INFLUENCE OF THE DEGREE OF RIPENESS OF COTTON SEEDS ON THE FATTY ACID COMPOSITION OF THE LIPIDS

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The total fatty acids of cotton seeds include 31 components. The 18:3 acid that is the main component of the early-ripe seeds is present mostly in the mono-, di-, and triacylglycerides. The distribution of the fatty acids in the triacylglycerides of the early-ripe seeds is not characterized by selectivity.

The fatty acid compositions of the lipids of developing seeds have been studied widely [1]. The oils of such industrially important crops as sunflower, soybean, safflower [2] contain large amounts of the 18:3 acid in the early stage of development and its amount decreases sharply as the seeds ripen and it is practically absent from the ripe seeds. In parallel with this, the amount of the 18:1 and 18:2 acids in the ripening seeds increases.

Similar characteristics of the change in the fatty acid composition of the total lipids have been observed in the study of vegetating cotton seeds [3]. However, as can be seen from the results of our previous paper [4], the composition of the total lipids of early-ripe cotton seeds differ substantially in its complexity from the lipid composition of seeds that have achieved final ripeness. The aim of the present investigation was to study the change in the fatty acid compositions of the individual classes of lipids of cotton seeds during their ripening.

The seeds of the cotton plant of variety Tashkent 1 were investigated.

The fatty acids were extracted from the lipids by alkaline hydrolysis and were analyzed in the form of the methyl esters (MEs) by the GLC method.

Table 1-3 give the fatty acid compositions of the total lipids and of the individual lipid classes of the 10-, 35-, and 70-day seeds, respectively. It follows from these figures

TABLE 1. Fatty Acid Composition of the Lipids of 10-Day Seeds

Acid	Total lipids		Sterol esters	FAMEs	PAGs		FFAs	DAGS + HAGs	MAGs	PLs
	wt.%	mg/100 seeds	wt.%		wt.%	mg/100 seeds	wt.%			
11:0	Tr.	Tr.	—	—	—	—	Tr.	—	—	—
12:0	Tr.	Tr.	6.2	0,7	—	—	—	—	—	—
13:0	Tr.	Tr.	—	0,7	—	—	Tr.	—	—	—
14:0	0,4	0,08	3,5	1,5	0.8	0,02	0,9	0 9	0,2	0,5
15:0	Tr.	Tr.	Tr.	—	—	—	Tr.	—	—	—
16:0	31,4	6,0	43.1	46,5	16,4	0,43	37,5	61,1	40,7	23,4
16:1	0,5	0,1	8,1	2,4	1,3	0,03	1,0	4,9	—	0.7
17:0	Tr.	Tr.	Tr.	—	—	—	Tr.	—	—	—
18:0	1,1	0.2	4,7	2.8	1,0	0,03	0,7	1,4	0,8	0,4
18:1	9,3	1,8	26,9	17,4	12,1	0,32	12,9	9,5	8,5	7,4
18:2 CPAs	19,8	3.8	7,5 —	24,2 —	23,3	0.61	31.0	11,8 —	12,3 —	20,8 —
18:3	37,5	7.2	—	3,8	45,1	1,17	16,0	10,4	37,5	46,8
20:0	Tr.	Tr.	Tr.	—	Tr.	Tr.	Tr.	—	—	—
Σ_{sat}	32,9	6,28	57,5	52,2	18,2	0,48	39,1	63,4	41,7	24,3
Σ_{unsat}	67,1	12,9	42 5	47,8	81,8	2 13	60,9	36,6	58,3	75,7

CPA — the cyclopropenoid malvic acid.

