Fatty Acid Composition of *Thalictrum* L. Seed Oils

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Abstract

The fatty acid composition of five representatives of the *Thalictrum* L. genus of the plant family *Ranunculaceae* has been investigated. The fatty acids include mainly acids with double bonds in the *trans*-5 position (about 60%). Although the main component of the fatty acids is a triene acid (*trans*-5,*cis*-9, *cis*-12-octadecatrienoic acid), the oils investigated are semidrying.

Introduction

M.O. Bagby et al. (1) have found that the fatty acids of oils of *Thalictrum polycarpum* include the *trans*-5-octadecenoic and *trans*-5,*cis*-9,*cis*-12-octadecatrienoic acids, unknown so far. M.K. Bhatty and B.M. Craig (2) have established that the oil of *Thalictrum venulosum* contains the unknown *trans*-5-hexadecenoic and *trans*-5,*cis*-9-octadecatrienoic acids.

We investigated a larger number of oils of the *Thalictrum* genus in order to determine the composition of the unusual fatty acids and to see whether there are other unknown fatty acids in these representatives. We studied oils of five plant representatives from various places of Bulgaria differing in their climate: Balchik (lying at sea-level), Pirin (a mountain, more than 1900 m), Sofia and Lozen (at 500–800 m).

Experimental Procedures and Results

Oil Extraction

The seeds were extracted in a Soxhlet apparatus with petroleum ether (bp 30–60 C). The latter was then distilled off in a vacuum rotatory evaporator. The oils obtained showed the characteristic values given in Table I.

Preparation of Methyl Esters

Five-gram samples of the oils were refluxed 1 hr in 1 n alcoholic potassium hydroxide under an atmosphere of nitrogen; the unsaponifiables were removed and the total fatty acids were isolated. Their methyl esters were then obtained by boiling for 2 hr in methanol containing 0.5% sulfuric acid.

Gas Liquid Chromatography of the Methyl Esters

The gas liquid chromatographic (GLC) analyses of the various methyl ester samples were performed with a Perkin-Elmer model F-11 apparatus under the following conditions: 1.80 m by 4 mm diameter column containing 9% PEGS on Chromosorb W (acid washed) and operating at 195 C and at 18.5 ml/min flow rate of N_2. The GLC analyses of the methyl esters of the mono- and dicarboxylic acids obtained after oxidation were performed with the same apparatus under the following conditions: 1.80 m by 4 mm diameter column containing 10% Apiezon L on Chromosorb W; linear programming, 80–195 C; rate, 2 C/min; 18.5 ml/min flow rate of N_2.

In the analyses of esters from transesterification of the oils, each sample showed seven well-defined peaks whose retention times were compared with those of five known methyl esters. The results are given in Table II.

All samples have the same components but differ only in their amounts.

Separation of the Methyl Esters of Three Representatives of the Thalictrum Genus by Chromatography on a Silica Gel-Silver Nitrate Column

The methyl esters of the total fatty acids from *Thalictrum minus, T. aquilegifolium* and *T. Glaucum* seed oils were separated into classes based on degree of unsaturation and configuration of the double bond according to B. de Vries (3) and M.K. Bhatty and B.M. Craig (2). We used the following procedure: a column (25 mm in diameter) with a cock was filled with silica gel silver nitrate (70 g) prepared according to de Vries (column length, 40 cm). The sample (about 0.5 g) was introduced into the column by means of a few milliliters of petroleum ether. The elution of the fractions was carried out as shown in Table III.

The fractions obtained were further studied by IR analysis and gas chromatography. The positions of the double bonds in the unsaturated acids were also determined using partial oxidation with performic acid according to F.D. Gunstone and P.J. Sykes (4). The results of this analysis are given in Table IV. The configuration of the *trans*-double bond in the diene and triene acids was determined by the IR spectra and by analogy with the data of M.K. Bhatty and B.M. Craig (2). The complete fatty acid composition of all samples is given in Table V.

Discussion

The investigations on the fatty acid composition of oils of five representatives of the *Thalictrum* genus have shown that about 60% of the fatty acids investigated have double bonds in the *trans*-5 position. The major component which determines the high iodine values of the oils is the *trans*-5,*cis*-9,*cis*-12-octadecatrienoic acid. Nevertheless, the oils cannot be considered drying ones since our previous investigations have shown that they belong rather closely to the group of semidrying oils.

