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DETERMINATION OF THE TRIGLYCERIDE COMPOSITION OF CERTAIN FATS

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Recently, new methods for determining the structure of glycerides have appeared which are based on the results of the enzymatic hydrolysis of fats [1-4]. The triglyceride composition of the majority of vegetable and animal fats calculated by this method proved to be similar to the composition determined by other methods: low-temperature crystallization; thin-layer chromatography, and various methods of destructive oxidation.

Table 1

Fatty Acid Composition of Cottonseed Oil

Acids	Triglycerides	Monoglycerides
$C_{10:0}$	0.33	0.65
$C_{12:0}$	0.09	0.18
$C_{14:0}$	0.81	0.17
$C_{16:0}$	22.57	2.62
$C_{18:0}$	2.19	—
$C_{16:1}$	2 26	0.71
$C_{18:1}$	18.31	22.54
$C_{18:2}$	53.44	73.13

Having developed new conditions for performing the hydrolysis and isolating and analyzing the resulting products by Coleman's method, we have calculated the glyceride composition of several vegetable oils, in particular cottonseed oil. Using this oil as an example, we shall show how it is possible to determine the glyceride composition of an oil or fat in a relatively simple manner, using the method of enzymatic hydrolysis. For this purpose, the glyceride fraction was isolated from the oil by the method of column adsorption chromatography. A mixture of fatty acids was isolated from a small amount of the glyceride fraction by cold saponification and its composition was determined by gas-liquid chromatography after methylation. Another part of the glyceride fraction was hydrolyzed to an acid number of 90-120 mg KOH/g. The hydrolysate contained, in addition to free fatty acids, mono- and diglycerides and a residue of triglycerides. The mixture was separated by thin-layer chromatography. Fatty acids were isolated from the monoglyceride fraction so obtained and, after methylation, were also subjected to gas-liquid chromatography. In this way the indices shown in Table 1 were obtained for cottonseed oil.

Table 2

Distribution of the Fatty Acid Radicals over the α-, α'-, and β-Positions

Composition	Index	P	O	L
Triglycerides	a	25.99	20.57	53.44
β-Monoglycerides	β	3.62	23.25	73.13
Acid in the α, α'-positions	$\frac{3a-\beta}{2}$	37.18	19.23	43.59

It can be seen from the tables how differently the saturated and unsaturated acids behave. With about 26% of saturated radicals and 74% of unsaturated radicals in the oil, more than 96% of the β-hydroxyls of the glycerol proved to be bound to the unsaturated acyl radicals, less than 4% being bound to saturated acids. Of the unsaturated acids the central position is occupied mainly by linoleic acid.

Having the indices of the fatty acid composition of the initial glycerides and, separately, those of the monoglycerides, and assuming that all the monoglycerides that we isolated were originally esterified in the β-position, we calculated the glyceride composition of the oil. For this purpose, the fatty acids were summed in groups: saturated (named after their main component "palmitic"—P); monoenic ("oleic"—O); and dienic ("linoleic"—L). The distribution of the acids over the α-, α'-, and β-positions is given by the figures of Table 2.

In addition, we made another assumption: all the acids not occupying the β-position are distributed between the glyceride molecules in the α, α'-positions proportionally to the indices 37.18, 19.23, 43.59. As a result, we obtain the following glyceride composition of cottonseed oil: S) saturated; and U) unsaturated fatty acids.

PPP	0.50	PPO	0.52	OPO	0.13	POP	3.21	POO	3.34	OOO 0.86
		PPL	1.17	OPL	0.61	PLP	10.11	POL	7.53	OOL 3.90
				LPL	0.69			PLO	10.46	OLO 2.70
								PLL	23.70	LOL 4.41
										OLL 12.26
										LLL 13.90
SSS	0.50	SSU	1.69	USU	1.43	SUS	13.32	SUU	45.03	UUU 38.03

The figures given characterize the content of each of the 18 groups of glycerides. However, from these it is possible to convert to the contents of the individual glycerides by distributing the figures for the content of each of the groups of components between the individual components within it according to the law of probability.

As an example, we shall distribute the PLL group between the individual glycerides which it contains just as was done in the distribution of the sum of the glycerides between the groups of components. Denoting the saturated acids

Table 3

Glyceride Types of Six Oils Taking Isomerism into Account

Oil-bearing plants	Type of glycerides						In the β-position	
	SSS	SSU	USU	SUS	SUU	UUU	S	U
Zea mays (corn)	0.46	2.30	2.83	7.81	38.64	47.96	5.59	94.41
Abutilon theophrasti (chingma abutilon)	0.41	2.46	3.65	5.95	35.28	52.25	6.52	93.48
Erysimum gypsaceum	0.39	2.34	3.57	5.74	34.90	53.06	6.30	93.70
Erysimum cuspidatum	0.28	1.96	3.45	4.60	32.46	57.25	5.69	94.31
Althaea nudiflora	0.33	1.90	2.71	6.37	36.46	52.23	4.94	95.06
Onopardon olgae	0.13	1.32	3.49	2.48	25.74	66.84	4.94	95.06

of the P group by the symbol C, with the number of carbon atoms as subscript, we find that the PLL group contains the following individual glycerides (%): $C_{10}LL$, 0.11; $C_{12}LL$, 0.03; $C_{1}LL$, 0.72; $C_{16}LL$, 20.74; and $C_{18}LL$, 2.10.

As can be seen from the glyceride composition of cottonseed oil, the overwhelming majority of the glyceride molecules (96.38%) is constructed in such a way that their β-positions are occupied by radicals of unsaturated fatty acids. A similar phenomenon has been observed previously in a number of oils that we have studied (Table 3).

Conclusions

Enzymatic hydrolysis, together with Coleman's method of calculation, as modified by us has been used to determine the glyceride composition of oils. It has been established that almost all (93–96%) of the β-positions of the glycerides of the coils studied are occupied by radicals of unsaturated acids.

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