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# A vibrational study of inulin by means of experimental and theoretical methods

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ABSTRACT

Inulin, a natural polymer formed by several units of fructose and just one unit of glucose, is found in different plants or directly in some fruits or vegetables. Due to its structure it has been used in many applications from medicine, pharmacology or food industry. In spite of this, a complete vibrational analysis of the molecule is missing in the literature. Moreover, there are contradictory results regarding the assignment of certain vibrational modes. Therefore, the aim of this study was to obtain a comprehensive vibrational investigation of inulin by means of experimental (FT-IR and Raman spectroscopy) and theoretical (density functional theory -DFT simulations) methods.



## 1. Introduction

Inulin is a naturally, linear polysaccharide [1] discovered in 1800s, which can be found in many plant roots such as dandelion, chicory, asparagus or dahlia; and in some cases, directly in fruits or vegetables: garlic, onion, wheat, rye, banana and so on [2].

The inulin molecule with the chemical formula $C_{6x}H_{10x+2}O_{5x+1}$, $x \geq 3$, is a polymer formed by several units of fructose and just one unit of glucose located at the group's end [2]. The length of the chain determines if inulin belongs to the oligosaccharide or polysaccharide groups. In order to be considered an oligosaccharide, inulin must have a maximum of 10 units of fructose. If the molecule of inulin has more than 10 units of fructose, it belongs to the polysaccharide group [3].

A previous study [3] reported that ingested inulin is not transformed in monosaccharaides by the digestives juices. Thus, the glycemia and insulin level in blood remain constant and the inulin goes in the large bowel where it is fermented [4]. This situation is caused by a specific bond, β(2−1) linked fructose present in the molecule of inulin [1], which confers the molecule a special property: it cannot be processed by the human digestive system so the inulin passes through stomach, small bowel and stops in the large bowel where it produces a healthy microflora (bifidobacterium). This means that inulin is a natural prebiotic (an ingredient that belongs to the prebiotic family requires two specifications: it should not be digested by the digestive enzyme, and it can only undergo fermentation in the colon [4]).

Nowadays inulin is an interest molecule with researches and applications in medicine, pharmacology or food industry, due to its bioactivity [2]. In medicine, inulin has multiple functions, such as: maintaining the microflora of the colon at some level, improving the metabolism, maintaining the gastrointestinal health [4]. A relative recent study [5] demonstrated that pure inulin promoted *Collinsella* growth in the gastrointestinal tract. Moreover, Smecuol et al. [6] found that inulin-type fructans contribute to the proliferation of *Bifidobacterium infantis* probiotic strains that have a beneficial effect on patients with active coeliac disease, a chronic inflammation of the intestinal mucosa resulting from an excessive immune response to a dietary gluten in genetically predisposed individuals. Colon diseases are quite difficult to treat because oral administrated drugs are absorbed at the stomach and intestine levels and they do not reach colon, whereas intravenous administrated drugs are eliminated from the body before reaching colon. Because inulin is not absorbed in the stomach or in the small intestine, and it is degraded by colonic bacteria, various inulin based hydrogels have been developed that can be used as potential carrier for introduction of drugs into the colon [1,7]. The strong antitumoral activity of inulin, has been recently established through *in vitro* experiments, and revealed that inulin is able to inhibit 4 different types of cancer cells [8]. In a recent study [9], an inulin tethered Ag- Graphene quantum dots nanocomposite for *in vivo*

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drug delivery application as a treatment of pancreatic cancer was reported. Inulin was also employed to mitigate the toxicity of silver nanocomposite [9] and was used to measure the glomerular filtration rate in kidney diseases [10,11]. In pharmacology, inulin is intensely used because of its longer molecular structure, for example in vaccines for the enhancement of the immune system [12,13]. In the food industry, inulin is commonly used as a sweetener, fat-replacer of for its capacity to induce the modification of textures [2,8,14,15].

There are several studies reporting about the FT-IR spectrum of inulin [1,16–19], but to the best of our knowledge there are no investigations reporting about the Raman spectrum and the complete assignment of the vibrational modes. Moreover, there are some different opinions concerning the assignment of a vibrational band around 1600 $cm^{-1}$ [8,16,17,20].

Having in view the large applicability area of inulin, the recent interest for this molecule (evidenced by the increasing number of papers about inulin) and the lack of a complete vibrational analysis of the molecule, we propose in the present study to obtain a comprehensive vibrational investigation of this molecule. In this respect Raman and IR absorption spectroscopy were applied and the assignment of the vibrational modes was performed by using the theoretical data of the density functional theory (DFT) based simulations.

## 2. Experimental section

### 2.1. FT-IR and FT-Raman measurements

Inulin was purchased from Alfa Aesar and used as received.

The FT-IR absorption spectrum of inulin sample was recorded with a JASCO 6200 spectrometer, at room temperature, in the 400–4000 $cm^{-1}$ range with a spectral resolution of 4 $cm^{-1}$, by using the KBr pellet technique.

FT-Raman spectrum was recorded by using a Bruker EQUINOX 55 spectrometer with an integrated FRA 160 Raman module, with the resolution 4 $cm^{-1}$. A radiation of 1064 nm was employed for excitation.

### 2.2. Computational details

Theoretical calculations of the vibrational wavenumbers of the model inulin molecule were performed with the Gaussian 03 W program package [21]. Having in view that inulin is a linear polysaccharide, its monomer was used as a model compound for theoretical simulations. Density functional theory (DFT) calculations were carried out with Becke's 1988 exchange functional [22] the Perdew-Wang 91 gradient corrected correlation functional (BPW91) [23] and Becke's three-parameter hybrid method using the Lee-Yang-Parr correlation functional (B3LYP) [24]. The 6-311 + G* basis set was used in the geometry optimization and normal-mode calculations. For the optimized structures of the examined species, no imaginary frequency modes were obtained, which proved that a local minimum on the potential energy surface was found.

