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PHENOLIC COMPOUNDS FROM *Pinus sibirica* SHELLS

E. A. Khamidullina,[1] M. Purevdash,[1] I. V. Ushakov,[2]
O. V. Neretina,[2] and S. A. Medvedeva[1]

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The chemical composition and properties of pinenut kernels and the oils obtained from them have been thoroughly investigated. The composition of secondary metabolites from shells, which contain 55-60% of the nut mass, has not been studied. We investigated compounds extracted from *Pinus sibirica* Du Tour shells in order to fill this gap.

Shells were ground to 0.5 × 0.5 ± 0.2 cm and extracted with aqueous MeOH (80%). High-molecular-weight tannins precipitated from the concentrated extract and were separated by filtration. The remaining extract was chromatographed over cellulose, polyamide, and silica gel to isolate **1-3**, the structures of which were established by spectral methods (UV and 1D and 2D NMR).

Cedrusin (1) [2-(3′-methoxy-4′-hydroxyphenyl)-3-hydroxymethyl-2,3-dihydro-7-hydroxybenzofuran-5H-propanol]: amorphous powder, [α] +2.47° (*c* 2.0, MeOH) [1].

PMR spectrum (400 MHz, DMSO-d_6, ppm, J/Hz): 6.95 (1H, br.s, H-2′), 6.80* (1H, d, J = 8.2, H-6′), 6.76* (1H, d, J = 8.2, H-5′), 6.54** (1H, br.s, H-4), 6.50** (1H, br.s, H-6), 5.39 (1H, d, J = 6.7, H-2), 3.75 (3H, s, OCH_3), 3.60 (1H, m, H-3), 3.41 (4H, m, 2×CH_2OH), 2.46 (2H, t, J = 7.3, 2H-γ), 1.65 (2H, m, 2H-β).

^{13}C NMR spectrum (ppm): 147.61 (C-3′), 146.40 (C-4′), 144.78 (C-8), 140.76 (C-7), 134.90 (C-9), 132.92 (C-1′), 129.17 (C-5), 118.73 (C-6′), 115.83 (C-4), 115.38 (C-5′), 114.99 (C-6), 110.51 (C-2′), 86.64 (C-2), 63.26 (CH_2OH), 60.34 (C-α), 55.77 (OCH_3), 53.69 (C-3), 34.81 (C-γ), 31.43 (C-β). Signals marked * and ** may be interchanged in pairs. Compound **1** was first isolated from *Cedrus deodara* and then from Siberian pine needles as the rhamnoside [2].

Eriodyctiol (2) (2*S*-5,7,3′,4′-tetrahydroxyflavanone): mp 248°C (MeOH) [3]. UV spectrum (MeOH, λ_{max}, nm): 280, 320 sh; +NaOAc, 280 sh, 325.

PMR spectrum (250 MHz, DMSO-d_6, ppm, J/Hz): 12.15 (s, 5-OH), 6.87 (1H, s, H-2′), 6.74 (2H, s, H-5′,6′), 5.86 (1H, s, H-6), 5.85 (1H, s, H-8), 5.36 (1H, dd, J = 12.4, J = 3.0, H-2), 3.17 (1H, dd, J = 12.6, J = 17.0, H-3_e), 2.66 (1H, dd, J = 17.1, J = 3.0, H-3_a).

^{13}C NMR spectrum (ppm): 196.20 (C-4), 167.25 (C-7), 163.58 (C-5), 162.96 (C-9), 145.80 (C-4′), 145.30 (C-3′), 129.59 (C-1′), 118.0 (C-6′), 115.45 (C-5′), 114.43 (C-2′), 101.73 (C-10), 95.96 (C-6), 95.17 (C-8), 78.50 (C-2), 42.17 (C-3).

The ^{13}C NMR spectrum agrees with that in the literature [4]. However, the PMR spectrum could be interpreted only after studying 2D correlation spectra. The absence of an *ortho* spin—spin coupling constant between H-5′ and H-6′ seemed unusual. The shape of the spectrum corresponded more with a 3′,5′-substituted ring B. However, there was no unambiguous evidence for the existence in nature of such a compound [5]. Our 2D NMR experiments enabled **2** to be identified as 2*S*-5,7,3′,4′-tetrahydroxyflavanone. Thus, signals for the three protons of ring B in this compound appeared as two singlets (1H, δ 6.87 ppm and 2H, δ 6.74 ppm). The signal with chemical shift (CS) 6.87 ppm gives cross peaks in the ^{1}H—^{13}C HMBC spectrum with those for C-3′, C-6′, and C-2; in the ^{1}H—^{1}H NOESY spectrum, for H-2, H-3_e, and H-8.

