Effect of Some Refining Steps on Rapeseed Oil Triacylglycerol Structures

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Abstract: Determination of fatty acids at *sn*-2 position in rapeeed oil triacylglycerols with low content of erucic acid is desribed. Oleic acid constitues of 48% of the fatty acids, linoleic acid 37.8%, linolenic acid 13.5%, and small amounts of the usual saturated acids make up the remainder. The effect of industrial alkali refining (degumming and neutralization), bleaching, deodorization and interesterification was studied. The use of different refining steps did not cause any or only mild triacylglycerol structure modification, other than interesterification, obviously.

Keywords: fats; oils; triacylglycerols; rapeseed; technology; refining; interesterification

INTRODUCTION

Oils and fats are an important part of the human diet and more than 90% of global production is used as food or as ingredients in food products. Nevertheless, relatively little investigation has been done on the possible changes in the triacylglycerol (TAG) structures caused by different refining procedures in the industrial edible oil and fat production. The positional distribution of the fatty acids within the TAG molecules can be determined in accordance with Vander Wal [1] distribution hypothesis, where content of every individual TAG structure is calculated as follows:

$$\%\ sn\text{-XYZ} = (\text{mol \% X in } sn\text{-1,3}) \times (\text{mol \% Y in } sn\text{-2}) \times (\text{mol \% Z in } sn\text{-1,3}) \times 10^{-4},$$

where: X, Y, Z – individual fatty acids

Comprehensive review of the methods for the analysis of triacylglycerols is given by Ruiz-Gutiérrez and Barron [2].

EXPERIMENTAL

The rapeseed oils used in this study were unrefined, partly refined (Alfa Laval degummed, neutralized and bleached as well), then physicaly refined (Lurgi deodorized) and lastly interesterified in Krupp apparatus. We obtained all oil samples from local Palma-Tumys factory in Bratislava during one processing batch. In course of the interesterification or randomization reaction the temperature was maintained at 90–95°C and catalyst sodium methoxide (0.2%) was added and continuosly stirred in tank.

The positional distribution of the fatty acids within the TAGs was determined by method described by Luddy [3]. The oils were hydrolyzed with crude pancreatic lipase type II (Sigma) and the degradation products were separated by TLC (hexane-diethyl ether-acetic acid in volume ratio 80:20:2) on silica gel plates modified with boric acid [4]. The isolated monoacylglycerol (MAG) bands were converted to fatty acid methyl esters [5], and then separated on a wide-bore capillary column Supelcowax 10 (30 m × 0.75 mm × 1 μm) in a Hewlett-Packard 5890 series II gas chromatograph (Hewlett-Packard, Palo Alto, USA) equipped with a flame-ionization detector [6].

RESULTS AND DISCUSSION

Pancreatic lipase catalyzed the hydrolysis of primary ester linkages in TAG molecules to produce *sn*-1,2(2,3)-diacylglecerols (DAG), *sn*-2-monoacylglycerol (MAG) and free fatty acids. The positional distribution and molecular association of fatty acids in the TAGs was obtained by enzymatic and

Table 1. Fatty acid distribution in rapeseed oil TAGs and their partial acylglycerols

Acylglycerols		Fatty acids (mole %)					
		palmitic	stearic	oleic	linoleic	linolenic	erucic
Original TAG		5.4	1.2	57.0	24.3	10.8	1.3
sn-1,2 (2,3)-DAG	found	4.2	0.9	54.7	27.7	11.5	1.0
	calculated*	4.8	0.7	53.4	28.1	12.2	0.8
sn-1,3-DAG	calculated*	7.8	1.8	61.4	17.6	9.4	2.0
Isolated *sn*-2-MAG		0.6	0.1	48.0	37.8	13.5	0

*DAG calculated = (3 TAG + MAG)/4 and (3 TAG – MAG)/2, where TAG and MAG represent original triacylglycerols and isolated monoacylglycerols [7]

chromatographic examination of the MAGs derived from the triacylglycerols by lipolysis. Table 1 indicates the different fatty acid (FA) compositions of the mono-, di-, and triacylglycerols produced by pancreatic lipolysis of examined rapeseed oils.

From FA positions on the glycerol backbone is evident, that linolenic acid and particularly linoleic acid were preferentially esterified in the *sn*-2 position, whereas erucic acid was completely absent from this position.

In order to compare possible alterations caused by different refining procedures, fatty acids in *sn*-2 positions of TAG has been determined. The results are shown in Table 2.

It is apparent that industrial degumming and alkali neutralization as well as bleaching and semicontinual Lurgi deodorization do not cause the migration of fatty acid acyl chains within molecules of triacylglycerols and so the structure is not changed. Otherwise, refining process does not affect the results obtained to a detectable extend. There are only a few publications in this field and the results are different. The exception is steam distillation or deodorization, where many literature sources in the last decade affirmed mild migration of fatty acid chains during laboratory/industrial deodorization, especially at temperatures above 220°C [8–10].

Determination of the percentage of FA at the *sn*-2 position of TAGs provides the possibilities to follow the progress of interesterification/randomization reaction in oil or oil and fat blends. Pancreatic lipase analysis in Table 2 showed, that the composition of FA in middle *sn*-2 position of rapeseed oil after randomization was almost the same as in the original rapeseed oil, so it is the proof, that reaction run into the equilibrium and can be used for detecting reaction endpoint. Importance of randomization of fats and oils rapidly increased nowadays, because the final product,

Table 2. Effect of processing on the percentage of fatty acids at *sn*-2 position in the triacylglycerols of low erucic rapeseed oil

Treatment		Fatty acids (mole %)				
		palmitic	stearic	oleic	linoleic	linolenic
Alkali refining	before	0.5	0.1	47.4	38.0	13.8
	after	0.6	0.1	48.4	37.3	13.3
Bleaching	after	0.6	0.1	49.2	37.2	12.9
	before	0.4	tr.	47.6	38.4	13.4
Deodorization	after	0.4	0.1	47.8	38.0	13.6
	before	0.5	0.1	48.4	37.5	13.4
Randomization	after	0.7	0.2	48.9	36.8	13.3
	before	0.5	0.3	49.3	35.9	13.8

margarine or plastic shortening, did not contain trans fatty acids, so it is much more suitable for health nutrition.

CONCLUSION

The results of this work confirmed that the conditions of industrial refining do not change the TAG molecular structures of rapeseed oil with low content of erucic acid. It was also determined that industrial randomization is running into the interchange equilibrium endpoint.

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