

We have investigated the glycoside composition of the roots of *Knautia arvensis* (L.) Coult, family Dipsacaceae, collected in the Tatar Autonomous Soviet Socialist Republic. In an aqueous methanolic extract of the plant we found a number of glycosides, three of which we succeeded in isolating by repeated chromatography in a column of silica gel in the ethyl acetate-methanol-water system. One of them is a monoglucoside of β -sitosterol (0.1% on the weight of the raw material) with mp 285-286°C, $[\alpha]_D -39^\circ$ (pyridine) — identified by comparison with an authentic sample. The other two have been isolated for the first time and we have called them knautiosides A and B (0.5% on the weight of the raw material); they have mp 208-213°C, $[\alpha]_D -10^\circ$ (pyridine) and mp 240-244°C $[\alpha]_D -13^\circ$ (pyridine), respectively. On treatment with mineral acid they formed the same aglycone $C_{30}H_{48}O_3$ with mp 255-256°C, $[\alpha]_D +188^\circ$ (pyridine). According to its chromatograph mobility (thin-layer chromatography) and IR spectrum and also from the constants of various derivatives (acetate, methyl ester, acetate of the methyl ester), this aglycone best corresponds with a triperpenoid described previously — randialic acid B [1].

Knautioside A contains four monosaccharide residues — D-glucose, L-arabinose, and D-xylose (2 : 1 : 1, densitometry on paper chromatograms) — which, on methylation of the glycoside by Hakomori's method [2], were converted into 3,4,6-tri-O-methyl-D-glucose, 2,3,4,6-tetra-O-methyl-D-glucose, 2,3-di-O-methyl-L-arabinose, and 2,3,4-tri-O-methyl-D-xylose. The alkaline hydrolysis of knautioside A formed a bioside with mp 223-228°C $[\alpha]_D -0^\circ$ (pyridine) containing L-arabinose and D-glucose residues. The facts given show the structure of the two carbohydrate chains of knautioside A: the O-glycosidic chain contains a L-arabinose residue directly attached to the hydroxyl of the aglycone, and the chain is terminated by a D-glucose residue; and the O-acylglycosidic chain contains a D-glucose residue attached directly to the carboxyl of the aglycone, and the terminal residue is that of D-xylose.

Knautioside B, according to the results of the hydrolysis, consists of a bioside containing two L-rhamnose residues. The glycoside is not cleaved by the action of alkali, and on acid hydrolysis its permethylate yielded 3,4-di-O-methyl-L-rhamnose and 2,3,4-tri-O-methyl-L-rhamnose. Consequently, knautioside B contains one carbohydrate chain attached to the hydroxyl of the aglycone and consisting of two L-rhamnose residues.

LITERATURE CITED

1. J. S. Tandon, K. P. Agarwal, and M. M. Dhar, *Indian J. Chem.*, **4**, 11, 483 (1966).
2. S. Hakomori, *J. Biochem. (Tokyo)*, **55**, 205 (1964).

A. E. Arbuzov Institute of Organic Physical Chemistry, Kazan' Branch of the Academy of Sciences of the USSR. Translated from *Khimiya Prirodnikh Soedinenii*, No. 5, pp. 661-662, September-October, 1975. Original article submitted April 17, 1975.

© 1976 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.