THE COUMARIN COMPOSITION OF Heracleum sosnowskyi

A. Z. Abyshev and P. P. Denisenko

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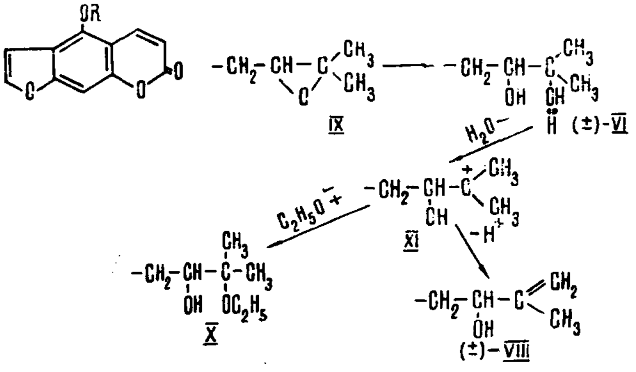
We have studied the chemical composition of the roots of Heracleum sosnowskyi Manden., which is widely distributed in Azerbaidzhan. Previously [1], several substances of a coumarin nature (pimpinellin, isopimpinellin, bergapten, and isobergapten) have been isolated from the roots of this plant.

From the roots of the plant investigated, which were collected in the Gusar region (village of Anykh), by extraction with chloroform and subsequent chromatography on a column of alumina we isolated eight substances of coumarin nature: (I) with mp 191-192°C; (II) 116-118°C; (III) 149-151°C; (IV) 223-224°C; (V) 81°C; (VI) 127-129°C; (VII) 189-190°C, (VIII) 125-127°C.

By comparing the results that we obtained with information in the literature [2-7], and also on the basis of an analysis of their IR and NMR spectra, (I)-(IV) were identified, respectively, as sphondin, pimpinellin, isopimpinellin, and isobergapten. The identification of substances (V)-(VIII) as osthole, (+)-oxypeucedanin hydrate, marmezin, and pangelin [(+)-5-(2″-hydroxy-3″-methylbutenyloxy)furo-2′,3′:7,6-coumarin], respectively, was performed with the aid of IR and NMR spectra, R_f values, and melting points of the compounds isolated with the same characteristics of authentic samples. Compounds (V-VIII) have not been found previously in the species studied, and this is the first time that (VI)-(VIII) have been found in the species Heracleum.

It must be mentioned that 5-(2″-hydroxy-3″-methylbutenyloxy)furo-2′,3′:7,6-coumarin has hitherto been isolated only from those plants in which, together with other coumarin derivatives, (±)-(VI) is present [8-10], in view of which may be assumed that the latter is a precursor of this compound in the plant organism. However, a paper has recently appeared reporting on the isolation of (±)-(VIII) from the products of the cleavage of natural oxypeucedanin (IX) with 1.5% oxalic acid, on the basis of which it was concluded that (±)-(VIII) is formed from (IX). At the same time, in the opinion of the authors, there is no similar information in the literature although we [12] have previously shown that when (IX) and (±)-(VI) are treated with 20% sulfuric acid, in addition to a series of known coumarin compounds, (±)-(VIII) (gosferol) and a new furocoumarin – 5-(3″-ethoxy-2″-hydroxy-3″-methylbutoxy)furo-2′,3′:7,6-coumarin (X) – are formed (see scheme). In our opinion, in the reaction of (IX) with 1.5% oxalic acid and with 20% sulfuric acid, in the first stage of the reaction the hydration of the epoxy group takes place with the formation of (±)-(VI), and this is followed by the nucleophilic substitution of the OH group in the latter by an S_N1 mechanism with the intermediate formation of the carbocation (XI) and the elimination of H^+ from one of the methyl groups in the gem-dimethyl grouping (scheme).



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