In the seed oil of the sea buckthorn, unlike the fruit flesh, there are three types of oxidized triacylglycerols with an increased amount of the products of incomplete esterification of glycerol and free fatty acids.

It has been shown that 80% of the carotenoids of the oil are epoxy derivatives of β-carotene.

In the seed oil, three groups of alcohols — alkanols, sterols, and triterpenols — are esterified by fatty acids in different ways.

Two saturated "isoprenologues," C_{20} and C_{25}, have been detected in the oil of the fruit flesh.

In one of the samples of seed oils, combined methyl and ethyl esters of fatty acids have been found.

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SPECTRAL CHARACTERISTICS OF C-METHYLFLAVONES

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A study has been made of natural C-methylflavones and their dealkylated analogues: 5-hydroxy-4',7-dimethoxy-7-methylflavone (noreucalyptin); 4',5,7-trihydroxy-6-methylflavone; 5-hydroxy-4',7-dimethoxy-6,8-dimethylflavone (eucalyptin); 4',5-dihydroxy-7-methoxy-6,8-dimethylflavone (sideroxylin); 4',5,7-trihydroxy-6,8-dimethylflavone; 4',5,6-trihydroxy-3-methoxy-8-methylflavone (silpin) and 3,4',5,6-tetrahydroxy-8-methylflavone.

Among natural flavonoids, C-methylated compounds form a fairly small group, and it is characteristic that the C-methylation of the flavonoid molecule takes place only in positions 6 and (or) 8 [1].

We have studied the properties of the following C-methylflavones: 5-hydroxy-4',7-dimethoxy-6-methylflavone, which for brevity we shall call noreucalyptin (II), 5-hydroxy-4',7-dimethoxy-6,8-dimethylflavone (eucalyptin, III), 4',5-dihydroxy-7-methoxy-6,8-dimethylflavone (sideroxylin, IV), and 4',5,6-trihydroxy-3-methoxy-8-methylflavone (silpin, VI). In the course of our study of these compounds, we have performed their dealkylation by heating with pyridine hydroxychloride, as in the conversion of silpin (VI) into demethylsilpin (VII) [2]. In this way, from noreucalyptin we obtained methylapigenin (II), and from eucalyptin and sideroxylin the same product, a dimethylapigenin (V).

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TABLE 1. Mass spectra of C-Methylflavones

Compound	Recording temperature, °C	Ions (m/z) and relative intensities, %					
		M^+	$(M-1)^+$	$(M-15)^+$	$(M-28)^+$	$(M-29)^+$	$(M-43)^+$
Noreucalyptin (I)	100	312 (100)	311 (47)	297 (9)	284 (4)	283 (23)	269 (8)
Methylapigenin (II)	180	284 (100)	283 (26)	—	256 (7)	255 (12)	—
Eucalyptin (III)	70	326 (100)	325 (18)	311 (70)	—	297 (11)	283 (5)
Sideroxylin (IV)	120	312 (82)	311 (20)	297 (100)	284 (3)	283 (15)	269 (8)
Dimethylapigenin (V)	180	298 (100)	297 (22)		270 (5)	269 (9)	—
Silpin (VI)*	120	314 (100)	313 (90)	299 (3)	286 (5)	285 (19)	271 (45)
Demethylsilpin (VII)	150	300 (100)	299 (21)	—	272 (10)	271 (12)	—

Compound	Ions (m/z) and relative intensities, %						
	A + H	A	A − 15	A − 28	A − 43	B_1	B ·
Noreucalyptin (I)	—	180 (2)	165 (2)	152 (4)	137 (5)	135 (14)	132 (5)
Methylapigenin (II)	—	166 (10)	—	138 (17)	—	121 (16)	118 (15)
Eucalyptin (III)	—	194 (2)	179 (4)	166 (5)	151 (10)	135 (10)	132 (5)
Sideroxylin (IV)	—	194 (3)	179 (8)	166 (5)	151 (12)	121 (10)	118 (5)
Dimethylapigenin (V)	—	180 (6)	—	152 (18)	—	121 (8)	118 (5)
Silpin (VI)*	167 (10)	166 (4)	—	138 (7)	—	121 (28)	118 (4)
Demethylsilpin (VII)	167 (5)	—	—	138 (4)	—	121 (22)	118 (2)

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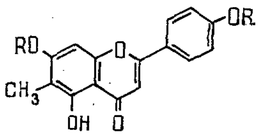
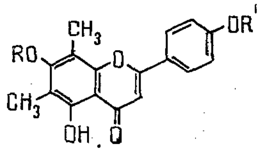
*The spectrum also contains the ions $(M - H_2O)^+$ 296(20), $(M - H - H_2O)^+$ 295(35), A - H 165(5), A - HCO 137(8).



