SEED OILS OF FOUR SPECIES OF THE FAMILY Caprifoliaceae

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UDC 547.915.665.31

Oil-bearing plants of the family Caprifoliaceae are grown in the European part of the USSR, in the Caucasus, in Western Europe, in the Mediterranean region, in North America, and in Asia.

The present paper gives the results of an investigation of the fatty-acid and triglyceride compositions of the seed oils of Central Asian representatives of all four genera of this family – Abelia corymbosa, Lonicera nummulariifolia, Sambucus nigra (European elder), and Symphoricarpus chenaultii (Chenault coralberry). The first two species of plants, growing wild, were collected on the northern slopes of the Bol'shoi Chimgan in the region of Lake Sarychelek. The other two species are cultivated as decorative plants and were collected in Tashkent.

We have previously published the characteristics of the seeds and the physicochemical indices of these oils [1, 2]. The seeds of Sambucus nigra and of Lonicera nummulariifolia are favorably distinguished by a high oil content (about 36% and about 33%, respectively). The low oil content of Abelia corymbosa (about 4%) is partially due to the high content of husk, which is difficult to separate from the kernels. The low saponification and iodine numbers of the same oil is due to the high content of total "unsaponifiables" (13%). These substances, extracted with ether from an aqueous solution of the potassium soaps of the fatty acids, likewise dissolve in ethanol and hot methanol but are insoluble in petroleum ether. They show positive qualitative reactions for polycyclic polyterpenes. Their IR spectra and rate of migration in a thin layer of silica gel in the chloroform–methanol (25 : 1) system [3] shows that they are substances of triterpenoid nature. The results of a comparison of the IR spectra of the oil and of the "unsaponifiables" of A. corymbosa confirm that the latter are present in this oil in considerable amount.

The IR spectra of the oils of S. chenaultii, S. nigra, and L. nummulariifolia have shown that their main component consists of fatty-acid triglycerides.

Mixtures of fatty acids have been isolated from all the oils. From three of the oils, not including that of the oil-poor A. corymbosa, we have obtained the total saturated and solid acids.

The gravimetric composition, according to GLC, and the chemical indices of all the mixtures isolated have been given previously [1, 2].

The identity of the composition and indices of the combined saturated and combined solid acids shows the absence of trans-ethylenic bonds and also the remoteness of cis-ethylenic bonds from the carboxy group in the unsaturated fatty acids.

The small and similar values of the iodine numbers of the combined saturated and the combined solid acids of all the oils can be explained by the incomplete removal of the saturated acids from the unsaturated by the methods of Bertram and of Twitchell, which provide for only twofold separation.

By gas–liquid and paper chromatography it is possible to determine the compositions of the acids only with respect to the number of carbon atoms and the number of multiple bonds, and no answer to the question of the position of the latter in the carbon chain is given. For this reason, to determine the positions of the multiple bonds we isolated the bromides of the mixtures of fatty acids of the four oils and studied the products of oxidative degradation of mixtures of acids.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 435-439, July-August, 1974. Original article submitted March 27, 1973.

From the mixtures of fatty acids of all the oils we isolated tetrabromides (mp 111-113°C; 111-112.5°C; 111-111.5°C; and 112-113.5°C), and from the oil of S. nigra a hexabromide (mp 175.5-176.5°C). The amounts of $C_{18:2}$ and $C_{18:3}$ acids calculated from the results of GLC correspond to the amounts of these acids calculated from the tetrabromine numbers (66.50, 61.78, 32.84, 69.76) and hexabromide number (32.00).

The degradation products of the mixtures of acids of each oil were investigated by gas–liquid and thin-layer (on cellulose) chromatography. An ethereal extract of the oxidized mixture was treated with diazomethane, and the mixture of methyl esters obtained was chromatographed at 198 and 122°C. In the first case azelaic acid and in the second case caproic and pelargonic acids were detected.

