

Synthesis of 6-*O*-vanillyl-D-glucose

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By the reaction of D-glucose with vanillyl alcohol in *N,N'*-dimethylformamide the 6-*O*-vanillyl derivative of D-glucose has been formed preferentially. The prepared ether was hydrolyzed both in acidic and alkaline media. The highest resistance to hydrolysis was observed in the pH range of 4—6.

The possibility of formation of ether bond between saccharide and lignin model compounds was demonstrated in the reaction of D-glucose with vanillyl alcohol in aqueous solution at moderate reaction conditions (pH 4, 60 °C) [1]. Relatively high yield of the reaction product was obtained after 10-day reaction. The reaction equilibrium was shifted in favour of formation of the product by using 36-fold excess of the starting saccharide component.

When using the above-mentioned type of reaction for large-scale preparation of 6-*O*-vanillyl-D-glucose, a model compound for following the properties of benzyl-ether bond between lignin and polysaccharides in plant material, it was shown that isolation of the product from the reaction mixture was rather difficult, because on removal of high excess of D-glucose in aqueous acid medium the prepared ether underwent hydrolysis. The observed hydrolysis of the prepared ether is in agreement with our previous results concerning the properties of methyl 4-*O*- and 6-*O*-(4-methoxybenzyl)- α -D-glucopyranosides [2, 3] which are, contrary to unsubstituted benzyl ethers of saccharides, little resistant to acid-catalyzed hydrolysis.

The aim of our work was to modify the direct acid-catalyzed etherification of glucose with vanillyl alcohol for large-scale use. The reaction performed in anhydrous *N,N'*-dimethylformamide, using Dowex 50 (H⁺) as the catalyst, made possible to reduce the concentration of the starting D-glucose, shorten the reaction time, and simplify the way of isolation. 6-*O*-Vanillyl-D-glucose was obtained in about 60 % yield. The reaction course was monitored by thin-layer chromatography and the expected structure was confirmed by elemental and ¹³C NMR spectral analyses of the prepared ether and of its peracetyl derivative (Table 1). The spectral data showed also that the product was a mixture of anomers. Since other positional isomers were not present in observable amount,

Table 1
 ^{13}C NMR chemical shifts (δ) for 6-*O*-vanillyl-D-glucose and its peracetyl derivative

Compound	C-1 α, β	C-2 α, β	C-3 α, β	C-4 α, β	C-5 α, β	C-6 α, β	C _{arom} -1	C _{arom} -2	C _{arom} -3	C _{arom} -4	C _{arom} -5	C _{arom} -6	CH ₂ benzyl	OCH ₃
6- <i>O</i> -Vanillyl-D-glucose ^a	93.30 97.20	74.20 75.23	72.64 77.06	70.82 70.82	71.08 75.89	69.93 69.93	130.85	113.96	148.53	145.93	116.43	122.93	74.20	57.05
1, 2, 3, 4-Tetra- <i>O</i> -acetyl-6- <i>O</i> -(3-methoxy-4-acetoxybenzyl)-D-glucose ^b	89.07 91.67	70.04 70.30	69.78 72.70	67.77 67.77	68.29 71.02	69.32 69.32	136.43	112.09	151.17	139.29	120.04	122.44	77.51	57.00

a) Solvent: water; internal standard: methanol. b) Solvent: chloroform; internal standard: TMS.

it is evident that only the primary hydroxyl group of D-glucose entered the reaction with the benzyl-alcohol group.

The hydrolysis of 6-O-vanillyl-D-glucose was studied at 60 °C in aqueous buffer solutions of pH 1.1–8.0. At higher pH values the hydrolysis was accompanied by side reactions of the aromatic moiety of the model compound. The reaction was monitored by spectrophotometric determination of the released benzyl-alcohol groups after copulation with quinone monochloroimide. From the results illustrated in Figs. 1 and 2 it follows that the prepared ether was hydrolyzed at all pH values, the reaction rate being the lowest in the pH range of 4–6. This range corresponds with that of the medium used in etherification of D-glucose with vanillyl alcohol described in [1].

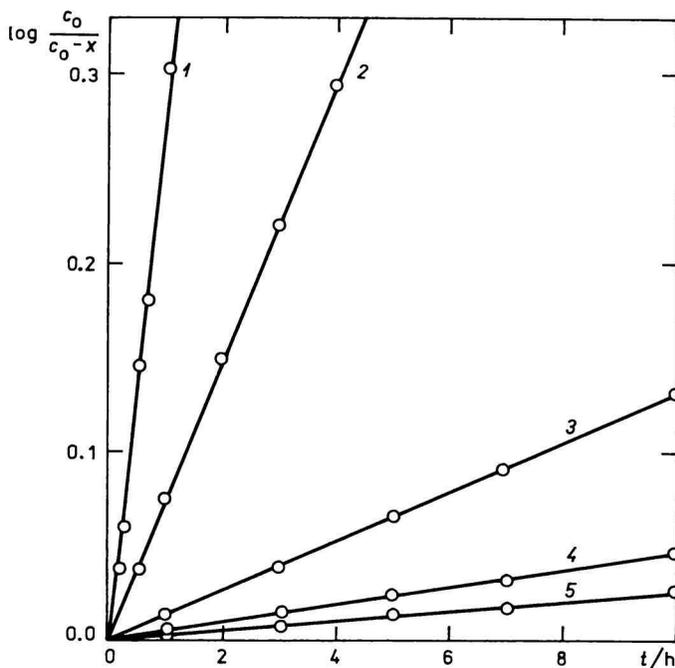


Fig. 1. Hydrolysis of 6-O-vanillyl-D-glucose.

c_0 — original concentration of the starting compound, x — determined concentration of vanillyl alcohol. pH: 1. 1.1, 2. 2.3, 3. 8, 4. 5.4, 5. 4.4.

