TABLE 2. Fatty Acid Compositions of Red Algae

Class of phospholipids	Ch. dasyphylla	C. granifera	O. latifolium	L. coronopus	P. elongata	C. corymbosum	C. strictum	Ph. nervosa
Phosphatidylglycerol	10,4	15,1	23,9	22,1	19,5	14,5	18,3	24,8
Diphosphatidylglycerol	—	0,7	—	—	—	1,3	—	—
Phosphatidylethanolamine	2,2	1,0	0,5	1,3	7,2	1,5	0,9	5,9
Phosphatidylinositol	2,8	3,1	2,2	5,7	6,4	3,2	4,2	3,8
Phosphatidylcholine	77,8	69,8	64,5	67,6	64,2	71,6	65,4	61,6
Phosphatidic acid	—	—	—	—	1,3	—	2,1	—
Unidentified polar phospholipid	6,8	10,3	8,9	3,3	2,7	7,9	9,1	3,9
Phospholipids, % of the sum of the total lipids	18,0	17,7	19,9	9,8	16,3	14,8	21,3	15,3
Total lipids, mg/g of the dry weight of the biomass	0,9	1,1	0,7	2,1	0,7	1,2	0,6	2,6

Thus, analysis of the fatty acid and phospholipid compositions of the red algae from the Black Sea has shown that the main fatty acids are the 16:0, 20:4, and 20:5 acids. The main phospholipid is phosphatidylcholine, its amount in different species of algae ranging from 61.6 to 77.8%.

LITERATURE CITED

1. R. G. Ackman, *New Sources of Fats and Oils*, American Oil Chemists Society, Champaign, Ill. (1981), p. 189.
2. J. M. Gennity, N. R. Bottino, R. A. Zingano, A. E. Wheeler, and K. J. Irgolic, *Phytochemistry* **24**, 2823 (1985).
3. S. Araki, T. Sakurai, T. Omana, A. Kawaguchi, and N. Murata, *Jpn. J. Phycol.* **27**, 94 (1986).
4. K. Stefanov, M. Konnaklieva, E. Y. Brechany, and W. W. Christie, *Phytochemistry* **27**, 3495 (1988).
5. V. E. Vaskovsky [Vaskovskii] and S. V. Khotimchenko, *J. High Resol. Chromatogr. Chrom. Commun.* **5**, 635 (1982).
6. M. I. Yur'eva, Biol. Morya, No. 1, 41 (1988).
7. V. E. Vaskovsky [Vaskovskii], E. Y. Kostetsky [Kostetskii], and I. M. Vasendin, *J. Chromatogr.* **114**, 129 (1975).
8. S. V. Khotimchenko, M. V. Vysotskii, V. I. Svetashev, and V. E. Vaskovskii, *Bioorg. Khim.* **11**, 103 (1985).

PHENOLIC COMPOSITION OF *Artemisia laciniata*

I. I. Chemesova, T. V. Bukreeva, and É. V. Boiko

UDC 547.972

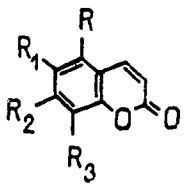
An investigation of *Artemisia laciniata* Willd. has shown that, in contrast to wormwoods that we have studied previously [1], which are flavonoid-containing, the main components of this species are coumarin compounds.

The epigeal part of *A. laciniata* was gathered on dry slopes in Maritime Territory, Ussuri region, village of Kuchuki, in August, 1982. The raw material was extracted successively with 96% ethanol and with 70% aqueous ethanol. As a result of the chromatographic separation of the ethanolic extract on a column of silica gel, substances (I) and (II), (VI) and (VII) were obtained while on a polyamide sorbent the aqueous ethanolic extract gave (III), (IV), and (V) and additional amounts of (VI)

V. L. Komarov Botanical Institute, Academy of Sciences of the USSR, Leningrad. Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Branch, Academy of Sciences of the USSR, Vladivostok.

Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 115-117, January-February, 1990. Original article submitted March 29, 1989.

and (VII). On the basis of an analysis of their IR spectra, compounds (I), (II), and (III) were determined as coumarins and (IV), (V), (VI), and (VII) as flavonoids.



