Thermal analysis of a calcium fructoborate sample

P. Rotaru [a,*], R. Scorei [b], Ana Hărăbor [a], M.D. Dumitru [c]

[a] University of Craiova, Faculty of Physics, Department of Physics II, A.I. Cuza Str., Nr. 13, Craiova, Romania
[b] University of Craiova, Faculty of Horticulture, Department of Biochemistry, A.I. Cuza Str., Nr. 13, Craiova, Romania
[c] INFLPR – National Institute for Laser, Plasma and Radiation Physics, PPAM – Lasers Department, 409 Atomistilor Bvd., Magurele RO-077125, Bucharest, Romania

ARTICLE INFO

ABSTRACT

A commercial calcium fructoborate dietary supplements with potential use in chemotherapy of diseases, was investigated by thermal analysis, XRD, FTIR, Raman spectroscopy and ICP. Measurements performed in air show that a commercial sample seems basically to be a hydrated calcium fructoborate. We have compared a commercial sample of calcium fructoborate with a sample produced in the laboratory and concluded that both lose the bonded water up to 150 °C and then degrades in six stages, more exactly one endothermic and five exothermic. By ICP and thermogravimetry (TG), the overall formula $Ca[(C_6H_{10}O_6)_2B]_2 \cdot 4H_2O$ is suggested. XRD indicates a highly amorphous nature of the sample.

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]. Such a compound as described above is the calcium fructoborate molecule, which may constitute a dietary supplement with potential use in chemotherapy of diseases. FutureCeuticals Inc. (USA), that marketed FruiteX B® [3], claims that the last is identical with the natural form of calcium fructoborate found in the edible plants [4].

Wagner et al. investigated calcium fructoborate prepared in their own laboratory based on the patent of Miljkovic [3], by using thermal analysis and established its molecular structure [5,6]. But this one does not correspond with the structure of the natural isolated compound [4]. Wagner et al. reached the conclusion that calcium fructoborate that they synthetized is mono-dentat and trigonal, different of the one found in the nature, bidentat and tetragonal [4].

In this paper we deeply investigate molecular composition of the FruiteX B® used as a dietary supplement for the human nutrition [7] by using thermal analysis and the X-rays diffraction technique. Its molecular composition is very important, since FruiteX B® has recently shown to posses an interesting anti-oxidant effect [8], anti-inflammatory [9,10] and anti-tumoral activity [11,12]. This is a real problem that has to be taken into account when preparing and labeling nutrient products to be further sold on the market. Also, it is necessary to establish whether FruiteX B® is identical with the natural one, or it is different as Wagner et al. claimed.

Thermal analysis is an useful method which helps determining calcium fructoborate molecular composition, since this method was used to find out quantitative information about the constituents of the organo-metallic complexes and of some biological active materials [13–17]. Thermal analysis is also used as method for the controlled step-wise obtaining of basic functional materials such as CaB_2O_3, CdS, ZnO, etc. [6,18–24].

2. Experimental

FruiteX B® (calcium fructoborate) has been purchased from the FutureCeuticals Company (USA) – commercial product [3]. Boric acid, fructose and calcium carbonate were purchased from Sigma–Aldrich. Additionally, a calcium fructoborate sample was prepared in the laboratory following the patent by Miljkovic [3], in order to compare with the commercial FruiteX B® sample.

Thermal analysis measurements were carried out on a "Diamond" Differential/Thermogravimetric PerkinElmer instrument that simultaneously provides the TG, DTG and DSC curves, in dynamic air atmosphere of $150 \, cm^3 \, min^{-1}$. For all experiments, the heating rate of $10 \, K \, min^{-1}$ was employed in the temperature range of RT–1000 °C, when placing the samples in alumina cru-

