenretinide	Retinoid, a vitamin A derivative	65646-68-6	
35	Stigmastane-6,22-diene	Cyclic compound with two double bonds, a derivative of phytosterols	107304-12-1	
36	Bicyclo [3.1.0] hexane-2-one dinitrile	Dinitrile of a cyclic ketone with a double bond	absent	Contains an eight-membered cycle with a double bond, a three- and five-membered cycle

According to the presented structural formulas, it can be seen that compound No. 26 contains an imine bond. The presence of these compounds indicates the contribution of nitrogen-containing substances, including those that are the products of oxidative and thermal transformations of lipids, to the provision of dark brown distillation lines.

The internal standard method was used to analyze the quantitative composition of the components of the unsaponifiable fraction.

Cholesterol has been chosen as the internal standard, since this substance is sterol and refers to unsaponifiable lipids, and it has a well-resolved peak; it does not react with other components of the sample and is absent in the mixture under analysis.

The concentration of the determined component in the mixture under analysis is calculated by the formula:

$$C_i = \frac{S_i \cdot K_i \cdot M_{st}}{S_{st} \cdot M_n} * 100, wt.\%$$

where S_i is the area of the relevant peak; K_i is the calibration factor; M_{st} is the mass of the added internal standard; S_{st} is the peak area of the standard; M_n is the mass of the sample of the mixture under analysis, to which an internal standard has been added.

In addition, the use of an internal standard makes it possible to verify the accuracy of the method for determining unsaponifiable substances.

During the analysis, an exact amount (0.10 g) of cholesterol was added to the test sample. The sample was then analyzed with and without the additive. Chromatograms of the unsaponifiable substances of the samples are presented in Figures 2 and 3. The results of the analysis are shown in Table 3.

The relative deviation of the result obtained from the absolute value is 5%, which is acceptable for this method of analysis.

Based on the results obtained, as well as using calibrations obtained using standard phytosterols, the composition of the sterols contained in the test samples of the distillation refining of heavy end samples has been determined.

Table 4 presents the results of determining the composition of phytosterols in individual samples of the heavy ends under analysis.

The analysis of the data presented shows that the phytosterols contained in the VOD contain campesterins, stigmasterols and β-sitosterols. For all samples, β-sitosterols predominate in phytosterols (from 70 to 75%), which is characteristic for lipids of sunflower seeds. Campesterol and stigmasterol are almost in equal quantities (from 10 to 20%) with a slight predominance of campesterols. Brassicasterols are not found, which is also characteristic of lipids of sunflower seeds. The mass spectra and structural formulas of the isolated phytosterols are shown in Figure 4.

