Preparation of some methyl α-D-glucopyranoside cyclic acetals by transacetalation

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Methyl 4,6-*O*-anisylidene-, *O*-vanillilidene-, *O*-syringylidene-, and *O*-veratrylidene-α-D-glucopyranosides have been prepared in 70—80% yields from methyl α-D-glucopyranoside and the corresponding dimethyl acetals of aromatic aldehydes by transacetalation. The substituted phenyl group on the acetal carbon in the produced acetals is in the equatorial position.

Приготовили в 70—80%-ных вытяжках 4,6-*O*-анисилиден-, *O*-ванилилиден-, *O*-сирингилиден- и *O*-вератрилиден-α-D-гликопиранозиды трансацеталацией из метил-α-D-глюкопиранозида с соответствующими диметилацеталами. Замещенная фенилгруппа на ацеталовом углероде помещена во всех приготовленных ацеталах в экваториальном положении.

Condensation of methyl α-D-glucopyranoside with anisaldehyde, vanilline, syringic aldehyde, and veratric aldehyde in the presence of zinc chloride gave the corresponding cyclic acetals in low yields [1]. These, rather labile derivatives, needed as models in the studies of the character of lignin—saccharide linkages in plant materials have been now conveniently prepared from methyl α-D-glucopyranoside and corresponding aromatic aldehyde dimethyl acetals by transacetalation. Methyl 4,6-*O*-benzylidene-α- and -β-D-glucopyranosides [2] as well as analogous substances derived from less reactive ketones [3, 4] were prepared in the same manner.

Experimental

The p.m.r. spectra for solutions in chloroform-d were obtained at 80 MHz with a Tesla BS 487 B spectrometer.

Methyl α-D-glucopyranoside (commercial product) was dried at 100°C for 12 h. The aromatic aldehydes (commercial products) were dried over phosphorus pentaoxide for 24 h. *N*,*N*-Dimethylformamide was purified by the standard method [5]. Trimethoxymethane was prepared by the described [6] procedure and *p*-toluenesulfonic acid was used as the catalyst.

The reactions were monitored by thin-layer chromatography as described [1].

The aromatic aldehydes were converted to the corresponding dimethyl acetals and reacted [3] with methyl α-D-glucopyranoside. The only difference between the original procedure and the one used throughout this work was the means of recovery of the unreacted methyl α-D-glucopyranoside; this was accomplished by dissolving the crude products in dry dichloromethane from which, when the solutions were kept at 0°C for 24 h, the substance crystallized.

The p.m.r. data:

Methyl 4,6-*O*-anisylidene-α-D-glucopyranoside (*I*): δ 6.80—7.40 (m, 4H aromat.); 5.45 (s, 1H, PhCH); 4.72 (d, H-1); 3.50—4.00 (m, H-2,3,4,5,6,6'); 3.42 (s, MeO-1); 3.76 (s, MeO aromat.); 2.42 (s, OH).

Methyl 4,6-*O*-vanillilidene-α-D-glucopyranoside (*II*): δ 6.80—7.28 (m, 3H aromat.); 5.45 (s, 1H, PhCH); 4.74 (d, H-1); 3.50—4.25 (m, H-2,3,4,5,6,6'); 3.42 (s, MeO-1); 3.82 (s, MeO aromat.); 3.14 (s, OH aromat.); 2.42 (s, OH).

Methyl 4,6-*O*-syringylidene-α-D-glucopyranoside (*III*): δ 6.78—7.25 (m, 3H aromat.); 5.45 (s, 1H, PhCH); 4.74 (d, H-1); 3.48—4.20 (m, H-2,3,4,5,6,6'); 3.42 (s, MeO-1); 3.82; 3.86 (2s, 2 MeO aromat.); 2.38 (s, OH).

Methyl 4,6-*O*-veratrylidene-α-D-glucopyranoside (*IV*): δ 6.76—7.30 (2s, 2H aromat.); 5.45 (s, 1H, PhCH); 4.73 (d, H-1); 3.48—4.24 (m, H-2,3,4,5,6,6'); 3.42 (s, MeO-1); 3.78; 3.82 (2s, 2 MeO aromat.); 3.16 (s, OH aromat.); 2.28 (s, OH).

Results and discussion

Owing to low reactivity of anisaldehyde, vanilline, syringic aldehyde, and veratric aldehyde as well as to the competing hydrolysis of the formed products the yields of the corresponding methyl 4,6-*O*-ylidene-α-D-glucopyranosides by the standard zinc chloride method were low [1]. Acid-catalyzed transacetalation in DMF under homogeneous conditions using aromatic aldehyde dimethyl acetals and methyl α-D-glucopyranoside gave acetals *I*—*IV* in 80, 70, 78, and 82% yields, respectively, as compared to 17, 9, 18, and 20% obtained by the original procedure.

Assuming chair conformation for the six-membered 1,3-dioxan ring in carbohydrate cyclic acetals the formation of one diastereoisomer, having the bulky group in the equatorial position, can be expected [7]. This was experimentally confirmed by *Foster et al.* [8] who assigned the signals at δ 5.46 in the p.m.r. spectrum of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside to the axially oriented benzylic proton. The same configuration for the C-2 in the 1,3-dioxan ring follows from the chemical shift observed for the benzylic proton of the acetals described herein. All prepared acetals revealed one singlet at δ 5.45 showing that the substitution on the aromatic ring has no effect upon the stereochemistry at the new centre of asymmetry. Hence, the isolated acetals can be characterized as a *trans*-decalin bicyclic system with an equatorially oriented phenyl group.

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