* Corresponding author. Tel.: +40 740905171.
E-mail addresses: protaru@central.ucv.ro, petrerotaru@yahoo.com (P. Rotaru).
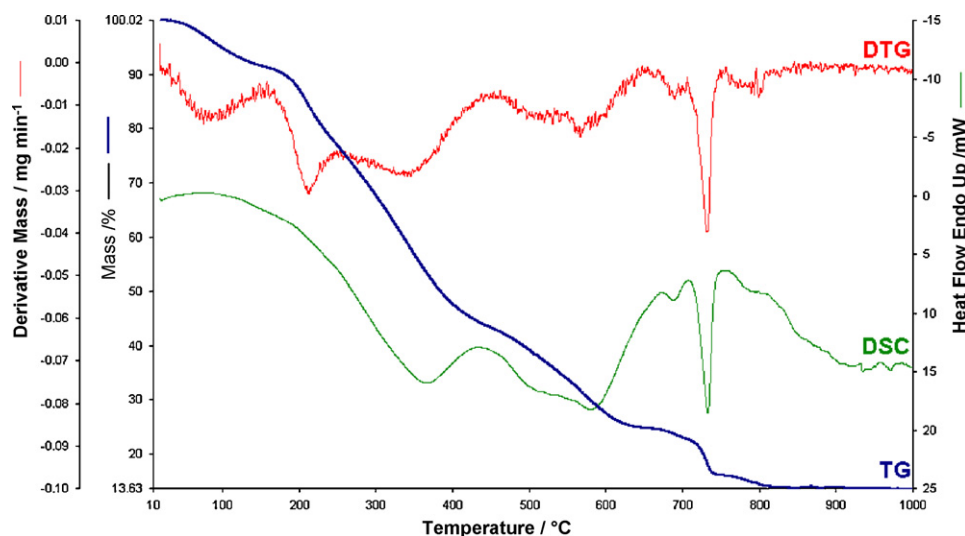
Fig. 1. Thermoanalytical curves of FruiteX B®, in air flow.

cibles. Gravimetric and enthalpic calculations were made using the specialized program Pyris Software.

Calcium and boron elemental analysis was carried out by Inductively Coupled Plasma Mass Spectrometry, using the ICP-MS PerkinElmer Elan 9000, with a known experimental protocol design [25].

Total organic carbon was measured on a Shimadzu TOC-VCSN analyzer and the hydrogen content was determined on a PerkinElmer 2400 CHN analyzer.

X-rays diffraction measurements were performed on powder samples, using a Shimadzu XRD-6000 X-rays diffractometer equipped with a vertical precision goniometer and a scintillation detector. The functioning parameters of the X-ray tube (A-40-Cu type) were established at a voltage of 40 kV and a current of 30 mA. A continuous scan measurement was chosen as operation mode in a geometry ($\theta/2\theta$) setting, a scan rate of $1°$ min^{-1} and a scan range from $3°$ to $50°$ (2θ). Divergence slit was of $1.0°$, scattering slit was of $1.0°$, and receiving slit of 0.15 mm.

FTIR measurements were performed on a Spectrum 100 apparatus from PerkinElmer Company, in absorption 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 min.

3. Results and discussion

3.1. Thermal analysis

A comparative thermal analysis of calcium fructoborate (FruiteX B®), fructose, boric acid and calcium carbonate was performed.

Thermoanalytical curves of FruiteX B® and of fructose are presented in Fig. 1 and respectively in Fig. 2. These figures show that after calcium fructoborate synthesis none of its precursors – fructose, boric acid or calcium carbonate – were retained in the final product.

In Fig. 2, the melting of fructose is identified between 115 and 155 °C, followed by the oxidative degradation in several stages, beginning with 155 °C. In the temperature range of 155–580 °C, Figs. 1 and 2 present some similar processes, those corresponding to the decomposition of fructose from the calcium fructoborate and can be easy identified.

Analysis of Fig. 1 allows the description of the calcium fructoborate decomposition and its molecular composition. TG and DTG curves show a continuous mass loss of calcium fructoborate, with 6 maximum values of decomposition at the temperatures of 83, 215, 342, 593, 690, 733 and 781 °C. The thermogravimetric and thermal effects are presented in Table 1.