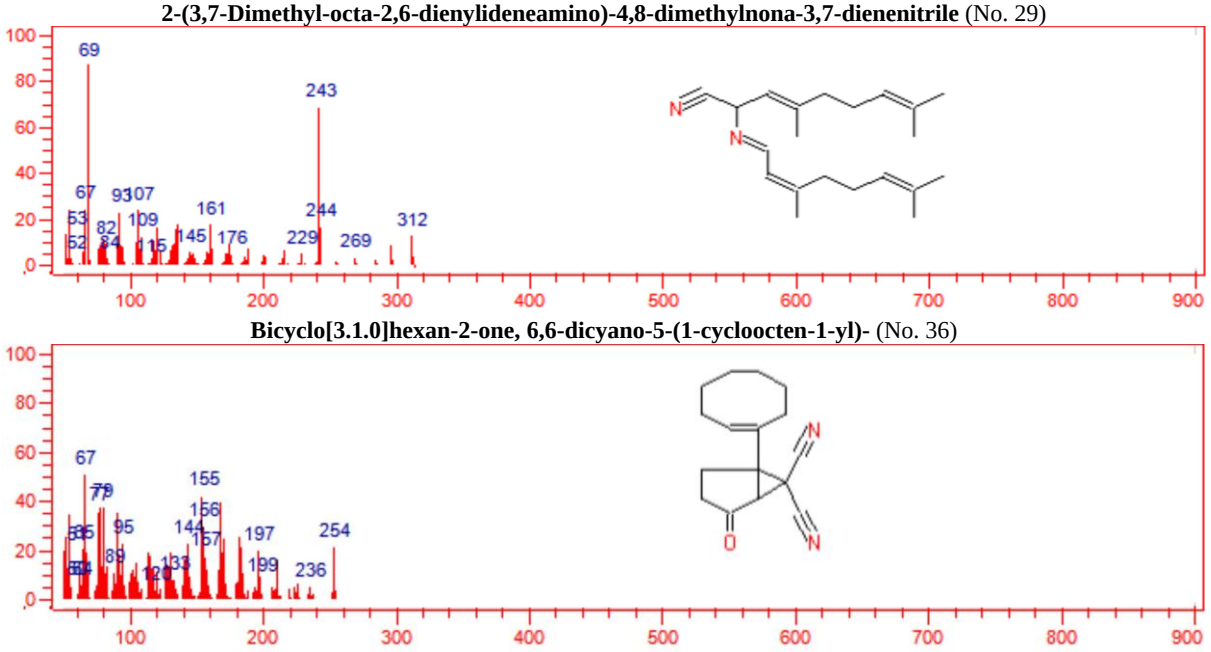


Figure 1 – Mass spectra of nitrogen-containing compounds

Table 3 - Analysis results

Indicator Name	Indicator Value	
	Sample without the additive	Sample with additive
Amount of additive (cholesterol), g	absent	0.10
content of unsaponifiable substances, %	4.2	7.6
Amount of unsaponifiable substances in a sample, g	0.13	0.23
Cholesterol content,% (calculated by chromatogram)	absent	0.09

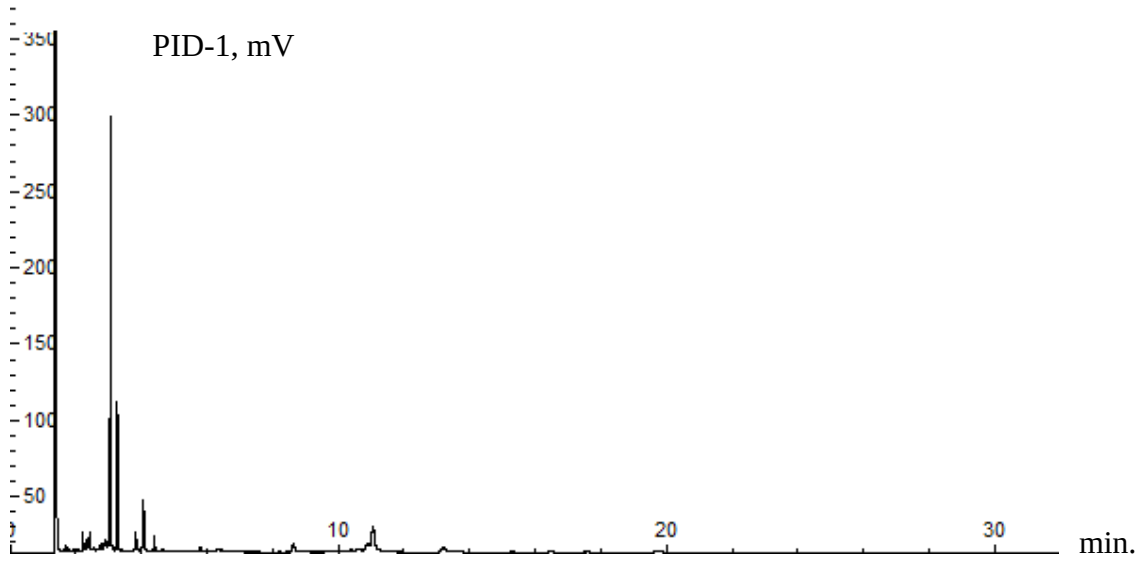


Figure 2 – Chromatogram of unsaponifiable substances of the analyzed sample without additive

