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CATALPA OIL SEEDS. II

L. N. Andrianova, A. L. Markman, and I. U. Yusupova

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Continuing an investigation of the seed oils of catalpa, we have studied the glyceroid composition of northern catalpa (Tashkent), oval-leaved catalpa (Kiev), and common catalpa (Voronezh) which, of those described previously [1], differ most considerably in fatty-acid composition. We used the method of enzymatic hydrolysis with porcine pancreatic lipase obtained in the Institute of Plant Substances of the Academy of Sciences of the Uzbek SSR [2].

The fatty acid compositions of the triglycerides and of the monoglyceride fraction of the oil, and also the enrichment factor are given in Table 1. The enrichment factor, which characterizes the affinity of each of the acids for the central or extreme positions of glycerol was calculated from the formula $EF = [A_2]/[A]$ [3], where $[A_2]$ is the amount of acid in position 2 and [A] is the amount of acid in the triglyceride. Obviously, EF can range from 0 to 3 (EF = 0 if the acid is present only in position 1 and 3, and EF = 3 if the acid occupies only position 2 of the glycerol). At EF = 1, the acid is present in all three positions of the glycerol equally.

As can be seen from Table 1, the saturated acids have an affinity for positions 1 and 3 of the glycerol that rises in the following sequence: palmitic, stearic, heneicosanoic. The unsaturated acids – oleic and linoleic – have an affinity for position 2 of the glycerol, that of oleic acid being greater than that of lineolic. The linolenic acid in the catalpa seed oil has no clearly marked specificity in its occupation of positions 1, 2, and 3 of the glycerol molecule. Eleostearic acid mainly esterifies the outer, 1,3, positions of the glycerol.

On the basis of the results on the fatty-acid compositions of the triglycerides and the monoglyceride fraction (see Table 1), the position-type composition of the triglycerides [3] of the oils has been calculated by Coleman's method, modified by A. L. Markman [4], using an M-222 digital computer, for which the program was drawn up in the language ALGOL-60.

The calculated figures for the position-type composition of the triglycerides of the oils of the seeds of northern catalpa are given below (because of their similarity to the figures for northern catalpa, the corresponding figures for oval-leaved catalpa and common catalpa are not given; the following abbreviations are used for the acid residues: P, palmitic; S, stearic; H, heneicosanoic; O, oleic; L, linoleic; Le, linolenic; X, unidentified; El, eleostearic):

Kalinin Polytechnic Institute. Moscow Branch of the All-Union Scientific-Research Institute of Fats.

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TABLE 1. Fatty-Acid Compositions of the Triglycerides and Monoglyceride Fraction of Catalpa Seeds

Acid	Northern catalpa			Oval-leaved catalpa			Common catalpa		
	amount of acids, %		enrichment factor	amount of acids, %		enrichment factor	amount of acids, %		enrichment factor
	in the triglycerides	in the 2-monoglycerides		in the triglycerides	in the 2-monoglycerides		in the triglycerides	in the 2-monoglycerides	
Palmitic	1,3	0,8	0,61	2,0	0,5	0,25	2,7	0,8	0,29
Stearic	1,9	0,2	0,11	1,7	0,0	0,00	2,1	0,4	0,19
Heneicosanoic	1,2	0,0	0,00	1,4	0,0	0,00	0,5	0,0	0,00
Oleic	7,7	16,4	2,13	5,8	14,8	2,55	7,0	11,8	1,69
Linoleic	46,8	80,3	1,71	39,9	81,0	2,03	50,2	75,5	1,51
Linolenic	1,8	0,4	0,22	1,7	1,1	0,65	0,9	1,2	1,33
Unidentified	1,7	0,3	0,18	1,5	0,6	0,40	0,6	0,7	1,16
Eleostearic	37,6	1,6	0,04	46,0	2,0	0,05	36,0	9,6	0,27
Total	100 0	100,0		100,0	100,0		100,0	100,0	

