The total fatty-acid compositions of the individual subfractions and the position distributions of the fatty acids in the glyceride moiety of the molecules have been determined, and on this basis the molecular compositions of the phosphatidylcholines have been established: for the DGs 46 species and for the MADGs 43 species. It has been shown that in the cotton plant two types of molecular species are synthesized (mainly to the extent of 85%): Disaturateds and monosaturated–monosaturateds, the disaturateds being characterized by a greater diversity of species but a low amount.

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THE SEED OIL OF Catalpa. I

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The decorative plant catalpa has a light and soft wood highly resistant to decay which has long been used as a material for railway sleepers, posts, and underwater structures [1].

The seed oil of catalpa has not been studied sufficiently deeply and, apparently, for this reason has not yet found a use. We have investigated samples of the seed oil from five species of catalpa: southern catalpa (C. bignonioides Walt. [C. syringaefolia]), northern catalpa (C. speciosa Word ex Engelm.), Chinese catalpa (c. ovata G. Don), the hybrid teas catalp (C. bignonioides × ovata), and Ducloux catalpa (C. duclouxii Dode [C. fargesi duclouxi]), which are cultivated in the Soviet Union (the towns of Kamyshin and Lipetsk) and in botanical gardens: the Main Botanical Garden (Moscow), those of Nikitskii (Yalta), Tashkent, Stavropol', and Voronezh, and the Central Republican Botanical Garden of the Academy of Sciences of the Ukrainian SSR (Kiev).

The oil content of the catalpa seeds varies between 21.2 and 36.7% (Table 1), which is not inferior to those of the oil crops most widely used in the Soviet Union for example, the oil content of linseed is 26.9-47.2%,

TABLE 1

Geographic site	Amt. of oil in the catalpa seeds, %				
	northern	southern	Chinese	teas	ducloux
Tashkent	29,9	—	—	—	—
Yalta	—	21,2	21,9	—	36,7
Stavropol'	36,1	—	—	—	—
Kamyshin	31,8	—	—	31,9	—
Kiev	33,1	34,3	26,3	—	—
Voronezh	—	29,9	—	—	—
Lipetsk	—	30,3	25,6	—	—
Moscow	—	10,1	—	—	—

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TABLE 2

Sample	Geographic site	Fatty acid content, %							
		palmitic	stearic	oleic	linoleic	linolenic	unidentified	heneicosanoic	eleostearic
Northern catalpa	Tashkent	1,3	1,9	7,7	46,8	1,8	1,7	1,2	37,6
	Stavropol'	2,4	1,5	5,5	50,1	0,7	0,7	0 6	38,5
	Kamyshin	2,8	1,7	7,5	46,8	1,1	1,1	0,9	36,0
	Kiev	2,2	1,2	5,7	47,6	1,4	0,9	0,8	40,2
	Yalta	3,4	2,2	8,1	44,6	1,7	1,5	5,2	33,3
Southern catalpa	Voronezh	2,7	2,1	7,1	50,3	0,9	0,4	0,5	36,0
	Lipetsk	4,3	2,5	9,8	48,0	0,6	0,8	1,2	32,8
	Moscow	4,1	1,6	6,3	40,2	1,0	0,7	1,0	45,1
Teas catalpa	Kamyshin	1,9	1,3	7,4	43,9	1,5	1,5	1,3	42,1
Chinese catalpa	Yalta	2,6	1,1	7,1	43,3	0,4	0,4	0,7	44,4
	Kiev	2,0	1,7	5,8	39,6	1,3	1,1	1,1	46,2
Ducloux catalpa	Yalta	2,1	1,2	9,0	42,2	0,4	0,6	0,7	43,8
Tung		1,1	1,8	5,5	7,0	—	1,0 (peak 6-gadoleic)	— —	83,6
Flax		5,7	3,1	19,2	18,4	53,6	—	—	—
Sunflower		4,8	4,7	21,9	68,6	—	—	—	—

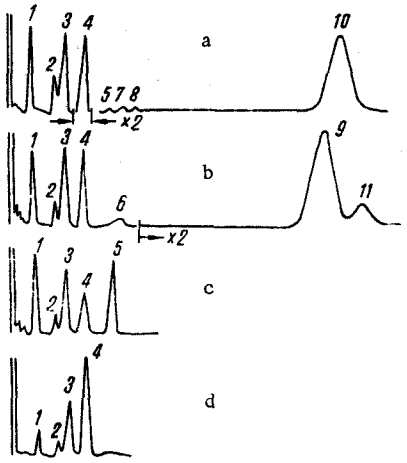

Fig. 1. GLC of the methyl esters obtained from the seed oils of catalpa (a), tung (b), linseed (c), and sunflower seed (d): 1) methyl palmitate; 2) methyl stearate; 3) methyl oleate; 4) methyl linoleate; 5) methyl linolenate; 6) methyl gadoleate; 7) unidentified peak; 8) methyl heneicosanoate; 9) methyl α-eleostearate; 10) methyl eleostearate; 11) methyl β-eleostearate.

of cottonseed 15.9-28.6%, of soybean 13.5-25.4%, and of sunflower seed 33.0-57.0% [2]). The oil content of the seeds of the various species of catalpa increases in the following sequence: Chinese, southern, teas, northern, Ducloux.