Results show that the formula $Ca[(C_6H_{10}O_6)_2B]_2 \cdot 4H_2O$ can be attributed to calcium fructoborate – FruiteX B®, due to the following reasons:

- in the first stage of decomposition (temperature up to 152 °C), the experimental mass loss is $8.5 \pm 1\%$ (theoretical value using the above formula is 8.5%). This loss is due to the four crystallization water molecules of the complex. The very small endothermic effect is due to the same process, identified in the DSC curve.
- next stages of decomposition correspond to the degradation of anhydrous complex; between 152 and 845 °C, the mass loss caused by fructose decomposition is of $77.8 \pm 1\%$, comparable with calculated value of 76.6%. The shift in decomposing temperature of the anhydrous calcium fructoborate (Fig. 1), compared to the fructose decomposition (Fig. 2) is due to the supplementary bonding within the inorganic complex, but exhibits however the same profile. The residue of $13.7 \pm 1\%$ is calcium borate, identified by X-ray diffraction. Using the previous formula, the theoretical mass of the residue is 14.8%.
- a supplementary confirmation of $Ca[(C_6H_{10}O_6)_2B]_2 \cdot 4H_2O$ formula is obtained when calcinating 1884.4 mg of calcium fructoborate in a Nabertherm furnace at 1000 °C, using the same heating program as the one used at the thermobalance. After the calcination, 275.8 mg of CaB_2O_4 were obtained, representing a residue of $14.7 \pm 1\%$, close to the values previously calculated.
- by Inductively Coupled Plasma mass spectrometry, we reached the conclusion that FruiteX B® contains $2.5 \pm 0.1\%$ boron and $4.6 \pm 0.1\%$ calcium. By calculation based on thermoanalytical curves, elemental content for molecular composition $Ca[(C_6H_{10}O_6)_2B]_2 \cdot 4H_2O$ is of 2.5% boron and 4.7% calcium.
- total organic carbon analysis shows $34.38 \pm 0.27\%$ carbon and $5.74 \pm 0.12\%$ hydrogen, while the calculated values are 34.05% carbon and 5.73% hydrogen with the proposed formula.

Since all boron content of the FruiteX B® is to be found completely in the decomposition product CaB_2O_4 (only one broad DTG peak Fig. 1 up to 152 °C) with no evidence of solely boric acid decomposition at low temperatures (as the sharp TG loss and sharp
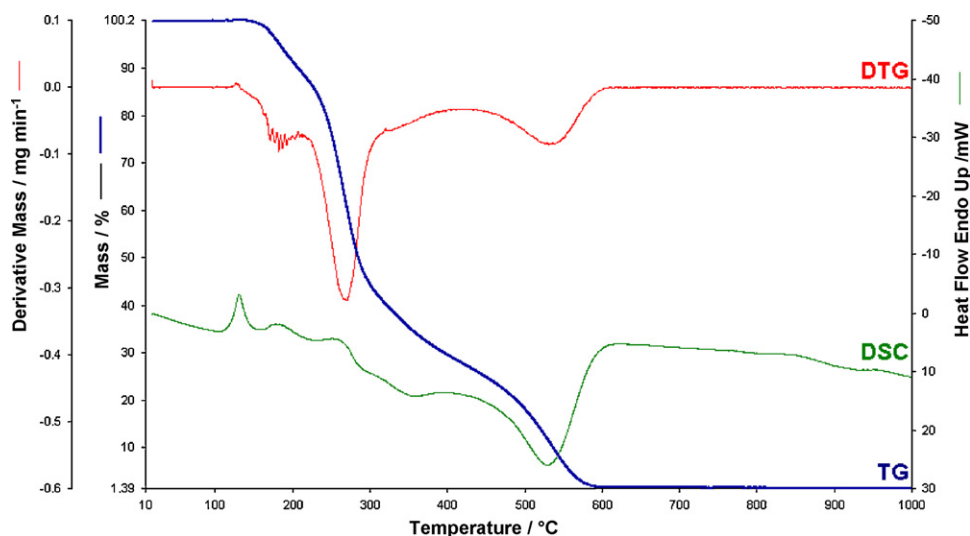
Fig. 2. Thermoanalytical curves of fructose, in air flow.

DTG peaks up to 120–130 °C), together with the last two arguments presented above, led to the conclusion that FruiteX B® [3] has $Ca[(C_6H_{10}O_6)_2B]_2 \cdot 4H_2O$ as molecular composition, identical with the natural product [4]. This formula reconfirms the expected content in boron [4] of the calcium fructoborate obtained in the chemical synthesis, which is two times higher than reported by Wagner et al. [5,6] and adequate to this type of boron compounds with glucides.