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TABLE 2. Fatty Acid Composition of the Lipids of the 35-Day Seeds

Acid	Total lipids		PAGs		FFAs	EAGs	DAGs+HAGs	MAGs	PLs
	wt.%	mg/100 seeds	wt.%	mg/100 seeds	wt.%				
11:0	Tr.	Tr.	—	—	Tr.	Tr.	—	—	—
12:0	Tr.	Tr.	—	—	Tr.	—	Tr.	Tr.	—
13:0	Tr.	Tr.	—	—	Tr.	—	—	Tr.	—
14:0	1.2	6,1	1.2	5,9	1.5	1,2	0,4	1,2	0,5
15:0	Tr.	—	—		Tr.	—	—	Tr.	—
16:0	29,2	149,6	29,9	146,5	30,3	26,8	30,0	26,5	27,4
16:1	1,4	7,1	1,4	6,9	0,9	1,5	1,6	1,6	0,6
17:0	Tr.	—	—	—	Tr.	—	—	0,9	—
18:0	2,1	10,7	2,0	9,8	0 5	3 1	1,7	2,9	2,4
18:1	20,2	103,6	21,0	102,9	19.8	19,7	27,3	20,6	11,5
18:2 CPAs	45,0	230,8	43,7	214,3	44,3	47,7	39,0	42,2	44,5
					—	—	—	—	—
18:3	0,9	4.6	0,8	3,9	2,7	—	—	4,1	13,1
20:0	Tr.	Tr.	Tr.	Tr.	Tr.	—	—	Tr.	—
Σ_{sat}	32,5	166,4	33,1	162,2	32,3	31,1	32,1	31,5	30,3
$\Sigma_{unsat.}$	67,5	346,1	66,9	328,0	67,7	68,9	67,9	68,5	69,7

TABLE 3. Fatty Acid Composition of the Main Lipid Classes of the 70-Day Seeds

Acid	Total lipids		TAGs		FFAs	PLs
	wt.%	mg/100 seeds	wt.%	mg/100 seeds	wt.%	
11:0	Tr.	Tr.	—	—	Tr.	—
12:0	Tr.	Tr.	Tr.	Tr.	Tr.	—
13:0	Tr.	Tr.	—	—	Tr.	—
14:0	1,1	29 2	1,0	25,0	1,5	1,0
15:0	Tr.	Tr.	—	—	Tr.	—
16:0	27,0	717,7	27,3	682,5	35.4	29,3
16:1	1,3	34,5	1,2	30,0	1,0	1,6
17:0	Tr.	Tr.	—	—	Tr.	—
18:0	2,6	69,1	2,7	67,5	1 1	2,2
18:1	17,9	475,8	18,9	472,5	37,2	18,1
18:2 CPAs	50,1	1331,6	48,9	1222,5	22,4	47,8
					—	—
18:3	Tr.	Tr.	Tr.	Tr.	1,4	Tr.
Σ_{sat}	30,7	816,0	31,0	775,0	38,0	32,5
Σ_{unsat}	68,3	1841,9	69 0	1725,0	61 0	67,5

that in the lipids of cotton seeds at all three stages of ripeness there are about 14 medium- and high-molecular-weight fatty acids half of which belong to the minor components. Traces of C_2-C_{10} low-molecular-weight acids were detected (GLC, TLC) in all the samples of total lipids [5]. The hydroxy acids of the monohydroxyacylidiacylglycerols (HAGs) consisted of eight components [6]. Thus, 31 acids have been identified in the total lipids of cotton seeds. The amount of predominating acids changes appreciably according to the class of lipids and the degree of ripening of the seeds.

In the lipids of the early-ripe seeds the free acids (FFAs) and the acids bound with sterols are distinguished by the greatest diversity, the total amount of unsaturated acids is highest in the triacylglycerols (TAGs), and of the 82% of unsaturated acids in the TAGs more than half (45%) consists of the 18:3 acid. Linolenic acid is also the main unsaturated acid in the polar lipids (PLs) and in the monoacylglycerols (MAGs) of the 10-day seeds, while in the FFAs the 18:2 acid predominates.

