SUMMARY

The carbohydrate complex of the epigeal part of Peganum harmala L. includes mono- and oligosaccharides, water-soluble polysaccharides, hemicelluloses, and an acidic polysaccharide similar to the pectin substances of higher plants. It is based on a fragment constructed of α-1 → 4-linked D-galacturonic acid residues in the pyranose form.

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NEUTRAL LIPIDS OF THE OIL OF TOMATO SEEDS

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The composition of the oil of tomato seeds with respect to the classes of lipids has been studied. The presence of less than 1% of oxidized triacylglycerides has been established. A stereospecific analysis of the main lipid component of the oil – triacylglycerols – has been performed. It has been shown that the first position is enriched with saturated fatty acids as compared with the third position, and the second position contains 95% of unsaturated fatty acid residues, as in the majority of plant triacylglycerols.

Every year in the USSR the gross tomato harvest amounts to more than 3.5 million tonnes [1], of which about 50% is processed in the preserving industry. When it is considered that their oil content is 25-30%, the seeds, which are obtained as a waste material (the proportion of seeds in tomatoes being 0.5-2.5%), are sufficient for the production of about 7 thousand tonnes of edible oil. Furthermore, this oil is recommended for use in the manufacture of cosmetic and pharmaceutical products and paints [2].

Information exists on the physicochemical properties, fatty-acid composition, and amount of unsaponifiables of the seed oil of tomatoes of various varieties, forms, and industrial samples. According to some figures, the seed oil contains oxidized lipids but their assignment to the classes of organic substances and the determination of the amounts of individual lipid components of the oil has not been carried out [2-7].

In order to evaluate tomato seed oil as a promising food product, we have studied it [3] in relation to the classes of lipids present in it. The oils were isolated from various of industrial waste seeds of the Tashkent preserving factory – samples I, II, and III. The oil from each of the samples was separated by column chromatography into a number of fractions by solvent systems 1-7. Complex fractions of the oil were additionally separated by comparative thin-layer chromatography in suitable solvent systems. The assignment of the chromatographically individual zones of the substances to various classes of lipids was made on the basis of a combination of the mobilities of the substances in a thin layer of silica gel in comparison with the mobility of model substances, of qualitative reactions, of spectral characteristics, and of the products of chemical reactions.

It was established that the lipids present in largest amount in these samples of oils belonged to the following classes:

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TABLE 1. Composition of the Unoxidized Free and Bound Fatty Acids

Lipids	Fatty acids, % on the total								
	12:0	14:0	16:0	17:0	18:0	16:1	18:1	18:2	18:3
Triacylglycerols									
II	—	0.4	15.0	—	4.8	0.5	22.0	56.7	0.6
III	—	0.6	12.	—	5.2	1.3	22.5	56.6	2.0
Position 1	Tr[a]	1.7	29.0	—	10.3	3.4	21.5	32.7	1.4
Position 2	—	—	3.7	—	1.6	0.5	27.1	64.6	2.5
Position 3	—	0.1	3.6	—	3.7	—	18.9	71.6	2.1
Epoxyacyldiacylglycerols									
I	2.3[b]	1.4	14.2	—	7.3	2.3	22.3	46.4	2.8
Free fatty acids									
II	—	0.1	16.5	0.3	5.6	0.6	20.0	55.3	1.6
III	0.1	0.2	12.8	0.6	6.4	0.7	24.5	53.3	1.4
Diacylglycerols									
II	0.8[c]	0.2	9.5	—	2.5	0.5	17.1	67.7	1.3
III	Tr.	Tr.	9.8	0.3	4.3	0.6	28.1	55.7	1.2
Monoacylglycerols									
II	1.0[d]	0.6	12.9	0.9	3.8	0.9	21.9	55.4	1.2
III	Tr.	0.2	9.7	—	4.3	0.6	26.2	57.2	1.8

In addition to the acids mentioned, the following were detected: a) traces of 13:0, 15:0, and 20:0; b) 1% of 13:0; c) 0.4% of 13:0; d) 1.4% of 10:0. The GLC figures for the triacylglycerols of III were recalculated to mol.% on the total.

