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FT-IR and Raman spectroscopic analysis of a calcium fructoborate sample

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Abstract

In this paper we deeply investigate molecular composition of the calcium fructoborate used as a dietary supplement for the human nutrition, by using FT-IR and Raman spectroscopic analysis. The experimental measurements agree very well with the molecular formula $Ca[(C_6H_{10}O_6)_2B]_2 \cdot 4H_2O$.

Keywords: calcium fructoborate, fructose, FT-IR, Raman spectrosopy.

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1 Introduction

Boron natural complexes have been isolated and characterized from the phloem sap of celery and floral nectar of peach as boric acid ester with fructose (fructose-B-fructose), glucose (glucose-B-glucose) and sorbitol (sorbitol-B-sorbitol), since it represents an essential nutrient and has curing effects [1], [2]. FutureCeuticals Company (USA), that marketed calcium fructoborate [3], claims that the last is identical with the natural form of calcium fructoborate found in the edible plants [4]. Calcium fructoborate is used as a dietary supplement for the human nutrition [5]. Its molecular composition is very important, since calcium fructoborate has recently shown to posses an interesting anti-oxidant effect [6], anti-inflammatory [7], [8] and anti-tumoral activity [9], [10].

By correlation of the results of thermogravimetric analysis with the elemental analysis, no precursors traces were found and the correct molecular formula of calcium fructoborate has been identified as $Ca[(C_6H_{10}O_6)_2B]_2 \cdot 4H_2O$, which contains two times more boron than reported in other researches [11], [12], [13].

In this paper we deeply investigate molecular composition of the calcium fructoborate used as a dietary supplement for the human nutrition, by using FT-IR and Raman spectroscopic analysis.

2 Experimental

2.1 Calcium fructoborate preparation

Calcium fructoborate sample was prepared from the FutureCeuticals Company (USA) following the patent by Miljkovic [3]. The precursors: boric acid, fructose and calcium carbonate were purchased from Sigma Aldrich.

2.2 Methods and technique

Spectral analysis was investigated by FTIR spectroscopy, with a PerkinElmer Spectrum 100 spectrometer in the range of 650-4000 cm^{-1}wavenumber. All spectra were obtained using universal attenuated total reflection infrared (UATR) accessory, at a resolution of 4 cm^{-1}, with 4 scans and CO_2/H_2O correction, in transmission mode. Raman spectra were recorded with a Jobin Yvon – HR640 spectrometer equipped with an Andor CCD detector (DU420A-BR-DD model). A laser source working at 532 nm with an average power of 63.02 mW was used during the experiment. The spectra were recorded at room temperature and an exposure time of 10 minutes.

3 Results and discussion

3.1 Fourier transform infrared spectroscopic studies

FT-IR is frequentely used to determine chemical bonds and functional groups of organic substances. FTIR spectra, in transmittance mode, of calcium fructoborate, fructose, boric acid and calcium carbonate in the wavenumbers range of 4000-650 cm^{-1} are shown in Figures (1) - (4).

In the transmission spectrum IR of calcium fructoborate, the vibrational bands of fructose are present due to the common functional groups, but the intensity of these bands is diminished by the new interactions in the calcium fructoborate molecule. The position of the most important IR bands for fructose and calcium fructoborate are presented in Table 1. The IR vibration frequency are given in cm^{-1}. Table 1 also presents an assignment of the most characteristic vibrations.

3.2 Raman spectroscopic studies

Raman spectroscopic analysis was performed for calcium fructoborate in the wavenumber range of 400-4000 cm^{-1}. Raman spectrum of calcium fructoborate is presented in Figure (5). However, the fluorescence and background were not extracted from the spectrum in Figure (5).

Table 1 Vibration wavenumbers of the fructose and calcium fructoborate exhibited in the FTIR spectra

Calcium fructoborate	Fructose	Assignments
3230s	3521s, 3401s	BO, H_2O, OH, CH_2OH
2936m	2990w, 2939w	CH, CH_2OH
2324w		
2163w	2163w	
2050w	2042w	
1652w		BO, H_2O
1429m	1427m, 1397m	BO, CH, OH, COH, OCH, CH_2OH
1336m	1332s	OH, CH_2OH
1251m	1250m, 1147s	H_2O, OH, CH_2, CH
1049vs	1077vs, 1048vs	H_2O, CH_2OH, CO
1025vs		H_2O, CH_2, CCH
976vs	976vs, 924m	H_2O, CH_2, CCH
822s	817m	H_2O, CC
779s	781s	COC
673vs	676m	BO, OH
614vs	625s	BO, H_2O

vs=very strong, s=strong, m=medium, w=weak; B-O and H:O bonds appear only in FruitexB.

The positions of the movement of the Raman intensities (Raman displacements) for calcium fructoborate are presented in Table 2. In Table 2 Raman displacements are given in cm^{-1}.

