inhibition pattern of GSH reported in the present paper. The data are consistent with a Theorell-Chance mechanism,[6] but it is evident that a simple Bi Bi mechanism will not suffice for a full description of the kinetics, as two molecules of GSH and one molecule of $NADP^+$ are liberated in the enzymatic reaction. Further experiments are required to demonstrate whether the complete rate equation is second order with respect to GSH.

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Synthesis of 2-*O*-β-D-Glucopyranosyl-L-arabinose

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Graded hydrolysis of an alkaloid glycoside, isolated from a *Malaxis* sp. (Orchidaceae), yielded, *inter alia* an amorphous disaccharide, $[\alpha]_{578}^{22}+23°$ (water).[1] Structural studies indicated that it was 2-*O*-β-D-glucopyranosyl-L-arabinose, a previously unknown disaccharide. In the present communication the synthesis of this disaccharide is reported.

Benzyl 3,4-*O*-isopropylidene-β-L-arabinoside[2] in benzene was condensed with tetra-*O*-acetyl-α-D-glucopyranosyl bromide, in the presence of silver oxide. The condensation product was isolated by column chromatography on silicic acid, deacetylated, and the isopropylidene groups removed by mild acid hydrolysis. The resulting benzyl 2-*O*-β-D-glucopyranosyl-β-L-arabinopyranoside crystallised from ethanol, m.p. 194–195°, $[\alpha]_{578}^{22}+132°$ (water).

The structure of the glycoside was confirmed by methylation analysis. The glycoside was methylated by the Hakomori procedure,[3] hydrolysed and the resulting methylated sugars reduced into alditols with sodium borodeuteride. These were then analysed, as their acetates, by GLC[4]-mass spectrometry.[5] On an ECNSS-column, two peaks were obtained with T-values (retention times relative to that of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol) of 1.00 and 1.38. From its mass-spectrum and T-value the component in the first peak was characterised as the alditol acetate of 2,3,4,6-tetra-*O*-methyl-D-glucose. From its mass-spectrum, the component in the second peak was identified as the alditol acetate of a 3,4-di-*O*-methyl-pentose. The possibility that this component was the alditol acetate of a 2,3-di-*O*-methyl-pentose was excluded because of the deuterium labeling at C-1. The identification of 3,4-di-*O*-methyl-L-arabinose is in agreement with the expected structure.

Debenzylation of the glycoside by catalytic hydrogenation yielded a disaccharide, $[\alpha]_{578}^{22}+29°$, which did not crystallise.

The disaccharide on hydrolysis afforded equimolar amounts of D-glucose and L-arabinose. Its electrophoretic mobility in germanate buffer[6] at pH 10.7, $M_G=0.6$, was of the order of magnitude expected for arabinose substituted in the 2-position. The same value, $M_G=0.6$, was obtained for 2-*O*-methyl-D-galactose.

The low optical rotation of the disaccharide indicates a β-glucosidic linkage. The Koenigs-Knorr reaction, under the conditions used, is also known to give almost exclusively β-glucosides.

The synthetic disaccharide and that obtained on graded hydrolysis of the alkaloid glycoside, were indistinguishable

by paper chromatography in several solvent systems and by paper electrophoresis in germanate buffer.

Experimental. General methods. Melting points are corrected. Solutions were concentrated under reduced pressure, at a bath temperature not exceeding 40°. Paper chromatography was performed on Whatman No. 1 paper, using the solvent systems; (*a*) ethyl acetate-pyridine-water, 8:2:1, (*b*) ethyl acetate-acetic acid-water, 3:1:1. Paper electrophoresis was performed on Whatman No. 1 paper, in 0.05 M germanate buffer of pH 10.7. *p*-Anisidine hydrochloride in ethanol and sodium periodate-benzidine were used as spraying reagents.

TLC was performed on silica gel G and silica gel G_{254} (E. Merck AG).

GLC was performed on ECNSS-M columns, using a Perkin-Elmer 881 instrument. A Perkin-Elmer 270 instrument was used for the combined GLC-mass spectrometry.

Benzyl 2-O-β-D-glucopyranosyl-β-L-arabinopyranoside. A mixture of benzyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside (13.4 g), silver oxide (9.3 g), and Drierite (35 g) in dry benzene (110 ml) was stirred in the dark over night. A solution of tetra-*O*-acetyl-α-D-glucopyranosyl bromide (26.4 g) in dry benzene (110 ml) was added over a period of 1 h, and stirring was continued for 96 h. The reaction mixture was filtered through a layer of Celite and the filtrate concentrated to a syrup (30.8 g).

Part of this syrup (27.7 g) was divided into three portions and each portion fractionated by chromatography on a silicic acid column (43×8 cm), using as irrigant ethyl acetate-light petroleum (60–71°), 1:2. The course of the fractionation was followed by measuring optical rotation of the effluent and by TLC with the same solvent system. The disaccharide derivative was further purified by chromatography on a silicic acid column (38×4 cm), irrigated with toluene-methanol, 7:1. The yield of the disaccharide, which was still not chromatographically pure, was 3.35 g.

This product was suspended in dry methanol (20 ml), sodium methoxide (from 30 mg sodium) in methanol (6 ml) was added and the mixture kept at room temperature for 18 h. It was then treated with methanol-washed Dowex 50 (H^+), and concentrated. The resulting syrup was dissolved in methanol (20 ml); 0.01 M aqueous oxalic acid (20 ml) was added and the solution was refluxed for 20 min, neutralised with barium carbonate, filtered and concentrated. Paper chromatography revealed that the crystalline product was a mixture of benzyl β-L-arabinopyranoside and the disaccharide benzyl glycoside. Part of the product (90 mg) was fractionated on a cellulose column, using solvent system *a*. The benzyl 2-*O*-β-D-glucopyranosyl-β-L-arabinopyranoside (66 mg), was crystallised from ethanol. The pure substance showed m.p. 194–195° and $[\alpha]_{578}^{22}+132°$ (*c* 0.3, water) (Found: C 53.2; H 6.40. $C_{18}H_{26}O_{10}$ requires: C 53.7; H 6.51).

2-O-β-D-Glucopyranosyl-L-arabinose. The remaining, non purified benzyl 2-*O*-β-D-glucopyranosyl-β-L-arabinopyranoside (1.31 g), in anhydrous ethanol (125 ml) was hydrogenated at room temperature and atmospheric pressure, using as catalyst 10 % palladium on charcoal (2 g). When hydrogen consumption had ceased (80 ml), the catalyst was filtered off and the solution concentrated to a syrup (1.00 g). This mixture of disaccharide and arabinose was added to the top of a Sephadex G 15 column (180×25 cm) and eluted with toluene-saturated water. A chromatographically pure disaccharide (460 mg) was then obtained. This disaccharide could not be crystallised. It showed $[\alpha]_{578}^{20}+29°$ (*c* 0.5, water) and its paper chromatographic mobility, relative to glucose in solvent systems *a* and *b* was 0.5 and 0.8, respectively.

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