300. *The Synthesis of 2-O-β-D-Xylopyranosyl-L-arabinose and its Isolation from the Partial Hydrolysis of Esparto Hemicellulose.*

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The structure of 2-*O*-β-D-xylopyranosyl-L-arabinose has been confirmed by a synthesis involving a Koenigs–Knorr condensation of 2 : 3 : 4-tri-*O*-acetyl-α-D-xylopyranosyl bromide with benzyl 3 : 4-*O*-*iso*propylidene-β-L-arabopyranoside, followed by removal of protecting groups. The disaccharide has also been identified as one of the products of partial acid hydrolysis of esparto hemicellulose.

The disaccharide, 2-*O*-β-D-xylopyranosyl-L-arabinose, was first isolated as a product of partial acid hydrolysis of corn-cob hemicellulose B,[1, 2] and the mode of linkage was established by methylation.[1] We have recently isolated the same compound from the partial acid hydrolysis of barley-husk hemicellulose.[3] Whistler and McGilvray [1] suggested that the positive rotation of the disaccharide was indicative of an α-D-xylopyranosyl

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[1] Whistler and McGilvray, *J. Amer. Chem. Soc.*, 1955, **77**, 2212.
[2] Whistler and Corbett, *ibid.*, p. 3822.
[3] Aspinall and Ferrier, *J.*, 1957, 4188.

linkage. Approximate calculations of the expected optical rotations of *O*-D-xylopyranosyl-L-arabopyranoses can be made by using Hudson's rule.[4] For example, the molecular rotation of *O*-β-D-xylopyranosyl-α-L-arabopyranose is given by the following expression, $[M]_D = B$(D-xylose) − A(methyl D-xylopyranoside) + B(L-arabinose) + A(L-arabinose). The Table shows the calculated optical rotations together with the observed physical constants for the known *O*-D-xylopyranosyl-L-arabinoses. Although the calculations do not take into account the relatively small differences likely to arise from linkages through different positions in the arabinose residue, the observed rotation for the 2-linked disaccharide is clearly consistent only with the presence of a β-D-xylopyranosyl linkage. Furthermore, the high optical rotation of 3-*O*-α-D-xylopyranosyl-L-arabinose, isolated from the partial acid hydrolysis of golden apple gum,[5] and of corn-fibre hemicellulose,[6] indicates that the two disaccharides probably have different configurations at the glycosidic linkage. We now report confirmation of the structure of the disaccharide by a synthesis of 2-*O*-β-D-xylopyranosyl-L-arabinose. Since the appearance of a preliminary account [7] of some of the following results, Charlson, Gorin, and Perlin [8] have proved the presence of a β-glycosidic link in the disaccharide by its degradation to 2-*O*-β-D-xylopyranosylglycerol.

Disaccharide	M. p.	$[\alpha]_D$	Source
2-*O*-β-D-Xylopyranosyl-L-arabinose (anhydrous form)	167—168°	+32·9°	Corn-cob hemicellulose B
monohydrate	80—81	+47·0° → +32·5°	—
trihydrate	97—99	+53·7° → +33·2°	Barley-husk hemicellulose
,, ,, ,,	96—98	+55° → +31·5°	Synthesis
,, ,, ,,	98—99	+49° → +30°	Esparto hemicellulose
3-*O*-α-D-Xylopyranosyl-L-arabinose	123	+173°	Golden apple gum
,, ,, ,,	117·5—119	+166° → +181·8°	Corn-fibre hemicellulose
O-α-D-Xylopyranosyl-α-L-arabopyranose	—	+131° (calc.)	—
O-α-D-Xylopyranosyl-β-L-arabopyranose	—	+191° (calc.)	—
O-β-D-Xylopyranosyl-α-L-arabopyranose	—	+2° (calc.)	—
O-β-D-Xylopyranosyl-β-L-arabopyranose	—	+63° (calc.)	—

Since *O*-acyl-α-D-glycosyl halides with alcohols give the corresponding β-glycosides,[9] the required glycosidic bond of the disaccharide was formed by a Koenigs–Knorr condensation [10] of 2 : 3 : 4-tri-*O*-acetyl-α-D-xylopyranosyl bromide with benzyl 3 : 4-*O*-*iso*propylidene-β-L-arabopyranoside. The condensation product, benzyl 3 : 4-*O*-*iso*propylidene-2-*O*-(2 : 3 : 4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-L-arabopyranoside, was isolated as a crystalline compound after chromatography on alumina; its deacetylation gave benzyl 3 : 4-*O*-*iso*propylidene-2-*O*-β-D-xylopyranosyl-β-L-arabopyranoside, which on hydrogenation (palladium–calcium carbonate) afforded 3 : 4-*O*-*iso*propylidene-2-*O*-β-D-xylopyranosyl-L-arabopyranose monohydrate. Mild acid hydrolysis of that monohydrate furnished the required disaccharide, which was readily separated from small amounts of xylose and arabinose and crystallised as 2-*O*-β-D-xylopyranosyl-L-arabinose trihydrate, identical (m. p. and mixed m. p., optical rotation, and *X*-ray single-crystal photograph) with the disaccharide previously isolated from the partial acid hydrolysis of barley-husk hemicellulose.[3]