I. Noreucalyptin, $R = CH_3$

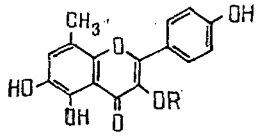
II. Methylapigenin, $R = H$



III. Eucalyptin, $R = R' = CH_3$

IV. Sideroxylin, $R = CH_3$ $R' = H$

V. Dimethylapigenin, $R = R' = H$



VI. Silpin, $R = CH_3$

VII. Demethylsilpin, $R = H$

We isolated the eucalyptin (III) and the sideroxylin (IV) by chloroform extraction of the leaves of ribbon eucalyptus (*Eucalyptus viminalis* L.) (family Myrtaceae) by chromatography on silica gel with subsequent fractionation by crystallization of the mixture of flavones using ethanol, chloroform, and petroleum ether as solvents.

The isolation of eucalyptin from the wax of the leaves of eight species of eucalyptus, including the ribbon eucalyptus has been reported in the literature [3, 4], but sideroxylin had not previously been isolated from it, being found in *Eucalyptus sideroxylon* [5]. Noreucalyptin (I) in a mixture with eucalyptin, had been detected previously in *Eucalyptus torelliana* and *E. urnigera* [4] but it was not found in the *Eucalyptus viminalis* we have studied. In the present investigation we used a sample of noreucalyptin (I) isolated from the leaves of *Ledum palustre* L. (family Ericaceae) [6] and a sample of silpin (VI) from the needles of *Pinus sylvestris* L. (family Pinaceae) [2].

In the study of compounds (I-VII) we used proton magnetic resonance, UV, and mass spectroscopy.

A characteristic feature of the PMR spectra of these compounds consisted of the signals of aromatic CH_3 groups (singlets), which were located in the 2.0-2.5 ppm region, while, as in the case of the H-6 and H-8 signals, the singlet of the 6-C-methyl protons was shifted upfield as compared with those of the 8-C-CH_3 group.

In the diagnosis of the functional groups of flavonoids it is traditional to use the characteristics of UV spectra with complex-forming reagents [1, 7]. For example, the presence of a 5-OH group in flavones and 3-substituted flavones is showen by a considerable bathochromic shift (35-55 nm) of the first (long-wave) band on the addition of $AlCl_3$/HCl. A shift of only 17-20 nm shows the presence of an additional oxygen function (OH or OMe) at C-6 [7]. The UV spectra of silpin (VI) agree with the results of this work (see below). The spectra of demethylsilpin (VII) in which there is a free 3-OH group and, therefore, the shift of the first band amounts to 67 nm, does not contradict it, either.

However, it has been shown [7] that a C-substituent at C-6 does not affect the spectra like an O-substituent, and this was confirmed for the case of 6-C-glucosides. In our investigation, the 6-C-substituent of compounds (I-V) was a methyl group, and it had the same influence on the UV spectrum as a 6-O-substituent. For these compounds we observed an anomalously small bathochromic shift of the long-wave band in the presence of $AlCl_3$/HCl as compared with methanol.

Compound	λ_{max}, nm		
	MeOH	$AlCl_3$/HCl	$\Delta\lambda$
Noreucalyptin (I)	329	352	23
Methylapigenin (II)	334	349	15
Eucalyptin (III)	325	347	22
Sideroxylin (IV)	330	352	22
Dimethylapigenin (V)	332	351	19
Silpin (VI)	338	356	18
Demethylsilpin (VII)	368	435	67

Analysis of the mass spectrum (Table 1) showed that each of these compounds gave the molecular ion as the main peak and also fragments from rings A and B and other ions corresponding to known pathways for the fragmentation of flavones [1]. The fragmentary ions had a low intensity, with the exception of certain peaks.

For example, the spectrum of silpin (VI) contained, in addition to the basic molecular ion, as the second most intense peak that of the ion $(M - R)^+$ with m/z 313, which is characteristic for 6-OR flavones and corresponds to the loss of a hydrogen radical from the 6-OH group of silpin. The third most intense peak, $(M - CH_3CO)^+$ with m/z 271, likewise corresponded to the structure of silpin since this ion is produced by flavonols containing a 3-OCH_3 group [1].

Unexpected were the intense peaks of the ions $(M - CH_3)^+$ in the spectra of eucalyptin (III) and of sideroxylin (IV). These peaks show a low intensity in the spectrum of noreucalyptin (I) and silpin (VI) and were completely absent in those of methyl- and dimethylapigenins (II and V). Since sideroxylin contains only one methoxy group, at C-7, and the $(M - 15)^+$ is the main ion in the spectrum, the presence of two neighboring C-methyl groups apparently activates the ejection of the methyl radical from the 7-OCH_3 group. These facts differ from information in the literature [1], since the ejection of the methyl radical with the formation of strong $(M - 15)^+$ ions usually characterizes the fragmentation of 6- and 8-methoxyflavones.