These results contradict Wagner et al. formula [5,6], where only 3.5 crystallization water molecules were reported. However, Wagner et al. papers [5,6] present the thermal analysis figures without even mentioning the actual values of the mass, mass loss (on the axis) or any other indication related to the registered mass that can sustain their conclusions.

The literature records do not refer to a calcium fructoborate sample which would be taken as reference and to which FruiteX B® could be compared. This is the reason why we have prepared a sample which perfectly reproduces Miljkovic [3]. The final step which implies the crystallization was performed when slowly drying the product at room temperature, known as freeze drying–liophilization process, which is recommended in the case of nutraceutics fabrication.

Thermoanalytical curves of calcium fructoborate obtained in the laboratory are presented in Fig. 3.

A comparative analysis of Figs. 1 and 3 shows that the processes involved in the two samples (FruiteX B® and the calcium fructoborate sample prepared in laboratory) are the same. The sample obtained in the laboratory looses $8.1 \pm 1\%$ of the total mass up to 152 °C, the process exhibiting a weak endothermic effect. Further, between 152 and 850 °C, the mass loss caused by fructose decomposition is of $74.8 \pm 1\%$. The residue of $17.0 \pm 1\%$ is calcium borate. The experimental measurements agree very well with the calculated values for the prepared calcium fructoborate when considering its molecular formula $Ca[(C_6H_{10}O_6)_2B]_2 \cdot 4H_2O$.

3.2. X-rays diffraction analysis

X-ray diffraction analysis was performed for calcium fructoborate (FruiteX B®), fructose, boric acid, calcium carbonate and the residue of calcium borate. Our results have been compared with those in the JCPDS database at the International Centre for Diffraction Data. For calcium carbonate (card 05-0586), boric acid (card 25-0097) and calcium borate (card 22-0141) XRD patterns are similar to those reported in the literature [26–29].

In the case of D-fructose used in the synthesis of calcium fructoborate, the X-ray diffraction analysis showed that D-fructose crystallizes in orthorhombic system (card 39-1839), with main XRD peaks very close to those of reference [30] (characteristic spreading of organic compounds).

When comparing crystallized fructose XRD patterns (for which diffraction peaks can be indexed), to the ones of small crystallized calcium fructoborate (Fig. 4), certain important peaks of bonded fructose may be identified (Table 2) within the diffraction peaks of calcium fructoborate (similarities sustained by common decomposition features of the thermal analysis results of the two).

The reason for this behaviour might be that the fructose represents 76.6% of the total mass of the complex and likely influences its crystalline structure. The diffraction maxima of free fructose were not identified in the XRD spectrum of calcium fructoborate. For calcium carbonate and boric acid there were not identified maximal values of the X-rays diffraction to be common to those of calcium fructoborate ones.

Table 1
Thermal parameters of decomposition in air flow for calcium fructoborate.