Lipids	Amount, % on the total		
	I	II	III
1. Hydrocarbons	0.3	0.3	0.1
2. β-Carotene	Tr.	Tr.	Tr.
3. Acylsterols	0.2	Tr.	0.4
4. Lycopene	Tr.	Tr.	Tr.
5. Acetyltriterpenols, lycopene	0	Tr.	Tr.
6. Triacylglycerols, lycopene	90.6	90.9	80.7
7. Tocopherol	0	Tr.	Tr.
8. Epoxyacyldiacylglycerols	0.8	0.4	Tr.
9. Free fatty acids	2.3	2.5	12.1
10. Chlorophyll a	Tr.	Tr.	Tr.
11. Triterpenols	0.5	Tr.	0.1
12. Diacylglycerols, pheophytin a	4.3	5.4	6.3
13. Free sterols	Tr.	0.2	Tr.
14. Chlorophyll b, pheophytin b	Tr.	Tr.	Tr.
15. Monoacylglycerols	0.2	0.3	0.3
16. Unidentified	0.8	Tr.	Tr.

As we see, the relative amounts in the lipids of samples I and II were almost the same. It must be mentioned that sample II, in contrast to I, was not studied immediately after it had been taken, but after storage for two years under laboratory conditions but, even so, the amount of oxidized lipids in it had not increased. Thus, not only the crude oil, but also that stored in the seeds, is stable to oxidation [6].

The compositions of the fatty acids of some lipids of the oil were determined in samples II and III (Table 1). The predominating component of the fatty acids was linoleic.

The products of alkaline hydrolysis and lipolysis with pancreatic lipase, chromatographic mobilities in a thin layer, the PMR spectra confirmed the structure of the substances of fraction 6, 12, and 15 of the oil as esters of fatty acids and glycerol, and showed the degree of esterification of the glycerol, which enabled them to be assigned to the triacylglycerols, diacylglycerols, and monoacylglycerols, respectively. The first of them formed the main component of the oil (80-90%).

The results of a determination of the stereospecies composition of the triacylglycerols showed that the first position was more enriched with saturated fatty acids then the third, and the second position contained 95% of unsaturated fatty acids, as in the majority of plant triacylglycerols. From these facts we calculated the stereospecies composition of the triacylglycerols of tomato seed oil. Among the 48 species of triacylglyc-

erols those in which the second and third positions were esterified with linoleic acid predominated (P – saturated; O – monoenoic; L – dienic; Le – trienic acids):

Species	Amount, % on the total	Species	Amount, % on the total	Species	Amount, % on the total
PPP	0.2	PPO	0.4	OPP	0.1
OPO	0.3	PPL	1.6	LPP	0.1
LPL	1.2	OPL	0.9	LPO	0.4
LePL	0.1	POO	2.1	OOP	0.5
POP	0.8	POL	8.2	LOP	0.6
POLe	0.2	OOL	4.8	LOO	1.7
OOO	1.3	OOLe	0.2	LeOO	0.1
LOL	6.6	LOLe	0.2	LeOL	0.3
PLP	2.0	PLO	5.1	OLP	1.2
OLO	3.1	PLL	18.9	LLP	1.6
LLL	15.2	PLLe	0.5	LeLP	0.1
PLeP	0.1	OLL	11.5	LLO	3.9
PLeO	0.2	OLLe	0.3	LeLO	0.2
PLeL	0.8	LLLe	0.4	LeLL	0.6
OLeO	0.1	OLeL	0.4	LLeO	0.2
LLeL	0.5	LeLeL	0.1	—	—
LLeP	0.1	—	—	—	—

The epoxyacyldiacylglycerols were identified as described previously [8-10]. The composition of the unoxidized fatty acids according to GLC is given in Table 1. The methyl esters of the epoxy acids were separated into five zones by the TLC/$AgNO_3$ method in system 8. Three of them were identified from their R_f values and relative retention times by the GLC method [8] in comparison with samples from other oils. According to GLC, the composition of the epoxy acids was as follows (% on the total): trans-epoxystearic – 5.9; cis-epoxystearic – 16.7; coronaric – 39.0; X_1 – 15.9; X_2 – 10.2; X_3 – 8.4; X_4 – 3.9. The mass spectrum of the total methyl esters of the epoxy acids showed the presence of molecular ions with mass numbers of 312, 310, and 308. The last-mentioned corresponded to an epoxydienic acid with two ethylenic bonds between the methyl terminus and the epoxy group (fragments m/z 199 and 155).