The amounts of oil in the catalpa seeds varies considerably according to the geographic coordinates, but no correlation was established between the oil content and the latitude. The oil content of the Moscow catalpa must apparently be considered as an exception due to the depletion of the seeds because of the absence of the necessary amount of heat in this geographic zone.

The fatty-acid compositions of the catalpa oils and also of comparison samples are given in Figure 1 and Table 2.

According to S. L. Ivanov's climatic theory, "The capacity of individual species and genera for elaborating certain fatty acids characteristic for them is a species or generic physiological-chemical characteristic" [3]. It can be seen from Table 2 that the qualitative compositions of the fatty acids of the seed oils of

different species of catalpa in different geographic zones are similar. Consequently, the physiological-chemical characteristic of catalpa is the presence of the following fatty acids: palmitic, stearic, heneicosanoic, oleic, linoleic, linolenic, and eleostearic; about 95% of them is made up of eleostearic, linoleic, and oleic acids.

In the quantitative respect, eleostearic acid has a tendency to a rise in its relative amount on passing from one species to another in the following sequence (%): southern – 32.8-36.0%, northern – 36.0-40.2%, teas – 42.1%, Chinese – 44.4-46.2%.

Peaks 7 and 10 (see Fig. 1) are of interest for the further study of geometric and position isomerism.

There is information [4, 5] on low values of the iodine numbers determined by the usual methods, as compared with the theoretically possible values, for oils which include fatty acids with conjugated double bonds. This is explained by the incomplete halogenation of conjugated double bonds [4], as a result of which the iodine number of eleostearic acid proves to be 1.5 times smaller than the true value. This is apparently why the literature figures for the iodine number of tung oil vary between 145 and 176 [4-7].

To select the optimum method of determining the degree of unsaturation of the oils studied, which is characterized by the iodine number, we performed a comparative investigation of results obtained by three methods: Kaufmann's (considered one of the most accurate methods) [2]. Dam's method (the fastest in performance of the methods described so far and requiring only small amounts of oil (0.002-0.005 g) [8], and Woburn's (recommended for the analysis of tung oil) [2] with the results obtained by the GLC method.

From the fatty acid compositions of the samples studied we calculated the theoretically possible values of the iodine numbers and then by the statistical treatment of the results we established a correspondence of the values of the iodine number for each sample obtained experimentally and by calculation.

The mean square deviations of the method of calculating iodine numbers were determined [9] from a performance in triplicate of the GLC of the methyl esters of the fatty acids of five samples – Chinese catalpa (Kiev), teas catalpa (Kamyshin), tung, linseed, sunflowerseed – and of the methods of experimental determination of the iodine numbers of the four last-mentioned samples by means of the following formula:

$$S = \sqrt{\frac{\sum_{1}^{m}\sum_{1}^{n_j} (x_{ji} - \bar{x}_j)^2}{n - m}},$$

where S is the mean square error of the method; x_{ji} is a single value; $\bar{x}_j$ is the mean of all the values; n is the total number of measurements; m is the number of samples; and $\sum_{1}^{m}\sum_{1}^{n_j}$ is the sum of the squares of the differences between the individual values and the mean.

The statistical dependence and independence of the differences between the square errors of the calculated values of the iodine numbers and those obtained experimentally were determined with the aid of Fisher's criterion $F = S_1^2/S_2^2$ [9] and a comparison of the value obtained with tables of F ($P = 0.95$; $f_1 = 10$; $f_2 = 8$) [9], where P is the probability with which the hypothesis of a statistically insignificant difference between the two square errors is adopted, f_1 and f_2 are the numbers of degrees of freedom, equal to $n-1$ and interpreted as the numbers of control measurements to which the result already obtained from the measurements corresponds [9].

For cases when the calculated values of the Fisher criterion were less than the tabular values, we used Student's criterion for determining whether the values of the iodine numbers for each sample of oil found experimentally and calculated belonged to one general set

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{S_{\bar{x}_1 - \bar{x}_2}} \sqrt{\frac{n_1 \cdot n_2}{n_1 + n_2}} \text{ [9]},$$

where $\bar{x}_1$ and $\bar{x}_2$ are the mean values of the two magnitudes being compared, and n_1 and n_2 are the number of measurements, $S_{\bar{x}_1 - \bar{x}_2} = \sqrt{(S_1^2/n_1) + (S_2^2/n_2)}$ is the mean square error of the difference of the two average values.

