COLLADOCIN – A NEW TRITERPENOID COUMARIN FROM Colladonia triguetra

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Continuing a study of the roots of Colladonia triguetra (Vent) DC [1, 2] – an endemic Bulgarian plant of the family Umbelliferae – we have isolated a new optically active crystalline substance with the composition $C_{26}H_{34}O_6$, mp 219°C (ethyl acetate), $[\alpha]_D^{20}$ −4.58° (c 0.55; ethanol); molecular weight 442 (mass spectrometrically), Rf 0.21 [TLC Silufol, benzene–chloroform–ethyl acetate–methanol (5 : 4 : 0.5 : 5)] which we have called colladocin.

The UV spectrum of the compound has maxima characteristic for a 7-O-alkylcoumarin, λ_{max}^{EtOH} 217; 243, 5; 254; 295; 326 nm (log ε 4.15; 3.55; 3.38; 3.90; 4.19).

IR spectrum ν_{max} cm^{-1} : 3510 (hydroxy group), 1720, 1735 (carbonyl of an α-pyrone and C = O of an acetyl group), 1620, 1515 (aromatic ring), 1250 (C–O of an acetyl group). The NMR spectrum of the compound (Varian, HA-100D, $CDCl_3$, 20°C, 0 – HMDS) showed the singlets of three quaternary CH_3 groups at 0.81, 0.84, and 0.92 ppm; of a CH_3 group geminal to a hydroxyl at 1.18 ppm (singlet, 3 H), of an acetyl CH_3 at 1.98 ppm (singlet, 3 H), and of an axial proton geminal to an acetyl group (broadened signal with its center at 4.46 ppm, $W_{1/2}$ = 16 Hz). A methylene group (Ar–O–CH_2–) appeared in the form of two quartets (intensity 1 H each) with centers at 4.08 and 4.34 ppm, J_{gem} = 10.5 Hz, J_{vic} = 6 Hz. There were signals of five protons of a 7-hydroxy-substituted coumarin: 6.16 ppm (d, 1 H), J = 9.3 Hz (H_a); 7.54 ppm (d, 1 H), J = 9.3 Hz (H_b); 7.27 ppm (d, 1 H), J = 9.0 Hz (H_c); 6.77 ppm (q, 1 H), J_{ortho} = 9.0 Hz, J_{meta} = 2.5 Hz (H_d); 6.72 ppm (d, 1 H), J = 2.5 Hz (H_e).

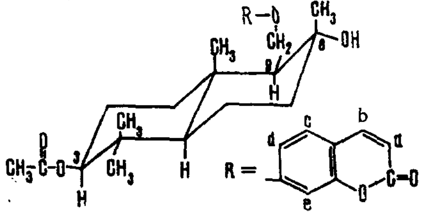
By acetylating natural isosamarcandin [3], we obtained a compound the physicochemical characteristics of which correspond to colladocin, but this compound differed from the latter by the small value and opposite sign of the optical rotation.

The coincidence of the NMR parameters of the signals from the C_3–H and C_9–CH_2– of colladocin and of isosamarcandin acetate show the identical (diaxial) arrangement of the protons at C_3 and C_9, but the different relative intensities (0.1 and 1.0%Σ, respectively) of the peaks of the ions (M – 18) in their mass spectra suggest epimerization at C_8.

It is most likely that colladocin has the cis-axial-equatorial orientation at C_9–H; C_8–OH, in contrast to the transdiaxial arrangement in isosamarcandin acetate, for which it is easier to effect elimination [4].

The less sterically hindered hydroxy group of colladocin leads to a decrease in the value of the optical intensity of the dehydration peak by an order of magnitude as compared with its epimer [5].

Thus, the following structure is proposed for colladocin:



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LITERATURE CITED

1. L. Bubeva-Ivanova and N. St. Pavlova, Farmatsiya (Sofia), No. 1, 30 (1969).
2. A. I. Ban'kovskii, N. E. Ermatov, M. E. Perel'son, L. Bubeva-Ivanova, and N. St. Pavlova, Khim. Prirodn. Soedin., 173 (1970).
3. V. N. Vorisov, A. I. Ban'kovskii, V. I. Sheichenko, and V. S. Kabanov, Khim. Prirodn. Soedin., 686 (1974).
4. E. Eliel, N. Allinger, S. Angyal, and G. Morrison, Conformational Analysis [Russian translation], Moscow (1969), p. 117.
5. K. Biemann and J. Seibl, J. Amer. Chem. Soc., 81, 3149 (1959).