The composition of the free fatty acids and that of the acids esterified in the monoacylglycerols did not differ from that of the fatty acids of the triacylglycerols.

Acylsterols and acetyltriterpenols were present in the oil in amounts of from 0.2% to traces. For this reason, the individual components were not identified. Their assignment to the corresponding classes of organic compounds was made from the nature of the qualitative reactions and their mobilities in a thin layer of silica gel in comparison with model samples.

The triterpenols were recrystallized from acetone. Their mass spectrum showed that they had a molecular weight of 426. However, in a thin layer of silica gel impregnated with silver nitrate the acetylated derivatives of the substances of fraction 11 were separated into several chromatographically individual zones. Consequently, the triterpenols consisted of a series of components of the same molecular weight. The main ones were amyrins (fragment with m/z 218, 100%).

The sterols were isolated by recrystallization of the substances of fraction 13 from acetone. On the basis of their mass spectrum, β-sitosterol was found as the main component, with minor amounts of campesterol and traces of sterols with molecular weights of 412 and 386.

EXPERIMENTAL

The isolation of the oils from the seeds, the recording of the spectra, GLC, alkaline and enzymatic hydrolysis, acetylation, and qualitative reactions have been described previously [8-10]. Stereospecific analysis was carried out by a well-known method [11]. Pigments were identified from their absorption in the ultraviolet in comparison with handbook information.

Chromatographic separation was carried out in a column containing silica gel L 100/250 μ and in a thin silica gel L 5/40 with 5% of gypsum on glass plates with 20% of silver nitrate and without it, and on Silufol.

Solvent systems: hexane–diethyl ether (10:0) (1), (9:1) (2), (8:2) (3), (7:3), (4), (6:4) (5), (5:5) (6), (0:10) (7); and benzene-chloroform–diethyl ether (50:50:2) (8).

Triacylglycerols. PMR spectrum (δ, ppm): t 0.86 (9 H); m 1.55; m 1.27; d 1.95; t 2.20; m 2.67; m 4.10 (4 H); m 5.10; m. 5.23.

Diacylglycerols. PMR spectrum (δ, ppm): t 0.85 (6 H); m 1.27; m 1.55; d 1.96; t 2.4; m 2.68; d 3.54 + m 4.10 (4-5 H); m 4.95; m 5.23.

Monoacylglycerols. PMR spectrum (δ, ppm): t 0.80 (3 H); m 1.24; m 1.55; d 1.98; t 2.24; m 2.68; d 3.70 + m comb. 3.90 (4-5 H); m 4.90; m 5.24.

Epoxyacyldiacylglycerols. PMR spectrum (δ, ppm): t 0.85 (9 H); m 1.26; m, 1.55; d 1.95; t 2.20; m comb. 2.68 and 2.70 (in the presence of trifluoroacetic acid, 2.70 and 2.90); m 4.14; m 5.10; m 5.24.

Hydrocarbons. Mass spectrum, 160°C, 40 V, m/z (relative intensity, %): M^+ 464 (79)–C_{33}, 450 (10)–C_{32}, 436 (100)–C_{31}, 422 (18)–C_{30}, 408 (55)–C_{20}. The intensities were calculated with respect to the peaks relating only to the molecular ions.

Triterpenols. Mass spectrum, 135°C, 40 V, m/z (% rel.): M^+ 425 (35.0), $(M-15)^+$ 411 (17.5), $(M-18)^+$ 408 (3.5), $(M-33)^+$ 303 (3.5), 304 (0), the ions 272 (5.2), d 257-259 (17.5-3.5), b 218 (100%), $(b-15)^+$ 103 (52.0), a 189 (58.0), 205 (75.0), 2.7 (38.6).

SUMMARY

The presence of about 11 classes of lipids in tomato seed oil has been established. The main components are unoxidized acylglycerols (80-90%). Oxidized components are represented by epoxyacyldiacylglycerols (0.4-0.8%). The compositions of the free fatty acids and those isolated from the triacyl- and monoacylglycerols are identical. A stereospecific analysis been made of the triacylglycerols, and it has been shown that the first position is esterified predominantly by saturated fatty acids, as compared with the third position, and the second position is 95% esterified by unsaturated fatty acids, as in the majority of plant triacylglycerols. The sterospecies composition of the triacylglycerols has been established – species with linolenic acid in the second and third positions predominate.

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