Glyceride	Amount, %	Glyceride	Amount, %	Glyceride	Amount, %
PPL	0,01	XPEl	0,02	POL	0,15
PPEl	0,01	HPEl	0,02	POLe	0,01
SPL	0,01	ElSEl	0,25	POX	0,01
SPEl	0,02	SSEl	0,01	POH	0,01
OPL	0,02	OSEl	0 01	POLe	0,28
OPEl	0,03	LSL	0,02	SOS	0,01
LPL	0,07	LSEl	0,07	SOO	0,03
LPLe	0,01	LeSEl	0,01	SOL	0,27
LPX	0,01	XSEl	0,01	SOLe	0,02
LPH	0,01	ELPEl	0,06	SOX	0,02
LPEl	0,27	POS	0,01	SOH	0,02
LePLe	0,02	POO	0,02	SOEl	0,50
OOO	0,02	SLL	1,33	LLeL	0,04
OOL	0,33	SLLe	0,11	LLeLe	0,01
OOLe	0,03	SLX	0,11	LLeX	0,01
OOX	0,03	SLH	0,08	LLeEl	0,13
OOH	0,02	SLEl	2,45	LeLeEl	0,01
OOEl	0,61	OLO	0,09	HLeEl	0,01
LOL	1,48	OLL	1,62	XLeEl	0,01
LOLe	0,25	OLLe	0,13	ElLeEl	0,12
LOX	0,24	OLX	0,13	SXEl	0,01
LOH	0,18	OLH	0,10	OXL	0,01
LOEl	5,48	OLEl	2,99	OLEl	0,01
LeOLe	0,01	LLL	7,25	LXL	0,03
LeOX	0,02	LLLe	1,21	LXEl	0,10
LeOH	0,02	LLX	1,16	LeXEl	0,01
LeOEl	0,46	LLH	0,87	XXEl	0,01
XOX	0,01	LLEl	26,83	HXEl	0,01
XOH	0,01	LeLLe	0,05	ElXEl	0,09
XOEl	0,44	LeLX	0.10	PElL	0,01
HOH	0,01	LeLH	0,07	PElEl	0,03
HOEl	0,33	LeLEl	2,23	SElL	0,03
ELOEl	5,07	XLX	0,05	SElEl	0,05
PLP	0,02	XLH	0,07	OElL	0,03
PLS	0,07	XLEl	2,14	OElEl	0,06
PLO	0,08	HLH	0,03	LElL	0,14
PLL	0,75	HLEl	1,61	LElLe	0,02
PLLe	0,06	ElLEl	24,82	LElX	0,02
PLX	0,06	LLeEl	0,01	LElH	0.02
PLH	0,04	SLeL	0,01	LElEl	0,53
PLEl	1,38	SLeEl	0,01	LeElEl	0,04
SLS	0,06	OLeL	0,01	XElEl	0,04
SLO	0,15	OLeEl	0,01	HElEl	0,03
				ElElEl	0,49

On summing the results for the characteristic of degree of saturation (S) and of unsaturation (U) of the fatty-acid residues and taking into account the total amount of glycerides, containing the unidentified acid (X_g), we obtain the following type composition for the glycerides of the catalpa oils (%):

Catalpa	S_3	S_2U	SU_2	U_3	X_g	Total
Northern	—	0,41	11,84	82,60	4,99	99,84
Oval-leaved	—	0,56	13,61	81,20	4,35	99,78
Common	—	0,63	14,22	83,18	1,68	99,71

The figures in "sum" columns cannot be compared with the sum of the constituents, since the computer rounds off the sum of the still unrounded percentage amounts of the glycerides.

Taking position isomerism into account, we obtain the position-type composition of the catalpa oil triglycerides (%):

Catalpa	SSS	SSU	SUS	SUU	USU	UUU
Northern	—	0,05	0.36	11,00	0,84	82,60
Oval-leaved	—	0,05	0.51	13,22	0,39	81,20
Common	—	0,13	0,50	13,21	1,01	83,18

On summing the triglycerides containing eleostearic acid in the extreme positions, and also in the extreme and central positions in one glyceride molecule, and the triglycerides containing eleostearic acid only in the central position, we obtain a pattern of the position specificity of the eleostearic acid in the triglycerides of the catalpa seed oils (%):

Catalpa	Triglycerides with eleostearic acid in an extreme position	Triglycerides with eleostearic acid in the central position
Northern	77.63	0,27
Oval-leaved	89,87	0,18
Common	74,06	2,40

As can be seen from the figures given above, the catalpa oils completely lack trisaturated glycerides and the overwhelming majority of the glycerides are triunsaturated (81–83%).

