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Preliminary communication

Isolation of new oligosaccharides from *Orthenthera viminea*

KAMAL N. TIWARI, ANAKSHI KHARE, and MAHESHWARI P. KHARE
Department of Chemistry. University of Lucknow, Lucknow (India)
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Chemical investigation of the aerial part of the plant *Orthenthera viminea* (Family *Asclepiadaceae*) afforded a mixture of glycosides which, on mild hydrolysis with acid, furnished four novel oligosaccharides. One of these was characterized as a trisaccharide of cymarose.

Powdered plant material (10 kg) was exhaustively extracted with 50–95% ethanol, and the crude glycosides were obtained by shaking with chloroform and chloroform–ethanol (20–40%) by using an earlier method[1,2]. These extracts contained an appreciable amount of 2-deoxyglycosides, as indicated by a strong, red coloration in the xanthydrol reaction[3]. The residue (12 g) from evaporation of the chloroform–ethanol extract, being the major part of the glycosides, was investigated in detail. This extract failed to be satisfactorily resolved by t.l.c. and p.c. It was, therefore, subjected to very mild hydrolysis with acid[4], which afforded a genin mixture (9 g) and a xanthydrol-positive, sugar mixture (2.2 g). The sugar mixture was nicely resolved by p.c. with 4:1 toluene–1-butanol, exhibiting eight spots when sprayed with vanillin–perchloric acid[5]; these were termed *A, B, C, D, E, F, G*, and *H* in the order of their decreasing mobilities.

Repeated chromatography of the sugar mixture on a column of SiO_2, with mixtures of chloroform and methanol afforded four chromatographically pure components *A, B, C*, and *F*. They failed to crystallize, and were characterized only by their specific rotation and mobility in p.c. In the present communication, some of the properties of the novel compound *C*, $[\alpha]_D$ +31°, an oligosaccharide, are reported.

A red coloration exhibited by compound *C* in the xanthydrol reaction indicated the presence of a 2-deoxy sugar in it. As compound *C* did not react with[6] $NaIO_4$, this suggested the absence of a vicinal diol grouping in the molecule. Drastic hydrolysis of compound *C* with acid by the Kiliani method[7] (2-deoxy sugars are decomposed under these conditions) completely decomposed *C*, suggesting that it contained only 2-deoxy sugars, but no normal sugars. To identify the sugar units of this oligosaccharide, it was completely hydrolyzed with 0.5mM H_2SO_4 in 1,4-dioxane within 30 min at 50°. In t.l.c. and p.c., the hydrolyzate showed the presence of only one product, which had the same mobility as

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cymarose. It was shown to be a reducing sugar by the Fehling test, and by its ready oxidation with bromine water to a lactone. Substance *C* was, therefore, a reducing oligosaccharide composed solely of cymarose residues.

The p.m.r. spectrum of substance *C* had a 9-H singlet at δ 3.43 which was assigned to the three methoxyl groups in the molecule. Its two signals to lower field were assigned to the three anomeric protons. One of them appeared as a 2-H, distorted doublet (*J* 3 Hz) at δ 5.37, and the other as a 1-H doublet of doublets (*J* 2 and 10 Hz) at δ 4.83. The multiplicity and coupling constants of the anomeric-proton signals of the three sugar units indicated that all of them existed in the pyranoid form. Its characteristic (2-deoxy) methylene signals appeared as two sets of multiplets, of 3 H each, in the regions of δ 2.29–2.46 and δ 1.39–1.54. In addition, a 3-H signal of a secondary CH_3 group as a doublet (*J* 6 Hz) at δ 1.37, and a 6-H signal of two secondary CH_3 groups as a doublet (*J* 6 Hz) at δ 1.30, substantiated that compound *C* contained three 2,6-dideoxyhexose units, each carrying a methoxyl group, which is in conformity with the analytical results, and that they were cymarose. The conclusion that compound *C* was a trisaccharide of cymarose was firmly substantiated by the observation of an M – 44 peak at 406 (42%) in its mass spectrum, due to the loss of CH_3CHO.

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