PROPERTIES OF OXIDIZED TRIACYLGLYCEROLS

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The property of oxidized triacylglycerols of being hydrolyzed faster than their unoxidized analogs has been established. The contribution of oxidized triacylglycerols to the acid number has been studied. The possibility has been shown of monitoring the amount of oxidized triacylglycerols in oils at all stages of the industrial process of oil production.

Oxidized triacylglycerols (o-TAGs) belong to the class of compounds isolated from the seed oils of a number of plants comparatively recently [1-8]. The properties of these compounds have therefore been studied to only a small extent.

The hydrolysis of unoxidized triacylglycerols (u-TAGs) is usually performed with a 1 M solution of KOH in methanol at the boil [9]. For o-TAGs, in order to retain the native structure of the oxidized fatty acids, we have used milder conditions of hydrolysis (a 0.1 N solution of KOH in methanol at a temperature of 37-40°C). After 10 min, the o-TAGs were hydrolyzed almost completely, while the u-TAGs were only half hydrolyzed during this period.

In order to study the reliability of this property of the o-TAGs and to obtain a clear interpretation of it, we isolated by the CC method the u-TAGs, the epoxyacyldiacylglycerols (EAGs), and the hydroxyacyldiacylglycerols (HAGs) from the seed lipids of the cotton plant, the Scotch thistle, and the sea buckthorn [8, 10-12]. The triacylglycerols were identified by analytical thin-layer chromatography, qualitative reactions, and IR and PMR spectra. In order to obtain comparative results, the alcoholysis of all these types of triacylglycerols was carried out under mild conditions. In each experiment, the reaction was stopped after the lapse of 5, 10, 15, etc., min. The results of the analysis are illustrated graphically in Fig. 1, where the percentage of the substance has been plotted along the axis of ordinates and the time in minutes along the axis of abscissas. The alcoholysis products were isolated by the usual method and their ratio was determined gravimetrically after separation in a thin layer.

As can be seen from Fig. 1, after 5 min the u-TAGs were 30% hydrolyzed, the EAGs 80%, and the HAGs almost completely. After 10 min, the products of the alcoholysis of the HAGs were found to contain not only FAMEs but also fatty acid salts, while in the products of the alcoholysis of the u-TAGs the latter appeared only after 20-25 min (Fig. 1, curve 1). The graphical dependence of the amount of reaction products on the time of the alcoholysis

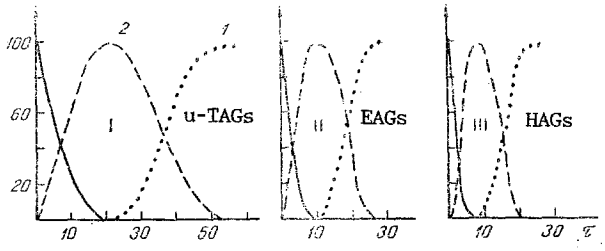

Fig. 1. Kinetics of the alcoholysis of the triacylglycerols u-TAGs, EAGs, and HAGs: 1) fatty acids (FAs), epoxy-FAs (EFAs), and hydroxy-FAs (HFAs); 2) FA methyl esters (FAMEs), EFAMEs, and HFAMEs.

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TABLE 1

Sample of cottonseed oil	Acid No., mg KOH		True acid No., mg KOH	Amount in the oil, %		Acid No. of the o-TAGs, mg KOH
	before treatment with diazomethane	after treatment with diazomethane		gossypol	phospholipids	
Forepressing oil before refining	2,64	1,37	1.27	0,22	0,08	0,87
The same after refining	0.34	0,18	0,16	0	0,05	0,16
Extraction oil before refining	3,79	1,32	2.47	0,12	0,06	1,04
The same after refining	0,40	0,15	0,25	0	0,05	0,13

