## Note

# The synthesis of 2-naphthyl α-L-arabinofuranoside

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While nitrophenyl glycosides and esters are now accepted substrates for the assay of hydrolytic enzymes, the naphthyl derivatives are of use as histochemical reagents in conventional methods[1] or, with suitable modifications, in electron microscopy[2]. Complexes formed by the enzymic cleavage of these naphthyl derivatives and subsequent coupling with suitable salts are generally of a greater colour density and have lower solubility and diffusion rates than the corresponding phenyl derivatives and are thus better suited for studies of enzyme localisation. In order to examine further the localisation of the enzyme α-L-arabinofuranosidase secreted by the fungus *Sclerotinia fructigena*[3], the synthesis of 2-naphthyl α-L-arabinofuranoside was investigated.

An attempt to prepare the glycoside by the method used for the corresponding *p*-nitrophenyl derivative, using a mercuric cyanide catalyst for the condensation of the α-L-arabinofuranose tetra-acetate with the phenol[4], proved unsuccessful. However, with toluene-*p*-sulphonic acid as catalyst, as used for the corresponding phenyl glycoside[5], condensation was successful, although on occasions some difficulty was encountered at the final deacetylation stage, probably as a result of base-catalyzed glycosidic cleavage[6].

The new compound showed a high negative optical rotation, of the same magnitude as other phenyl derivatives of α-L-arabinofuranosides[4,5]. The furanose structure was confirmed by the 100-MHz n.m.r. spectrum of the naphthyl glycoside in $Me_2SO$-$d_6$. The signals due to the hydroxyl protons[7] were well resolved, OH-5 as a triplet at $\tau'$ 4.8 ($J$ 3 Hz) and OH-3 and OH-2 as doublets ($J$ 2 Hz) at $\tau'$ 5.3 and 5.6 which disappeared on equilibration with $D_2O$. The small coupling constant for H-1 at $\tau'$ 5.65 ($J_{1,2}$ 2 Hz), consistent[8] with *trans* H-1 and H-2, confirmed the α-configuration. Similar coupling constants ($J_{1,2}$ ~2 Hz) were observed for the phenyl and the *p*-nitrophenyl α-L-arabinofuranosides at $\tau'$ 5.6 and 5.7, respectively.

2-Naphthyl α-L-arabinofuranoside was shown to be hydrolysed to 2-naphthol and L-arabinose by an enzyme preparation from *S. fructigena*, and its use as a histochemical substrate for α-L-arabinofuranosidase is now being investigated.

## EXPERIMENTAL

Thin-layer chromatography (t.l.c.) was carried out at each stage, using silica gel G (Merck) and ethyl acetate–chloroform (1:1, v/v).

*2-Naphthyl α-L-arabinofuranoside.* — L-Arabinose (20 g) was acetylated under conditions which gave predominantly L-arabinofuranose tetra-acetate[5]. A mixture of the resulting syrup (11 g) with 2-naphthol (15 g) and toluene *p*-sulphonic acid (0.1 g) was melted to a homogeneous mixture and heated at 100° for 25 min under reduced pressure (water pump) with continuous rotation. Benzene (60 ml) was then added to the hot mixture, and after cooling a further quantity (100 ml) was added. The benzene solution was washed with M sodium hydroxide (4 × 10 ml) and then with water until the washings were neutral, dried ($MgSO_4$), and concentrated under reduced pressure to a yellow syrup (18 g). This syrup was dissolved in anhydrous methanol (500 ml) to which sodium methoxide (from 0.3 g of sodium) in methanol (50 ml) was added. After 3 h at room temperature, the methanol was distilled off, the residue was dissolved in water (100 ml), and this solution was extracted with ethyl acetate (8 × 100 ml) to remove the glycoside (the Dowex ion-exchange and chloroform extraction stages used for the isolation of the corresponding phenyl glycosides[5] were omitted). The ethyl acetate extract was dried ($MgSO_4$) and concentrated to a syrup. This was taken up in ethyl acetate (40 ml) and freed of 2-naphthol and other impurities by chromatography on a column (70 × 4 cm) of silica gel with ethyl acetate as solvent. T.l.c. indicated the appearance of the required glycoside after 700 ml of eluate had been collected.

Evaporation of the appropriate fractions under reduced pressure gave a syrup (2.5 g) from which 2-naphthyl α-L-arabinofuranoside slowly crystallised. After washing with ether, the crystals (0.75 g) were obtained as light, buff-coloured needles, m.p. 108–111°, $[\alpha]_D^{20}$ −206.5° (*c* 0.5, methanol) (Found: C, 65.2; H, 5.9; $C_{15}H_{16}O_5$ calc.: C, 65.0; H, 5.8%). *p*-Nitrophenyl α-L-arabinofuranoside[4] had $[\alpha]_D^{20}$ −212° (*c* 0.5, methanol).

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