ODONTOSIDE: A NEW IRIDOID FROM ODONTITES SEROTINA

A. V. Degot', V. I. Litvinenko, and I. P. Kovalev

Khimiya Prirodnykh Soedinenii, Vol. 6, No. 4, pp. 474–475, 1970

UDC 547.918

Aucubin has previously been found in Odontites serotina (Lam.) Dum. [1, 2]. In the course of the present investigation, together with aucubin we found a series of iridoids, one of which proved to be new and has been called "odontoside" (I). For the isolation of I, a 50% aqueous ethanolic extract of the epigeal part of the plant was evaporated to an aqueous residue and freed from lipophilic and phenolic substances, and the odontoside (I) was extracted from the aqueous solution of iridoids with ethyl acetate.

In a second method, the total iridoids were chromatographed on a column of Kapron. The water-soluble impurities were separated off and substance I was desorbed with 30% ethanol. The iridoid I, after recrystallization from ethyl acetate, had mp 145–147° C (decomp); $[\alpha]_{589}^{20}$ −92°, $[\alpha]_{546}^{20}$ −107°, $[\alpha]_{491}^{20}$ −136°, $[\alpha]_{455}^{20}$ −159°, $[\alpha]_{436}^{20}$ −179°, $[\alpha]_{420}^{20}$ −195°, $[\alpha]_{407}^{20}$ −212°, $[\alpha]_{390}^{20}$ −231°, $[\alpha]_{380}^{20}$ −248°, $[\alpha]_{370}^{20}$ −268°, $[\alpha]_{360}^{20}$ −280°, $[\alpha]_{350}^{20}$ −294°, $[\alpha]_{340}^{20}$ −320°, and $[\alpha]_{330}^{20}$ −340° (c 0.1, ethanol). UV spectrum: λ_{max} (in ethanol) 232, 273, and 282 mμ (log ε 3.66, 2.61, and 2.56); R_f 0.70 [paper chromatography in system 1: butan-1-ol–acetic acid–water (4 : 1 : 5)], 0.76 [system 2: butan-1-ol–methanol–water (4 : 1 : 5)], and 0.82 [system 3: propan-1-ol–water (4 : 1)].

The Stahl reagent [3] revealed it in the form of a dark blue spot and the Bacon-Edelman reagent [4] in the form of a dark brown spot.

On acid (1 N HCl, 90° C, 30 min) and enzymatic (emulsin, 30° C, 12 hr) hydrolyses, the reaction mixture became dark blue, and a black precipitate deposited. The sugar liberated on hydrolysis was identified as D-glucose.

The alkaline saponification of I (25% ammonia, 90° C, 3 hr) led to the formation of an iridoid (II), which was identified (R_f and UV and IR spectra) as aucubin and had mp 180° C; $[\alpha]_{589}^{20}$ −117°, $[\alpha]_{546}^{20}$ −131°, $[\alpha]_{491}^{20}$ −164°, $[\alpha]_{455}^{20}$ −191°, $[\alpha]_{436}^{20}$ −209°, $[\alpha]_{420}^{20}$ −227°, $[\alpha]_{407}^{20}$ −247°, $[\alpha]_{395}^{20}$ −262°, $[\alpha]_{390}^{20}$ −275°, $[\alpha]_{380}^{20}$ −291°, $[\alpha]_{370}^{20}$ −310°, $[\alpha]_{360}^{20}$ −322°, $[\alpha]_{350}^{20}$ −346°, $[\alpha]_{340}^{20}$ −367°, $[\alpha]_{335}^{20}$ −380°, $[\alpha]_{330}^{20}$ −387°, $[\alpha]_{325}^{20}$ −405°, $[\alpha]_{320}^{20}$ −420°, $[\alpha]_{315}^{20}$ −431°, and $[\alpha]_{310}^{20}$ −445° (c 0.1, ethanol). UV spectrum: λ_{max} (in ethanol) 270 mμ (log ε 2.31); R_f 0.36 (1), 0.54 (2), 0.41 (3).

The alkaline saponification of I formed p-hydroxycinnamic acid, which was identified by its physicochemical properties and its UV and IR spectra.

The results of a comparison of the optical rotatory curves and also those of a polarimetric analysis in a determination of the influence of the acyl group on the optical activity of the aglycone showed that I is a new iridoid, which has been characterized as 5-p-coumaroylaucubin.

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5 May 1970

Zaporozh'e Medical Institute

Khar'kov Scientific-Research Chemical and Pharmaceutical Institute