A second crystalline condensation product (*A*) was isolated in low yield from the Koenigs–Knorr reaction. It is probable that this compound is a partially acetylated benzyl di-*O*-xylosylarabinose since hydrolysis gave xylose and arabinose in the proportion

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[4] Hudson, *J. Amer. Chem. Soc.*, 1916, **38**, 1566.
[5] Andrews and Jones, *J.*, 1954, 4134.
[6] Whistler and Corbett, *J. Amer. Chem. Soc.*, 1955, **77**, 6328.
[7] Aspinall and Ferrier, *Chem. and Ind.*, 1957, 819.
[8] Charlson, Gorin, and Perlin, *Canad. J. Chem.*, 1957, **35**, 365.
[9] Haynes and Newth, *Adv. Carbohydrate Chem.*, 1955, **10**, 207.
[10] Koenigs and Knorr, *Ber.*, 1901, **34**, 957.

of 1·8 to 1, and since the infrared spectrum contained a sharp absorption at 3531 cm.$^{-1}$ showing the presence of a single hydroxyl group in the molecule. The product (*B*) of deacetylation consumed 4·4 mol. of periodate, slightly more than the expected 4 mol. Methylation and deacetylation of material *A* gave a methylated trisaccharide, whose hydrolysis gave 2 : 3 : 4-tri-*O*-methylxylose and a mono-*O*-methylarabinose. The latter was shown to be the 2-methyl ether since chromatography of the products of periodate oxidation [11] showed methoxymalondialdehyde and since the derived mixture of methyl pyranosides was attacked by periodate. Although insufficient of the trisaccharide derivative (*A*) was available for a complete characterisation, these experiments suggest that compound *B* is benzyl 3 : 4-di-*O*-β-D-xylopyranosyl-β-L-arabopyranoside and that material *A* is a partially acetylated derivative. Although there is no apparent reason for the instability of benzyl 3 : 4-*O*-*iso*propylidene-β-L-arabopyranoside during the Koenigs–Knorr reaction, it is clear that some hydrolysis of the *iso*propylidene group took place since benzyl β-L-arabopyranoside was also isolated from the mixture. The trisaccharide derivative (*A*) must have been formed by condensation of tri-*O*-acetyl-α-D-xylopyranosyl bromide with benzyl β-L-arabopyranoside.

During the isolation of xylobiose and xylotriose from the partial acid hydrolysis of esparto hemicellulose,[12] a small fraction was obtained which contained xylobiose and a second disaccharide having the same chromatographic mobility as 2-*O*-β-D-xylopyranosyl-L-arabinose.* This compound was separated chromatographically and was isolated as the crystalline 2-*O*-β-D-xylopyranosyl-L-arabinose trihydrate. It is clear that this disaccharide arises from a hitherto unrecognised structural feature of esparto hemicellulose. Previous investigations have shown that esparto hemicellulose contains at least two xylans, one [13] devoid of and one [14] containing arabinose residues, the majority of which are present as end groups in the furanose form. The structural significance of the isolation of 2-*O*-β-D-xylopyranosyl-L-arabinose from esparto hemicellulose is not yet clear. It may be recalled, however, that a small quantity of an unidentified di-*O*-methylarabinose was isolated from the hydrolysis of methylated esparto araboxylan; [14] the optical rotation and chromatographic mobility of this sugar were similar to those of 3 : 5-di-*O*-methyl-L-arabinose. 1 : 2-Linked L-arabofuranose residues would be present in esparto hemicellulose if 2-*O*-β-D-xylopyranosyl-L-arabofuranosyl side-chains were attached to the backbone of 1 : 4-linked β-D-xylopyranose residues as in barley-husk hemicellulose.[3]

EXPERIMENTAL

Alumina, Type H, 100/200 S mesh, supplied by Peter Spence and Sons, Ltd., was shaken with N-acetic acid, washed with water by decantation until free from acid, and dried at 260°. Optical rotations were observed at 18° ± 2°.