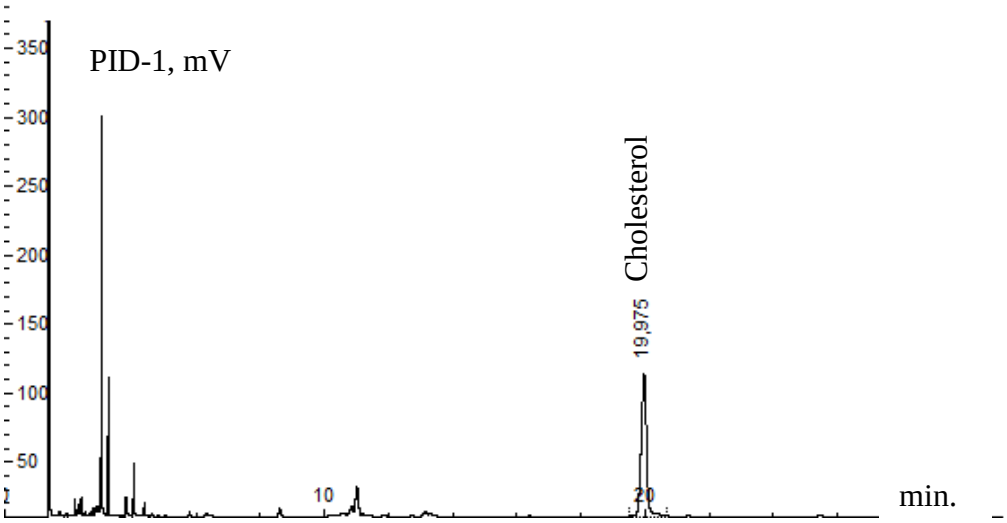
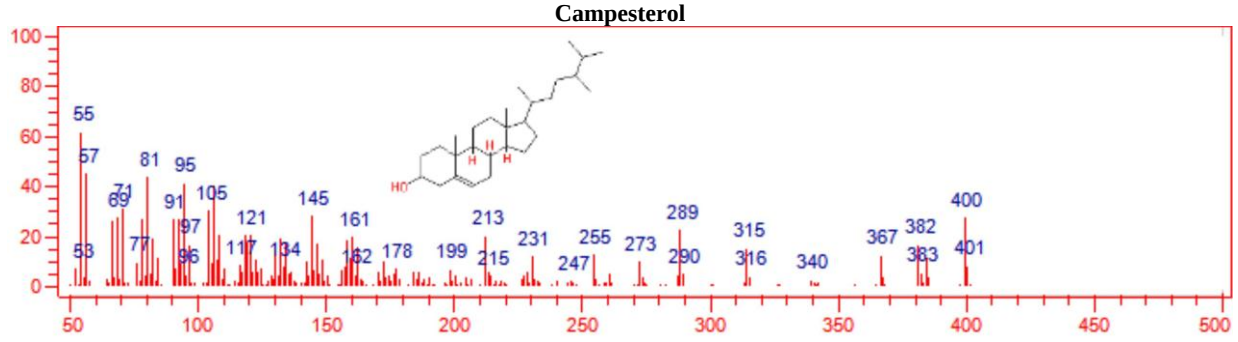
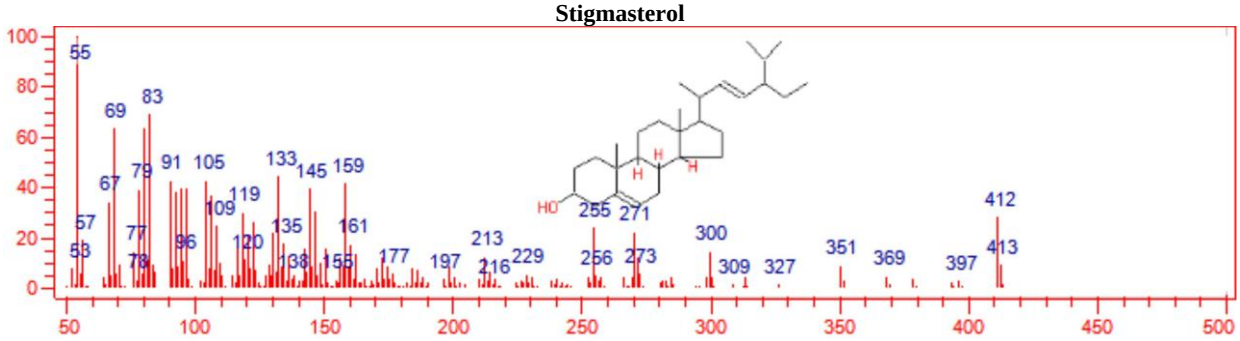


Figure 3 – Chromatogram of unsaponifiable substances of the analyzed sample with the addition of cholesterol

