STUDY OF THE OILS OF PLANTS OF THE FAMILY UMBELLIFERAE

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Characteristic for plants of the family Umbelliferae is the presence of resins, aliphatic and cyclic terpenes, and, to a smaller extent, alkaloids. These substances are used in the food industry, in perfumery, and in medicine [1, 2]. This paper gives the results of a study of the fatty oils of three representatives of the family Umbelliferae growing wild under the conditions of Soviet Central Asia, namely Ligusticum discolor (multicolored ligusticum), Daucus carota (wild carrot), and Eremodaucus lehmannii (desert carrot of Lehman). These oils have been described previously, although there has been a number of publications concerning the essential oils of these plants [3].

The oil contents of the seeds are as follows: for Ligusticum discolor 16.5%, for Daucus carota 13.0, and for Eremodaucus lehmannii 6.7%.

The oils of Daucus carota and Eremodaucus lehmannii are light-yellow mobile liquids with a herbaceous odor. The oil of Ligusticum discolor is dark green with a sharp peppery smell.

We give the analytical results for these oils and the fatty acids isolated from them, and also for the fractions of saturated acids obtained by Bertram's method and the solid acids isolated by Twitchell's method [4] (Table 1).

Table 1

Index	Units of measurement	Ligusticum discolor		Daucus carota		Eremodaucus Lehmannii	
		Oil	Acids	Oil	Acids	Oil	Acids
Density	g/cm³	0.9411	—	0.9452	—	0.9390	—
Refractive index	—	1.4705	—	1.4826	—	1.4810	—
Hehner number	%	94.0	—	95.09	—	95.57	—
Neutralization number	mgKOH/g	—	199.91	—	201.89	—	200.8
Mean molecular weight	—	—	280.6	—	277.9	—	279.3
Iodine number	% I_2	107.6	110.01	105.00	111.30	106.25	109.3
Thiocyanogen number	% I_2	78.2	81.03	77.90	78.55	76.15	80.32
Yield of saturated acids	%	—	7.56	—	12.9	—	5.9
Neutralization number of the saturated acids	mgKOH/g	—	214.8	—	210.9	—	223.08
Mean molecular weight of the saturated acids	—	—	261.3	—	266.0	—	250.7
Yield of solid acids according to Twitchell	%	—	24.4	—	14.0	—	11.6
Iodine number of the solid acids	% I_2	—	83.2	—	78.6	—	85.4

The fatty acid compositions of the oils determined by gas-liquid chromatography are given in Table 2. The high iodine number of the fractions of solid acids shows that they contain solid unsaturated acids in addition to saturated acids. The former include petroselic (octadec-6-enoic), which is characteristic for the oils of plants of the family Umbelliferae. The compositions of the solid acid fractions determined by the GLC method are given in Table 3.

The octadecenoic acid contained in the Twitchell fraction of the acids is pure petroselic acid uncontaminated by oleic acid, which is confirmed by the destructive oxidation [5] of its methyl ester, since, among the fragments of the dicarboxylic acids formed in the destructive process we found only adipic and not azelaic acid, and among the monocarboxylic acid fragments we found only lauric and not pelargonic acid.

$$CH_3(CH_2)_{10}CH{=}CH\,(CH_2)_4COOCH_3 \xrightarrow{KMnO_4} CH_3(CH_2)_{10}COOH + HOOC\,(CH_2)_4COOCH_3$$

When the content of petroselic acid in the solid fraction was recalculated as a percentage in the whole, we found that, of the octadecenoic acids in the oil, the oleic and petroselic acids were present in the amounts shown in Table 4.

