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## Abstract

## Full Text

## Chemistry

**V. A. Derevitskaya, G. S. Smirnova, and Z. A. Rogovin**

# Comparative Acidity of the Hydroxyl Groups of *D*-Glucose, $\alpha$- and $\beta$-Methyl Glucosides, Maltose, and Cellobiose

*(Presented by Academician M. M. Shemyakin, May 4, 1961)*

In connection with the study of the reactivity of individual hydroxyl groups in carbohydrate molecules, data on the comparative acidity of carbohydrate hydroxyls are of special interest; at present such data are practically lacking. For some carbohydrates, measurements of the electrical conductivity of dilute alkaline solutions have been used to determine dissociation constants ($^1$) of the order of $10^{-14}$–$10^{-13}$. Attempts to determine the dissociation constants of polysaccharide hydroxyls ($^2$) did not give satisfactory results.

We have begun work on studying the degree of dissociation of the hydroxyl groups of glucose and some of its derivatives, namely partially methylated glucoses, methyl glucosides, and disaccharides. The present communication gives data obtained for *D*-glucose, methyl glucosides, cellobiose, and maltose.

The acidity of the hydroxyls was determined by the method of nonaqueous titration ($^3$), namely by electrometric titration in an ethylenediamine medium with a 0.1 $N$ solution of KOH in absolute propyl alcohol at 20° with oxide-metal electrodes ($^4$) *. The measuring circuit consisted of an indicating molybdenum electrode and a calomel reference electrode. A type M-198 galvanometer with a sensitivity of $10^{-8}$ A was used as the null instrument, and a saturated KCl solution served as the electrometric bridge. A resistance of about 1 megohm was included in the circuit. For the study, 0.1, 0.01, and 0.001 $N$ and 0.001 $M$ solutions of the corresponding substances in ethylenediamine were prepared. The indicating molybdenum electrode, the bridge with saturated KCl solution, a glass stirrer, and the end of the burette containing the titrant were immersed in the solution. The titration was carried out with complete isolation of the system from air. The relative dissociation of the hydroxyls of the substances studied was determined from the magnitude of the current at the equivalence points. The most distinct curves are obtained when titrating 0.001 $N$ carbohydrate solutions, when it is possible to titrate even the most weakly dissociating hydroxyls. All the substances studied behave in ethylenediamine medium as polybasic acids, as evidenced by the presence of several inflection points on the titration curves. For a more precise determination of the equivalence points in the titration of mixtures of acids or of individual polyfunctional compounds,

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Fig. 1. Titration curve of 0.001 N solutions of $\beta$-methylglucoside (a), D-glucose (b), $\alpha$-methylglucoside (c), cellobiose (d), maltose (e)

Figure 1: Fig. 1. Titration curve of 0.001 N solutions of $\beta$-methylglucoside (a), D-glucose (b), $\alpha$-methylglucoside (c), cellobiose (d), maltose (e)

such as the carbohydrates studied here, curves are plotted for the dependence of the derivative of the current strength with respect to volume on the volume of titrant. The titration curves of 0.001 $N$ carbohydrate solutions constructed in this way are shown in Fig. 1. On all curves several peaks are visible, characterizing the equivalence points of different hydroxyls. In glucose, for example, all five are titrated hydroxyls (Fig. 1). The titration curves show that the acidity of the hydroxyls changes on going from glucose to glucosides and depends both on the nature of the aglycone (a methyl group or a second monosaccharide molecule in disaccharides) and on the type of linkage ($\alpha$ or $\beta$).

Fig. 1. Titration curve of 0.001 $N$ solutions of $\beta$-methylglucoside (a), $D$-glucose (b), $\alpha$-methylglucoside (c), cellobiose (d), maltose (e)

At present there are no data that would make it possible to assign all equivalence points to definite hydroxyls of the carbohydrate molecule. However, there is every reason to believe that the most acidic hydroxyls are the anomeric hydroxyl and the hydroxyl at $C_2$. The acidic properties of the anomeric hydroxyl are clearly manifested in the reaction of glycoside formation, which proceeds analogously to the interaction of alcohols with the hydroxyl of a carboxyl group. The increased acidity of the hydroxyl at the second carbon atom ($C_2$) is apparently due to the proximity of the acetal group.

···tion and is manifested in the increased reactivity of this hydroxyl in glycosides and polysaccharides in reactions with bases (5).

The first, highest peaks on the titration curves of glucose, maltose, and cellobiose, characterizing the degree of dissociation of the anomeric hydroxyls, differ greatly from one another. For a more rigorous comparison of the degree of dissociation of the anomeric hydroxyls of glucose, maltose, and cellobiose, titration was carried out of 0.001 $M$ solutions of these compounds with the same concentration of anomeric hydroxyls. According to the degree of dissociation of the anomeric hydroxyl, these compounds are arranged in the following series: $D$-glucose $>$ cellobiose $>$ maltose.

On the titration curves of 0.001 $N$ solutions of $\alpha$- and $\beta$-methylglucosides (Fig. 1), the first maxima should be attributed to the hydroxyls at $C_2$, just as the

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second maxima on the glucose titration curves. According to the degree of dissociation of the hydroxyl at $C_2$, these compounds are arranged in the following series: $\beta$-methyl-$D$-glucoside > cellobiose > $\alpha$-methyl-$D$-glucoside > maltose > glucose.

From the data obtained it follows that, in going from free glucose to glucosides, the degree of dissociation of the hydroxyl at $C_2$ increases sharply; moreover, the degree of dissociation of $\beta$-glucosides is considerably higher than the degree of dissociation of $\alpha$-glucosides. The nature of the aglycone also strongly affects the acidity of the hydroxyl at $C_2$. Thus, the degree of dissociation of the hydroxyl at $C_2$ of $\beta$-methylglucoside is considerably higher than the degree of dissociation of the corresponding hydroxyl of cellobiose.

These results agree well with data obtained earlier by us on the comparative reactivity of the hydroxyls of cellulose ($\beta$-glucosidic bonds) and amylose ($\alpha$-glucosidic bonds). Owing to the considerably greater acidity of the hydroxyls at $C_2$ of cellulose than of amylose, reactions with bases proceed at the first stage almost selectively at the expense of the hydroxyl at $C_2$; for amylose such selectivity is not observed.

The reason for the differences in the acidity of the hydroxyl at $C_2$, depending on substitution at the glycosidic center and on the configuration of the glycoside, has not yet been established. However, it may be assumed that it is determined to a significant extent by the presence and strength of hydrogen bonds arising between the substituent at $C_1$ and $C_2$. Thus, for example, the lower degree of dissociation of the hydroxyl at $C_2$ in $\alpha$-glucosides as compared with the $\beta$-isomer can be explained by the greater probability of formation of a hydrogen bond between the hydroxyl at $C_2$ and the oxygen of the glucosidic group, which is in the axial position.

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