A GLUCOEMODIN FROM THE ROOTS OF RHEUM PALMATUM

A. S. Romanova, A. I. Ban'kovskii, M. E. Perel'son, and A. A. Kir'yanov

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We have previously reported the preparation from the roots of Rheum palmatum L. var. tanguticum Maxim (Tangut rhubarb) of a monoglucoside of emodin of the composition $C_{21}H_{20}O_{10}$ with mp 176°-178° C which is an O-glucoside and which we have called glucoemodin [1]. In 1956, Schultz and Mayer [2] isolated a glucoside of emodin from the leaves of Rheum undulatum L. They did not give data on its physicochemical properties but, on the basis of the IR spectra, they stated that the sugar residue in the emodin glucoside was in position 1 or position 8. Later, Hörhammer et al., [3] succeeded in isolating from the roots of Tangut rhubarb an emodin monoglucoside ($C_{21}H_{20}O_{10} \cdot 0.5\,H_2O$) with mp 189°-190° C identical with Schultz and Mayer's glucoside and also with a 1-(or 8-)-monoglucoside of emodin synthesized by Mühlemann [4].

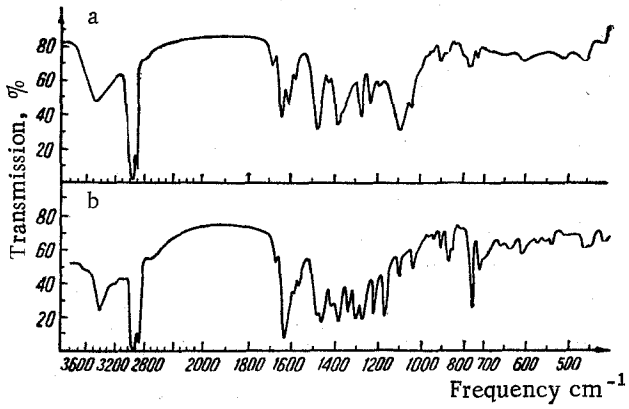

Fig. 1. IR spectra of a) glucoemodin and b) emodin. (UR-10 spectrophotometer, mull in paraffin oil).

The position of the sugar residue in Schultz and Mayer's emodin glucoside was established by comparing its IR spectrum with the spectrum of the aglycone. The band at 1613 cm^{-1}, assigned to the vibrations of the two C=O groups splits into two components at 1618 and 1587 cm^{-1} on passing to the glycoside, and this, in the opinion of the authors mentioned, shows the presence of the sugar residue in the glycoside at position 1 or 8. This proof is unsatisfactory: in the first place, the band at 1613 cm^{-1} belongs to only one carbonyl group, which is connected by an internal-complex

Aglycone	λ_{max}, mμ	log ε	Glucoside	λ_{max}, mμ	log ε
Chrysophanic acid	435	3.87	Chrysophanein	411	3.94
Aloeemodin	431	4.04	Glucoaloeemodin	412	3.95
Rhein	436	4.04	Glucorhein	413	3.96
Emodin	438	4.03	Glucoemodin	434	3.90
Physcion	436	3.99	Rheochrysin	420	3.96

hydrogen bond with the hydroxyl group in the α position [5, 6] while the band of the nonbound carbonyl group is in the 1690-1660 cm^{-1} range; in the second place, the band at 1587 cm^{-1} is assigned to the vibrations of the ring of the molecule and its position does not give direct information on the position of the link with the sugar residue. A similar picture is observed in the glycoside that we isolated from Tangut rhubarb. Its IR spectrum (Fig. 1) has bands of a nonbound carbonyl group (1673 cm^{-1}), a carbonyl group bound by an internal-complex hydrogen bond (1636 cm^{-1}), and bands at 1605 and 1573 cm^{-1} due to vibrations of the skeleton of the molecule. In the spectrum of emodin, the corresponding bands are at 1673, 1633, 1595, and 1570 cm^{-1}. Thus, it is difficult to draw any conclusions whatever on the position of the sugar residue in this compound from the IR spectrum.

Considerably more information in this respect can be obtained from a study of the UV spectra of the substances under investigation. Using some hydroxyanthraquinones having hydroxyl groups in the α position to a carbonyl group as examples, it has been shown [7–9] that the long-wave band in the UV spectra of these substances is shifted in the direction of longer wavelengths as compared with the corresponding methoxyl derivatives. This shift is explained by Shcheglova et al., [9] by the formation of intramolecular hydrogen bonds between the OH and C=O groups, which leads to the appearance of additional rings and to a lengthening of the chain of conjugation of the system. Consequently, the position of the long-wave maximum does not depend on the type of substituent of the hydroxyl group but is determined only by its presence or absence. The addition of a sugar residue in position 1 or position 8 must also lead to a shift in the long-wave maximum in the short-wave direction in the spectrum of the glucoside as compared with the corresponding aglycone.

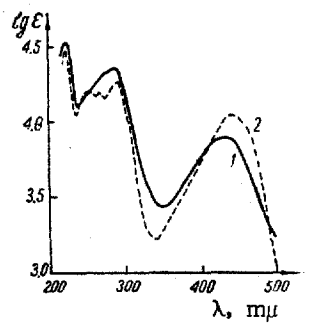

Fig. 2. UV spectra of 1) glucoemodin and 2) emodin in aqueous ethanol.

To confirm this hypothesis, we have measured the IR spectra of a series of derivatives of 1,8-dihydroxyanthraquinone with unsubstituted hydroxyl groups (chrysophanic acid, aloeemodin, etc.) and monoglucosides of these aglycones (chrysophanine, glucoaloeemodin, etc.). In all cases, the long-wave bands of the aglycones were in the 431–438 mμ range and those of the glycosides in the 411–413 mμ range (table).

In the UV spectrum of the glucoemodin that we isolated from Tangut rhubarb, the long-wave maximum is found at 434 mμ (Fig. 2), while for emodin it is located at 438 mμ. It follows from this that the sugar residue in the glucoemodin is attached to the aglycone in position 6; glucoemodin has the structure of 1, 8-dihydroxy-3-methyl-6-glucosyloxyanthraquinone.

Summary

The glucoemodin isolated from the roots of roots of Rheum palmatum L. var. tanguticum Maxim is 1,8-dihydroxy-3-methyl-6-glucosyloxyanthraquinone.

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