I. R=OH, R_2=R_3=OCH_3

II. R=R_1=OCH_3, R_2=O—CH_2—CH(OH)—C(OH)(CH_3)(CH_3)

III. R=OH, R_1=OCH_3, R_3=O—CH_2—CH_2—CH(CH_3)—CH_2OH

Coumarin (I), $C_{11}H_{10}O_5$, mp 242°C (chloroform—ethanol). Mass spectrum, m/z (%): 222 (M^+, 100). UV spectrum, λ_{max}^{MeOH}: 261, 318 nm (log ε 3.65, 3.85). In the presence of NaOMe, (I) showed a bathochromic shift of Δ 85 with a decrease in the intensity of the long wave band, λ_{max}^{NaOMe} 370 nm (log ε 3.52), which is characteristic for coumarins having an OH group at C-5 [2]. PMR spectra (60 MHz, DMSO): 3.60 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 6.13 (d, J = 10 Hz, H-3), 6.46 (s, H-6), 8.06 (d, J = 10 Hz, H-4). ^{13}C NMR spectrum (25.15 MHz, DMSO): 56.2 (q, OCH_3 at C-7), 60.88 (q, OCH_3 at C-8), 95.3 (d, C-6), 102.6 (s, C-10), 109.8 (d, C-3), 128.4 (s, C-8), 139.8 (d, C-4), 148.0 (s, C-9), 151.3 (s, C-5), 156.2 (s, C-7), 160.4 (s, C-2). Having studied the spectral characteristics of (I), we determined its structure as 5-hydroxy-7,8-dimethoxycoumarin. Its acetate had mp 157°C, close to the melting point of the acetate of this compound obtained synthetically [3].

Coumarin (II), $C_{16}H_{20}O_7$, mp 110°C (ethanol), $[\alpha]_D^{20}$ −60.6° (c 0.33; ethanol—water). UV spectrum, λ_{max}^{MeOH}: 298, 348 nm (log ε 3.62). With NaOMe, (II) gave no shift of the absorption maximum, which indicates the absence of free hydroxy groups in the coumarin nucleus. The mass spectrum contained the peak of its molecular ion — at m/z 324 (M^+) — which permitted the assumption that an aliphatic chain was present in (II).

The fragment corresponding to a peak at m/z 222 was formed as the result of the splitting out of the side chain and the migration of a hydrogen atom and most probably contained two OCH_3 groups and one OH group attached to the coumarin skeleton, while the side chain was a $C_5H_{11}O_2$ fragment. The presence of OCH_3 groups in the molecule was confirmed by the appearance of two singlets of 3H each in the PMR spectrum (60 MHz, DMSO): 3.96 and 3.86.

The substituents in the aromatic ring were located in positions 5, 6, and 7, a one-proton singlet at 7.10 ppm relating to H-8, since the H-4 signal was present in a weak field — 7.96 ppm — because of the anisotropic influence of the substituent at C-5 [2]. The positions of the substituents were confirmed by the cleavage of the molecule of (II) (50% solution of H_2SO_4, room temperature, 5 min), as a result of which a coumarin identical with umckalin, 7-hydroxy-5,6-dimethoxycoumarin (mp 146°C), was obtained [4].

In the region of the PMR spectrum where aliphatic protons appear, doublets with an intensity of one proton each were observed (4.76 ppm, J = 4 Hz and 4.24 ppm, J = 4 Hz) which showed the presence of a methylene group attached to the aromatic rings through an O atom and, together with this group, a methine proton, i.e., R—O—CH_2—CH(. The signal of the methine group proton appeared in the form of double doublet at 4.20 ppm, while two singlets, each with an intensity of three protons, at 1.10 and 1.04 ppm corresponded to two CH_3 groups at C-3′. In the ^{13}C NMR spectrum (25.15 MHz, DMSO), the carbon atoms of the aliphatic chain appeared in the form of a triplet at 75.9 ppm (O—CH_2—), a doublet at 76.6 ppm (CH_2—CH—), a singlet at 70.8 ppm (CH—C≡), and two quartets at 27.2 and 24.6 ppm (2 CH_3). All this confirmed the presence of the elements of the side chain.

Thus, on the basis of the results obtained, compound (II) was determined as 7-(2′,3′-dihydroxy-3′-methylbutoxy)-5,6-dimethoxycoumarin.

Coumarin (III), $C_{15}H_{18}O_6$, mp 103°C (water), $[\alpha]_D^{20}$ −6.06° (c 0.33; ethanol). Mass spectrum, m/z (%): 294 (M^+, 100). UV spectrum, λ_{max}^{MeOH} 265, 322 nm (log ε 3.55, 3.58). After a study of the PMR and ^{13}C NMR spectra of (III) and its acetate (mp 90°C), the coumarin was identified as lacarol, which has been isolated previously from this species [5].

The two flavonoids (IV) and (V) were identified as quercitin and isorhamnetin. The two others had absorption maxima in their UV spectra considerably shifted in the long-wave direction: λ_{max}^{MeOH} 280, 405 nm (VI) and λ_{max}^{MeOH} 237, 372 nm (VII). In the ^{13}C NMR spectrum (25.15 MHz, DMSO) a singlet corresponding to C-4 was observed in the weak field, at 191.6 ppm. These characteristics enabled (VI) and (VII) to be determined as chalcones [6].