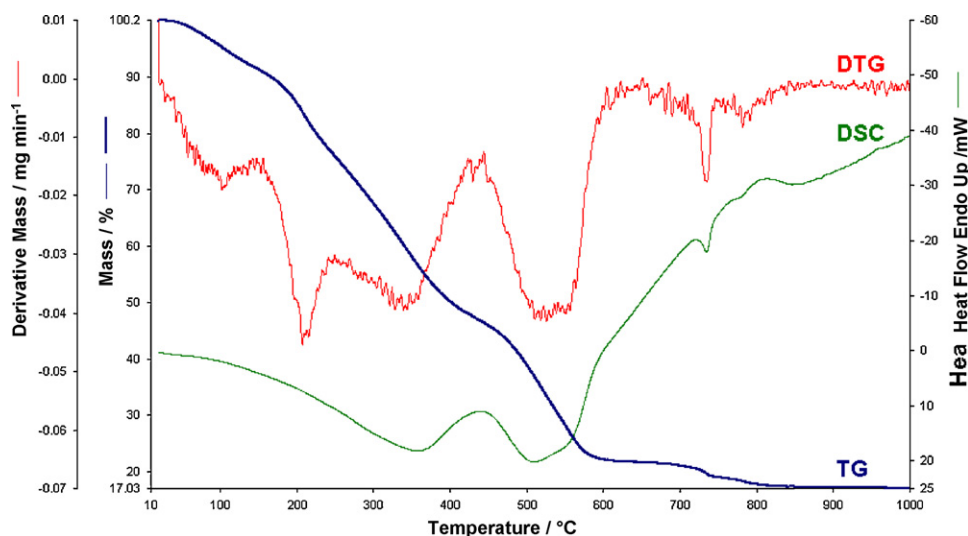| Temperature range (°C)	Temperature of the maximum decomposition rate (°C)	Mass loss (%)	Thermal effect endo/exo	ΔH (kJ kg^{-1})
RT–152	83	8.5	endo weak	–
152–253	215	15.0	endo weak	–
253–457	342	33.6	exo weak	–
457–650	593	18.1	exo moderate	−585.0
650–707	690	2.1	exo moderate	−115.2
707–757	733	6.7	exo strong	−987.5
757–845	781	2.3	exo moderate	−53.5

Fig. 3. Thermoanalytical curves for calcium fructoborate prepared in laboratory, in air flow.
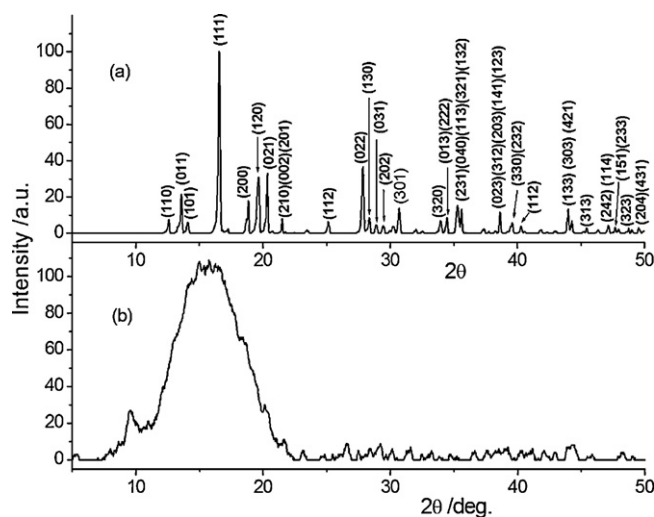

Fig. 4. XRD patterns of the fructose (a) and calcium fructoborate (b).

3.3. FTIR and Raman spectroscopic studies

Vibrational spectroscopy enhances the information on metal–organic complexes. FTIR analysis was performed for calcium fructoborate (FruiteX B® and calcium fructoborate prepared in laboratory), fructose, boric acid and calcium carbonate in the wavenumber range of 4000–600 cm^{-1}. FTIR spectra of FruiteX B® and calcium fructoborate prepared in laboratory are almost identical, therefore we will refer further only to FruiteX B®. Raman spectroscopic analysis was performed for FruiteX B® and fructose in the wavenumber range of 400–4000 cm^{-1}.

FTIR and Raman spectra were compared with those of similar compounds investigated by the same methods [5,31]. FTIR spec-trum of FruiteX B® is shown in Fig. 5, while Raman spectrum of FruiteX B® is presented in Fig. 6.

In the absorption spectrum of calcium fructoborate, the vibra-tional 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 IR absorption bands and the movement of the Raman intensities (Raman displacements) for fructose and FruiteX B® are presented in Table 3, where the IR vibration frequency and Raman displace-ment are given in cm^{-1}. Table 3 also presents an assignment of the most characteristic vibrations.

Wagner et al. performed a comparative spectroscopic study (FTIR and Raman) of calcium fructoborate and D-fructose – observ-ing similarities, while the most interesting FTIR spectral range

Table 2

Comparison of some main XRD peaks of fructose and of calcium fructoborate (FruiteX B®).

