Carbohydrate Research 407 (2015) 5–9

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Mass spectrometry-based method to investigate the natural selectivity of sucrose as the sugar transport form for plants

Hang Yuan [a], Yile Wu [a], Wu Liu [c], Yan Liu [a,*], Xiang Gao [b], Jinming Lin [c], Yufen Zhao [a,c,*]

[a] Department of Chemical Biology, College of Chemistry and Chemical Engineering, Key Laboratory for Chemical Biology of Fujian Province, Xiamen University, Xiamen, Fujian 361005, China

[b] School of Pharmaceutical Sciences, Xiamen University, Xiamen, Fujian 361005, China

[c] Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China

A R T I C L E I N F O

Article history:
Received 21 November 2014
Received in revised form
20 January 2015
Accepted 21 January 2015
Available online 29 January 2015

Keywords:
Sucrose transport
Glycosidic bond
Potassium ions
Mass spectrometry

A B S T R A C T

Sucrose is the carbon skeletons and energy vector for plants, which is important for plants growth. Among thousands of disaccharides in Nature, why chose sucrose for plants? In this paper, we analyzed the intrinsic structural characteristics of four sucrose isomers with different glycosidic linkage by mass spectrometry (MS) technique. Our results show that sucrose has the most labile glycosidic bond compared with other three isomers, which is helpful for releasing glucose and fructose unit. Besides, sucrose has the most stable integral structure, which is hard to dehydrate and degrade into fragments through losing one or three even four-carbon units, just as its three isomers. In other words, sucrose is more easily holds an integral structure during the transport process, whenever it is necessary, and sucrose can be cleaved into glucose and fructose easily. Besides, we also investigate the internal relationship of sucrose with K^+ by tandem mass spectrometry and viscosity measurement. The related results have shown that the K^+ can stabilize sucrose to a greater extent than the Na^+. Furthermore, under the same conditions, K^+ ions reduce the viscosity of sucrose–water system much more than Na^+. These results suggest that K^+ is a better co-transporter for sucrose.

Of course, the transport of sucrose in plants is a very complicated process, which is involved in many proteins. This paper directly accounts for the basic structure feature of sucrose, and the results discovered could provide the novel insight for the answer why Nature chose sucrose for plants.

1. Introduction

When we eat fruit or vegetables, their sweet taste tells us the presence of sucrose. It is amazing that among all possible isomers of disaccharides sucrose has been chosen as the major sugar transport form in high plants. As a source of carbon skeletons and an energy vector[1] for plants, sucrose is a non-reducing disaccharide consisting of glucose and fructose in an α 1, 2-linkage, the latter being the major material source of ribose synthesis. In the phloem sap of plants, sucrose is the main soluble component.[2] Sucrose is produced in the photosynthesis and must be transported through the phloem to other parts of the plant for utilization and storage. As one kind of protected derivatives of glucose and non-reducing sugar, the unique structure of sucrose makes it transported over long distances in the plant,[3] without the problem of metabolism commonly encountered with glucose. In 1968, Arnold investigated the selection of sucrose as the major transport sugar through the analysis of acid hydrolysis of four sucrose isomers and comparing some physical parameters of sucrose and glucose solution, such as density, viscosity and osmotic pressure etc. These research results indicate the selection of sucrose has been evolved from its non-reducing and easy hydrolysis nature,[4] which is related to the inherent structure feature of sucrose.

In the sucrose transport process, alkali metals, especially potassium, has vital functions. Potassium can activate the enzymes that are involved in the sugar transport process. Also Potassium can regulate the photosynthesis, which can trigger enzyme function and provide ATP for the plant's transportation.[5] In addition, it was reported that potassium and sucrose have a co-transport

* Corresponding authors.
E-mail addresses: stacyliu@xmu.edu.cn (Y. Liu), yfzhao@xmu.edu.cn (Y. Zhao).

http://dx.doi.org/10.1016/j.carres.2015.01.011
0008-6215/

relationship across the plasma lemma of mesophyll protoplasts.[6] Thus, it's interesting and worthy to know at molecule level if there are some preference relations between sucrose and potassium ion.

It is well known that the properties of compounds are determined by their structures. Investigation on the molecular structures in the gas phase without solvent effects is helpful in assessing their intrinsic structural proprieties, such as chemical bond stability, and the interaction between the molecule and other molecules or ions, etc.

Mass spectrometry (MS) is a highly-efficient analytical technique for studying molecules in the gas state.[7] MS, particularly tandem mass spectrometry, is a widely applied and effective method to analyze the structure of oligosaccharides, due to its capability of providing detailed molecular information and its high sensitivity.[8–13] Through collision-induced dissociation (CID)-MS/MS, a very common but important tandem mass technique, glycosidic bond cleavages and cross-ring cleavages are typically observed for saccharides. The relative abundance of glycosidic bond cleavage fragment ions can reflect the stability and the position of glycosidic bond efficiently.[9]

Furthermore, it is reasonable to expect that viscosity is a vital factor to determine the efficiency of sucrose transport. The lower the viscosity of the transport system, the better translocation rate of sucrose becomes.