In an aqueous dioxane extract from the oxidized mixture of acids, malonic and propionic acids were detected, in addition to those already mentioned. Thus, in the oxidation products of all the mixtures of fatty acids we found the usual fragments from the oxidation of oils containing linolenic, linoleic, and oleic acids. The results obtained permit the $C_{18:0}$, $C_{18:2}$, and $C_{18:3}$ acids detected to be identified as oleic, α-linoleic, and α-linolenic acids.

As can be seen from the results obtained, in its fatty-acid composition the S. nigra oil is close to the linseed type and the other oils to the poppyseed type.

All the mixtures of fatty acids isolated, including the combined saturated and combined solids acids, were separated by paper chromatography. The chromatograms obtained confirmed the results of GLC. In addition, on paper chromatograms of the mixture of fatty acids from the S. nigra oil traces of arachidic and behenic acids were detected (from their R_f values and the absence of unsaturation), although these were not detected by a gas–liquid chromatograph. Paper chromatography, unlike gas–liquid chromatography, showed that the mixtures of fatty acids of all the oils contained a substance giving a zone with R_f 0.98. Such an R_f value is not characteristic for the usual monocarboxylic acids.

In all the mixtures of fatty acids, the presence of hydroxy acids was shown on a thin layer of silica gel. In the UV region of the spectra, these four oils and the mixtures of fatty acids absorbed at 230 and 280 nm (log ε 4.85, 2.9). Such absorption is characteristic for conjugated dienes and α,β-unsaturated ketones. However, the negative reaction of all the oils and the mixtures of fatty acids isolated from them with maleic anhydride shows the absence of conjugated ethylenic bonds that permits the assignment of the bands observed to α,β-unsaturated keto groups.

On this basis, we have suggested that keto hydroxy acids containing α,β-unsaturation with respect to the carbonyl group are present in the oils of the four species of plants. According to the UV spectra it was found that the oils of S. chenaultii, L. nummulariifolia, and A. corymbosa contain about 1%, and the oil of S. nigra about 2%, of keto hydroxy acids calculated as an 18-C acid.

A keto hydroxy acid has been isolated from the oil of S. nigra and a most probable structure has been put forward for it [4].

The oils investigated were subjected to enzymatic hydrolysis with pancreatic lipase, which splits the acyl radical from the α-position in triglycerides [5]. By hydrolysis and TLC on silica gel, we obtained monoglycerides with the acyl radical in the β-position. From the molar composition of the mixtures of acids isolated both from the monoglycerides and from the triglycerides by a modified Coleman calculation [6] we determined the triglyceride compositions of all the oils with respect to the four and to the 18 types of triglycerides (Table 1). As can be seen from the table, all the oils contain about 70% of triunsaturated glycerides. This corresponds to the pronounced drying properties of the oils: the oil of S. nigra is a drying oil, forming a dry film twice as fast as linseed oil; the other three oils are semidrying.

The triglyceride compositions of all the oils with respect to the four types of triglycerides (Table 1) found by enzymatic hydrolysis (columns I) were identical with the compositions (columns II) calculated by the law of random distribution [7]. This shows that the distribution of the acyl radicals in the synthesis of the triglycerides of the oils that we studied takes place according to the principle of random distribution under natural conditions.

On comparing the paper chromatograms of the mixtures of acids from the monoglyceride fraction and the combined di- and triglyceride fractions of hydrolyzates of all the oils, we found that the keto hydroxy acids appeared predominantly in the monoglyceride fraction, which corresponds to the β-position of the keto hydroxy acids found in the triglycerides.