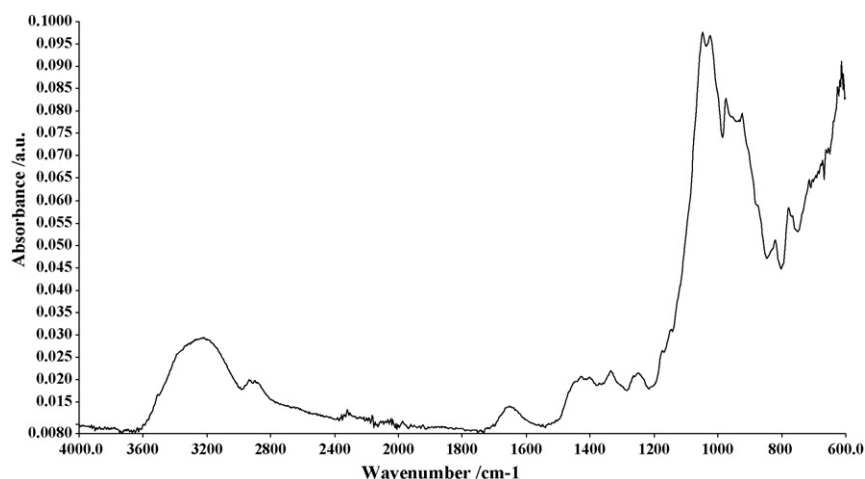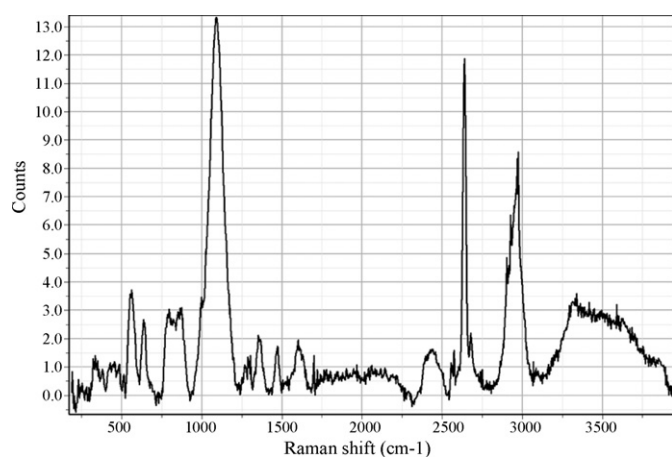| D-Fructose			Low crystallized calcium fructoborate		
Relative intensity	2θ (°)	D (Å)	Relative intensity	2θ (°)	D (Å)
100	16.86	5.254	93	16.90	5.242
38	19.92	4.453	34	19.92	4.453
38	28.14	3.168	6	27.77	3.210

Fig. 5. FTIR spectrum of FruiteX B®.

Fig. 6. Raman spectrum of FruiteX B®.

appearing between 500 and 2000 cm^{-1} [5]; however, when examining their FTIR figure [5], it is obvious that they have reported a much broader range instead of the real one 600–1800 cm^{-1}, which is to be found in our study. For the Raman spectroscopy no figure

was provided, with only comparing the obtained values for calcium fructoborate to the fructose ones in a table [5]. In both cases, the characteristic peaks resemble, with only small differences of their positions which are due to the different composition and structure of the investigated compounds.

From the values of vibration frequencies one can identify the functional groups of studied compounds:

- High frequency domain (4000–2000 cm^{-1}) contains for both IR and Raman (Table 3) wide and intense bands [5,32,33]. The peak at 3314 cm^{-1} in the Raman spectrum is related to B–O bond and for 3550–3145 cm^{-1} in IR spectrum, one can identify the crystallization water of metal complexes of saccharides. In the same domain functional groups like: CH$_2$OH, OH and CH can be identified.
- In the IR spectrum, between 1770 and 1200 cm^{-1} one can identify CH, OH, COH, CH$_2$OH, CH$_2$ groups and once more the crystallization water at 1250 cm^{-1}.
- In the Raman spectrum of calcium fructoborate, the B–O bond is exhibited by the weak peaks from 1602 to 1471 cm^{-1}.
- The IR spectrum of fructose and calcium fructoborate contains in the 1050–600 cm^{-1} range the vibrational bands characteristic to groups like: CO, CH$_2$OH, C–CH, CH$_2$, C–C and C–O–C.