Chalcone (VI), $C_{15}H_{12}O_5$, mp 216-218°C (acetate, mp 126°C), mass spectrum, m/z (%): 272 (M^+, 100) was identified on the basis of its spectra and physicochemical properties and a comparison with literature information, as butein [7].

Chalcone (VII), $C_{15}H_{12}O_4$, mp 204°C, mass spectrum, m/z (%): 256 (M^+, 100) was identified as isoliquiritigenin [8, 9]. This is the first time that chalcones have been detected in representatives of the genus *Artemisia*; and this is the first time that coumarins (I) and (II) have been found in nature.

LITERATURE CITED

1. I. I. Chemesova, "Phenolic compounds of representatives of the wormwood genus *Artemisia* L. of the Flora of the Mongolian Peoples' Republic," Author's abstract of Candidate's Dissertation, Pharmaceutical Sciences, Leningrad (1987).
2. M. E. Perel'son, Yu. N. Sheinker, and A. A. Savina, *The Spectra and Structures of Coumarins, Chromones, Xanthones* [in Russian] (1975).
3. V. K. Ahluwalia and Prakas Chandra, *Indian J. Chem., Sec. B* **15B**, No. 9, 808 (1977).
4. H. Wagner and S. Bladt, *Phytochemistry* **14**, No. 9, 2061 (1975).
5. G. Szabo, H. Greger, and O. Hofer, *Phytochemistry* **24**, No. 3, 537 (1985).
6. K. R. Markham and B. Ternai, *Tetrahedron* **32**, 2607 (1976).
7. T. A. Geissman, *J. Am. Chem. Soc.* **63**, 2689 (1941).
8. C. Van Hiille, P. Braeckman, and M. Vandewalle, *Planta Med.* **20**, No. 1, 278 (1971).
9. V. I. Litvinenko, *Farmats. Zh.* **18**, No. 5, 20 (1963).

FLAVONOIDS OF *Caragana spinosa*

G. A. Shpekina

UDC 547.972

The epigeal part of *Caragana spinosa* (L.) DC. (spiny pea shrub) gathered in the Buryat ASSR on the shores of Lake Gusinoe was exhaustively extracted with 70 and 96% ethanol. The ethanolic extract was concentrated in vacuum to an aqueous residue, which was treated with chloroform to eliminate ballast substances. Flavonoids were extracted from the purified aqueous solution with ethyl acetate. To isolate individual compounds, the combined flavonoids were deposited on a column of polyamide sorbent and were eluted successively with chloroform and mixtures of ethanol and chloroform. As a result six substances of flavonoid nature were isolated and identified.

Substance (I) – $C_{15}H_{10}O_7$, mp 308-310°C, λ_{max} 374, 255 nm (ethanol) – was identified as quercetin.

Substance (II) – $C_{15}H_{10}O_6$, mp 274-275°C, λ_{max} 368, 267 nm (ethanol) – was identified as kaempferol.

Substance (III) – $C_{27}H_{30}O_{16}$, mp 185-187°C, λ_{max} 362, 259 nm (ethanol) – was identified as rutin (quercetain 3-O-rutinoside).

Substance (IV) – $C_{28}H_{32}O_{16}$, mp 175-177°C, λ_{max} 360, 256 nm (ethanol) – was identified as narcissin (isorhamnetin 3-O-rutinoside) [1, 2].

Substance (V) – $C_{21}H_{20}O_{12}$, mp 210-212°C, λ_{max} 367, 255 nm (ethanol) – was identified as isoquercitrin (quercetin 3-O-glucoside).

Substance (VI) – $C_{21}H_{20}O_{12}$, mp 185-187°C, λ_{max} 350, 257 nm (ethanol) – was identified as quercetin 3-O-rhamnoside.

The structures of all the substances isolated were confirmed by the results of elementary elements, UV and IR spectroscopy, and a study of the products of acid and enzymatic hydrolysis, and also their comparison with authentic specimens.

LITERATURE CITED

1. L. A. Klyshev, V. A. Bandyukova, and L. S. Alyukina, *Plant Flavonoids* [in Russian], Alma-Ata (1978).
2. A. E. Polovinko and G. P. Yakovlev, *Khim. Prir. Soedin.*, 268 (1985).

Leningrad Institute of Pharmaceutical Chemistry.

Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 117-118, January-February, 1990. Original article submitted March 27, 1989.

0009-3130/90/2601-0095$12.50