The fatty acid composition of the lipids of the medium-ripe seeds was practically the same as that of the lipids of the 10-day seeds while the total amount of the unsaturated

acids in all classes of lipids was twice as great as that of the saturated acids. The acid present in largest amount in the lipids of the 35-day seeds had become linoleic (18:2), and the 18:3 acid was present in appreciable amounts only in the PLs.

The fatty acids of the lipids of the ripe (70-day) seeds were close in quantitative and quantitative composition to the acids of the lipids of the 35-day seeds. The greatest amount of saturated acids was present in the FFAs, and the dominating acids remained the 16:0 and 18:2 acids.

The degree of saturation (or of unsaturation) of the fatty acids of the total lipids scarcely changed as a function of the phase of development of the seeds, but in the individual lipids these changes were considerable. The greatest changes in the fatty acid composition were undergone by such classes of lipids as the PAGs, the diacylglycerols (DAGs), the MAGs, and the PLs. As the seeds ripened, the proportion by weight of the 16:0 acid in the PAGs increased nonuniformly, reaching a maximum level in the medium-ripe seeds (30%), the 18:3 acids disappeared almost completely, and the amounts of the 18:1 and 18:2 acids doubled. In the MAGs the amounts of 18:1 and 18:2 acids almost doubled, that of the 16:0 acid halved, and that of the 18:3 acid fell by a factor of 9 (Table 2). The same laws were traced in the DAGs as in the MAGs. In the FFAs the total saturation scarcely changed, the amount of 18:3 acid fell 11-fold and that of the 18:1 acid doubled. The amount of 16:0 acid changed nonuniformly in the course of ripening: it first fell by 7% in the FFAs of the medium-ripe seeds and then increased somewhat (by 5%) in the ripe seeds. The opposite situation was observed in the quantitative changes of the 18:2 acid, the amount of which in the free acids of the 35-day seeds was 45% while in the FFAs of the 70-day seeds it had become 1.5 times smaller than in the analogous fraction of the 10-day seeds.

The amounts of acids with unusual functional groups changed dissimilarly during ripening. Thus, the hydroxy acids were present in the form of traces in the early-ripe seeds and their amount increased during ripening, while the amount of cyclopropenoid acid (CPAs) had fallen almost twofold by the moment of full ripeness [7].

It can also be seen from the tables that the amounts of individual acids in the combined lipids (with the exception of the 18:3 acid), calculated to the mass of 100 seeds increased as they ripened, and this at the highest rate between the 10th and 35th days from the moment of flowering. Between the 35th and 70th days from the moment of flowering, the rate of accumulation of the individual acids fell sharply and became practically the same for all the components. The same characteristics were observed in the changes of the absolute amounts of the fatty acids of the PAGs, but here they were even more pronounced. Thus, the amounts of the main 16:0, 18:0, 18:1, and 18:2 acids in the PAGs rose at the highest rate between the 10th and 35th days from the moment of flowering. The amount of the 18:3 acid had trebled by the 35th day, and by the 70th day this acid had practically disappeared.

In order to establish which acids esterified the central position of the PAG molecule in the various stages of development, pancreatic hydrolysis of the PAGs of two samples was performed. The fatty acid compositions of the β-MAGs were as follows (wt.%):

Seeds	*14:0*	*16:0*	*16:1*	*18:0*	*18:1*	*18:2*	*18:3*
1-day	1,1	7,6	1,4	0,7	7,9	21,6	59,7
35-days	0,9	8,5	1,1	1,3	27,7	54,9	5,6