Table 3
Vibration wavenumbers of FruiteX B® and fructose exhibited in the FTIR and Raman spectra.

Fructose		FruiteX B®		Assignments
FTIR	Raman	FTIR	Raman	
3521s, 3401s	3420m	3230s	3314s	BO, H$_2$O, OH, CH$_2$OH
2990w, 2939w	2942w	2936m	2975vs, 2640vs	CH, CH$_2$OH
		2324w	2490w, 2344w	
2163w	2168w	2163w		
2042w	2047w	2050w		
		1652w	1602w	BO, H$_2$O
1427m, 1397m	1470s, 1450m	1429m	1471w	BO, CH, OH, COH, OCH, CH$_2$OH
1332s	1337m	1336m	1352w	OH, CH$_2$OH
1250m, 1147s	1265s, 1251m	1251m		H$_2$O, OH, CH$_2$, CH
1077vs, 1048vs	1081s, 1041m	1049vs, 1025vs	1086vs	H$_2$O, CH$_2$OH, CO
976vs, 924m	979s	976vs		H$_2$O, CH$_2$, CCH
817m	821s	822s	851m	H$_2$O, CC
781s		779s	796m	COC
676m				
		673vs		BO
625s	604m			OH
		614vs	627m	BO, H$_2$O
	527m			CCH
			513w	CCO

vs: very strong; s: strong; m: medium; w: weak; B–O and H$_2$O bonds appear only in FruiteX B®.

- Raman spectrum contains two additional peaks at 851 and 627 cm^{-1}, attributed to the crystallization water of the complex [31]. As well, some works [34–36], 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}.

4. Conclusions

Thermal analysis of FruiteX B$^{®}$ – a product of chemical synthesis – and of boric acid and calcium carbonate showed that there are no similarities between their thermoanalytical curves. Only with fructose, similarities appear, but shifted to higher temperatures as a result of the bonding influences in the calcium fructoborate complex. Mass loss is of 8.5% up to 152 °C, when the experiment is performed in air. This loss is due to the crystallization water of the compound. By correlation of the results of thermogravimetric analysis with the elemental analysis, no precursors traces were found and the correct molecular formula of FruiteX B$^{®}$ 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. Above 152 °C, the decomposition in air occurs in six stages: first stage is weakly endothermic, the second is weakly exothermic, and the following four are exothermic. For the last 4 stages, the exchanged heat was determined as well. Gravimetric effects of the last six stages are due to decomposition of fructose from the complex with a mass loss of 77.8 ± 1%, compared to the 76.6% (calculated on the basis of the proposed formula). Residue of 13.7 ± 1% is calcium borate (theoretical 14.8%). XRD results show a weak crystallinity of calcium fructoborate and confirmed the thermal analysis results when no evidence of fructose, boric acid and calcium carbonate were found. FruiteX B$^{®}$ comes therefore as the calcium fructoborate found in natural products.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.04.006.

