Phenolic compounds, carotenoids, vitamin C and fatty acids from organic and conventional goji berry: biological activities, chromatographic profile and thermal stability

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Abstract

Goji fruits grown in the organic and conventional systems were investigated for phenolic content (TPC), antioxidant activity (AA), carotenoid and ascorbic acid profile, fatty acid composition (FA), and thermal stability. Phenolic extracts and solid samples were analyzed, comparing the use of shaker and ultrasound for Folin-Ciocalteu, Fast Blue BB, and FRAP methods. HPLC and GC-FID were used to determine the profile of carotenoids, ascorbic acid and FA, and oil thermal stability was determined by TG-DTG. Ultrasound showed a higher content of TPC and AA in organic (803.34–7076.43 mg GAE/100 g, 11.45–234.11 mmol TE/100 g) and conventional (763.01–6366.30 mg GAE/100 g, 10.27–117.12 mmol TE/100 g) samples in relation to the shaker. The Folin-Ciocalteu showed higher values (912.42 – 6350.54 mg/100 g) than the Fast-Blue BB method. The content of TPC and AA were 3–20 times higher in solid samples (Quencher) compared to extracts. (all-*E*)-lutein and (all-*E*)-zeaxanthin were the main carotenoids identified. Organic and conventional fruits showed a high vitamin C content (101.83 and 80.46 mg/100 g). Linoleic acid was the main FA, and the ω-6/ω-3 ratio was 0.13 and 0.12.

Thermal decomposition for organic and conventional oils started at 130 and 170 °C, respectively. Organic fruits had a higher TPC, AA, (all-E)-zeaxanthin, vitamin C, and linoleic acid than conventional fruits. The results presented in this work show the potential of goji fruits, mainly cultivated in the organic system, as antioxidants and natural functional ingredients. Therefore, goji berry can be considered a food and a promising functional ingredient for developing products in different industrial segments with cosmetic, food, and pharmaceutical purposes.

Keywords: Quencher, Fast Blue BB, ascorbic acid, TG-DTG, safe ingredient, *Lycium barbarum* L.

Introduction

The consumption of foods rich in phytochemicals has been increasing worldwide. Phytochemicals are synthesized during the development of the plant in response to different stress situations, such as infections, injuries, and ultraviolet radiation [1]. In the human body, these compounds inhibit reactive oxidative species associated with diseases [2]. Goji berries are fruits rich in phytochemicals with important biological functions in the human body and industrial applications. Phenolic extracts of goji fruits (*Lycium barbarum* L.) have been associated with antitumor and antimicrobial (*Staphylococcus aureus*, *Salmonella Typhi*, *Escherichia coli*, and *Bacillus subtilis*) effects [3, 4] and have antioxidant properties in vegetable oils [5].

Ascorbic acid (vitamin C), found in large quantities in goji fruits, has important biological functions, such as inducing cell death from cancerous tumors of the Hela type-cervical adenocarcinoma [6]. Carotenoids are natural pigments responsible for the intense orange color of goji berries. Zeaxanthin, the main carotenoid in goji fruit, is associated with protection against ocular retinal degeneration in the elderly [7]. Unsaturated fatty acids from goji fruits also have important physiological functions in the human body, such as strengthening the epithelial tissue. Furthermore, they have potential technological characteristics for industrial applications [8, 9].

Different industrial sectors have widely used natural antioxidants, and it is essential to obtain extracts with high yield and quality. Thus, the selection of the raw material, extraction method, and technological applications are extremely relevant [10]. Studies show that plants grown in the organic system tend to produce more nutritious and safer extracts than those produced with pesticides (conventional cultivation system) [11]. In addition, there are desirable methods that use shorter extraction times, such as ultrasound. This method maintains the main biological functions of natural sources [12]. For industrial applications, it is crucial to highlight that the obtained vegetable extracts and oils have a certain degree of stability. Some analyses are important to prove this characteristic. Therefore, thermogravimetric analyses (TG-DTG) are fast and simple techniques often used by the food and pharmaceutical industry to determine the thermal stability of phytochemicals [13].

Few studies relate the differences in phytochemical composition between vegetables and fruits grown with different cultivation techniques in the literature. In addition, no study has been found regarding the thermal stability of oils extracted from the goji berry. Therefore, this study aimed to evaluate goji fruits produced organically and conventionally regarding: (1) different methods of extraction and determination of total phenolics and antioxidant activity *in vitro*; (2) chromatographic profile of carotenoids and ascorbic acid (L-ascorbic and L-dehydroascorbic); (3) fatty acid profile and thermal stability of the goji berry oils.