Dreiding models have shown that these cross peaks may be only for C-2′ with the *S*-configuration for the C-2 asymmetric center. The 2H singlet with CS 6.74 ppm gives cross peaks with C-2, C-1′, and C-4′ in the ^{1}H—^{13}C HMBC spectrum. This enabled it to be assigned as H-5′ and H-6′ (Fig. 1). This assignment was confirmed by the presence of through-space interactions of these protons with H-2 and H-3_e in the ^{1}H—^{1}H NOESY spectrum.

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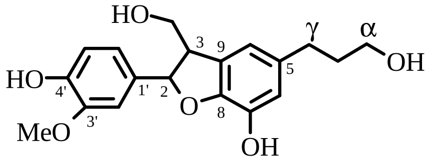
1) A. E. Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, 664033, Irkutsk, ul. Favorskogo, 1, e-mail: zoya@irk.ru; 2) Irkutsk State Technical University, 664074, Irkutsk, Lermontova, 83. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 81-82, January-February, 2005. Original article submitted October 8, 2004.



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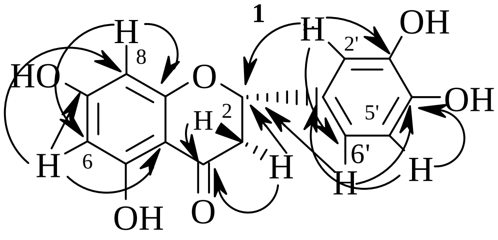

Fig. 1. ^{1}H—^{13}C HMBC interactions of atoms in **2**.

2-Hydroxy-(4-octyloxy)benzophenone (3): film, UV spectrum (MeOH, λ_{max}, nm): 290, 325 sh.

PMR spectrum (250 MHz, $CDCl_3$, ppm, J/Hz): 6.49 (1H, d, J = 2.3, H-3), 6.39 (1H, dd, J = 2.4, 8.6, H-5), 7.46 (1H, m, H-6), 7.47 (2H, m, H-2′, H-6′), 7.62 (2H, dd, J = 7.0, 8.3, H-3′,5′), 7.55 (1H, m, H-4′), 4.01 (1H, t, J = 6.5), 1.79 (1H, m, H-9), 1.43 (1H, m, H-10), 1.25-1.30 (4H, m, H-11—H-14), 0.86 (3H, m, H-15).

^{13}C NMR spectrum (ppm): 113.0 (C-1), 166.40 (C-2), 101.50 (C-3), 165.90 (C-4), 107.90 (C-5), 135.30 (C-6), 131.50 (C-1′), 128.94 (C-2′), 128.39 (C-3′), 138.40 (C-4′), 128.39 (C-5′), 128.94 (C-6′), 200.07 (C-7), 68.58 (C-8), 29.04 (C-9), 26.03 (C-10), 29.81 (C-11), 29.39 (C-12), 31.89 (C-13), 22.76 (C-14), 14.21 (C-15).

The site of attachment of the aliphatic chain to the aromatic ring was determined using ^{1}H—^{13}C HMBC and 2D NOESY. We did not find data in the literature on the isolation of this compound from natural sources [6].

All compounds from pine nut shells were isolated for the first time.

REFERENCES

1. P. K. Agrawal, S. K. Agarwal, and R. P. Rastogi, *Phytochemistry*, **19**, 1260 (1980).
2. S. Z. Ivanova, S. A. Medvedeva, V. A. Babkin, A. I. Rezvukin, and I. V. Volkova, *Khim. Prir. Soedin.*, 560 (1985).
3. R. M. Horowitz and B. Gentili, *J. Am. Chem. Soc.*, **82**, 2803 (1960).
4. H. Wagner, V. M. Chari, and J. Sonnenbichler, *Tetrahedron Lett.*, **21**, 1799 (1976).
5. L. Lin, *Yaoxue Xuebao*, **36**, 393 (1994); A. Uffe, E. D. Rosalba, H. N. Per, and C. Carsten, *Acta Chem. Scand.*, **52**, 1243 (1998).
6. N. A. Larin, E. N. Matveeva, and V. S. Smirnova, *Zh. Obshch. Khim.*, **30**, 2377 (1960).