References

[1] P.H. Brown, H. Hu, Ann. Bot. 77 (1996) 497.
[2] P.H. Brown, B.J. Shelp, Plant Soil 193 (1997) 85.
[3] D. Miljkovic, US Patent 5,962,049 (1998).
[4] H. Hu, S.C. Penn, C.B. Lebrilla, P.H. Brown, Plant Physiol. 113 (1997) 649.
[5] C.C. Wagner, V. Ferraresi Curotto, R. Pis Diez, E.J. Baran, Biol. Trace Elem. Res. 122 (2008) 64.
[6] C.C. Wagner, E.J. Baran, Mater. Res. 11 (2008) 493.
[7] D. Miljkovic, R. Scorei, V.M. Cimpoiasu, I.D. Scorei, J. Dietary Suppl. 6 (2009) 211.
[8] R. Scorei, V.M. Cimpoiasu, D. Iordachescu, Biol. Trace Elem. Res. 107 (2005) 127.
[9] R. Scorei, R. Ciubar, C. Ciofrangeanu, V. Mitran, A. Campean, D. Iordachescu, Biol. Trace Elem. Res. 118 (2007) 27.
[10] R.I. Scorei, C. Ciofrangeanu, R. Ion, A. Cimpean, B. Galateanu, V. Mitran, D. Iordachescu, Biol. Trace Elem. Res. (2009), doi:10.1007/s12011-009-8488-5, Online.
[11] R. Scorei, R. Ciubar, C. Ciofrangeanu, V. Mitran, A. Campean, D. Iordachescu, Biol. Trace Elem. Res. 122 (2008) 197.
[12] R.I. Scorei, R. Popa, Anti-Cancer Agents Med. Chem. 10 (2010), doi:10.2174/1871210199121035206.
[13] M. Tătucu, P. Rotaru, I. Rău, C. Spînu, A. Kriza, J. Therm. Anal. Calorim. (2009), doi:10.1007/s10973-009-0276-0, Online.
[14] M. Olczak-Kobza, Thermochim. Acta 419 (2004) 67.
[15] M.A. Haroun, P.K. Khirstova, G.A. Gasmelseed, A.D. Covington, Thermochim. Acta 484 (2009) 4.
[16] M. Badea, R. Olar, D. Marinescu, E. Segal, A. Rotaru, J. Therm. Anal. Calorim. 88 (2007) 317.
[17] M. Badea, R. Olar, D. Marinescu, G. Vasile, J. Therm. Anal. Calorim. 92 (2008) 205.
[18] E. Szunyogova, D. Mudronova, K. Gyoryova, R. Nemcova, J. Kovarova, L. Piknova-Findorakova, J. Therm. Anal. Calorim. 88 (2007) 355.
[19] Z.R. Tian, J.A. Voigt, J. Liu, B. McKenzie, M.J. McDermott, M.A. Rodriguez, H. Konishi, H. Xu, Nat. Mater. 2 (2003) 821.
[20] P. Gerstel, R.C. Hoffmann, P. Lipowsky, L.P.H. Jeurgens, J. Bill, J.F. Aldinger, Chem. Mater. 18 (2006) 179.
[21] L.P. Bauermann, J. Bill, F. Aldinger, J. Phys. Chem. B 110 (2006) 5182.
[22] A. Kropidlowska, A. Rotaru, M. Strankowski, B. Becker, E. Segal, J. Therm. Anal. Calorim. 91 (2008) 903.
[23] A. Rotaru, A. Mietlarek-Kropidłowska, C. Constantinescu, N. Scarisoreanu, M. Dumitru, M. Strankowski, P. Rotaru, V. Ion, C. Vasiliu, B. Becker, M. Dinescu, Appl. Surf. Sci. 255 (2009) 6786.
[24] A. Rotaru, C. Constantinescu, A. Mândruleanu, P. Rotaru, A. Moldovan, K. Győryová, M. Dinescu, V. Balek, Thermochim. Acta 498 (2010) 81.
[25] A.S. Al-Ammar, E. Reitznerova, R.M. Barnes, J. Radioanal. Nuclear Chem. 244 (2000) 267.
[26] H.E. Swanson, R.K. Fuyat, Natl. Bur. Stand. (US) 539 (1953) 61.
[27] H. Effenberger, Z. Kristallogr. 156 (1981) 233.
[28] J. Zachariassen, Acta Crystallogr. 7 (1954) 305.
[29] F. Marezio, Acta Crystallogr. 25 (1969) 955.
[30] Y. Rosenstein, Am. Cryst. Assoc. 1 (1968) 92.
[31] S. Söderholm, Y.H. Roos, N. Meinander, M. Hotokka, J. Raman Spectrosc. 30 (1999) 1009.
[32] S.B. Etcheverry, P.A.M. Williams, E.J. Baran, Carbohydr. Res. 302 (1997) 131.
[33] R.P. Bandwar, M.S.S. Raghavan, C.P. Rao, Biometals 8 (1995) 19.
[34] M. Hineno, Carbohydr. Res. 56 (1977) 219.
[35] M. Mathlouthi, D.V. Luu, Carbohydr. Res. 78 (1980) 225.
[36] J.P. Huvenne, G. Vergoten, G. Fleury, J. Mol. Struct. 74 (1981) 169.