Note

Formation of hydrogen-bonded complexes of D-galactose, D-glucose, D-mannose, and maltose with ethylenediamine

S. P. MOULIK, A. K. MITRA, AND K. K. SEN GUPTA

Carbohydrate Research Unit, Department of Food Technology & Biochemical Engineering, and Department of Physical Chemistry, Jadavpur University, Calcutta-32 (India)

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As a proton-withdrawing agent, ethylenediamine is known to activate D-glucose and make its hydroxylic hydrogen atoms more dissociative[1]. It is considered that calcium hydroxide forms a different type of adduct with D-glucose in the presence than in the absence of ethylenediamine[2]. We therefore anticipated complexing of the amine, alone, with carbohydrates, and we now describe physicochemical evidence for formation of hydrogen-bonded complexes of D-galactose, D-glucose, D-mannose, and maltose with ethylenediamine.

EXPERIMENTAL

The carbohydrates used were of either Pro Analyse (E. Merck) or Analar (BDH) grade. Pure ethylenediamine (Riedel, Germany) was redistilled prior to use.

Spectrophotometric and paper-chromatographic methods were used in the study. Spectral measurements were made with a Beckman DBf spectrophotometer with 1-cm silica cells. Descending paper-chromatography was performed on Whatman No. 3 paper, with 8:2:1 ethyl acetate–pyridine–water as the solvent medium. The paper was sprayed with ninhydrin solution, and with alkaline silver nitrate solution, for detection of the amine part and the carbohydrate part, respectively.

RESULTS AND DISCUSSION

A distinct absorption band for each carbohydrate, mixed with ethylenediamine in different molar proportions, indicated formation of a complex with each. The concentration was so adjusted that the carbohydrate and the amine had practically negligible absorption in the wavelength range at which the new band appeared. A band at 325 nm in the experiments with D-glucose, D-mannose, and D-galactose, and at 340 nm with maltose, indicated formation of a complex. The product in solution was not of the chromophoric type observed during the transformation of D-glucose, D-mannose, and D-fructose[3] in the presence of sodium hydroxide; this chromophore gives peaks at 270 and 310 nm (a band at 290–310 nm is characteristic of saturated aldehydes[4]). We observed similar bands for D-glucose in the presence of ammonia.

As representative examples, the spectra of the carbohydrates mixed in equimolar proportions with ethylenediamine are shown in Fig. 1. Pretreatment of the mixtures by heating in a water bath for 4 h at ~60° was found necessary in order to provide a stable optical absorbance; this was then stable for several hours. By use of Job's method of continued variation, formation of a 1:1 complex was observed in each case.

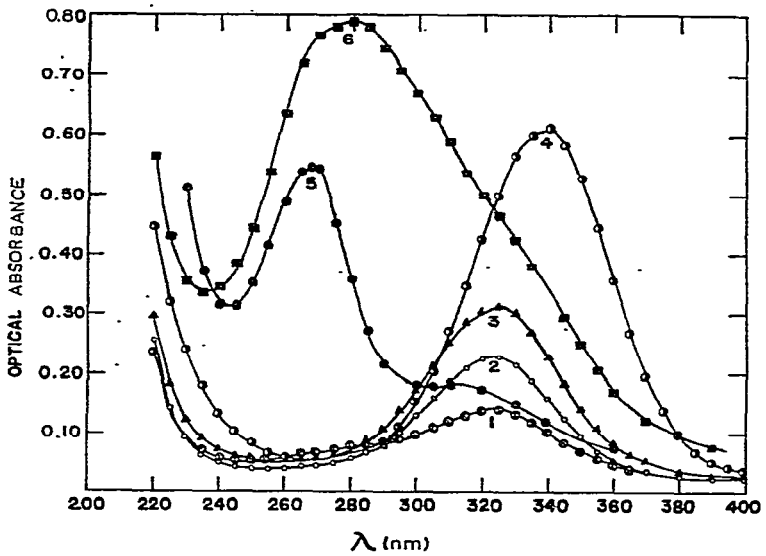

Fig. 1. U.v. spectra of the carbohydrates: *1*, D-mannose–ethylenediamine (1:1) at 0.01M; *2*, D-glucose–ethylenediamine (1:1) at 0.01M; *3*, D-galactose–ethylenediamine (1:1) at 0.01M; *4*, maltose–ethylenediamine (1:1) at 0.01M; *5*, 0.04M D-glucose in 0.1M NH_4OH; and *6*, 2mM D-glucose in 0.02M NaOH.

In the paper chromatography, tailing of the carbohydrate front occurs in the presence of the amine. However, if the amine is present in large excess, almost all of the carbohydrate is arrested by the amine, resulting in practically no tailing. At moderate concentrations of the amine, a weak spot may appear for unreacted carbohydrate at an R_F value similar to that of the carbohydrate employed. Use of NaOH, NH_4OH, $Ca(OH)_2$, $Ba(OH)_2$, or $Sr(OH)_2$ instead of the amine did not result in any of the above characteristics. It should be mentioned that, had this been a reaction involving alkaline transformation[3], a spot for D-fructose should also have been found, starting from either D-glucose or D-mannose, but in no experiment was even a weak spot for D-fructose found.

The complexes observed are, presumably, of a hydrogen-bonded type similar to those given by a phenol and an amine[5–7]. However, the carbohydrates studied had no effect on the u.v. spectrum of 2-aminoethanol; this observation supports the concept that the observed interaction is not an aldose–ketose transformation[3], an α–β transformation, or ring opening[4] due to the influence of a base. The complex may be a proton-transfer type of complex (of an initially formed, hydrogen-bonded intermediate[8]), in which the carbohydrate moiety is the proton donor and the amine

is the proton acceptor. At room temperature, the hydrogen-donating capability may be weak, and, therefore, energization by increasing the temperature may be necessary in order to increase the proton dissociation[7] of the carbohydrate so that it may form an appreciable proportion of the interaction product. Any difference in the respective stability of the complexes of D-glucose, D-mannose, and D-galactose may be attributable to their conformational differences. The effect of the solvent[8] may also be a factor influencing their formation. The kind of complex reported here may be related to the unknown intermediate compounds[3] that occur in alkaline degradations.

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