Campesterol



Stigmasterol



β-sitosterol

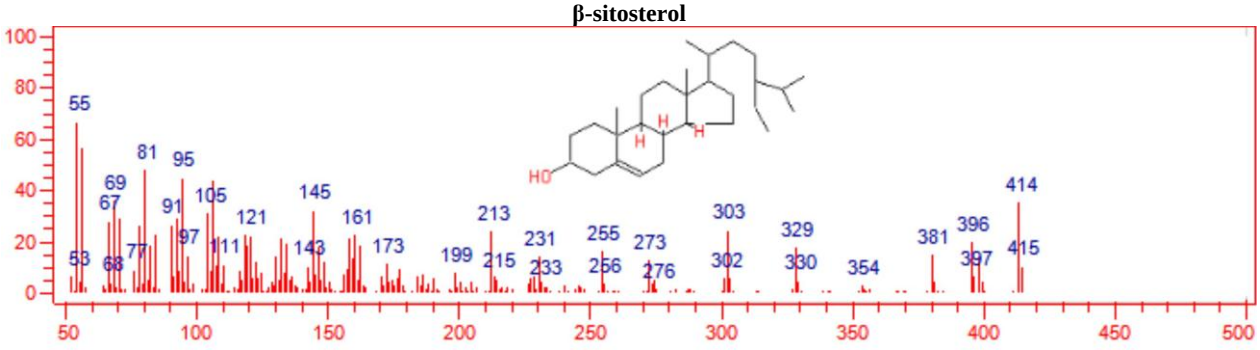


Figure 4 – Mass-spectra and structural formulas of isolated phytosterols

Table 4 - The composition of phytosterols contained in the VOD

Indicatorname	Indicator Value				
	HE2	HE4	HE5	HE6	HE11
content of phytosterols,%, including:	4.5	3.0	4.7	5.0	3.7
campesterol	0.6	0.5	0.8	0.6	0.5
stigmasterol	0.5	0.4	0.5	0.6	0.4
β-sitosterol	3.4	2.1	3.4	3.8	2.8
brassicasterol	Abs.	Abs.	Abs.	Abs.	Abs.

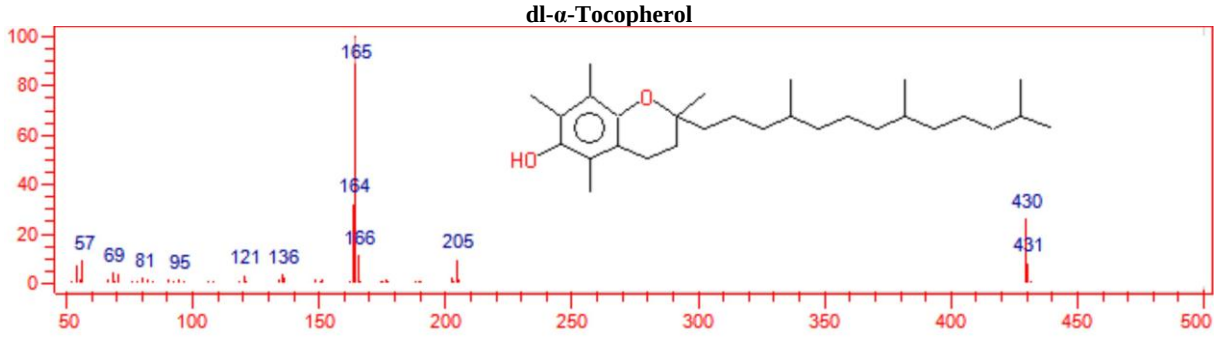


Figure 5 – Mass-spectra and structural formula of isolated tocopherol

The composition of tocopherols was also analyzed by chromatography-mass spectrometry with parallel determination applying the HPLC methods with the use of the standard samples in accordance with GOST EN 12822.

The results obtained by different methods were characterized by high convergence (the relative error was not more than 5% with a confidence level of 0.95).

It has been established that the tocopherols present in the analyzed samples of the VOD are mainly represented by α-tocopherols, which is characteristic of the lipids of sunflower seeds.

The mass spectra and structural formula of the isolated tocopherols are shown in Figure 5.

The analysis of the obtained results has shown that the majority of the test samples of the distillation refining of VOD contain the target components - fatty acids, phytosterols and tocopherols in significant amount as compounds with native structure and chemical composition.

This confirms the advisability of using the VOD by Russian oil processing refineries as feedstock for obtaining high-tech innovative products - concentrates of purified fatty acids, as well as concentrates of natural phytosterols and tocopherols.

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