Figure 1: FT-IR spectrum of calcium fructoborate

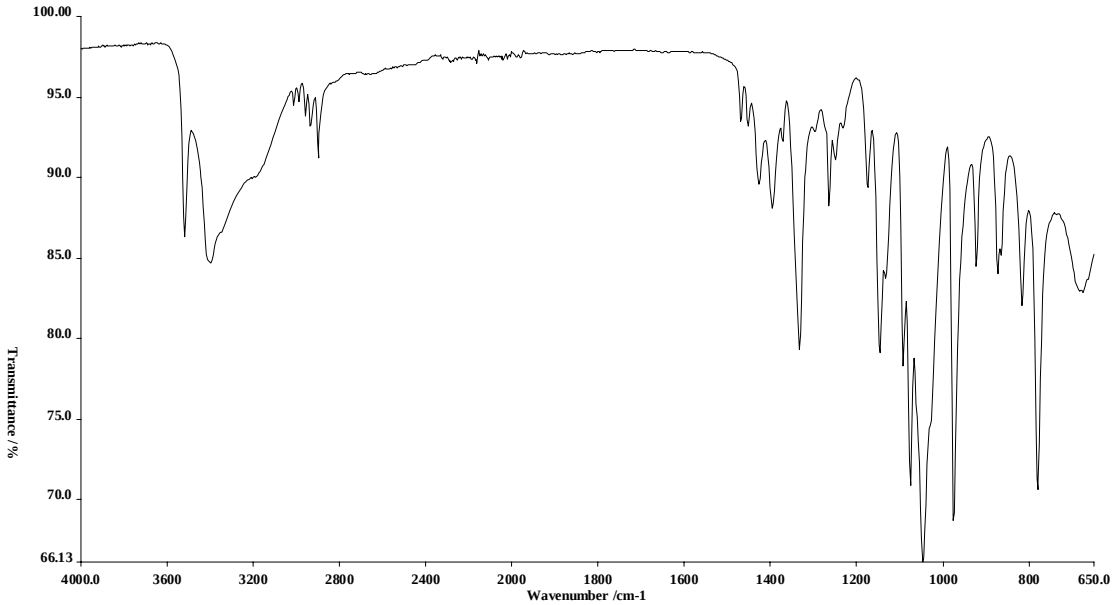

Figure 2: FT-IR spectrum of fructose

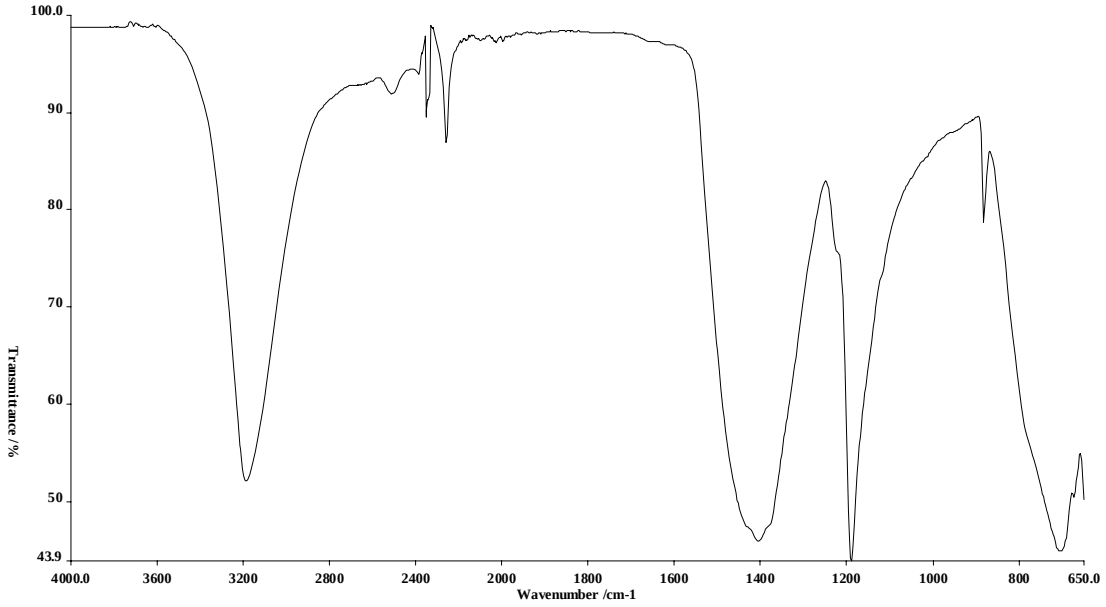

Figure 3: FT-IR spectrum of boric acid

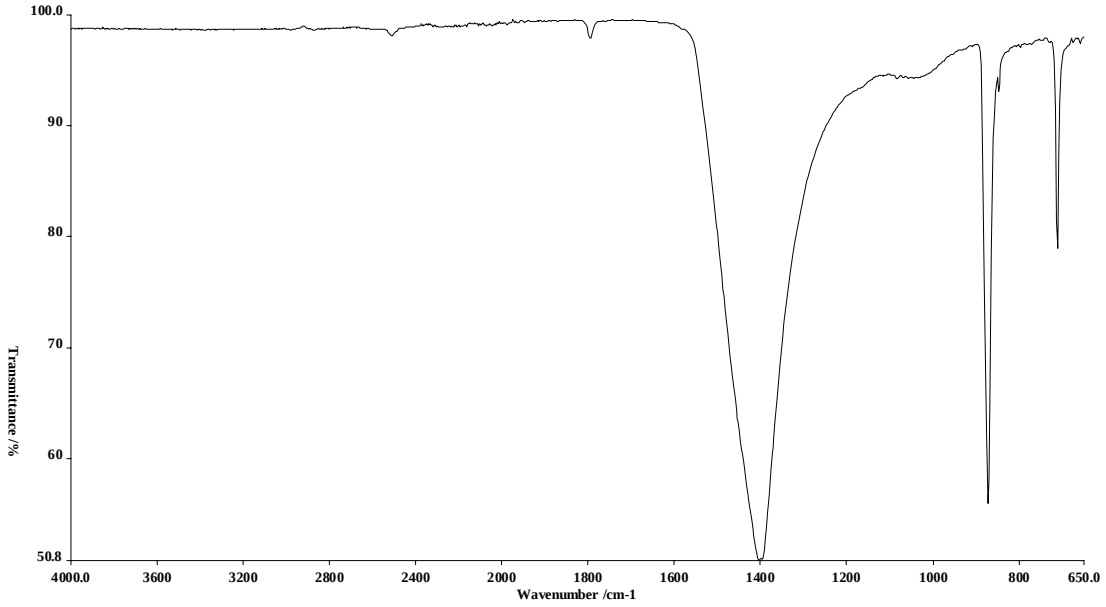

Figure 4: FT-IR spectrum of calcium carbonate

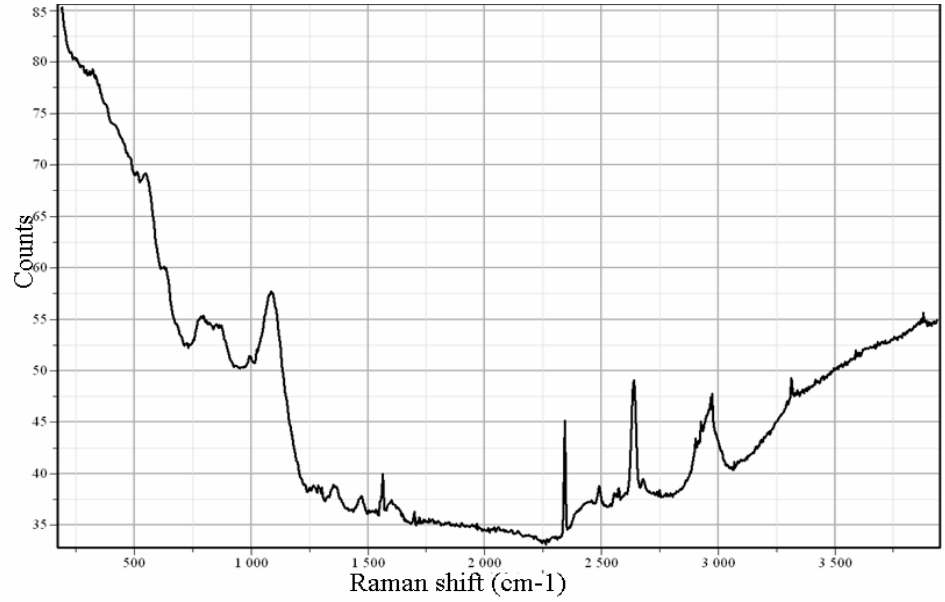

Figure 5: Raman spectrum of calcium fructoborate

Table 2 – Raman displacements of calcium fructoborate exhibited in the Raman spectra

Counts	Raman shift (cm^{-1})
513.2	69.3
544.1	69.1
627.2	60.1
851.0	54.5
1077.9	57.4
1086.2	57.7
1351.8	39.0
1471.9	37.8
1602.0	37.4
2344.2	45.2
2490.0	38.8
2640.2	49.1
2969.1	47.5
2975.8	47.8
3313.9	49.3

The peak at 3314 cm^{-1} in the Raman spectrum is related to B-O bond. In the Raman spectrum of calcium fructoborate, the B-O bond is exhibited by the weak peaks from 1602 to 1471 cm^{-1}. Raman spectrum contains two additional peaks at 851 and 627 cm^{-1}, attributed to the crystallization water of the complex [14]. As well, some works [15], [16], [17] have suggested that the O-H$\cdots$O out-of-plane bending motions contribute to the Raman spectra of fructose in the region 400-550 cm^{-1}.

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