## FLAVONOIDS OF THE LEAVES OF POLYGONUM CORIARIUM. II.

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From a methanolic extract of the leaves of <u>Polygonum coriarium</u> [1] by adsorption chromatography on polyamide we have isolated a flavonol glycoside  $C_{21}H_{20}O_{12}$  with mp 238-240° C. On the basis of the hydrolysis products, UV spectra, and specific and molecular rotations, it has been established that it is a hyperoside (quercetin 3-O- $\beta$ -D-galactopyranoside).

From an aqueous methanolic extract of the leaves previously extracted with ether and ethyl acetate, by chromatography on polyamide (desorption with 50% aqueous methanol) and preparative paper chromatography in an ethyl acetate-formic acid-water (10:2:3) system we have isolated a glycoside with mp 203-205° C,  $[\alpha]_D^{23}$ -21.5° (c 0.68, dimethylformamide), Rf 0.38 (BAW 4:1:5), 0.68 (15% CH<sub>3</sub>COOH), and 0.22,  $\lambda_{max}$  362 and 256 m $\mu$ , CH<sub>3</sub>COONa  $\lambda_{max}$  376 and 262 m $\mu$ ; CH<sub>3</sub>COONa + H<sub>3</sub>BO<sub>3</sub>  $\lambda_{max}$  382 and 256 m $\mu$ ; C<sub>2</sub>H<sub>5</sub>ONa  $\lambda_{max}$  412 and 276 m $\mu$ ; and zirconyl chloride  $\lambda_{max}$  392 and 262 m $\mu$ .

The products of acid hydrolysis (2% HCl) were found to contain an aglycone with mp  $310-312^{\circ}$  C, identified as quercetin, and arabinose and galactose as sugar components. According to UV spectroscopy, the sugar components are present in position 3 in the form of a biose. This was confirmed by the oxidative degradation of the bioside with hydrogen peroxide [2]. Hydrolysis with 1% formic acid  $(100^{\circ} \text{ C})$  [3] also gave the aglycone and a biose. The R<sub>f</sub> of the biose in BAW (4:1:5) was 0.18. The same products were obtained by enzymatic hydrolysis with rhamnodiastase although hydrolysis took place fairly slowly. With aniline phthalate, the biose appeared in the form of a brown spot, and with diphenylamine reagents as a pink spot (with urea) and a blue-green spot (with p-anisidine). To determine the nature of the bond between the sugars, stepwise hydrolysis was carried out by Fox's method [4]. After hydrolysis for 5 hr, traces of biose were still present and after 10 hr, quercetin, arabinose, and galactose were obtained. Neither could the intermediate monoglycoside be obtained on hydrolysis with 1% formic acid at 65-70° C [3].

Thus, the nature of the linkage of the sugars in the bioside has not been established. Judging from the rate of hydrolysis of the bioside and from the formation of a fairly stable biose, we may assume that the sugar which is directly attached to the aglycone is in the furanose form and that the second sugar is in the pyranose form. They are probably connected to one another by a 1-6 glycoside bond. An analogous bioside of quercetin has been described in the literature [5].

## REFERENCES

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