

ANTHRAQUINONES OF GALIUM DASYPODUM. II

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By paper chromatography in a number of solvent systems of ethanolic extracts of fresh roots of Galium dasypodum Klok, family Rubiaceae, we have detected ten substances of anthraquinone nature—(I)–(X) (some of which have been described previously [1]). In this paper we give the results of a study of substances VII and VIII.

Substance VII; composition  $C_{27}H_{30}O_{13}$  (the molecular weights of the biosides and monoglycosides were determined spectrophotometrically [2-3] on an SF-4A instrument) has mp 227–229° C (from ethanol);  $[\alpha]_D^{20} -140^\circ$  (c 0.1; ethanol); and is readily soluble in methanol, ethanol, and water, and sparingly soluble in acetone and chloroform.

Compound VII gives no coloration with solutions of alkalis and it may therefore be assumed that the compound lacks free phenolic hydroxyls [4]. From the products of the hydrolysis of VII with 15% sulfuric acid we have isolated and identified the aglycone  $C_{16}H_{12}O_4$  (1-methoxyrubiadin), D-xylose, and D-glucose.

To elucidate the sequence of addition of the sugars in the glycoside, we have carried out stepwise hydrolysis with 1% sulfuric acid, which yielded a monoglycoside  $C_{22}H_{22}O_9$  with mp 245–247° C (from ethanol) and D-xylose.

One enzymatic hydrolysis with rhamniidastase and primeverase, substance VII is cleaved into the same aglycone and a biose identical with primeverose. Consequently, compound VII is 1-methoxyrubiadin 3-O- $\beta$ -primeveroside (longifloroside) [5].

Substance VIII has the composition  $C_{26}H_{28}O_{13}$ , mp 248–250° C (from aqueous ethanol),  $[\alpha]_D^{18} -133.3^\circ$  (c 0.1; 60% ethanol) and is readily soluble in aqueous ethanol, less readily in methanol and ethanol, and sparingly in water. Alkaline solutions of VIII have a red coloration, which shows the presence of free phenolic hydroxyls in the substance. The hydrolysis of VIII with 15% sulfuric acid leads to the aglycone  $C_{15}H_{10}O_4$  (rubiadin), D-glucose, and D-xylose.

The methylation [6] of the glycoside under investigation and subsequent hydrolysis gave the aglycone 1-methoxyrubiadin, which shows that the carbohydrate moiety is attached at C<sub>3</sub>.

Stepwise hydrolysis with 1% sulfuric acid split VII into a monoglycoside  $C_{21}H_{20}O_9$  with mp 270–271° C (from ethanol), identical with rubiadin glucoside and D-xylose, and enzymatic hydrolysis with rhamniidastase and primeverase gave the aglycone rubiadin and primeverose.

Thus, substance VIII has the structure of rubiadin 3-O- $\beta$ -primeveroside.

## REFERENCES

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