The results of a comparative examination of the iodine Nos. of samples of sunflower seed, linseed, tung, and catalpa oils by the Kaufmann, Dam, and Woburn methods and those calculated on the basis of the results of a gas-chromatographic analysis, also the statistical treatment of these results are given in Tables 3 and 4.

As can be seen from the results of a statistical treatment of the figures, the values of the Fisher criterion (F criterion) calculated in order to compare the mean square errors of the experimental methods of determining iodine numbers with the results of the gas-chromatographic method are less than the tabular

TABLE 3

Acid	Sample	Single values of the I. No. x_1	x_2	x_3	Mean value of the I. No. ($\bar{x}_j$)	$\Sigma(x_j-\bar{x}_j)^2$
GLC	Chinese catalpa, Kiev	199,4	199,0	196,9	198,4	3,61
	Teas catalpa (Kamyshin)	196,1	194,9	192,8	194,6	4,58
	Tung	233,1	235,6	234,0	234,2	3,21
	Linseed	188,3	186,7	189,5	188,2	3,95
	Sunflower seed	137,4	137,5	136,1	137,0	1,22
	$\sum_{1}^{m}\sum_{1}^{n_j}(x_{jl}-\bar{x}_j)^2$	=16,57;	S^2=1,66;		S=1,29;	f=10
Kaufmann	Sunflower seed	136,9	137,9	137,1	137,3	0,56
	Linseed	192,0	191,8	190,7	191,5	0,98
	Tung	164,0	165,0	163,5	164,2	1,17
	Teas catalpa (Kamyshin)	169,9	168,5	170,1	169,5	1,52
	$\sum_{1}^{m}\sum_{1}^{n_j}(x_{jl}-\bar{x}_j)^2$	=4,12;	S^2=0,52;		S=0,72;	f=8
Dam	Sunflower seed	136,1	137,9	136,5	136,8	1,79
	Linseed	188,1	187,0	189,2	188,1	2,42
	Tung	165,1	165,1	163,5	164,5	1,72
	Teas catalpa (Kamyshin)	169,4	170,0	170,0	169,8	0,24
	$\sum_{1}^{m}\sum_{1}^{n_j}(x_{jl}-\bar{x}_j)^2$	=6,17;	S^2=0,77;		S=0,88;	f=8
Woburn	Sunflower seed	139,6	138,5	139,3	139,1	0,65
	Linseed	189,0	192,7	189,6	190,4	7,89
	Tung	234,8	234,1	233,2	234,0	1,29
	Teas catalpa (Kamyshin)	193,5	192,9	194,1	193,5	0,72
	$\sum_{1}^{m}\sum_{1}^{n_j}(x_{jl}-\bar{x}_j)^2$	=10,55;	S^2=1,32;		S=1,15;	f=8

TABLE 4. Values of the Fisher Criterion (F Criterion) and the Student Criterion (t-Criterion)

Sample	Method	Calculated value* F-criter.	t-criter.
Sunflower seed	Kaufmann	3,19	2,03
	Dam	2,16	0,27
	Woburn	1,26	2,58
Linseed	Kaufmann	3,19	2,73
	Dam	2,16	0,14
	Woburn	1,26	2,71
Tung	Kaufmann	3,19	58,00
	Dam	2,16	94,80
	Woburn	1,26	0,25
Catalpa	Kaufmann	3,19	20,70
	Dam	2,16	33,80
	Woburn	1,26	1,35

*Tabular value of the F criterion 3.3472, and of the t criterion 2.78.

value of F (P = 0.95; f_1 = 10; f_2 = 8) = 3.3472 in all cases. Consequently, the mean values of the iodine numbers determined experimental and calculated are comparable with one another according to Student's criterion (t criterion).

The values of t-criterion calculated for the iodine numbers of sunflower seed oil, which possesses a relatively low degree of unsaturation of the fatty acids, are less than the tabular value of t (P = 0.95; f = 4) = 2.78, i.e., the values of the iodine numbers belong to one general set. Consequently, all the experimental methods mentioned can be used to determine the iodine number of a sunflower seed oil.

For linseed oil, the same picture is observed (the oil is highly unsaturated but does not contain acids with a conjugated system of double bonds).