The results of the investigation have shown that the oil of the perennial S. nigra can be recommended for trial as a raw material for the preparation of varnishes and paints, including artists' materials. The

TABLE 1. Triglyceride Compositions of the Oils

Triglyceride	Composition of the triglycerides, mole %							
	S. chenaultii		S. nigra		L. nummulariifolia		A. corymbosa	
PPP	0,05		0,17		0,11		0,17	
PPO	0,14		0,49		0,72		0,34	
PPL	1,01		2,15		2,61		2,23	
POP	0,07		0,14		0,11		0,11	
POO	0,17		0,39		0,69		0,24	
POL	1,27		1,71		2,52		1,50	
PLP	0,68		1,03		0,44		1,08	
PLO	1,76		2,92		2,80		2,21	
PLL	12,77		12,96		10,21		14,24	
OPO	0,09		0,28		0,58		0,15	
OPL	1,31		2,98		4,48		2,23	
OOO	0,11		0,22		0,57		0,10	
OOL	1,64		2,37		4,33		1,49	
OLO	1,13		1,66		2,30		0,98	
OLL	16,52		17,94		17,53		14,27	
LPL	4,11		6,75		8,50		7,28	
LOL	5,15		5,36		8,21		4,89	
LLL	52,48		40,48		33,29		46,49	
	I	II	I	II	I	II	I	II
GIS^3	0,05	0,06	0,17	0,17	0,11	0,20	0,17	0,17
GIS^2U	1,90	1,98	3,81	3,83	3,88	4,17	3,76	3,78
$GISU^2$	21,48	21,31	27,31	27,94	29,78	28,91	27,85	27,81
GIU^3	76,57	76,65	67,97	68,05	66,23	66,72	68,22	68,24

Note. I – results of enzymatic hydrolysis; II – results of calculation by the law of random distribution; P – saturated acids; O – monoenic acids; L – polyenic acids.

oil of L. nummulariifolia can be used in the pharmaceutical industry as a source of linoleic acid – for example, in the manufacture of preparations for lowering the cholesterol content in the blood and for treating radiation and heat burns and other skin lesions.

EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument in a thin layer, and the UV spectra on a Hitachi spectrophotometer in hexane and 96% ethanol at concentrations of 0.1-0.2 mg/ml.

The elementary analyses of the bromides corresponded to the calculated figures. The melting points are not corrected.

The oils were extracted in the cold with light petroleum ether.

The mixtures of fatty acids and unsaponifiables from the oils and from fractions of the hydrolyzate were isolated by cold saponification with 1 N KOH in methanol and the decomposition of the potassium soaps under a layer of diethyl ether with 15% hydrochloric acid. The mixtures of acids were esterified with diazomethane.

The gas–liquid chromatography of the mixtures of methyl esters was performed on UKh-2 and LKhM-7A chromatographs with columns 2.5 m long and 0.4 cm in diameter. The solid phase was INZ-600 (60 mesh), the liquid phase was poly(ethylene succinate) in an amount of 17%, and the carrier gas was helium at a rate of flow of 80-90 ml/min.

The triglycerides were hydrolyzed by a modified method using pancreatic lipase from cattle pancreatic gland [6]. The mixtures of fatty acids were separated by paper chromatography [8].

For thin-layer chromatography, activated KSK silica gel (150 mesh) and cellulose were deposited on plates by the wet method. For the separation of the monoglyceride fraction of the hydrolyzate from the combined di- and triglyceride fraction we used 5% of gypsum and the diethyl ether–light petroleum ether (9 : 1) system. The mixtures of C_1–C_6 dicarboxylic and monocarboxylic acids were separated in the form of the ammonium salts on cellulose in the ethanol–ammonia–water (20 : 30 : 2) system. The bromides were isolated from the mixtures of fatty acids of all the oils, and the hexabromine and tetrabromine numbers were determined, by a handbook method [9].

The destructive oxidation of the mixtures of fatty acids was performed by the periodate-permanganate method [10].

The drying properties of the oils were determined in the presence of 1.5% of red lead as the siccative in the light at 20 and 30°C. Linseed oil was used as standard.

SUMMARY

The fatty-acid and triglyceride compositions of the oils of the seeds of four species of Central Asian representatives of the family Caprifoliaceae have been studied. A great diversity of the fatty acids in the oil of Sambucus nigra has been established; this differs from the other oils studied by a high content of linolenic acid (more than 30%). It has been shown that the distribution of the acyl radicals in the triglycerides corresponds to the law of random distribution. All the oils contain about 1-2% of hydroxy keto acids occupying the β-position in the triglycerides.

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