TABLE 2

Amounts of substance in the sample, %			Acid No., mg KOH	Amounts of substance in the sample, %		Calculated amounts of substances in the sample, g	
u-TAGs	o-TAGs	FAs		o-TAGs	FAs	o-TAGs	FAs
100,00	0	0	0,01	0	0	0	0
96.44	3,56	0	0,23	0,072	0	0,007	0
95,01	4,99	0	0,30	0,100	0	0,010	0
90,65	9,35	0	0,36	0,202	0	0,011	0
89,66	10,34	0	0,37	0,207	0	0,012	0
85,46	14,54	0	0,45	0.295	0	0,014	0
96,54	0	3,46	5,78	0	0,100	0	0,101
94,27	0	5,73	9,46	0	0,149	0	0,150
80,75	0	19,25	31,78	0	0,627	0	0,627
78,41	11,23	10,36	17,51	0,464	0,428	0,025	0,428
			After treatment with diazomethane				
			0,41				

clearly demonstrates the capacity of the o-TAGs for being hydrolyzed faster than the u-TAGs. The reason for the change in the rate of hydrolysis of the o-TAGs is apparently their increased emulsifying capacity, as in the case of the di- and monoacylglycerols [13].

Since the o-TAGs are readily hydrolyzed, we assumed that the presence of these components in oils will affect the acid number. We determined the acid numbers of the individual groups of triacylglycerols of cottonseed oil: u-TAGs, 0.01; EAGs, 1.62; HAGs, 4.85 mg of KOH. As we see, the acid numbers of the triacylglycerols rise in the same sequences as the rate of hydrolysis.

It is known that in the determination of acid numbers in unrefined plant oils, alkali is consumed in the titration not only of the free fatty acids but also of other substances. For cottonseed oil, such substances are phospholipids and gossypol.

The true acid number is calculated from Rzhekhin's formula [14]: acid number of the FFAs = acid number of the oil $-(0.32\ P + 2.17\ G)$, where P is the percentage of phospholipds and G that of gossypol.

In order to study the magnitude of the contribution of o-TAGs, we investigated samples of cottonseed oil taken in the Yangiyul' oils and fats combine. We determined their acid numbers before and after three treatments with diazomethane in order to convert the FFAs into their methyl esters, and their gossypol and phospholipid contents. The results of the analysis are given in Table 1. The difference between the acid numbers before and after methylation corresponds to the true acid number of the oils, which depends on the amount of FAAs. The acid number after methylation is due to the presence of phospholipids, gossypol, and o-TAGs. The corrections to the acid numbers due to the presence of phospholipids and gossypol are small. Consequently, the o-TAGs make a definite contribution to the acid numbers of oils.

However, the question arises as to whether the o-TAGs can react with alkali in the titration process. In order to answer this, we prepared model mixtures of definite amounts of u-TAGs, o-TAGs, and a FFA (behenic acid), and determined the acid numbers of these mix-

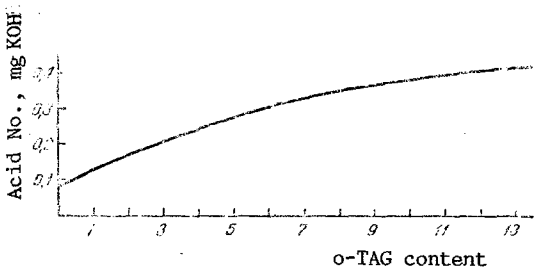

Fig. 2. Curve of the dependence of the acid numbers of oils on the amount of oxidized triacylglycerols in them.

tures. The results of the analysis are presented in Table 2. The amount of titratable substances in the model mixtures was calculated from the stoichiometric equation for the hydrolysis of o-TAGs and the neutralization of fatty acids with alkali, and also in the light of the acid numbers of the mixtures and the mean molecular weight of the o-TAGs (883.31). The latter was calculated by using the mean molecular weight of the fatty acids of cottonseed oil (273.61) and the molecular weight of ricinoleic acid, as the predominating component of the oxidized lipids [15, 16].