## 3. Results and discussion

As already mentioned [3] the inulin molecule is a polymer,

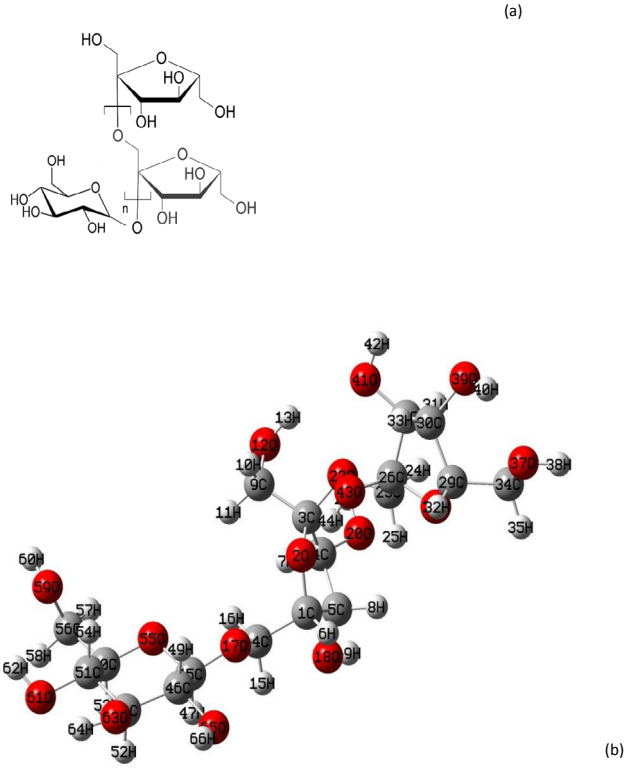


**Fig. 1.** Chemical structure of the inulin molecule (a) and the optimized geometry of the model compound (b) obtained at the BPW91/6-311 + G* theoretical level with the labeling of the atoms.

**Table 1**
Selected calculated bond lengths (Å)) and angles (°) of inulin model compound compared to the experimental data.

| | Calc.[a] | Calc.[b] | Exp.[c] |
|---|---|---|---|
| *Bond lengths (Å)* | | | |
| β-fructose | | | |
| $C_1O_2$ | 1.456 | 1.447 | 1.427 |
| $C_3O_2$ | 1.444 | 1.431 | 1.458 |
| $C_3C_4$ | 1.565 | 1.560 | 1.517 |
| $C_4C_5$ | 1.530 | 1.526 | 1.513 |
| $C_3C_9$ | 1.535 | 1.529 | 1.541 |
| $C_{29}O_{27}$ | 1.448 | 1.439 | 1.444 |
| $O_{27}C_{26}$ | 1.451 | 1.435 | 1.427 |
| $C_{26}C_{28}$ | 1.543 | 1.538 | 1.524 |
| $C_{28}C_{30}$ | 1.535 | 1.531 | 1.513 |
| $C_{29}C_{34}$ | 1.524 | 1.519 | 1.497 |
| -glucose | | | |
| $O_{55}C_{50}$ | 1.436 | 1.427 | 1.428 |
| $C_{51}C_{48}$ | 1.523 | 1.519 | 1.536 |
| $C_{46}C_{48}$ | 1.531 | 1.527 | 1.504 |
| $C_{46}C_{45}$ | 1.534 | 1.529 | 1.522 |
| $C_{50}C_{56}$ | 1.526 | 1.523 | 1.513 |
| $C_{45}O_{17}$ | 1.389 | 1.382 | 1.417 |
| *Angles (°)* | | | |
| β-fructose | | | |
| $C_1O_2C_3$ | 112.587 | 112.046 | 109.9 |
| $O_2C_3C_4$ | 105.303 | 105.298 | 104.0 |
| $C_3C_4C_5$ | 104.632 | 104.490 | 100.9 |
| $O_2C_3C_9$ | 109.725 | 109.609 | 109.3 |
| $C_{29}O_{27}C_{26}$ | 108.143 | 108.541 | 110.1 |
| $C_{26}C_{28}C_{30}$ | 102.714 | 102.663 | 102.6 |
| $C_{34}C_{29}O_{27}$ | 108.866 | 108.905 | 111.0 |
| -glucose | | | |
| $C_{51}C_{48}C_{46}$ | 111.095 | 111.000 | 110.0 |
| $C_{48}C_{46}C_{45}$ | 110.234 | 110.490 | 108.6 |
| $C_{46}C_{45}O_{17}$ | 108.560 | 108.645 | 105.0 |
| *Torsion angles (°)* | | | |
| $C_1O_2C_3C_4$ | −3.214 | −2.820 | 11.5 |
| $O_2C_3C_4C_5$ | −16.777 | −16.81 | −34.1 |
| $C_{23}C_{26}C_{28}C_{30}$ | 26.48 | −26.024 | 33.5 |
| $C_{29}O_{27}C_{26}C_{23}$ | 160.975 | 161.589 | 142.2 |
| $C_{51}C_{48}C_{46}C_{45}$ | −51.654 | −51.369 | −57.4 |

[a] Calculated with: BPW91/6-311 + G*.
[b] B3LYP/6-311 + G*.
[c] Ref. [25].