Benzyl 3 : 4-O-iso*propylidene*-β-L-*arabopyranoside*.—Benzyl β-L-arabopyranoside (20 g.) in acetone (1 l.) was shaken with cupric sulphate (60 g.) and concentrated sulphuric acid (1 ml.) for 24 hr. The acetone solution was separated, acid was neutralised by passing in dry ammonia, salts were removed by filtration, and the solution was concentrated to a syrup. The syrup was extracted with ether and the extract (23 g.) was redissolved in ether and chromatographed on alumina (25 × 5 cm.). Elution with ether containing 5% ethanol, followed by two recrystallisations from light petroleum (b. p. 60—80°)–ether (3 : 1), afforded *benzyl* 3 : 4-O-iso*propylidene*-β-L-*arabopyranoside* (10 g.), m. p. 57—58°, $[\alpha]_D$ +187° (*c* 0·9 in $CHCl_3$) (Found: C, 64·7; H, 7·2. $C_{15}H_{20}O_5$ requires C, 64·3; H, 7·2%). Ballou [15] reports m. p. 55—58°, $[\alpha]_D$ −208° (EtOH), for benzyl 3 : 4-*O*-*iso*propylidene-β-D-arabopyranoside.

Condensation of 2 : 3 : 4-*Tri*-O-*acetyl*-α-D-*xylopyranosyl Bromide and Benzyl* 3 : 4-O-iso*propylidene*-β-L-*arabopyranoside*.—Benzyl 3 : 4-*O*-*iso*propylidene-β-L-arabopyranoside (9·2 g.), freshly

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* We are grateful to Dr. Mary E. Carter for drawing our attention to the presence of this disaccharide.

[11] Lemieux and Bauer, *Canad. J. Chem.*, 1953, **31**, 814.

[12] Aspinall, Carter, and Los, *J.*, 1956, 4807.

[13] Chanda, Hirst, Jones, and Percival, *J.*, 1950, 1289.

[14] Aspinall, Hirst, Moody, and Percival, *J.*, 1953, 1631.

[15] Ballou, *J. Amer. Chem. Soc.*, 1957, **79**, 165.

prepared silver carbonate (15 g.), and anhydrous calcium sulphate (40 g.) were shaken overnight in benzene (100 ml.). After addition of iodine (3 g.), a solution of 2 : 3 : 4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (11·1 g.) in benzene (100 ml.) was added slowly with stirring during 1 hr. The mixture was shaken in the dark for 3 days (with occasional release of carbon dioxide); the benzene solution then gave no opalescence with ethanolic silver nitrate. Filtration of the mixture followed by concentration of the filtrate yielded a syrup (16 g.), which was chromatographed in benzene on alumina (25 × 5 cm.) to give 6 fractions.

Fraction 1. The solid [1·8 g.; eluted with light petroleum–benzene (1 : 1)] after two recrystallisations from light petroleum containing a little ethanol gave *benzyl* 3 : 4-O-iso*propylidene*-2-O-(2 : 3 : 4-*tri*-O-*acetyl*-β-D-*xylopyranosyl*)-β-L-*arabopyranoside* (1·35 g.), m. p. 110—111°, $[\alpha]_D$ +71° (*c* 1·0 in $CHCl_3$), $[\alpha]_D$ +78° (*c* 1·0 in MeOH) (Found: C, 58·3; H, 6·4. $C_{26}H_{34}O_{12}$ requires C, 58·0; H, 6·4%).

Fraction 2. The syrup [0·6 g.; eluted with light petroleum–benzene (1 : 3)] was dissolved in ethanol, crystals were deposited, and recrystallisation from ethanol gave compound *A* (200 mg.), m. p. 154—155°, $[\alpha]_D$ +38° (*c* 1·0 in $CHCl_3$). Hydrolysis of a sample of *A* gave xylose and arabinose in the ratio of 1·8 : 1 (quantitative chromatography [16]). Deacetylation of *A* with sodium methoxide gave compound *B*, which after recrystallisation from ethanol–water had m. p. 261—263° [Found: C, 52·0; H, 6·3. Benzyl di-*O*-β-D-xylopyranosyl-β-L-arabopyranoside ($C_{22}H_{32}O_{13}$) requires C, 52·4; H, 6·3%)]. The benzyl glycoside *B* consumed 4·4 mol. of periodate (spectrophotometric determination [17]). Direct methylation of *A* with methyl sulphate and sodium hydroxide and hydrolysis of the methylated trisaccharide gave two components *a* and *b*, R_G 0·95 (cf. 2 : 3 : 4-tri-*O*-methyl-D-xylose) and 0·37 in butan-1-ol–ethanol–water (4 : 1 : 5; upper layer). Chromatography [11] of the product of the periodate oxidation of *b* showed methoxymalondialdehyde. Demethylation of *b* with hydrobromic acid gave arabinose. The derived syrup of methyl pyranosides consumed *ca.* 1 mol. of periodate.

Fractions 3 *and* 4. Benzyl β-L-arabopyranoside, m. p. and mixed m. p. 172—173°, was deposited from ethanolic solutions of fractions 3 (2·1 g.; eluted with benzene) and 4 [1·6 g.; eluted with benzene–ether (1 : 1)].