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TABLE I
Properties of *Thalictrum* Oils

No.	Representative of *Thalictrum*	Location	Per cent oil	n_D^{20}	Iodine value (Kaufmann)	Acid value	Unsaponifiables, %
1	*T. adiantifolium*	Balchik	17.8	1,4786	162.5	7.4	2.0
2	*T. Glaukum*	Balchik	21.1	1,4780	160.8	19.1	3.7
3	*T. minus*	Balchik	15.0	1,4782	169.6	7.4	3.6
4	*T. minus*	Lozen	13.8	1,4790	163.2	13.4	2.6
5	*T. minus*	Sofia	19.9	1,4790	173.0	6.8	1.9
6	*T. foetidum*	Vidin	15.0	1,4785	166.0	21.8	3.8
7	*T. aquilegifolium*	Pirin	29.3	1,4805	183.0	4.2	2.0

TABLE II
GLC Peaks for Methyl Esters From *Thalictrum* Oils

Peak No.	Thalictrum: Retention time relative to 16:0	Thalictrum: ECL[a]	Thalictrum: Fatty acids	Standard mixture: Fatty acids	Standard mixture: Retention time relative to 16:0	Standard mixture: ECL[a]
1	1.00	16.00	16:0	16:0	1.00	16.00
2	1.11	16.36	16:1	.....	.....	.....
3	1.78	18.00	18:0	18:0	1.78	18.00
4	1.93	18.28	18:1	18:1 Δ9*c*	1.97	18.36
5	2.15	18.66	18:2	.....	.....	.....
6	2.37	19.00	18:2	18:2 Δ9*c*, 12*c*	2.37	19.00
7	2.61	19.33	18:3	18:3 Δ9*c*, 12*c*, 15*c*	2.92	19.70

[a] Equivalent chain length.

TABLE III

Fraction	Per cent fraction with respect to the initial methyl esters: *T. minus*	*T. aquilegifolium*	*T. glaucum*	Solvent	Peak No. (in Table II)	Per cent composition by GLC: *T. minus*	*T. aquilegifolium*	*T. glaucum*
I	9.1	7.2	6.5	Skellysolve "B"	1.3	14:0 3.5 15:0 0.7 16:0 60.0 17:0 1.0 18:0 33.6 20:0 1.2	14:0 1.5 15:0 0.6 16:0 54.7 17:0 0.3 18:0 42.0 20:0 0.9	14:0 0.3 15:0 0.6 16:0 75.1 17:0 0.9 18:0 22.1 20:0 1.0
II	12.0	6.5	16.5	10% Benzene[a] 20% Benzene[a]	2.4	14:1 0.9 16:1 Δ*t* 10.0 18:1 Δ*t* 89.1 20:1 Trace	14:0 0.5 16:1 7.2 18:1 92.3	14:1 0.3 16:1 7.0 18:1 92.7
III	10.1	7.0	14.0	40% Benzene[a]	2.4	16:1 Δ*c* 25.0 18:1 Δ*c* 75.0	16:1 60.0 18:1 40.0	16:1 15.3 18:1 84.7
IV	4.5	1.3	4.1	50% Benzene[a]	5.6	18:2 Δ*c* 4.0 18:2 Δ*t*,*c* 96.0	18:2 3.8 18:2 96.2	18:2 2.8 18:2 97.2
V	21.0	21.4	18.5	Benzene 5% Ether[b]	6	18:2 Δ*c*,*c* 100	18:2 100	18:2 100
VI	43.3	56.6	40.4	10% Ether[b] Ether	7	18:3 Δ*c*,*t*,*c* 100	18:3 100	18:3 100

[a] In Skellysolve "F".
[b] In benzene.

TABLE IV
Products From Oxidative Cleavage of Fractions in Table III

Fraction	Monocarboxylic acids, %: C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	Dicarboxylic acids, %: C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}
II						3.0		23.5			5.1		46.0	22.4								
III				18.5		7.2					14.0		38.5	6.4				15.4				
IV	Trace			10.7				11.1					55.0	10.5				12.7			1.0	
V	8.0			13.8									61.0					9.3			7.9	
VI	5.7			7.4				9.9					54.0	3.1				9.5			10.4	

TABLE V
Fatty Acid Composition (%) of Oils of the *Thalictrum* Genus

Fatty acids	Structure	*T. minus* (Balchik)	*T. minus* (Lozen)	*T. adiantifolium* (Balchik)	*T. minus* (Sofia)	*T. foetidum* (Vidin)	*T. glaucum* (Balchik)	*T. aquilegifolium* (Pirin)
14:0	.....	0.3	0.1	0.2	0.1	0.2	0.1	Trace
16:0	.....	5.4	5.1	6.7	6.9	3.2	4.8	3.7
16:1	Δ5t	1.2	2.3	3.9	2.0	2.3	1.5	0.5
16:1	Δ5c	2.5	2.3	3.9	2.0	2.3	1.3	2.8
18:0	.....	3.0	1.8	2.2	3.0	3.2	1.5	2.7
18:1	Δ5t	10.7	21.8	20.1	22.8	21.8	15.0	6.6
18:1	Δ9c	7.6	21.8	20.1	22.8	21 8	12.6	4.3
18:2	Δ5t, 9c	4.6	6.0	4.4	4.5	5.3	4.0	1.4
18:2	Δ9c, 12c	22.0	16.6	17.6	20.5	20.0	18.5	21.3
18:3	Δ5t, 9c, 12c	42.6	46.2	44.9	40.1	43.9	40.7	56.7
20:0	.....	0.1	0.1	Trace	0.1	0.1	0.1	Trace

It has also been established that the oils from the various representatives do not differ qualitatively from each other but the percentage of the *trans*-5, *cis*-9,*cis*-12-octadecatrienoic acid varies considerably (from 40.1% to 56.7%).

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