

(H⁺ form). The ash content of the demineralized PSs was 0.4-0.5%. The amounts of uronic anhydride in the WSPSs were determined by complexometric titration [2] (cowberries 73.7%; myrtle whortleberries, 75.1%; small cranberries, 78.2%).

The hydrolysis of the demineralized PSs, the neutralization of the hydrolysates, and the subsequent operations with them were carried out as described previously [1]. The WSPSs of the hydrolysates obtained were investigated by descending PC in the butan-1-ol-pyridine-water (6:4:3) system at 19-21°C for 42-47 h (Leningrad type M ["slow"] paper, density 80 g/m²). The monosaccharides were revealed with aniline phthalate. It was found that PCs of the cowberry, myrtle whortleberry, and small cranberry consisted of seven monosaccharides: D-galacturonic acid, D-galactose, D-glucose, L-arabinose, D-xylose, and L-rhamnose and one unidentified monosaccharide present in traces which was chromatographically more mobile than L-rhamnose.

The amounts of the neutral sugars - galactose, glucose, arabinose, xylose, and rhamnose - were determined by direct densitometry of the chromatograms on an automatic integrating microdensitometer of type 3 CS (Joyce-Loebl); in the WSPSs of the cowberry they were present in a ratio, respectively, of 2.5:1.9:2.2:1.0:1.0; in the myrtle whortleberry, 5.0:1.1:3.2:1.9:1.0; and in the small cranberry, 1.8:1.2:3.3:1.3:1.0. The figures obtained permit the PSs of the fruit of these plants to be assigned to the class of pectin substances.

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STEREOSPECIFIC ANALYSIS OF TRANSESTERIFIED TRIACYLGLYCEROLS

V. Sh. Salidzhanova, S. G. Yunusova,
S. D. Gusakova, and A. I. Glushenkova

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The transesterification of fats is discussed in many publications [1], but inadequate attention has been devoted to the structures of the triacylglycerols (TAGs). In order to determine the recombination of acyl radicals, we have studied their distribution in the molecules of the TAGs in the process of transesterification in a model mixture consisting of triolein (TO) and tripalmitin (TP), synthesized by ourselves.

For the synthesis we used dynamite-quality glycerol and the 16:0 and 18:1 fatty acids. The latter was obtained by fractionating olive oil fatty acids as described by Jantzen and Andreas [2]. The TO and TP were synthesized at 180°C in a current of nitrogen for 5 h, using as catalyst K₂CO₃ in an amount of 0.2-0.3% on the mass of the fatty acids. The glycerol was added in 30-40% excess as compared with the amount calculated theoretically. The completeness of esterification was checked by TLC [3]. The reaction products were separated by column chromatography (CC), the homogeneity of the fractions being checked by TLC in comparison with model samples, and their quantitative ratios were determined gravimetrically. The following results were obtained (wt. %): TAGs, 40-57; sum of 1,3- and 1,2(2,3)-diacylglycerols (DAGs), 33-26; free fatty acids (FFAs) 21-13.5; and monoacylglycerols (MAGs) 6.5-4.0. These results show that in addition to the desired product - triacylglycerols - there was a considerable amount of intermediate products resulting from incomplete acylation. Consequently the completeness of esterification was judged only from the results of TLC and not from the acid No. [4].

The pure TO and TP were transesterified in a ratio of 4:1 at 65°C using sodium ethanoate as catalyst (0.2% calculated as sodium on the total mixture) with stirring for 50 min and subsequent 10-min standing. Then the reaction mixture was extracted with hexane, washed with distilled water, and dried over Na₂SO₄.

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The reaction products were freed from impurities by CC, their purity being checked by TLC. The result showed that the transesterificate contained, in addition to TAGs (30-70%) DAGs (mainly the 1,3-isomer), MAGs, and traces of FFAs.

The structure of the TAGs was calculated by means of the formulas of mathematical statistics [5], and they were also determined by stereospecific analysis [6]. The distribution of the fatty acids over the three positions of the transesterified TAGs are given below (mole %):

	16:0	18:1
TAGs	20.5	79.5
sn-1 position	24.9	75.1
sn-2 position	13.4	86.6
sn-3 position	22.9	77.1

From the results obtained we calculated the stereospecific composition of the TAGs in the transesterificate. The eight individual TAGs given below (with their amounts, mole %) were obtained:

Species of TAG	Calculated statistically	Found experimentally
PPP	0.8	0.8
OOO	51.2	50.1
PPO	3.2	2.6
OPP	3.2	2.3
POP	3.2	4.9
OOP	12.8	14.9
POO	12.8	16.7
OPO	12.8	7.7

Under these conditions of transesterification, the recombination of the acyl radicals was close to the statistical distribution. The difference in the amounts of the species POP and OPO can be explained by the fact that fatty acyl radicals in the sn-1 and sn-3 positions of TAGs are less mobile than in the sn-2 position.

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