The properties of the model compound observed in the followed pH range are important for better understanding of the behaviour of lignin-poly-saccharide complex of wood in delignification processes.

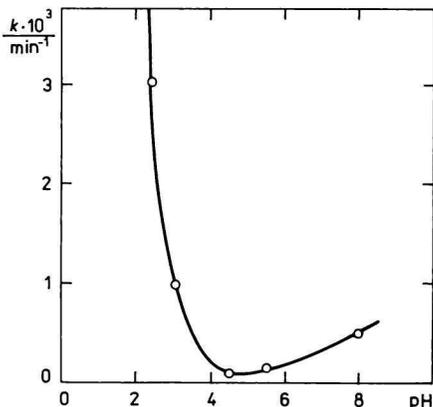


Fig. 2. Dependence of rate constant of hydrolysis of 6-*O*-vanillyl-D-glucose on pH.

Experimental

Optical rotations were measured on a Perkin—Elmer 141 automatic polarimeter. The content of free benzyl-alcohol groups was determined with a universal spectrophotometer (Zeiss, Jena). The ^{13}C NMR spectra were measured at 22 °C with a Jeol FX-100 spectrometer (spectral width 6000 Hz, pulse width 12 s, data points 8000), using the noise-decoupling off resonance method. Chemical shifts are given with the accuracy of $\delta = 0.06$. Thin-layer chromatography was performed on silica gel PF₂₅₄ (Merck) and column chromatography on silica gel PF₂₅₄ (grain size 0.063—0.1 mm) in the systems *A* (chloroform—methanol, $\varphi_r = 5:1$) and *B* (chloroform—petroleum ether, $\varphi_r = 2:1$), respectively.

Kinetics of hydrolysis of 6-O-vanillyl-D-glucose

The 0.0015 M aqueous solution of the sample (1 cm³) and the buffer (0.5 cm³) were heated in the atmosphere of N₂ at 60 °C (± 0.1 °C) in sealed tubes. The buffers used were the following: hydrochloric acid—potassium chloride (pH 1.1 and 4.4), sodium dihydrogen phosphate—citric acid (pH 2.3 and 3.0), sodium dihydrogen and disodium hydrogen phosphates (pH 5.4 and 8.0). At time intervals the tubes were cooled down to room temperature, then 0.043 M aqueous solution of NaOH (7 cm³) and 0.5 % ethanolic solution of quinone monochloroimide (0.01 cm³) were added to the content of the tube. After 10 min reaction the content of the released benzyl-alcohol groups was determined spectrophotometrically at $\lambda = 640$ nm. Quinone monochloroimide was prepared from 4-aminophenol [4].

6-O-Vanillyl-D-glucose

D-Glucose (18 g; 0.1 mol) was dissolved in anhydrous *N,N'*-dimethylformamide (250 cm³), then vanillyl alcohol (7.7 g; 0.5 mol) and Dowex 50 W \times 8 (H⁺; 0.1 g) were

added to the solution. After 10 h heating of the reaction mixture at 60 °C the cation-exchanger was filtered off and the solvent was removed at reduced pressure. The oily residue was extracted with anhydrous diethyl ether ($2 \times 200 \text{ cm}^3$) and subsequently with anhydrous dioxane ($3 \times 200 \text{ cm}^3$). The filtered, joined dioxane extracts were concentrated to give a crude oily product which was purified on a silica gel column (system A). The yield of the obtained product was 60 %, $[\alpha]_D(20, \rho = 10 \text{ g dm}^{-3}, \text{methanol}) = +42.7^\circ$. For $\text{C}_{14}\text{H}_{20}\text{O}_8$ ($M_r = 316.31$) $w_i(\text{calc.})$: 53.16 % C, 6.37 % H; $w_i(\text{found})$: 53.12 % C, 6.39 % H. ^{13}C NMR spectrum, $\delta = 50.15$.

1, 2, 3, 4-Tetra-O-acetyl-6-O-(3-methoxy-4-acetoxybenzyl)-D-glucose

Conventional esterification of 6-O-vanillyl-D-glucose with the mixture of acetic anhydride—pyridine resulted in a crude product which was purified on a silica gel column (system B). The sirup obtained in 86 % yield had $[\alpha]_D(20, \rho = 10 \text{ g dm}^{-3}, \text{methanol}) = +31.2^\circ$. For $\text{C}_{24}\text{H}_{30}\text{O}_{13}$ ($M_r = 526.50$) $w_i(\text{calc.})$: 54.80 % C, 5.75 % H; $w_i(\text{found})$: 54.86 % C, 5.71 % H.

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