Materials and methods

Chemicals

The TPTZ, Fast Blue BB, Folin-Ciocalteu reagents and chromatographic grade chemical standards (purity ≥ 95%) were purchased from Sigma-Aldrich (St. Louis, MO,

89 USA). Solvents, hexane (C_6H_{14}), ethanol (C_2H_6O), acetone (C_3H_6O), acetonitrile (C_2H_3N)
90 and methanol (CH_3OH) were purchased from J.T.Baker (Loughborough, USA). The other
91 reagents were of analytical grade and ultrapure water was obtained by a Milli-Q water
92 system (Millipore, Bedford, MA, USA).
93
94 **Goji berry samples**
95 Goji berry (*Lycium barbarum* L.) samples grown in organic (organic certificate:
96 IMO Control, Manufactured: Qingdao Ri Tai Food Co., Ltd) and conventional systems
97 were purchased at the Municipal Market of Curitiba/PR (2015 harvest). The fruits were
98 lyophilized (L101-Liotop, São Carlos - São Paulo, Brazil), ground in a 10 mesh analytical
99 mill (MA630/1-Marconi, Piracicaba - São Paulo, Brazil) and stored in amber glass
100 containers at 4 ± 2 °C until the time of analysis.
101
102 **Preparation of solid samples and extract**
103 The determination of total phenolic compounds (TPC) and antioxidant activity
104 (AA) *in vitro* was performed on extracts and solid samples obtained from goji berry
105 grown in organic and conventional systems.
106 The extracts were obtained according to the methodology proposed by Liyana-
107 Pathirana and Shahidi [14], with modifications. The extraction conditions were according
108 to Pedro et al. [5]. One gram of sample was mixed with 10 mL of ethanol (70%, v/v). The
109 mixture was stirred in a shaker (Memmert WB14, Schwabach, Germany) at 45 °C for 162
110 min. The same conditions were applied for the extraction by ultrasound (Selecta
111 Ultrasons-H 288071, Barcelona, Spain). The supernatant was obtained by centrifugation
112 (MPW-350R, Warsaw, Poland) at 4300 rpm for 20 min and the volume was made up to

50 mL with ethanol (70%, v/v). Solid samples were also analyzed according to the Quencher method, proposed by Condezo-Hoyos et al. [15].

Quantification of total phenolic compounds (TPC)

The Fast Blue BB and Folin-Ciocalteu methods were applied to extracts and solid samples. The quantification of TPC by the Fast Blue BB method was applied according with Medina [16]. For the extracts, a mixture of 4 mL of diluted sample (1/10, v/v), 0.4 mL of Fast Blue BB (0.1%, v/v) and 0.4 mL of NaOH (5%, m/v) were stirred for 90 min and the absorbance determined at 420 nm. TPC in solid samples were determined by adding 1 mg of sample, 0.4 mL of Fast Blue BB reagent (0.1%, v/v), 0.4 mL of NaOH (5%, m/v) and 4 mL of water. The mixture was stirred for 1 h, filtered and the absorbance determined at 420 nm. The results were expressed in milligram of gallic acid equivalent per 100 g of dried fruit (mgGAE/100 g).

Folin-Ciocalteu method [17] was performed as follows: in tubes, 600 µL of water, 200 µL of diluted sample (1/20, v/v), 50 µL of Folin-Ciocalteu and 150 µL of Na_2CO_3 (15%, w/v) were added, followed by agitation. After 60 min of reaction, the absorbance was monitored at 760 nm (ThermoFisher-Scientific, Genesys-105, Waltham, Massachusetts, USA). For solid samples, 1 mg of sample was mixed with 600 µL of water, 200 µL of Folin-Ciocalteu, and then stirred. Then 4 mL of Na_2CO_3 (75 g/L, m/v) and 5 mL of water were added and kept under stirring for 35 min. Finally, the mixture was filtered and the absorbance determined at 760 nm. The results were expressed in milligram of gallic acid equivalent per 100 g of dried fruit (mgGAE/100 g).