EXPERIMENTAL

Spectral characteristics were obtained on the following instruments: Varian HA-100D at 100 MHz with TMS as internal standard (PMR); Varian CH-8 at 70 eV (mass spectra); and Hitachi EPS-3T (UV).

4',5,7-Trihydroxy-6-methylflavone (6-Methylapigenin, II). This was obtained by the demethylation of noreucalyptin (I). Light yellow acicular crystals with the composition $C_{16}H_{12}O_5$, mp 289-292°C. UV spectrum, λ_{max} (nm): MeOH 272, 334; NaOMe 277, 327, 392; NaOAc 276, 370; NaOAc + H_3BO_3 272, 334; $AlCl_3$ 280, 303, 352; $AlCl_3$ + HCl 280, 303, 349. PMR spectrum in DMSO (ppm): 13.2 (s, 5-H); 7.90 (d, 9 Hz, H-2',6'); 6.92 (d, 9 Hz, H-3.5'); 6.70 (s, H-3 and H-8); 2.00 (s, CH_3); in deuteropyridine: 7.64 (H-2',6'); 6.96 (H-3',5'); 6.70 (H-3); 6.66 (H-8); 2.38 (CH_3).

The Triacetate of (II). PMR spectrum in $CDCl_3$ (ppm): 7.90 (H-2',6'), 7.30 (H-3',5'), 6.82 (H-8), 6.72 (H-3), 2.12 (CH_3), 2.40 (s, CH_3CO), 2.36 (s, $2CH_3CO$).

4',5,7-Trihydroxy-6,8-dimethylflavone (6,8-dimethylapigenin, V). This was obtained by the demethylation of eucalyptin (III) and of sideroxylin (IV). Light yellow crystals with the composition $C_{17}H_{14}O_5$, mp 292-295°C (decomp). UV spectrum, λ_{max} (nm) MeOH 279, 332; NaOMe 284, 333, 398; NaOAc 284, 380; NaOAc + H_3BO_3 279, 332; $AlCl_3$ 290 sh, 309, 354; $AlCl_3$ + HCl

290 sh, 309, 351. PMR spectrum in deuteropyridine (ppm); 7.92 (d, 9 Hz, H-2',6'); 7.20 (d, 9 Hz, H-3'5'); 6.77 (s, H-3); 2.50 (s, 8-CH_3); 2.44 (s, 6-CH_3).

The Triacetate of (V). PMR spectrum in $CDCl_3$ (ppm): 7.90 (H-2',6'), 7.30 (H-3',5'), 6.72 (H-3), 2.27 (8-CH_3), 2.10 (6-CH_3), 2.42 (s, CH_3CO), 2.35 (s, $2CH_3CO$).

CONCLUSION

The spectral properties of a number of C-methylflavones have been studied.

It has been shown that, in contrast to literature statements, the 6-C-methyl group has the same influence on the UV spectra as 6-O-substitution in producing a shift with $AlCl_3/HCl$.

In the mass spectra of the flavonoids, the production of intense $(M - 15)^+$ ions is usually connected with the presence of a 6-OCH_3 or an 8-OCH_3 group. For the 6,8-di-C-methylflavones, similar ions are characteristic in the presence of a 7-OCH_3 group.

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X-RAY STRUCTURAL STUDY OF SESQUITERPENE ESTERS FROM PLANTS OF THE GENUS *Ferula*.

I. CRYSTALLINE AND MOLECULAR STRUCTURES OF THE CAROTANE ESTER LAPIDOLIN

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An x-ray structural study has been made of the carotane ester lapidolin: diffractometer: Mo K_α radiation, 1601 reflections, direct method, R factor 0.099. The spatial structure of the lapidolin molecule has been determined. The orientation of the ester group in position 10 has been found.

Structure (I) has been proposed on the basis of spectral characteristics and chemical transformations for lapidolin, $C_{24}H_{26}O_8$ — a carotane ester isolated from the roots of *Ferula lapidosa* [1].

A comparative analysis of the PMR spectra of lapidolin and compounds close to it in structure, lapidolinol (II), lapidolinin (III), has enabled the most probable orientations of the substituents and the type of linkage of the rings to be determined. Conclusions relating to the stereochemistry of lapidolin have been made on the basis of the following facts. The characteristic pattern of the splitting of the signal at C(6) with its neighbors (m: 5.32 ppm; $W_{1/2}$ = 24 Hz) shows the axial orientation of H(6) and the α-pseudoequatorial orientation of the angeloyl residue geminal to the proton, with the trans-linkage of the cyclopentane and the cycloheptane rings [2]. The presence in the spectrum of (I) of two doublets (2.8 and 4.87 ppm) is the result of the interaction of the epoxide proton with the vicinal

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