The results of the calculation are also presented in Table 2, from which it can be seen that the calculated amount of o-TAGs in the model mixtures was 10-20 times smaller than that taken. We are therefore unable to introduce a correction into Rzhekhin's formula for the acid numbers of the o-TAGs. However, with the aid of the figures of Table 2 we have plotted a curve of the dependence of the acid numbers of cottonseed oil on the amount of o-TAGS in it (Fig. 2).

By making use of this curve it is possible to determine the amount of o-TAGS in cottonseed oil. A curve for any other oil can be plotted similarly. This provides the possibility of monitoring the amount of oxidized triacylglycerols in an oil at any stage of the industrial process.

EXPERIMENTAL

The isolation of the oil, column, and thin-layer chromatography, qualitative reactions, and spectral analyses were performed by methods described previously [11]. The alkaline hydrolysis of the u-TAGs was carried out by a handbook method [9]. The o-TAGs were hydrolyzed with 0.1 M solution of caustic potash in methanol at a ratio of sample to solution of 1:10. The reaction mixture was stirred with a magnetic stirrer at 37-40°C. The reaction products were isolated in the usual way [9].

The acid numbers and gossypol and phospholipid contents were determined by methods given in a handbook [17].

SUMMARY

1. Oxidized triacylglycerols are hydrolyzed faster than unoxidized ones.

2. The presence of oxidized triacylglycerols in oils affects the acid number.

3. The possibility has been shown of monitoring the amount of oxidized triacylglycerols in oils at all stages of the industrial process of oil production.

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NEW GLYCOSIDES FROM PLANTS OF THE GENUS Phlojodicarpus

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From plants of the genus Phlojodicarpus have been isolated the new coumarins umbelliferone β-D-apiosyl(1 → 6)-β-D-glucopyranoside (I) and 8-(2',3'-dihydroxy-3'-methylbutyl)umbelliferone 7-O-β-D-glucopyranoside (II) and also the flavone glycoside diosmetin 7-O-β-D-glucopyranoside (III). The result of IR, UV, PMR, and ^{13}C NMR spectroscopy are given.

Investigating the coumarins from plants of the genus Phlojodicarpus, we turned our attention to the fact that the chemical composition of even a single species may undergo considerable changes according to the conditions of growth. Thus, Ph. turczaninovii Sipl. growing in the arid regions of Mongolia contained substances not found in this plant collected on the territory of the USSR [1-3]. In the present paper we describe the isolation and chemical structures of two coumarin glycosides and one flavonoid glycoside from Ph. villosus (Turcz. ex Fischer et Meyer) Ledeb. and Ph. sibiricus (Steph. ex Speng.) K.-Pol.

The first species was collected in the period of flowering in the western part of Mongolia. Decursinol and esters of it have been isolated from it previously [4]. It has now been established that, in addition to these components, the plant contains a polar coumarin with the composition $C_{20}H_{24}O_{12}$. On the basis of the results of IR, UV, PMR, and ^{13}C NMR spectroscopy it was assigned the structure of a bioside of umbelliferone (I). The UV spectrum of the compound coincided with the absorption of O-substituted umbelliferone derivatives and no displacement of the absorption bands in the presence of diagnostic additives was observed. The IR spectrum revealed bands typical for the unsaturated lactone ring of a coumarin. In the PMR spectrum, the nature of the spin-spin interactions showed the presence of one substituent in position 7. Hydrolysis with dilute hydrochloric acid formed umbelliferone and two carbohydrates. One of them was identified by paper chromatography as glucose, and the other had the same mobility as rhamnose. However, this should have been a pentose, as follows from the empirical formula of the glycoside and the SSCC of the anomeric proton, 3 Hz. We assumed that the second carbohydrate was apiose which, as is known [5], has the same chromatographic mobility as rhamnose. A study of the ^{13}C NMR spectrum confirmed this assumption: the pentose contained two CH_2O groups and one quaternary carbon atom and, consequently, was a branched sugar. The attachment ofthe apiose at position 6 of the glucosyl residue was determined from the chemical shift of the C-6' signal (68.3 ppm). An interpretation of the ^{13}C NMR spectrum is given in Table 1.

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