Antioxidant activity (AA)

The ferric reducing antioxidant power (FRAP) method was applied to extracts and solid samples [18]. The FRAP reagent was prepared by a mixture of acetate buffer (300 mmol/L, pH 3.6), TPTZ (10 mmol/L, w/v) in HCl (40 mmol/L, v/v), and $FeCl_3$ (20 mmol/L, w/v). In tubes were added 700 µL of acetate buffer (pH 3.6), 200 µL of FRAP and 100 µL diluted samples (1/20, v/v). The tubes were shaken, incubated for 40 min at 37 ± 1 °C and the absorbance was monitored at 596 nm (ThermoFisher-Scientific, Genesys-105, Waltham, Massachusetts, USA). The results were expressed in millimol equivalents of trolox per 100 g of fruit (mmolTE/100 g).

Extraction and profile of carotenoids

The carotenoids were extracted according to Nagata and Yamashita [19], with modifications. Approximately 150 mg of the samples were slowly agitated with 10 mL of acetone/hexane (4/6, v/v) for 5 min. The solution was filtered and saponified according to Zhao et al. [20]. To the extracts were added 1.3 mL of KOH in methanol (40%, w/v) and stirred at 56 °C for 20 min. The extracts were cooled, 10 mL of hexane added and the volume made up to 30 mL with Na_2SO_4 (10%, w/v). The solution was stirred and allowed to stand for phase separation. Finally, the supernatant was collected for analysis.

The carotenoid profile was evaluated by High Performance Liquid Chromatography with UV-Vis detector (HPLC/UV-Vis), PU II isocratic pumping system (Micron Analitica, SA, Spain) and 100 UV ultraviolet detector (Knauer, Germany) [21]. The extracts were filtered (PTFE 0.45 µm) and 30 µL were injected into the chromatograph. The column used (300 x 2 mm, 10 µm) was Bondapack C18 (Milford, MA, USA) at 30 °C. The mobile phase consisted of acetonitrile/methanol (95/5, v/v),

flow 0.9 mL/min at 475 nm. The peak areas of the chromatograms were quantified by standard curves of zeaxanthin and lutein.

Vitamin C analysis: Ascorbic and dehydroascorbic acid

Ascorbic and dehydroascorbic acids were determined by HPLC/UV [22]. 25 mL of HPO_3 (4.5%, w/v) was added to the 0.5 g sample. The mixture was stirred for 15 min (protected from light) and filtered through a 0.45 µm PVDF membrane. To a 3 mL aliquot, 2.5 mL of the L-cysteine solution (4%, m/v) was added, and adjusted to pH 7. After 5 min, was adjusted to pH 3 and the volume completed with water to 10 mL. The extract was filtered (PVDF 0.45 µm) and 40 µL were injected into the chromatograph. The column used (250 x 4.60 mm, 5 µm) was ODS II from Phenomenex (Torrance, CA, USA) and the mobile phase consisted of H_2SO_4 (1.8 mmol/L, v/v) (pH 2.6), flow 0.9 mL/min at 245 nm. Peak areas in chromatograms were quantified using a standard ascorbic acid curve.

Oils extraction and profile of fatty acids (FA)

Goji berry oils were extracted according to Bligh and Dyer [23]. Approximately 3.5 g of samples (organic and conventional) were mixed with chloroform/water/methanol (20/10/8, v/v/v) and homogenized at 25 ± 2 °C, 200 rpm for 30 min (Marconi MA420, São Paulo-SP, Brazil). Then, 10 mL of chloroform and 10 mL of Na_2SO_4 (1.5%, m/v) were added and mixed for 5 min. The solution was decanted and a three-phase system was formed. The chloroform phase was collected in tubes with 1 g of Na_2SO_4 and then the mixture was filtered. The solvent was evaporated under reduced pressure at 50 °C (Fisatom–model802, São Paulo-SP, Brazil) and the residual solvent was removed with

forced air circulation at 50 ± 2 °C for 1 h. The FA were transferred into amber vials with nitrogen and stored at -18 °C.

The capillary column gas chromatograph with a flame ionization detector (GC-FID) (Varian, CP3900, USA) was used for determined FA profile [24] (with modifications). Approximately 250 mg of oils were saponified with NaOH (0.5 mol/L, w/v) for 10 min. The mixture was boiled for 2 min with CH_4BF_3O (14%, w/v) following by the addition of n-hexane. Saturated NaCl (30 mL) was added and mixed, and 1 μL of the upper phase was injected in a GC-FID with ZB-WAX capillary column (Phenomenex, USA) (60 m x 0,25 I.D., 0,25 μm). The temperature program as follows: 60 °C (2 min) to 160 °C at 20 °C/min, to 240 °C at 2.5 °C/min, hold 31 min; carrier gas: nitrogen 3 mL/min; detector temperature: 300 °C. FA quantification was by comparing the retention time of the standard mix C4-C24 (Supelco FAME, Bellafonte, PA, USA).

