Computer modelling of the structure of sucrose-water complexes

Computer-Modellierung der Struktur von Saccharose-Wasser-Komplexen

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The spatial structure of 1:1 sucrose/water complexes was obtained with the help of the molecular mechanics method and the energy levels were determined. Complexes in which a water molecule forms hydrogen bonds: a) with hydroxyl groups 4 and 6, b) with the hydroxyl group 6' and the "bridge" oxygen have the lowest energy levels. The hydrogen bonds between the hydroxyl group 3 of the glucose moiety and the 4' hydroxyl group of the fructose moiety have the highest energy levels. The importance of these considerations in relation to the structure of sucrose monohydrate is discussed.

Die dreidimensionale Struktur von 1:1 Saccharose-Wasser-Komplexen wurde mit Hilfe einer Computersimulierung der molekularen Mechanik bestimmt und das Energieniveau der 12 untersuchten Konfigurationen ermittelt. Das niedrigste Energieniveau haben Komplexe mit Wassermolekülen, die Wasserstoffbrückenbindungen zwischen den Hydroxylgruppen 4 und 6 der Glucoseeinheit und zwischen dem Brücken-Sauerstoffatom und der 6'-Hydroxylgruppe der Fructoseinheit bilden. Das höchste Energieniveau haben die Wasserstoffbrückenbindungen zwischen der 3-Hydroxylgruppe der Glucoseeinheit und der 4'-Hydroxylgruppe der Fructoseeinheit.

Introduction

Obtaining knowledge about sucrose hydration not only has theoretical but also important practical significance for sugar production. Sucrose hydration has an influence on the viscosity of its solutions, on its solubility and, in connection with this, reflects on the process of crystallization. It is known that normally formed sucrose crystals do not contain water of crystallization. Thus, before association and the formation of seeds, or a crystal lattice, sucrose molecules must free themselves from water molecules. The dehydration of sucrose monohydrate is a stage which precedes the appearance of a new phase and its development.

In a well-known review by *Allen* et al. [1] the main articles in which hydration numbers for sucrose molecules were determined by different indirect methods are cited. *Davidova* et al. [2] obtained hydration numbers for sucrose directly with the help of scanning calorimetry. The authors of a more recent paper [3] calculated correlations between water and sucrose molecules in saturated and supersaturated sucrose solutions at different temperatures from literature data. They reached the conclusion that the degree of a hydration evidently led to the existence of three zones for water-sucrose solutions: the stable zone, the metastable zone and the labile zone. The labile state occurs under conditions when the relationship of number of water molecules (N_w) to number of sucrose molecules (N_s), i.e. when N_w/N_s, is < 1.

But data about spatial positions of water molecules in sucrose-water complexes are absent in the above-mentioned papers. In particular it is not known which water molecule leaves a sucrose molecule last during its complete dehydration. The aim of this paper is to establish the structure of sucrose monohydrate, to obtain its spatial structure by the molecular mechanics method and determination of the configuration of the complexes having the lowest steric energy.

Materials and methods

The numbering of carbon atoms in the glucose and fructose moieties is according to Figure 1 [1]. An isolated sucrose molecule with one water molecule which joins to different hydroxyl groups was studied.

Calculations were based on the standard molecular mechanics method (program MMX, version 88.9) [4]. The computer program finds the optimal structure and energies which correspond to a given steric model. Different starting positions for hydroxyl groups and the hydroxymethyl group were chosen. The calculated energy minima did not depend on the geometry of the starting complex.

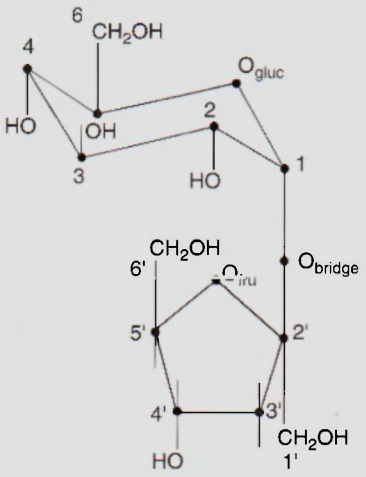

Fig. 1:
Numbering of the atoms in a sucrose molecule

Description of the molecular mechanics method

Molecular mechanics consider the molecule as an aggregate of atoms which are described with the help of classical potential functions. The combination of potential functions describing distortions of bonds, valence and torsion angles deformations is called the valence force field. The force field determines the mechanical model of a molecule (cluster). The computer program realizing the method of molecular mechanics finds the optimal structure and energies which correspond to a given mechanical model. In the first stage of calculations, bond lengths, valence and torsion angles are determined for the starting model of the molecule. Obtained values are used in the expressions for the potential function with the purpose of determining the starting value for to steric energy of a molecule. The last item can be written as the sum of potential energies calculated for all bonds, valence and torsion angles, pairs of untied atoms, etc. A steric energy has a meaning only in the framework of given force field and is connected with the heat of formation via a simple expression. Ultimately, the minimum steric energy was found (all other factors were constant during optimization of the structure).

Table 1: Steric energies for complexes of sucrose with water molecules

No	Scheme of connections of water molecules to hydroxyl groups	Steric energy of a complex (arbitrary units)
1	$3 - H_2O$	3.82
2	$4' - H_2O$	3.52
3	$1' - H_2O$	3.04
4	$2_O - H_2O - 3_H$	2.74
5	$O_{gluc} - H_2O$	2.21
6	$2_H - H_2O - 3_O$	1.78
7	$6 - H_2O$	1.75
8	$O_{fru} - H_2O - 1'$	1.23
9	$3' - H_2O$	1.08
10	$O_{fru} - H_2O - 6'$	1.07
11	$O_{bridge} - H_2O - 6'$	– 0.09
12	$4 - H_2O - 6$	– 0.4

Results and discussion

The results of calculations of steric energies for sucrose-water complexes are given in Table 1 (the results were obtained with a dielectric constant of 1.5 which was distance-dependent (–1.0)).

Some peculiarities were found:

1) the most unfavourable is the joining of a water molecule to hydroxyl groups 3 and 4;
2) the lowest energies have complexes in which a water molecule forms hydrogen bonds:
   a) with hydroxyl groups 4 and 6,
   b) with the hydroxyl group 6' and the "bridge" oxygen.

Thus it is possible to suppose that the monohydrate of sucrose contains the water molecule in the position between C4 and C6.

Literature

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