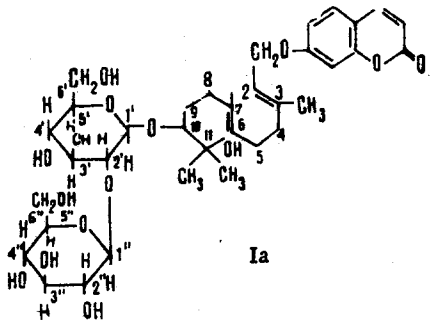
THE STRUCTURE OF THE COUMARIN GLUCOSIDE REOSELIN FROM THE ROOTS OF *Ferula pseudooreoselinum*

N. P. Kir'yalov, T. V. Bukreeva,
V. A. Gindin, G. Mamatov,
and I. S. Kozhina

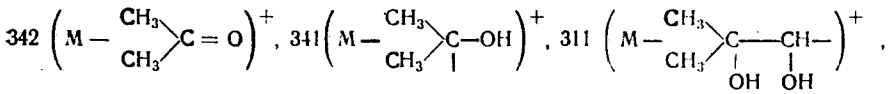
UDC 547.587.668.5.918

It has been shown previously [1] that reoselin is an umbelliferone derivative the side chain of which includes a sesquiterpenoid part and two molecules of glucose. We have continued investigations with a view to determining its structure (Ia).



Ia

The IR spectrum (Fig. 1b) of the aglucone of reoselin obtained by enzymatic hydrolysis with the stomach juice of the grape snail and its NMR spectrum, and those of karatavikinol from *Ferula karatavika* (Rgl. et Schmalh.) are very similar. But differences are observed in their IR spectra in the ratios of the intensities of some absorption bands. It is possible that this difference is due to a different geometry of the double bonds in karatavikinol and in the aglycone of reoselin. The melting points of these compounds are also different (53 and 62°C, respectively) [2, 1]. The mass spectrum of the aglucone shows the fragments



238 (M − umbelliferone)$^+$, 162 (umbelliferone)$^+$, confirming its identity with karatavikinol or an isomer of it.

The very close similarity of the IR spectra (Fig. 1) and NMR spectra of reoselin, its monoglucoside (amorphous product, mp 108-110°C, $[\alpha]_D^{20}$ −15° (c 1; methanol) and its aglucone, with the exception of the region characteristic for the carbohydrate moiety, show the invariability of the structure of the aglucone in enzymatic hydrolysis. However, the acid hydrolysis of reoselin gives the aglucone in very small amount, the umbelliferone is split off, and a sesquiterpene ketone is formed which probably consists of the product of the dehydration of a glycol, as in the pinacolin rearrangement in an acid medium, and cyclization also takes place, since the NMR spectrum of the ketone has the signal of only one of the two olefinic protons.

When the products of the partial hydrolysis of reoselin were chromatographed on paper,

V. L. Komarov Botanical Institute, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 87-89, January-February, 1975. Original article submitted August 3, 1974.

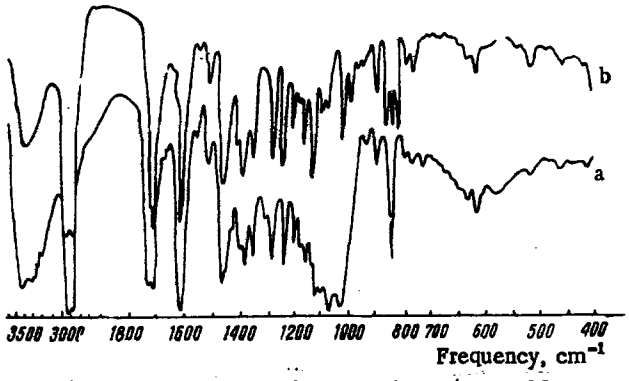


Fig. 1. IR spectra of reoselin (paraffin oil, UR-10) (a) and the aglycone of reoselin (paraffin oil, UR-10) (b).

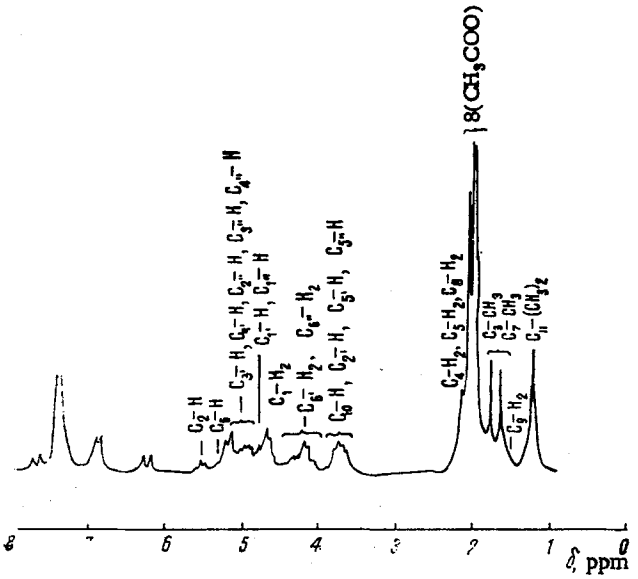


Fig. 2. NMR spectrum of acetylated reoselin ($CDCl_3$, Varian HA-100).

glucose and a biose were found. Judging from the rate of acid hydrolysis, the glucose residues in the glucoside are present in the pyranose form. The negative contribution of each glucoside residue to the total specific rotation, and also the position and coupling constants of the signals of the C_1, —H and $C_{1''}$ —H protons of the glucopyranosides, appearing particularly clearly in the NMR spectrum of methylated reoselin (δ 4.53 ppm, J = 8 Hz, and δ 4.73 ppm, J = 8 Hz), show their β configuration.

On the basis of a color reaction of the products of the hydrolysis of methylated reoselin with triphenyltetrazolium chloride, we assumed that the biose in the glucoside is β-sophorose. This was confirmed by gas–liquid chromatography [3] of the products of the methanolysis of methylated reoselin. The α and β anomers of methyl 2,3,4,6-tetra-O-methyl-D-glucoside and 3,4,6-tri-O-methyl-D-glucoside were identified by comparison with authentic samples, i.e., the glucose residues in the biose are connected by 1–2 bond (β-sophorose). This does not agree with statements in the literature [4]. However, individual samples of reoselin contained small amounts, difficult to separate, of other glucosides with 1–4 and 1–6 bonds between the glucose residues.

In the NMR spectrum of acetylated reoselin (Fig. 2), in the region of weaker bonds the signals of protons appeared at δ 4.8-5.2 ppm (5 H) (C—H in CH_3COO), δ 3.85-4.5 ppm (4 H) (C—H_2 in CH_3COOH), and signals in the δ 3.5-3.85 ppm region (4 H) (C—H at substituted C—O groups in reoselin) remained in their previous position. Consequently, the β-sophorose is attached at the secondary OH group of karatavikinol (or a double-bond isomer of it).

LITERATURE CITED

1. N. P. Kir'yalov and S. D. Movchan, Dokl. Akad. Nauk SSSR, 148, 1081 (1963).
2. N. P. Kir'yalov and V. Yu. Bagirov, Khim. Prirodn. Soedin., 225 (1969).
3. D. M. W. Anderson and A. Hendrie, Carbohydrate Research, 22, 265 (1972).
4. Kh. M. Kamilov and G. K. Nikonov, Khim. Prirodn. Soedin., 85 (1974).