Thermal stability of goji berry oils

For the study of thermal stability and losses of mass of goji berry oils, the following parameters were used: sample mass of approximately 10 mg (organic and conventional goji berry oils); atmosphere at a flow rate of 150 mL/min; heating rate of 10 °C/min, from 30–700 °C. The TG curves were obtained by the TGA-50 thermal analysis system and the mass loss percentages were determined using the TA-60 WS data analysis software. The same software was used to generate the DTG curve providing the peak temperatures of the maximum rate of loss.

Statistical analysis

Results were expressed as means (n = 3) ± standard deviation (SD), by analysis of variance (ANOVA) followed by the Fisher LSD test at 5% probability ($p \leq 0.05$). The *t*-

student test was also used and $p \leq 0.05$ values were considered significant. The Statistica 7.0 software (StatSoft Inc. South America, Oklahoma, USA) was used.

3 Results and Discussion

Total phenolic compounds (TPC) and antioxidant activity (AA)

The TPC content and AA of the goji berry samples were strongly influenced by the extraction processes and by the determination methods employed. In addition, significant differences ($p \leq 0.05$) were also observed between extracts and solid samples (Quencher), as shown in Table 1.

The ultrasound method showed a higher ($p \leq 0.05$) TPC in extracts and solid (Quencher) samples of organic (803.34–7076.43 mgGAE/100 g) and conventional (763.01–6366.30 mgGAE/100 g) fruits compared to the shaker shaking process. AA (FRAP) was also higher for extracts and solid samples of organic (11.45–234.11 mmol TE/100 g) and conventional (10.27–117.12 mmol TE/100 g) goji fruits obtained by ultrasound. These results can be explained by the cavitation that occurs in the ultrasound process. Cavitation produces shear forces that mechanically disturb plant cell walls and increase mass transfer processes. As a result, the leaching of organic and inorganic compounds from the plant matrix is intensified [25].

The Folin-Ciocalteu method, traditionally used to quantify phenolic compounds, showed higher ($p \leq 0.05$) TPC contents (912.42–6350.54 mgGAE/100 g) when compared to Fast Blue BB (712.88–7076.43 mgGAE/100 g). This is because it has recently been proposed as a method for antioxidant activity determination, rather than phenolic compounds content, due to the chemical reaction mechanisms. Folin-Ciocalteu is an oxidizing reagent based on phosphomolybdic and phosphotungstic acids, which are reduced in the presence of antioxidants, and blue molybdenum-tungsten complexes

236 ($(PMoW_{11}O_4)^{4-}$) are formed. As a result, the analysis detects the presence of a wide
237 variety of compounds, such as phenols, reducing agents, and possible metal chelators
238 [26]. However, some of these compounds can interfere with the analysis, forming a blue-
239 colored complex, such as non-phenolic antioxidants and reducing ascorbic acid, glucose,
240 fructose, sulfites, amino acids (tyrosine, tryptophan), and proteins that contain these
241 amino acids [16].

242 On the contrary, the Fast Blue method is based on the direct interaction between
243 phenolics and the diazonium salt, present in the reagent Fast Blue BB. Therefore, ascorbic
244 acid and other reducing compounds interfering with the analysis do not react with the
245 diazonium salt. This salt contains a diazonium group (-+N=N-), wherein alkaline
246 medium, nitrogen is retained in coupling with the reactive activator group (-OH) of the
247 phenolic, causing an aromatic electrophilic substitution in the *ortho* or *para* position and
248 formation of azo compounds [16]. This phenomenon can be observed in Fig. 1, where
249 chlorogenic acid, one of the main phenolic acids in *Lycium barbarum* L. fruits, reacts
250 with the diazonium salt in the *para* position to activate the -OH group.

251 Samples of goji berry have high sugar and ascorbic acid content [6], which are
252 important factors in the quantification of total phenolics. Thus, the method applied may
253 have had a strong influence on the results obtained. For example, the Folin-Ciocalteu
254 method would conduct an overestimation of TPC. Therefore, the Fast Blue BB method is
255 the most suitable for TPC determination, both in extracts and in solid samples of organic
256 and conventional goji fruits.