Fraction 5. The syrup [2·1 g.; eluted with ether–ethanol (1 : 1)] was dissolved in ethanol; crystals were deposited, m. p. 141—142°, $[\alpha]_D$ +69° (*c* 1·3 in $CHCl_3$) {cf. 2 : 3 : 4-tri-*O*-acetyl-D-xylose, m. p. 138—141°, $[\alpha]_D$ +70° ($CHCl_3$) [18]}.

Fraction 6. The mobile oil (3·6 g.; eluted with acetone), $[\alpha]_D$ +10° (*c* 1·2 in H_2O), when hydrolysed, gave approximately equal amounts of xylose and arabinose.

Benzyl 3 : 4-O-iso*propylidene*-2-O-β-D-*xylopyranosyl*-β-L-*arabopyranoside*.—Methanolic 0·1N-sodium methoxide (6 ml.) was added to benzyl 3 : 4-*O*-*iso*propylidene-2-*O*-(2 : 3 : 4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-L-arabopyranoside (1·20 g.) in methanol (60 ml.), and after the mixture had been shaken for 6 hr. crystals separated. Recrystallisation from methanol afforded *benzyl* 3 : 4-O-iso*propylidene*-2-O-β-D-*xylopyranosyl*-β-L-*arabopyranoside* (0·75 g.), m. p. 216—217°, $[\alpha]_D$ +132° (*c* 0·5 in MeOH) (Found: C, 58·2; H, 6·6. $C_{20}H_{28}O_9$ requires C, 58·3; H, 6·8%).

2-O-β-D-*Xylopyranosyl*-L-*arabinose*.—The above benzyl glycoside (0·72 g.) in ethanol–water (100 ml.) was shaken in hydrogen at atmospheric pressure in the presence of palladium hydroxide (5%)–calcium carbonate (4 g.) for 6 hr. Catalyst was filtered off and the filtrate concentrated to a syrup (0·55 g.). Extraction of the product with boiling acetone, followed by removal of solvent, afforded a crystalline *compound* (0·50 g.), m. p. 141—143°, $[\alpha]_D$ +53° (equil.) (*c* 0·7 in H_2O). Although no satisfactory solvent could be found for recrystallisation, this substance was probably 3 : 4-*O*-*iso*propylidene-2-*O*-β-D-xylopyranosyl-L-arabinose monohydrate (Found: C, 45·3; H, 7·0. $C_{13}H_{22}O_9,H_2O$ requires C, 45·9; H, 7·1%). This substance (0·28 g.) was heated at 100° for 40 min. with 0·005N-oxalic acid (10 ml.), the solution was neutralised with Amberlite resin IR-4B(OH), and the filtrate was concentrated to a syrup (0·20 g.). Recrystallisation from ethanol–water furnished 2-*O*-β-D-xylopyranosyl-L-arabinose trihydrate (120 mg.), which had m. p. and mixed m. p. 96—98°, $[\alpha]_D$ +55° (3 min.) $\longrightarrow$ +31·5° (90 min., const.) (*c* 1·5 in H_2O), and gave an *X*-ray single-crystal photograph identical with that of an authentic sample.

Isolation of 2-O-β-D-*Xylopyranosyl*-L-*arabinose from the Partial Hydrolysis of Esparto Hemicellulose*.—During the isolation of xylobiose and xylotriose from the partial acid hydrolysis of esparto hemicellulose,[12] a small fraction (350 mg.) was obtained from the fractionation on

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[16] Flood, Hirst, and Jones, *J.*, 1948, 1679.

[17] Aspinall and Ferrier, *Chem. and Ind.*, 1957, 1216.

[18] Hudson and Dale, *J. Amer. Chem. Soc.*, 1918, **40**, 997.

charcoal–celite which was shown by paper chromatography in ethyl acetate–pyridine–water (10 : 4 : 3) to contain two components, xylobiose and an unidentified sugar, having R_{xylose} 0·59 and 0·67. The sugars were separated chromatographically on filter sheets and the faster-moving component (50 mg.) crystallised from ethanol–water to give 2-*O*-β-D-xylopyranosyl-L-arabinose trihydrate (20 mg.), m. p. 98—99°, $[\alpha]_D$ +49° (3 min.) $\longrightarrow$ +30° (1 hr., const.) (*c* 1·0 in H_2O). The sugar was chromatographically indistinguishable in three solvent systems from the authentic disaccharide, hydrolysis gave xylose and arabinose, and hydrolysis of the derived aldobionic acid (bromine oxidation) gave only xylose. An *X*-ray single-crystal photograph was identical with that of the disaccharide isolated from barley-husk hemicellulose.[3]

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