TABLE 5

Species of catalpa	Geographic site	n_D^{20}	Iodine No.		t-criterion
			exptl.	calc.	
Northern	Tashkent	1,4920	189,8	190,1	0,37
	Stavropol'	1,4990	193,9	193,5	0,49
	Kamyshin	1,4968	191,5	190,2	1,59
	Kiev	1,4993	197,2	196,4	0,98
Southern	Yalta	1,4905	177,4	175,2	2,70
	Voronezh	1,4960	191,0	189,2	2,21
	Lipetsk	1,4985	177,0	178,7	2,09
Chinese	Yalta	1,4995	198,5	197,3	1,47
	Kiev	1,5000	198,4	199,0	0,74
Teas	Kamyshin	1,4994	194,2	196,1	2,34
Ducloux	Yalta	1,4941	194,4	195,9	1,84

The results of the determination of the iodine number of tung oil show that the Kaufmann and Dam methods, which are the best-reproducible methods (the values of the F criterion less than the tabular value) give systematically low values of the iodine numbers for an oil with a high content of acids having systems of conjugated double bonds (calculated values of the T criterion greater than the tabular values). Only the Woburn method gives iodine numbers agreeing well with the calculated values (calculated value of the t criterion less than the tabular value).

A similar result was obtained for the catalpa oil, and therefore in the subsequent determination of the iodine numbers of oils of catalpas from different geographic zones the Woburn method was selected (Table 5).

As can be seen from Table 5, the values of the t-criterion for all the catalpa samples are less than the tabular values of t ($P = 0.95$; $f = 4$) = 2.78. Consequently, the values of the iodine numbers calculated from the results of GLC and obtained by Woburn's method for catalpa seed oils belong to one general set.

Since "the iodine number and the refractive index are mutually supplementing constants which permit the nature of the oil in relation to the amount of unsaturated acids in it to be judged" [3], Table 5 gives, in addition to the iodine numbers, the values of the refractive indices.

The degree of unsaturation of the fatty acids of the catalpa seed oils increase on passing from one species to another in the following sequence: Southern, northern, teas, Chinese, i.e., the sequence similar to that of increasing eleostearic acid content in the oil, and on passing to more northern latitudes a slight tendency to an increase in the degree of unsaturation of the fatty acids is observed (see Table 5).

EXPERIMENTAL

In view of the presence of eleostearic (octadeca-9,11,13-trienoic) acid, which is capable of rapid oxidation and isomerization, particularly at elevated temperatures, in catalpa oil [7, 10], we avoided extraction of the oil in a Soxhlet apparatus [8]. The oil was extracted from seeds freed from the fruit coating and finely ground in an electric mill by three extractions with freshly distilled hexane, bp 68.5°C, which had been deaerated in a current of nitrogen, at room temperature, with constant stirring. The hexane was distilled off at a residual pressure of 10-20 mm Hg of nitrogen and at a water-bath temperature not exceeding 40°C.

The refractive indices of the oils were determined on a RPL-3 refractometer.

To determine their fatty-acid compositions, samples of the seeds were saponified with an ethanolic solution of caustic soda by the VNIIZh [All-Union Scientific-Research Institute of Fats] method [2] and methylated with diazomethane [11] followed by analysis of the fatty acid methyl esters by the GLC method on a Varian Aerograph, series 1400, chromatograph. The column had a length of 1.5 m and a diameter of 3 mm, the liquid phase was diethyleneglycol succinate (20% on the weight of the solid support). The solid support was Chromosorb W, 60-80 mesh, the temperature of the column was 185°C and of the evaporator 250°C, and the rate of flow of air was 300 ml/min and of helium and hydrogen 30 ml/min each.

The acids were identified from the logarithms of the relative retention volumes ($VR_{\text{methyl palmitate}} = 1$). The areas of the peaks were used for quantitative calculation [11].

SUMMARY

1. The fatty-acid compositions of the seed oils of catalpas cultivated in the Soviet Union have been studied.

2. The oil content of the seeds is 21.2-36.7%, the refractive index 1.4905-1.5400, and the iodine number 184.8-201.7.

3. The following fatty acids have been found in catalpa oil (%): palmitic – 1.3-4.3; stearic – 1.1-2.5; heneicosanoic – 0.5-5.2; oleic – 5.5-9.8; linoleic – 39.6-50.3; linolenic – 0.4-1.8; and eleostearic – 32.8-46.2.

4. The most accurate results for characterizing the degree of unsaturation of the fatty acids of the catalpa seed oils are given by Woburn's method of determining iodine numbers. The iodine numbers obtained experimentally agree with those calculated and consequently the addition of halogen to the system of double bonds takes place at all the double bonds.

5. The degree of unsaturation of the fatty acids of catalpa oil characterized by the iodine numbers and refractive indices increases in the sequence of species southern, northern, teas, Chinese and has a tendency to rise on passing to more northerly zones, which is one more piece of evidence confirming the correctness of S. L. Ivanov's climatic theory of the structure of fats.

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