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Synthesis of *O*-β-D-Xylopyranosyl-L-serine

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In several glycoproteins the sugar and the aminoacid involved in the carbohydrate-protein linkage are *N*-acetyl-D-glucosamine and L-aspartic acid, linked as a 2-acetamido-1-(L-β-aspartamido)-1,2-dideoxy-β-D-glucose residue.

Recent studies, by Rodén and coworkers,[1-3] have indicated that heparin and chondroitin 4-sulphate are linked to protein by a different type of linkage, involving a xylose residue glycosidically linked to the hydroxyl group of L-serine. The synthesis of *O*-β-D-xylopyranosyl-L-serine, which possibly represents the branching point, is therefore a matter of some interest and is reported in the present communication.

Tri-*O*-acetyl-α-D-xylopyranosyl bromide and the methyl ester of *N*-tosyl-L-serine, in a Koenigs-Knorr reaction gave a 70 % yield of the corresponding glycoside. Removal of the protecting groups was expected to offer difficulties, as the electronegative methyl ester group would render the C(3)-*O*-linkage in the serine residue labile to alkali. The ester linkages were hydrolysed by treatment with sodium hydroxide in aqueous methanol and then the *N*-tosyl group was removed by treatment with sodium in liquid ammonia. The yield of the crystalline substance, m.p. 230–240° (decomp.), $[\alpha]_{578}$ −65° (water), was low (1.2 %). On hydrolysis with acid it yielded xylose and serine. It was unaffected by a commercial emulsin preparation which hydrolysed phenyl-β-D-xylopyranoside.

The methyl ester of β-D-glucopyranosyl-L-serine has recently been prepared by Kochetkov and coworkers.[4]

Experimental. Concentrations were carried out under reduced pressure at 40°. Melting points are corrected.

2,3,4-Tri-O-acetyl-β-D-xylopyranosyl-N-tosyl-L-serine methyl ester. A mixture of *N*-tosyl-L-serine methyl ester[5] (3.9 g), Drierite (14 g) and freshly prepared silver oxide (3.6 g) in dry, ethanol-free chloroform (14 ml) was stirred in the dark for 1 h. A solution of tri-*O*-acetyl-α-D-xylopyranosyl bromide (5.1 g) and iodine (0.7 g) in chloroform (25 ml) was then added during 1 h and stirring continued for 24 h. After filtration through a layer of Celite, the solution was washed with aqueous sodium thiosulphate and concentrated. Crystallisation from ethanol yielded a product (5.6 g) which gave only one spot on thin layer chromatography (Kieselgel G, ethyl acetate-light petroleum [b.p. 40–60°], 1:1). The crystals melted at 56–60° and on further heating the melt recrystallised at about 100°. When these crystals were used for seeding purposes a product was obtained which melted at 138–139° and had $[\alpha]_{578}^{20}$ −32° (*c* 2.0, chloroform). [Found: C 49.9; H 5.59; O 36.1; N 2.72; S 6.21. $C_{22}H_{29}O_{12}NS$ requires: C 49.8; H 5.50; O 36.1; N 2.64; S 6.02].

O-β-D-Xylopyranosyl-L-serine. The above substance (4.6 g) was dissolved in methanol (20 ml), M aqueous sodium hydroxide (38 ml) was added and the mixture was kept at room temperature under nitrogen for 1 h. Water (50 ml) was added and the solution was

extracted with ethyl acetate. The aqueous phase was then filtered through a column of Dowex 50 (H^+) and concentrated to a syrup (2.4 g). This syrup was dissolved in liquid ammonia (100 ml) and sodium (1.3 g) was added in small pieces over a period of 3 h with stirring. Dowex 50 (NH_4^+) (24 g) was added and stirring was continued for 1 h, after which time the ammonia was allowed to evaporate. The last traces were removed over sulphuric acid in a vacuum. The product was treated with water (150 ml) and filtered. The filtrate and washings were concentrated to 25 ml and the thiocresol present was extracted with ethyl ether (3 × 25 ml). Paper chromatography (ethyl acetate-acetic acid-water, 3:1:1) of the aqueous phase revealed the presence of several components, two of which appeared in the region where xylosylserine could be expected. These spots were developed with ninhydrin and with silver nitrate—ethanolic sodium hydroxide.

The substance giving the stronger and slightly faster spot was isolated chromatographically pure after repeated fractionations on thick filter paper, using the same solvent system. It crystallised from aqueous ethanol and the substance (25 mg) melted at 230—240° (decomp.) and had $[\alpha]_{578}^{20} - 65°$ (*c* 0.1, water). [Found: N 5.9. $C_8H_{15}O_7N$ requires: N 5.9].

The substance (1 mg) was dissolved in M hydrochloric acid (0.1 ml) and kept at 100° overnight. The hydrolysate was treated with Dowex 3 (free base) and concentrated. A paper chromatographic examination revealed the presence of xylose and serine.

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Studies on Components in Wood

3. Gas-Chromatographic Separation of Resin Acids of the Pimaric Acid Type

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In a previous article [1] we have presented some studies of the gas-chromatographic separation of mixtures containing those resin acids which constitute the main components of resin acid material both of native and of industrial origin. In the present communication we wish to report briefly on some gas-chromatographic separation experiments with a number of pimaric acids, partly with different degree of hydrogenation.

The pimaric acids constitute one of the two main groups of resin acids from softwood trees such as pine (*Pinus*), spruce (*Picea*), douglas-fir (*Pseudotsuga*) and larch (*Larix*) as well as from industrial products made from these species. The pimaric acids are characterized by the presence of a vinyl group which is absent in the acids belonging to the second main group, the abietic acids. The pimaric acids are in several cases more stable toward thermal isomerization than the abietic acids and they show certain individual characteristics which deserve attention with regard to their utilization in the pulp industry.

Pimaric acid and isopimaric acid are contained in many resin products [2] and recent gas-chromatographic analyses indicate that this may be the case with sandaracopimaric acid also.[1] Whether hydrogenated pimaric acids are present in such materials has not been established but it seems probable that technical products contain these acids at least in small amounts. Analytical methods suitable for their determination have not yet been developed.*

* Regarding analytical methods for the two ordinary pimaric acids, *i.e.* pimaric and isopimaric acid, see Ref. 2; for separation of these acids in the presence of sandaracopimaric acid, see Refs. 3, 4, and for gas-chromatographic separation of these three acids from abietic acids, see Ref. 1.