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POSITION DISTRIBUTION OF PETROSELINIC ACID IN THE TRIACYLGLYCEROLS OF *Acanthopanax sessiliflorus*

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There is almost no information in the literature on the nature of the distribution in triacylglycerols (TAGs) of acids of unusual structure such as isooleic acids. One of such acids is the 18:1(6) acid (petroselinic), which is found mainly in the lipids in the seeds of representatives of the families *Umbelliferae*, *Garryaceae*, and *Araliaceae* [1].

Our aim was to ascertain the order of distribution of the 18:1(6) acid over the three positions of the TAGs of the seeds of *Acanthopanax sessiliflorus* (Purp. et Maxim) Seem. (family *Araliaceae*).

The triacylglycerols isolated from the seed lipids by the usual method [2] contained 52.8% of the 18:1(6) acid (wt.%, GLC). The analysis of the structure and compositions of the TAGs was carried out by Brockerhoff's method [3]. The amounts of the 18:1(6) acid in the TAGs, the monoacylglycerols (MAGs), the D-phosphatidylphenols (D-PPs), and the lysophosphatides (LPs) were calculated from the results of the GLC analysis of the fragments of periodate-permanganate oxidation of each group of acids isolated from the given fractions [2]. The calculation was based on the molecular mass of the methyl esters of the 9:0 and 12:0 acids. The results obtained are shown in Table 1.

The results show that in the TAGs of *A. sessiliflorus* the 16:0 and 18:0 saturated acids and the 16:1 monoenoic acid occupy the sn-1 position, and the 18:3 acid the sn-3 position. In the sn-2 position are bound 2/3 of the total amount of the 18:2 acid, and the remainder

TABLE 1. Fatty Acid Compositions of the Products of the Stereospecific Analysis of the TAGs of *Acanthopanax sessiliflorus*

Sample	Acid, moles-%, GLC						
	16:0	16:1	13:0	18:1 (b)	13:1 (a)	18:2	18:3
TAGs	3,1	Tr..	Tr..	52,8	8,9	34,1	1,1
DAGs	2,2	Tr..	Tr..	55,2[a]		42,6	Tr.
FFAs of phospholipolysis	2,7	Tr..	—	32,2		65,1	—
D-PPs	1,9	Tr..	Tr..	47,9	8,5	40,2	1,5
Positions in the TAGs:							
sn-1	8,4 (90,3)[b]	Tr.	Tr.	57,2 (36,1)	10,5 (39,3)	23,9 (23,4)	—
sn-2	—	—	—	20,3 (12,4)	9,8 (36,7)	69,9 (68,3)	—
sn-3	0,9 (9,7)	—	—	80,9 (51,5)	6,4 (24,0)	8,5 (8,3)	3,3 (100)

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of it is distributed unsymmetrically over the extreme positions of the acylglycerols with a preference for sn-1.

The bulk of the oleic — the 18:1(9) — acid is distributed almost uniformyl between the sn-1 and sn-2 positions, and only 24% of its total amount is bound in the sn-3 position. The distribution of the 18:1(6) acid is distinguished by a far higher specificity in relation to the extreme positions. Only 13% of the 18:1(6) acid sterifies the secondary hydroxyl of sn-glycerol, and more than half of its total amount is bound in the sn-3 position.

Thus, petroselinic acid is distributed nonuniformly over all the positions of sn-glycerol with a preference for the sn-3 position.

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PHOSPHORYLATION OF DIACYLGLYCEROLS

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The value of fats and their resistance to oxidation on storage are determined to a large extent by how the fatty acids are distributed between the sn-1, sn-2, and sn-3 positions of the triacylglycerols (TAGs).

The set of acids in each of three positions of the TAGs are determined by stereospecific analysis by Brocherhoff's method [1]. The method includes several stages: the production of racemic mixture of sn-1,2- and sn-2,3-diacylglycerols (DAGs) by pancreating hydrolysis or with the aid of a Grignard reagent, phosphorylation of the mixture of DAGs in order to obtain the total L- and D-phosphatidylphenols, and the lipolysis of this mixture with phospholipase A.

Phenyl phosphorodichloridate is the most frequently used phosphorylating agent for DAGs. As a rule, the reaction is performed at room temperature for a time ranging from 30 min [2, 3] tp 14-20 h [1, 4].

Phosphorylation under these conditions is accompanied by the formation of an artefactual compound of phenolic nature which it is not always possible to eliminate completely from the phospholipids by treatment with Na_2CO_3 and by adsorption chromatography. In the subsequent GLC analysis of the methyl esters of the fatty acids isolated from the synthetic phospholipids, this compound issues together with methyl palmitate, distorting the results of analysis.

We have succeeded in eliminating the formation of the artefact by modifying the method in the following way.

A weighed sample (20-150 mg) of a racemic mixture of sn-1,2- and sn-2,3-DAGs was dissolved in 0.5 ml of dry diethyl ether and the solution was cooled in ice. All the reagents and solvents were also cooled to 0°C. The mixing of the reagents was carried out at —5°C by the dropwise addition of a solution of the substance to a mixture of 2 ml of dry pyridine and 0.25 ml of freshly distilled phenyl phosphorodichloridate with shaking. The reaction mixture was kept at —5°C for 15-20 min and was then left at room temperature for 10-12 h. The subsequent treatment of the products and the isolation of fatty acid methyl esters from them were carried out as described previously [5].

TLC analysis was performed on a Chrom-4 instrument with a flame-ionization detector in the isothermal regime, using a 2.5 m × 4 mm column filled with 17% of poly(ethylene succinate)

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