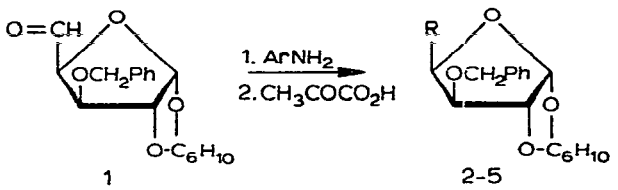
Preliminary communication

The Doebner synthesis in the carbohydrate series

We have examined the behaviour of 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-*xylo*-pentodialdo-1,4-furanose[1] (1) with various arylamines in the Doebner synthesis. The condensation proceeds in the usual way, giving the corresponding substituted cinchoninic acids (2–5).



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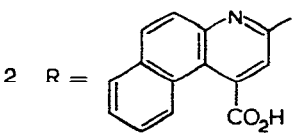

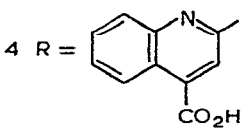

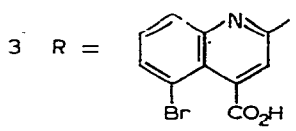

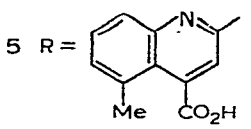

This synthesis was accomplished by preliminary storage of a mixture of compound 1 and the arylamine in ether for 24 h to form the Schiff base, with subsequent addition of freshly distilled pyruvic acid and storage of this mixture for 10 days; all operations were performed at room temperature. Preparative fractionation of the final mixture on alumina gave the following products:

3-*O*-Benzyl-4-(4-carboxybenzo[*f*]quinol-2-yl)-1,2-*O*-cyclohexylidene-α-D-*xylo*-tetrofuranose (2) (27.5%), white needles from ethyl acetate, m.p. 198° (decomp.), $[\alpha]_D^{15}$ −7° (*c* 0.6, chloroform); λ_{max} 243 (inflection) (ε 33,400) and 256 nm (ε 36,000); ν_{max} 1710 (medium), 1670 (weak), and 1599 cm^{-1} (medium) (Found: C, 72.45; H, 5.59; N, 2.40. $C_{31}H_{29}NO_6$ calc.: C, 72.79; H, 5.67; N, 2.74%).

3-*O*-Benzyl-4-(5-bromo-4-carboxyquinol-2-yl)-1,2-*O*-cyclohexylidene-α-D-*xylo*-tetrofuranose (3) (10.9%), an amorphous powder, $[\alpha]_D^{15}$ −125° (*c* 1.2, chloroform); λ_{max} 252 (ε 9900) and 304 nm (ε 3900); ν_{max} 1709 (medium) and 1592 cm^{-1} (medium) (Found: C, 59.85; H, 4.76; Br, 14.26. $C_{27}H_{26}BrNO_6$ calc.: C, 60.0; H, 4.81; Br, 14.81%).

3-*O*-Benzyl-4-(4-carboxyquinol-2-yl)-1,2-*O*-cyclohexylidene-α-D-*xylo*-tetrofuranose (4) (13.9%), an amorphous powder, $[\alpha]_D^{15}$ −102° (*c* 1, chloroform); λ_{max} 235 (ε 9700) and 308 nm (ε 3800); ν_{max} 1710 (medium), 1594 (medium), and 1510 cm^{-1} (medium) (Found: C, 69.71; H, 6.18. $C_{27}H_{27}NO_6$ calc.: C, 70.28; H, 5.85%).

3-*O*-Benzyl-4-(4-carboxy-5-methylquinol-2-yl)-1,2-*O*-cyclohexylidene-α-D-*xylo*-tetrofuranose (5) (24.4%), white needles from ethyl acetate, m.p. 158° (decomp.), $[\alpha]_D^{15}$ −143° (*c* 1.4, chloroform); λ_{max} 236 (ε 13,000) and 322 nm (ε 5300); ν_{max} 1709 (medium), 1601 (medium), and 1512 cm^{-1} (medium) (Found: C, 70.58; H, 6.14. $C_{28}H_{29}NO_6$ calc.: C, 70.73; H, 6.10%).

Removal of the cyclohexylidene residue was accomplished by methanolysis of compound 2 in the presence of dry hydrogen chloride.

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REFERENCE

1 Yu.A. Zhdanov, Yu.E. Alexeev, and G.N. Dorofeenko, *Zh. Obshch. Khim.*, 37 (1967) 98.

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