$-H_2O]^+$ (6) ($C_{15}H_{24}O$), 205 $[220-Me]^+$ (3), 177 $[220-C_3H_7]^+$ (8), 57 $[C_4H_9]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+7 \quad +9 \quad +10 \quad +16}\ (\text{CHCl}_3;\ c\ 0.1).$$

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FLAVONOIDS FROM *RHAMNUS PALLASII*

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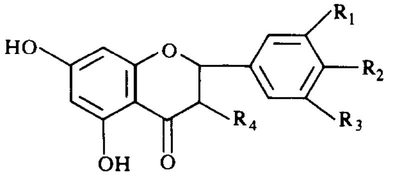
Key Word Index—*Rhamnus pallasii*; Rhamnaceae; flavonoids; pallasiin; 2,3-dihydromyricetin 4′-*O*-methyl ether; kaempferol; quercetin; isorhamnetin; mearsetin; aromadendrin; eriodictyol; taxifolin.

Abstract—A new dihydroflavonol, pallasiin, together with kaempferol, quercetin, isorhamnetin, mearnsetin, aromadendrin, eriodictyol and taxifolin, has been isolated from the bark of *Rhamnus pallasii* and its structure elucidated as 2,3-dihydromyricetin 4′-*O*-methyl ether.

Rhamnus species (Rhamnaceae) are known to be rich sources of anthraquinones and to produce flavonols, i.e. kaempferol, quercetin and their methyl ethers [1]. There is, however, no report on the constituents of *Rhamnus pallasii* Fisch. et Meg., a species from Turkey, as far as we know. The present paper describes the isolation of seven known flavonoids, kaempferol (**1**), quercetin (**2**), isorhamnetin (**3**), mearnsetin (**4**), aromadendrin (**5**), eriodictyol (**6**) and taxifolin (**7**), and a new flavonoid, pallasiin (**8**), from the bark of *Rhamnus pallasii.*

Compounds **1**–**3**, and **5**–**7** were identified by direct comparison with respective authentic samples. The spectral data (UV, ^{1}H NMR and mass spectra) of **4** were in good agreement with those of mearnsetin (myricetin 4′-*O*-methyl ether) in the literature [2].

Furthermore, the structure of **4** was confirmed by correlating its ^{13}C NMR chemical shifts with those of myricetin (Table 1). This represents the first report of a myricetin-type flavonol in this genus.



5 $R_1 = R_3 = H,\ R_2 = R_4 = OH$
6 $R_1 = R_2 = OH,\ R_3 = R_4 = H$
7 $R_1 = R_2 = R_4 = OH,\ R_3 = H$
8 $R_1 = R_3 = R_4 = OH,\ R_2 = OMe$

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Table 1. ^{13}C NMR chemical shifts of **4** and myricetin

	4	Myricetin	$\Delta\delta$
C-2	145.8	146.8	—
C-3	136.4	135.9	—
C-4	175.8	175.8	—
C-5	156.1	156.1	—
C-6	98.0	98.1	—
C-7	164.1	163.9	—
C-8	93.1	93.2	—
C-9	160.4	160.7	—
C-10	102.9	102.9	—
C-1′	119.8	120.9	−1.1
C-2′	107.1	107.2	−0.1
C-3′	125.7	135.9	−10.2
C-4′	150.3	145.7	+4.6
C-5′	125.7	135.9	−10.2
C-6′	107.1	107.2	−0.1
OMe	59.6	—	—

Compound **8** was recrystallized from aqueous ethanol to give a white powder, mp 237–239°. (Found: $[M]^+$ at *m/z* 334.0703; $C_{16}H_{14}O_8$ requires: 334.0690.) The IR spectrum showed absorption bands at 3400 (OH), 2900 (CH), 1630 (C=O), 1590 (C=C) and 1160 (C–O) cm^{-1} in potassium bromide. The UV spectrum showed maximum absorption at 291 and 330 (sh) nm in ethanol, 311 and 380 (sh) nm with the addition of aluminium chloride, 330 nm with the addition of sodium acetate and 295 and 329 nm with boric acid. The ^1H NMR spectrum gave signals at δ 3.78 (3H, *s*, OMe), 4.38 (1H, *d*, $J = 11.0$ Hz, H-3), 4.81 (1H, *d*, $J = 11.0$ Hz, H-2), 5.83 (2H, *br s*, H-6, H-8) and 6.47 (2H, *s*, H-2′, H-6′). The mass spectrum gave significant peaks at *m/z* 334 $[M]^+$, 332 $[M-2]^+$, 305 $[M-CHO]^{+\cdot}$, 182 $[B_1]^{+\cdot}$ and 153 $[A_1+H]^+$. All this evidence suggested that **8** was either 2,3-dihydromyricetin 3′-*O*-methyl ether or 2,3-dihydromyricetin 4′-*O*-methyl ether. However, the identity of the H-2′ and H-6′ signals in the ^1H NMR spectrum supported the 4′-methyl ether structure since, in the 3′-methyl ether, the H-2′, H-6′ signal would appear as a finely separated doublet [3].

Compound **8** was also found to be identical with synthetic 2,3-dihydromyricetin 4′-*O*-methyl ether obtained from **4** by Pew's flavonol reduction method [4, 5].

EXPERIMENTAL

^1H NMR spectra were run on a 90 MHz instrument and ^{13}C NMR spectra on a 15 MHz instrument in CD_3OD with TMS as int. standard. MS were obtained by direct inlet, electron energy 70 eV, ion source temp. 200°.

Plant material. Rhamnus pallasii Fisch. et Meg. was collected on 11 Sept. 1980 at Artuin near Ardanuc, Turkey. A voucher specimen is retained in Ankara Üniversitesi Eczacilik Fakültesi Herbaryumu.

Isolation. Dry powdered bark (100 g) was extracted × 3 with MeOH. The concd extract plus H_2O was extracted successively with Et_2O, $CHCl_3$ and EtOAc. The EtOAc extract was chromatographed on a Si gel column with a $CHCl_3$–MeOH gradient, collecting those fractions which gave a positive Mg–HCl reaction. These fractions were rechromatographed on a Si gel column with $CHCl_3$–EtOH (19:1) to be eluted in the order of **8** (4 mg), **7** (5 mg), **3** (1.5 mg), **6** (2 mg), **5** (2 mg), **1** (5 mg), **2** (3 mg) and **4** (30 mg).

Reduction of mearnsetein (**4**) *to pallasiin* (**8**). Compound **4** (10 mg) was dissolved in H_2O with H_3BO_3 (4 mg) and Na_2CO_3 (100 mg) and the mixture was treated with $Na_2S_2O_4$ (100 mg) according to a variation of Pew's flavonol reduction method [5]. The product obtained was purified by Si gel CC to afford a dihydroflavonol, 2,3-dihydromyricetin 4′-*O*-methyl ether. The spectral and physical data of the synthetic dihydroflavonol were in good agreement with those of **8**.

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