ACYL ISOMERIZATION OF TRIGLYCERIDES DURING THEIR CHROMATOGRAPHY ON Al_2O_3

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The capacity of Al_2O_3 for causing the hydrolysis of esters and isomerizing the acyl residues in diglycerides (DGs) and monoglycerides (MGs) is well known [1], but this adsorbent is used for the isolation of triglycerides (TGs) [2] and some classes of phospholipids (PLs) [3]. The position-species compositions are determined in TGs and PLs desorbed from Al_2O_3.

In a determination of the position-species composition of the TGs isolated by chromatographing the oil of the seeds of *Nepeta cataria* L. (catnip) on columns containing Al_2O_3 and silica gel, we found that, in addition to hydrolyzing properties, Al_2O_3 possesses the capacity for causing the isomerization of the acyl radicals in triglycerides.

The position-species compositions of the natural TGs (silica gel) of this oil is represented by 38 main species, among which LeLLe, LeLeLe, LeOLe, and LLLe predominate [4].

The fatty-acid composition of the TGs isolated from the Al_2O_3 was as follows (%, GLC): 16:0, 7.1; 18:0, 1.7; 18:1, 12.5; 18:2, 25.5; 18:3, 53.2. It differs from the composition of the natural TGs by a lower amount of the 18:3 acid and an increase in the amount of saturated acid. The changes in fatty-acid composition can be explained by a loss as the result of hydrolysis of TG species containing the 18:3 acid.

The fatty-acid composition of the 2-monoglycerides obtained from the TGs (Al_2O_3) after specific enzymatic hydrolysis is represented by the following acids (%): 16:0, 2.6; 18:0, 0.9; 18:1, 20.5; 18:2, 32.4; 18:3, 43.6.

The position-species composition of the TGs (Al_2O_3) calculated from these results is characterized by 50 species (Table 1). The other 10 possible species are present in the total in an amount of less than 0.1%.

TABLE 1. Position-Species Composition of the Triglycerides (Al_2O_3) of the Oil of the Seeds of *Nepeta cataria* L. (mole %)

Glyceride with P* and S* in position 2	Amount	Glyceride with O* in position 2	Amount	Glyceride with L* in position 2	Amount	Glyceride with Le* in position 2	Amount
PPL	0.2	OOO	0.2	LLL	1.6	LeLeLe	14.7
PPLe	0.2	POO	0.4	PLS	0.2	PLeS	0.2
OPL	0.2	POL	0.8	PLO	0.6	PLeO	0.8
OPLe	0.2	POLe	2.2	PLL	1.4	PLeL	1.8
LPL	0.1	SOL	0.2	PLLe	3.6	PLeLe	4.8
LPLe	0.6	SOLE	0.6	SLO	0.2	SLeO	0.1
LePLe	0.9	POP	0.2	SLL	0.3	SLeL	0.4
PSLe	0.2	OOL	0.8	SLLe	0.8	SLeLe	1.0
LSLe	0.2	OOLe	2.1	OLO	0.2	OLeO	0.3
LeSLe	0.3	LOL	1.0	OLL	1.2	OLeL	1.6
		LOLe	5.2	OLLe	3.2	OLeLe	4.2
		LeOLe	6.9	PLP	0.3	LLeL	2.1
				LLLe	8.2	LLeLe	11.2
				LeLLe	10.9	PLeP	0.4

*P — 16:0; S — 18:0; O — 18:1; L — 18:2; Le — 18:3;

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On comparing the glyceride compositions of the natural TGs and the TGs (Al_2O_3) we can see that the total amount of glyceride species when the oil was chromatographed on Al_2O_3 increased by 12 through the appearance of new species containing in position 2 the 16:0, 18:0, and 18:3 acids (three species each), the 18:2 acid (two species), and the 18:1 acid (one species). The species predominating in the natural TGs are retained in the TGs (Al_2O_3), but their amount decreases; for example, LeLLe by 13.3% and LeOLe by 4.3%. On the other hand, there are increases in the amount of such species of the natural TGs as LeLeL (by 6%) and LeLeO (by 2%) in which L and O occupy position 1 or 3 and Le is present in position 2.

The formation of new species and the considerable decrease in the amount of species with Le in position 1 with a simultaneous increase of species with Le in position 2 shows the occurrence of intra- and intermolecular isomerization of the TGs consisting in an exchange of acyl groups between positions 1 or 3 and position 2 of the glycerides.

We have previously detected natural DGs (~2%) and MGs (~0.3%) in the seed oil of *N. cataria*. When this oil was chromatographed on a column of Al_2O_3 we obtained about 16% of DGs and 4% of MGs with acid compositions differing from the compositions of the analogous natural fractions [4].