Among the disaturated-monounsaturated triglycerides an increase is found on passing from SSU to SSS, which agrees well with existing ideas on the affinity of unsaturated acids having a carbon chain with a length of < 18 for the central position of a glyceride [3]. However, among the monosaturated monosaturated-diunsaturated triglycerides this rule is not observed because of the high content of eleostearic acid in the extreme position (averaging 80% of the total amount of glycerides).

EXPERIMENTAL

The main methods of isolating the oils and of determining their fatty-acid compositions have been described previously [1].

The monoglyceride fraction of the products of the lipase hydrolysis of the triglycerides was isolated by the GLC method on a fixed layer of silica gel of the Chemopol L5/40 μ type using the diethyl ether–petroleum ether (9 : 1) solvent system [5].

The gypsum was prepared by the action of sulfuric acid on a solution of calcium chloride [6]. As the revealing agent we used a 10% ethanolic solution of phosphomolybdic acid [7].

After the monoglyceride fraction had been extracted from the plates with diethyl ether, it was subjected to saponification, methylation, and GLC as described previously [2].

SUMMARY

The results of the investigation of the glyceride composition of three samples of the seeds oils of various species of catalpa from different growth sites have shown a great similarity in the amounts of certain groups of triglycerides that they contain, in spite of the considerable differences in the fatty-acid compositions of these samples. An unusual affinity of unsaturated acids for the central position of the glycerol molecule and also a specificity of eleostearic acid in esterifying the extreme positions of the glycerol molecule in catalpa seed oils have been found.

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SEED OILS OF FIVE SPECIES OF THE FAMILY ROSACEAE

É. I. Gigienova, E. I. Kiryushina, and A. U. Umarov

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The family Rosaceae includes about 3000 species, and of them more than 150 grow in the territory of Uzbekistan. The fatty-acid compositions of the seed oils of woody-bushy species of plants have been studied in most detail [2-8], while herbaceous species have been less studied [9, 10].

We give information on the seed oils of herbaceous species of the family Rosaceae collected in the central band of mountains of the western Tien-Shan (Uzbek SSR) in 1975-1976.

The results of the thin-layer chromatography of the oils according to the classes of lipids showed that the neutral lipids contain predominantly triglycerides (main zone). In fact, all the oils investigated have low acid numbers and a low content of unsaponifiables. In the remaining 6-7 zones of neutral lipids of each of the oils, by comparing the R_f values with those of model samples (the hydrocarbons of the seed oil of the Scotch thistle, the free fatty acids of cottonseed oil, β-sitosterol) we identified hydrocarbons, free fatty acids, and free sterols.

The total fatty acids were isolated from the oils by cold saponification. Part of the combined fatty acids was methylated with diazomethane and investigated by gas–liquid chromatography (GLC) and thin-layer chromatography (TLC). The peaks of the fatty acid methyl esters in GLC were identified from their relative retention times using the linear dependence of the logarithms of these magnitudes on the number of carbon atoms [11-14]. As model samples we added the methyl esters of the fatty acids of the seed oil of Lindelofia macrostyla (Bunge) M. Pop., family Boraginaceae [15]. Another part of the total fatty acids was separated by paper chromatography (PC). This gave 5-6 fatty-acid zones, which confirmed the GLC results and additionally showed the presence of traces of arachidic and behenic acids in the oils.

The characteristics, the oil content of the seeds, and some physicochemical indices of the oils isolated and of the mixtures of fatty acids are given in Table 1.

No oxidized fatty acids were detected by PC and TLC.

The satisfactory correlation between the refractive index, the iodine number, and the IR and UV spectra of each oil leaves no doubt on the main components of the fatty-acid composition found by the GLC method. For correlation we used the regression equation: I. No. = $8555.559 \cdot n_D^{40} - 12425.928$.

The results of analyses of the fatty-acid compositions of the five oils show that the triglycerides of these oils contain considerable amounts of linolenic acid.

Information on the fatty-acid composition of the seed oil of Poterium polygamum was obtained previously [9] by calculation using the iosmerization of the oil and of the mixture of fatty acids followed by spectrophotometry in the near ultraviolet. These results concerning the amount of linolenic acid agree well with those which we have obtained by the GLC method. We also found similarly the amount of linolenic acid in the fatty acids of the seed oil of Potentilla transcaspica Th. Wolf. (~ 50%) [10]. At the same time, we found no linolenic acid whatsoever in the seed oils of woody-bushy species of plants, for example, in the cherry [8], or found it in an amount of about 2% in four species of almond [7].

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