257 There was a wide variation ($p \leq 0.05$) in the content of TPC (Folin-Ciocalteu and
258 Fast Blue BB) and AA (FRAP) between solid samples (2265.95–7076.43 mgGAE /100
259 g and 38.78–234.11 mmol TE/100 g) and extracts (712.88–1094.92 mgGAE/100 g and
260 10.09–11.45 mmol TE/100 g) of organic and conventional goji fruits (Table 1). The

content of phenolic compounds and antioxidant activity were between 3 and 20 times higher in solid samples (Quencher), compared to extracts. Fruits, vegetables, and cereals have a large amount of insoluble compounds, such as bound phenolics. These compounds are not easily extracted with the use of chemical solvents and therefore are not quantified. Therefore, alternative methods such as Quencher can be used. This method is a rapid and direct test that determines insoluble compounds in the solid plant matrix [15]. Therefore, the highest TPC content obtained for solid samples (Quencher) may be related to phenolics linked to the plant matrix. In addition, carotenoids and ascorbic acid, antioxidants present in high concentrations in goji fruits, may have contributed to the high antioxidant activity [27].

Extracts and solid samples (Quencher) of organic goji berry showed higher ($p \leq 0.05$, *t*-student) contents of TPC (740.34–7076.43 mgGAE /100 g) and AA (10.72–234.11) mmol TE/100 g) compared to conventional goji (71.88–6366.30 mgGAE/100 g and 10.09–117.12 mmol TE/100 g), as shown in Table 1. These results can be explained by the response of plants to stressful physiological and environmental situations. Plants grown in the organic system do not use agrochemicals in their cultivation and tend to be more susceptible to the attack of pathogens and fragile to adverse climatic conditions. As a result, the organic plants tend to produce a large amount of defense compounds derived from secondary metabolism, showing higher content of TPC compared to plants grown in the conventional system [28].

Carotenoids

The main carotenoids present in organic and conventional goji samples were identified and quantified by HPLC. In the unsaponified extracts, 2 xanthophylls ((all-*E*)-lutein and (all-*E*)-zeaxanthin) (Supplementary material, Fig. S1) were identified, and in

286 the saponified extract only (all-*E*)-zeaxanthin was detected (Supplementary material, Fig.
287 S2). The saponification process resulted in a higher content of (all-*E*)-zeaxanthin and
288 possible degradation of lutein and another unidentified compound (peaks 1 and 3,
289 respectively) in the samples, as this process involves an exothermic chemical reaction.
290 According to Zhao et al. [20] the zeaxanthin present in goji berry is available as an ester
291 and can be converted to free zeaxanthin through the chemical saponification process. In
292 addition, compounds such as chlorophyll, lipids, and impurities can be removed through
293 this process, reducing interferences in the analysis.

294 Table 2 shows the content of organic and conventional goji berry carotenoids.
295 Unsaponified extracts showed (all-*E*)-lutein and (all-*E*)-zeaxanthin contents ranging from
296 0.13–0.16 and 0.24–0.28 mg/100g, respectively. Saponified extracts showed only (all-*E*)-
297 zeaxanthin, with levels of 8.36 and 6.61 mg/100 g for organic and conventional fruits,
298 respectively. Zhao et al. [29] observed a high reduction in lutein content in goji berry
299 extracts after saponification and related it to a molecular degradation process.

300 In the study by Wong et al. [30], the lutein and zeaxanthin content in goji fruits
301 ranged from 0.14–0.68 and 0.23–0.47 mg/100 g, respectively. In contrast, Zhao et al. [29]
302 determined in different samples of goji berry contents of 0.33–1.87 and 6.49–152.29
303 mg/100 g of lutein and zeaxanthin, respectively. The carotenoid content in the
304 unsaponified extract showed no significant difference ($p > 0.05$, *t-student*) between
305 organic and conventional samples (Table 2). However, organic fruits showed a higher
306 content of (all-E)-zeaxanthin for the saponified extract. Differences observed in the
307 content of carotenoids can be explained by different varieties, storage conditions,
308 cultivation systems, temperature, and main exposure to light [31]. Carotenoids have
309 chromophoric groups in the molecule responsible for absorbing sunlight and transforming
310 it into chemical energy.

