OIL OF THE SEEDS OF Hibiscus syriacus

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Hibiscus syriacus L. (shrub althea; rose of Sharon) is a well-known decorative plant. Its oil contains biologically active cyclopropenoid acids (CPAs) [1]. We have investigated the oil of the seeds of this plant growing in the environs of Tashkent. Its physical and chemical indices are given in Table 1.

The UV spectrum of the oil showed that it contained 0.92% of dienic acids with conjugated double bonds. The IR spectrum showed absorption bands at 1010 and 1869 cm^{-1} which are characteristic for the cyclopropenoid grouping $-C=C-$ (CH_2) [2], which change after the hydrogenation of the oil into a band at 1021 cm^{-1} corresponding to a cyclopropane group $-CH-CH-$ (CH_2).

The Halphen reaction [3] for CPAs was positive. It was shown by titration with hydrogen bromide in glacial acetic acid [4] that the oil contained 16.87% of CPAs. The mass spectrum of the methyl esters of the CPAs showed molecular peaks with m/e 308 and 296, which correspond to the methyl esters of sterculic (a) and malvalic (b) acids:

$$CH_3\cdot(CH_2)_7\cdot C=C\cdot(CH_2)_7\cdot CO\cdot O\cdot CH_3 \quad (a)$$
(CH_2)

$$CH_3\cdot(CH_2)_7\cdot C=C\cdot(CH_2)_6\cdot CO\cdot O\cdot CH_3 \quad (b)$$
(CH_2)

The methyl esters of the CPAs, after recrystallization, were subjected to degradation by periodate–permanganate oxidation. The results of an investigation of the degradation products by the GLC method are given in Table 2.

TABLE 1

Index	Units of measurement	Oil	Fatty acids
Oil content of the seeds	%	21,20	—
Density of the oil	g/ml	0,9250	—
Refractive index	n_D^{20}	1,4712	—
Acid No.	mg KOH/g	4,61	—
Hehner No.	%	93,58	—
Saponification No.	mg KOH/g	183,02	—
Iodine No.	% I_2	108,61	112,04
Unsaponifiables content	%	1,33	—
Phosphatides content	%	1,58	—
Neutralization No.	mg KOH/g	—	200,04
Mean MW	—	—	280,53

The only monocarboxylic acid found was pelargonic.

The products of the incomplete oxidation of the methyl esters of the CPAs gave a positive qualitative reaction with ferric chloride characteristic for β-diketo compounds. On this basis, it may be assumed that the oxidation of the CPAs takes place through the intermediate formation of the compounds $CH_3\cdot(CH_2)_7\cdot C(=O)\cdot CH_2\cdot C(=O)\cdot(CH_2)_n\cdot CO\cdot O\cdot CH_3$, the further oxidation of which forms the acids shown in Table 2.

Since, under our conditions of analysis by the GLC method, the methyl esters of the CPAs issued

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TABLE 2

Crystallization temperature,°C	Dicarboxylic acids	
	suberic	azelaic
−50	45.61	54.39
−70	86.30	13.70

from the chromatogram as a common peak with those of linoleic acid, knowing the total amount of CPAs (16.87%) it is not difficult to calculate the fatty acid composition of the oil (%):

$C_{14:0}$ – 0.31	$C_{18:1}$ – 18.09
$C_{16:0}$ – 18.32	$C_{18:2}$ – 40.59
$C_{16:1}$ – 1.25	$C_{18:3}$ – 1.83
$C_{18:0}$ – 2.74	CPAS – 16.87

The glyceride composition of the oil (%) was determined by enzymatic hydrolysis [5]:

GlSSS	0.31	GlUSU	1.10
GlSSU	1.14	GlSUS	44.28
GlSUS	11.86	GlUUU	41.31

EXPERIMENTAL

The oil was extracted from the comminuted seeds in the cold with petroleum ether (40-50°C), and the solvent was distilled off in vacuum. The physical and chemical indices of the oil were determined by generally adopted methods [6]. The mass spectra were taken on an MKh-1303 instrument fitted with a system for the direct introduction of the sample into the ion source at a voltage of 40 eV. Gas–liquid chromatography was performed on a UKh-2 apparatus using a thermal-conductivity detector. The methyl esters of the acids were separated by the use of a copper column (2.5 m × 0.4 cm) filled with 17% of poly(ethylene succinate) on TND-TSM (60-80 mesh). The temperature of the column was 198°C and the rate of flow of helium 80 cm^3/min. The IR spectra were recorded on a UR-10 apparatus.

Determination of the Amount of CPAs. A 2-g sample of the oil was passed through a column 8 mm in diameter filled with 8 g of alumina; the neutral lipids were eluted with petroleum ether, which was then distilled off in a current of nitrogen, and 0.5 g of the purified oil was dissolved in 0.7 ml of benzene, and 1.7 ml of glacial acetic acid and 1-2 drops of the indicator Crystal Violet were added and the mixture was titrated at 55°C with 0.1 N hydrogen bromide in glacial acetic acid.

Hydrogenation. A 2-g sample of the oil was hydrogenated in ethanol solution at 60°C and normal pressure with palladium on wood charcoal as catalyst. The iodine number of the hydrogenizate was found to be 32.40% of I_2.

Preparation of the Methyl Esters and Their Fractionation [7]. A mixture of 180 ml of a 0.35% solution of sodium methoxide in absolute methanol and 20 g of the oil was stirred and was left in the dark at room temperature for three days. Then the mixture was neutralized with glacial acetic acid, and 24 g of urea in 30 ml of methanol was added. The solution was kept at −16°C for 2 h. The precipitate was separated off on a Schott filter, and the filtrate was cooled successively to −30, −50, and −70°C; the complexes of the methyl esters obtained at −50 and −70°C were washed with water and were twice recrystallized from acetone. The final products were freed from acetone residues by purging with a jet of nitrogen.

SUMMARY

The physical and chemical properties and the fatty acid and triglyceride compositions of the oil of Hibiscus syriacus L. have been investigated. The oil was found to contain 16.87% of the cyclopropenoid acids malvalic and sterculic acids.

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