From these figures we calculated the position-species composition of the PAGs. Information on the position-species composition of the ripe seeds has been published previously [5]. In contrast to the 29 species of PAGs of the ripe seeds, the PAGs of the 10-day seeds were represented by 60 species and those of 35-day seeds by 37 species. Thus, the composition of the PAGs simplified as the seeds ripened. By comparing the compositions of the acids of the β-MAGs in the corresponding TAGs, and also the amounts of TAG species in the 10- and 35-day seeds it is possible to deduce that esterification of glycerol by acids in the early period of the development of the seeds takes place less selectively than in the later stages. The main acids predominantly esterifying the β positions of the TAGs are distributed in the following way: for the TAGs of the 10-day seeds — Le > L > O > P; for the 35-day seeds — L = O > P; and for the 70-day seeds — L > O > P [8]. Consequently, in the early stages of the development of the seeds the central position of the TAGs is occupied predominantly by the 18:3 acid, in the PAGs of medium-ripe seeds by equal amounts of the 18:2 and 18:1 acids, and in the PAGs of the ripe seeds by the 18:2 acid, as in many other plant oils. It must be men-

tioned that in spite of the minor amount of the 18:3 acid in the PAGs of the 35-day seeds, all of it is present in the central position of the PAGs, as can be seen from a comparison of the fatty acids of the TAGs and β-MAGs of the medium-ripe seeds.

Thus, although the qualitative fatty acids compositions of the total lipids at all stages of development of cotton seeds are practically the same, the individual lipid classes differ appreciably in relation to this composition both in the individual periods and with respect to one another within a single period of development. The most considerable qualitative and quantitative changes in the composition of the fatty acids take place in the intermediate products of the biosyntheses of the glycerides — MAGs, DAGs, and PLs — and in the triacylglycerols themselves.

EXPERIMENTAL

The conditions for performing GLC have been described previously [5].

All the lipids with the exception of the fatty acid methyl esters were hydrolyzed with a 10% methanolic solution of KOH, and the fatty acids were methylated with diazomethane, and analyzed by GLC.

CONCLUSION

The total fatty acids of cotton seeds consist of 31 components, including cyclopropenoid acids, hydroxy acids, low-molecular-weight acids, and fatty acids with odd numbers of carbon atoms.

It has been established that the 18:3 acid, which is the predominating acid in the lipids of the early-ripening seeds, is concentrated in the triacylglycerols and the intermediate products of their biosynthesis, while the 18:2 acid predominates in the free acids.

The distribution of the acids in the triacylglycerols in the early stages of the development of the seeds takes place less selectively than by the end of their ripening.

LITERATURE CITED

1. P. K. Stumpf, "Lipid biosynthesis in developing seeds," in: Lipids and Lipid Polymers in Higher Plants (ed. H. Tevini and H. Lichtentaler), Springer, Berlin (1977).
2. J. A. Robertson, G. W. Chapman, and R. L. Wilson, J. Am. Oil Chem. Soc., 55, 266 (1978); O. S. Privett, K. A. Dougherty, and W. L. Erdahi, J. Am. Oil Chem. Soc., 50, 516 (1973); K.-I. Ichihara and M. Noda, Phytochemistry, 19, 49 (1980).
3. S. V. Skvortsova, R. R. Rakhmanov, and A. G. Vereshchagin, Dokl. Akad. Nauk USSR, No. 7, 57 (1966); A. G. Vereshchagin, S. V. Skvortsova, and N. I. Ishakov, Biokhimiya, 28, 868 (1968).
4. S. G. Yunusova and S. D. Gusakova, Khim. Prir. Soedin., No. 1, 40 (1982).
5. S. G. Yunusova, I. P. Nazarova, S. D. Gusakova, and A. I. Glushenkova, Khim. Prir. Soedin., 319 (1980).
6. S. G. Yunusova, S. D. Gusakova, and Ya. V. Rashkes, Khim. Prir. Soedin., 436 (1981).
7. G. A. Preobrazhenskaya, S. G. Yunusova, A. I. Glushenkova, and A. L. Markman, Maslozhir. Promst., No. 11, 11 (1973).
8. F. D. Gunstone, R. J. Hamilton, F. B. Padley, and M. J. Qureshi, J. Am. Oil Chem. Soc., 42, 965 (1965).