The fatty-acid composition of the DGs (Al_2O_3) was as follows: 16:0, 6.0; 16:1, 0.7; 18:0, 1.3; 18:1, 12.7; 18:2, 25.8; 18:3, 53.5. The acid composition of the MGs (Al_2O_3) was (in %): 16:0, 5.3; iso-17:0, 0.3; 18:0, 0.8; 18:1, 13.4; 18:2, 24.7; 18:3, 55.5.

As mentioned above, on Al_2O_3 it is mainly the linolenic-containing TG species that are hydrolyzed on Al_2O_3. In the natural TGs these are species containing Le in position 1 or 3. Thus, the increase in the yield of DGs is evidence of the splitting out of Le from either terminal position of the TGs, as is also confirmed by the fall in the amount of this acid in the total acids of the DGs (Al_2O_3).

In the total natural DGs, the 1,3 isomer predominates (TLC, H_3BO_3). In the DGs (Al_2O_3), one might expect an increase in the amount of the 1,2 isomer. However, the presence in this fraction (Al_2O_3) of a large amount of the 1,3 isomer (ATLC) confirms the previously known property of this sorbent for isomerizing acyl groups in diglycerides.

Information on the isomerization of the TGs was confirmed by chromatography on columns containing silica gel and Al_2O_3 of the oil of the seeds of *Eremostachys moluccelloides* Bge. [5]. Here the change in the species of the TGs is shown in the following way:

TG species	Amount, mole % (silica gel)	Amount, mole % (Al_2O_3)
OP*O	2.8	0.9
POO	1.2	5.8
OOL*	20.0	26.8
OLO	21.2	10.0
LOL	2.9	4.8
OLL	12.2	7.2

In the TGs of *E. moluccelloides* eluted from Al_2O_3 the amount of species with O in the extreme positions decreases (OLO — by 11.2%) and the isomeric species where O occupies the central position increases (OOL — by 6.8%). In this case migration takes place of the predominant 18:1 acid from position 1 or 3 to position 2.

Thus, the quantitative compositions of fatty acids and the position—species compositions of TGs eluted from Al_2O_3 do not correspond to the compositions of the native TGs isolated from silica gel.

EXPERIMENTAL

The method of isolating the oils from the seeds, the conditions for GLC analysis, and also the conditions for enzymatic hydrolysis have been described previously [4, 5].

The oils were chromatographed on a "Woelm" silica gel column in the manner described previously [5].

*Because of their small proportion of the total, the 18:0 and 18:3 acids were combined with the 16:0 and 18:2 acids, respectively.

When the oil of *N. cataria* (17 g) was chromatographed on a column (22 × 0.5 cm) of Al_2O_3 (neutral, "Chemapol"), hexane (720 ml) eluted the TGs, diethyl ether (700 ml) eluted the DGs together with the free fatty acids and β-sitosterol, and chloroform (300 ml) eluted the MGs. The DGs were purified as described previously [5].

SUMMARY

In a study of the position-species and fatty-acid compositions of the glyceride fractions of the oils of the seeds of *N. cataria* and *E. moluccelloides*, desorbed from silica gel and from neutral Al_2O_3, it was found that on Al_2O_3 isomerization of the TGs takes place with a change in their fatty acid composition consisting in the migration of acyl groups from positions 1 and 3 to position 2 both within the molecule and between the molecules of the TGs.

These properties exclude the use of this sorbent for the isolation and purification of the glyceride fractions with the aim of establishing their molecular structure.

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VITAMINS OF THE OIL OF THE FRUIT OF *Hippophaë rhamnoides*

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The fat-soluble vitamins of *Hippophaë rhamnoides* L., which belongs to the family Elaeagnaceae, have been studied inadequately [1-5]. On the one hand, this is due to their extreme instability to oxidation during the isolation and storage of the oil and juice of the fruit and, on the other hand, to the fact that the oil of common sea buckthorn fruit has been of great interest to botanists, pharmacists, and technologists. The composition of the oils of the juice and the seeds have not been studied separately.

The causes of the high biological activity of the oil from the fruit of the sea buckthorn have not been elucidated [3]. The wide use of this oil [6, 7] in medicine and the shortage of it make it necessary to study its chemical composition in detail in order to search for or create an adequate substitute.

We have studied the oil of the juice and the oil for the seeds of the fruit of the plant collected at the end of August—beginning of September in the valley of the R. Paltau (Chatkal range).

The oil of the juice was isolated from the juice of the fruit by the method of Bligh and Dyer. The amount of oil was 7.4% of the weight of the juice, its refractive index n_D^{22} 1.4646, and its acid No. 14.19 mg of KOH/g.

The seed oil consisted of the sum of the neutral lipids isolated from the seeds by hexane. The amount of oil was 11.8% of the weight of the absolutely dry seeds, n_D^{22} 1.4740, acid No. 23.23 mg of KOH/g.

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