Table 2

Acid	Ligusticum discolor	Daucus carota	Eremodaucus Lehmannii
Pelargonic	—	1.35	—
Capric	—	3.29	—
Undecyclic	—	2.90	—
Lauric	—	2.50	—
Tridecylic	—	—	0.49
Myristic	0.90	—	—
Palmitic	4.60	4.85	3.72
Palmitoleic	1.29	—	1,29
Stearic	1.01	2,94	1.89
Octadecenoic	56.40	67.41	66.11
Linoleic	30.40	14.76	26.50
Linolenic	5.40	—	—

Table 3

Acid	Composition of the solid acid fraction		
	Ligusticum discolor	Daucus carota	Eremodaucus Lehmannii
Palmitic	5.46	2.95	1.30
Stearic	0.74	0.15	0.09
Octadecenoic	93.80	96.90	98.61

Table 4

Acid	Ligusticum discolor	Daucus carota	Eremodaucus Lehmannii
Oleic	33.52	53.75	54.68
Petroselic	22,88	13.66	11.43

Table 5

Glycerides	Ligusticum discolor	Daucus carota	Eremodaucus Lehmannii
Gl SSS	0,01	0,58	0,32
Gl SSU	0,72	2,64	1,4
Gl SUS	0.05	5.19	0,50
Gl SUU	4.26	29.10	0,58
GlUSU	14.70	7.01	15,64
Gl UUU	80.26	55.48	82,00

Note: Gl denotes the glycerol radical, S saturated, and U unsaturated acyl radicals.

The triglyceride compositions of the oils, which are shown in Table 5, were calculated on the basis of the fatty acid composition of the total mixture of acids and of the acids of the monoglyceride fraction [6].

EXPERIMENTAL

Preparation of the oils and separation of the resinous substances. The oils were extracted from the seeds with cold petroleum ether, bp 50–60° C, the ether was distilled off under vacuum, and the extract was concentrated in a vacuum-drying chest.

When the oil of Ligusticum discolor was saponified with ethanolic alkali, a dark resinous product was formed. After the decomposition of the soap with mineral acid, the carboxylic acids liberated were brown, which made it difficult to determine the refractive index. The dark color of the acids is apparently due to the presence of resinous substances in them. We determined the amount of these substances by Wolf's method [7]; it was 20.1% of the total weight of the carboxylic acids.

To separate the resinous substances from the oil [8], a 15–20% petroleum ether miscella was passed through a column of alumina which was then eluted with a four- to fivefold amount of petroleum ether (bp 40° C). The ether was distilled off from the resulting miscella; the oil dried under vacuum proved to be suitable for further investigations.

The fatty acid compositions of the oils were determined by gas-liquid chromatography and in a LKhM-7A chromatograph. For this purpose, the fatty acids were methylated with diazomethane and the esters were separated on a column (3 m × 0.5 cm) filled with INZ-600 brick. The stationary phase was poly(ethylene glycol succinate) and the mobile phase helium at the rate of 80–100 cm^3/min with a column temperature of 200° C (see Table 2).

Oxidation of the solid fraction of the acids. A sample of the solid acids (0.4 g) was methylated with diazomethane. The resulting methyl esters were dissolved in 9 ml of acetone and transferred to a flask for oxidation. Potassium permanganate (3.3 g) was added to the flask in portions with careful shaking. After the end of the addition of the oxidizing mixture, the flask was fitted with a stirrer and placed in a water bath and oxidation was continued at 50° C for 1 hr. Then 150 ml of water was added and the solution was decolorized with sodium bisulfite under acid conditions. The fragments formed as the result of degradation were extracted with ether and saponified. The oxidation products isolated were separated into mono- and dicarboxylic acid fractions.

Hydrolysis of the triglycerides. A sample of oil (about 1 g) dissolved in chloroform was passed through a column of silica gel. Then the column was eluted with benzene, the benzene was distilled off, and the triglyceride fraction was hydrolyzed.

Hydrolysis was performed in a round-bottomed flask fitted with a stirrer to which the triglycerides isolated from the column were added. The flask was kept in a thermostat and hydrolysis was carried out at 37° C for 0.5 hr with the addition of 0.4 g of purified lipase obtained from the pancreas of large-horned cattle.

The hydrolysis products were separated by thin-layer chromatography on silica gel [solvent system: diethyl ether–petroleum ether (9 : 1)]; the monoglyceride fraction was isolated and chromatographed [9].

CONCLUSIONS

The oils of three species of plants of the family Umbelliferae have been studied. Their analytical characteristics and fatty acid and glyceride compositions have been determined.

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