Here, in order to further understand the function of K^+ in the sucrose transport process at molecular level, the interaction of K^+ with sucrose was investigated through MS analysis and viscosity titration. By comparison with Na^+ or Li^+, we found that K^+ can stabilize sucrose better than Na^+ or Li^+. Furthermore, under similar conditions, K^+ can reduce the viscosity of the sucrose–water system much more than Na^+. These results imply that K^+ is a better co-transporter for sucrose.

Moreover, the intrinsic structural properties of sucrose was obtained by comparing the ESI-CID tandem mass spectra of four sucrose isomers with different linkage pattern, namely sucrose (α1-2), turanose (α1-3), maltulose (α1-4), and palatinose (α1-6) (Fig. 1). The present research results show that sucrose is the most resistant to dehydration in the gas phase among the four isomers. On the other hand, sucrose has the most labile glycosidic bond among the four sucrose isomers. These two features can be the structural merits of sucrose for its critical role as the sugar transport form in plants.

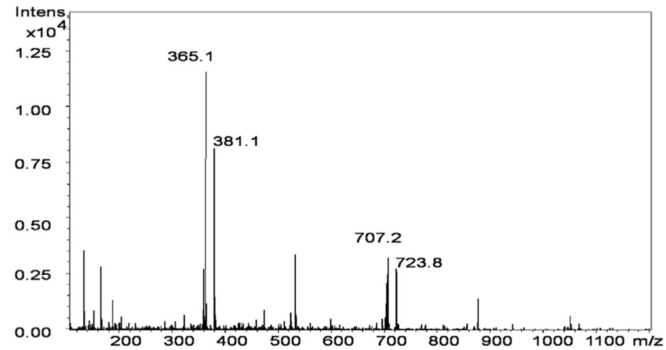

Fig. 2. The ESI-MS spectrum of fresh sugarcane juice in positive-ion mode.

2. Results and discussion

2.1. Interaction between sucrose and potassium ion

Mass spectrometry is one of reliable methods to demonstrate the intrinsic character of a complex without the interference of solvent.[14] Therefore, we adopted ESI-MS/MS to study the inwardness in the sucrose–metal ion complex here.

As one of the highest-sugar-yielding plants on the earth, sugarcane is a major sweetener source for mankind. In Fig. 2, the mass signals at *m/z* 365.1, *m/z* 381.1, *m/z* 707.2 and *m/z* 723.8 correspond to $[sucrose+Na]^+$, $[sucrose+K]^+$, $[2sucrose+Na]^+$ and $[2sucrose+K]^+$, respectively. For direct analysis of fresh sugarcane juice, paper spray ambient ionization mass technique was performed with 50% methanol as ionizing solvent. The results show that only $[sucrose+K]^+$, $[2sucrose+K]^+$ and $[3sucrose+K]^+$ can be observed (Fig. S1). These results indicate that sugarcane juice contains a small amount of potassium ions natively, which can be adducted with sucrose in the gas phase.

In addition, through ESI-MS analysis of 2 mmol L^{-1} sucrose aqueous solution with 0.5 mmol L^{-1} KCl, we also observed a series of mass peaks ranged from two to five sucrose molecules non-covalent aggregation adducted with K^+ (Fig. S2). The interaction of alkali metal ions with saccharides was oriented from its non-specific binding to the hydroxyl groups of saccharides in gas phase.[15,16]

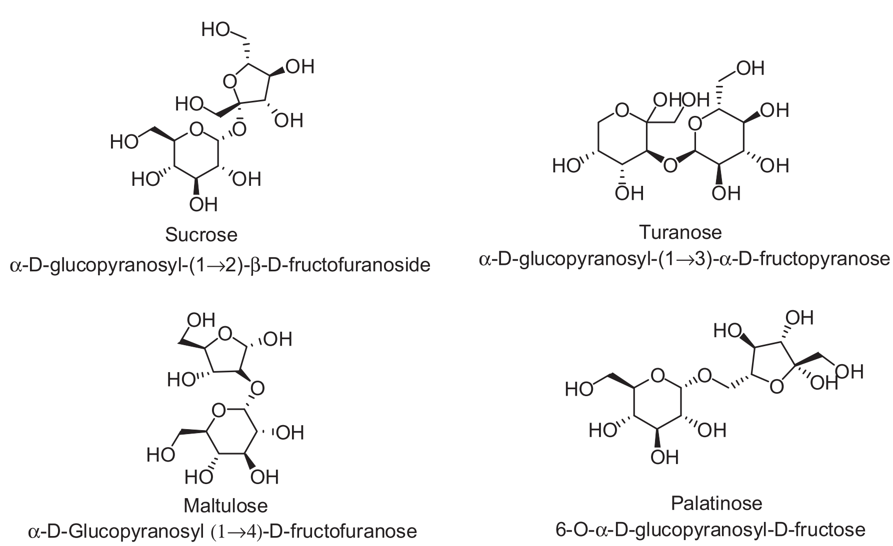

Fig. 1. Structures of four sucrose isomers with different linkage patterns.