In the literature, different authors have also identified zeaxanthin (~ 80%) as the major carotenoid in goji berries [32, 27]. In a lower concentration, β-carotene, β-cryptoxanthin, violaxanthin, and lutein were identified [9, 33]. Zhao et al. [29] showed that goji fruits had between 60 to 70 times more zeaxanthin than other food sources of this carotenoid, such as egg yolk. Therefore, goji berry can be considered an excellent source of zeaxanthin. This pigment, in addition to increasing the color of the egg yolk of birds, and enhancing the pigmentation of the epithelial tissue of fish and pigs [34], also provides effects for human health, as protection against macular degeneration in the elderly [35] and anti-hyperglycemic, anti-aging and antioxidant activities [36].

Vitamin C: Ascorbic and dehydroascorbic acid

Vitamin C is widely distributed in products of plant origin and can be found in reduced form (L-ascorbic acid), which occurs more naturally in plant sources or oxidized form (L-dehydroascorbic acid). The oxidation of the L-ascorbic acid molecule causes its conversion to L-dehydroascorbic acid through reversible electron transfer [37].

The reduced and oxidized forms of vitamin C were identified and quantified in organic and conventional samples of goji berry by HPLC-IR. The L-ascorbic acid chromatogram (Supplementary material, Fig. S3) shows retention times of 3.65 and 3.66 min for organic and conventional fruits, respectively. After the oxidative process of the extracts, the L-ascorbic acid was converted to L-dehydroascorbic acid, and the obtained chromatograms (Supplementary material, Fig. S4) showed retention times of 5.22 and 4.42 min for organic and conventional samples, respectively.

Table 3 shows the contents of total ascorbic acid and the two forms found in organic and conventional goji fruits. Organic fruits showed a significant difference ($p \leq 0.05$) between the total content of ascorbic acid, L-ascorbic acid, and L-dehydroascorbic

acid (101.83, 34.88, and 66.95 mg/100 g, respectively). Conventional fruits did not show a significant difference ($p > 0.05$) between the two forms of ascorbic acid (40.87 and 39.60 mg/100 g). Different Vitamin C contents were determined for goji fruits. Donno et al. [38] determined a Vitamin C content of 48.90 mg/100 g of dried fruit, while Kulaitienė [39] obtained low Vitamin C contents, approximately 4.3–5.8 mg/100 g. These results demonstrate that the high values of vitamin C obtained for the goji berry samples contribute considerably to daily ingestion [38].

The contents of total ascorbic acid and the oxidized form, L-dehydroascorbic acid, were significantly higher ($p \leq 0.05$) in organic fruits when compared to fruits grown in the conventional system. Similar results were obtained by Pertuzatti et al. [40], who reached the content of phytochemicals in samples of passion fruit (*Passiflora edulis*) grown in the organic and conventional system. According to Genovese et al. [41], the levels of vitamin C in fruits are subject to a wide variety of environmental factors, including light, temperature, salts, and the presence of air pollutants, metals, and agrochemicals.

Fatty acids (FA)

The FA composition of goji fruit oils grown in the organic and conventional system is shown in Table 4. Significant differences were identified between the composition of FA ($p \leq 0.05$, ANOVA) and between the different forms of cultivation ($p \leq 0.05$, *t-student*). The oils from fruits grown in the organic and conventional systems showed low saturated fatty acids (SFA) levels, 18.43 and 21.27%, respectively. Therefore, it can be said that organic and conventional goji fruits are sources of unsaturated fatty acids (UFA = monounsaturated (MFA) + polyunsaturated (PFA)), 83.57

and 78.24%, respectively. These results are similar to the results obtained by Endes et al. [42], Blasi et al. [43], and Skenderidis et al. [44].

Vegetable oils with a high UFA content are important for human health to demonstrate a reduction in the triglyceride index, inflammatory processes, arrhythmias, and blood pressure. Such characteristics arouse broad interest for technological applications in the pharmaceutical, cosmetic, and food industries. In addition, the World Health Organization [45] recommends a PFA/SFA ratio above 0.5 for optimal physiological conditions in the human body, such as gene modulators and important sources of energy. In this study, the PFA/SFA ratio for organic and conventional goji berry samples was 3.39 and 2.73, respectively. Skenderidis et al. [44] showed that the PFA/SFA ratio ranged from 1.38 to 1.95 in *Lycium barbarum* L. of Mongolia. Ilić et al. [46] studied different types of goji berry and determined a PFA/SFA ratio of 2.52, 3.59, and 1.86 for red, yellow, and black goji berry cultivated in Serbia, respectively. These results show that FA of goji fruits are important compounds for promoting human health since they can contribute to a better diet's fatty acid profile.

Approximately 80% of the lipid fraction of goji fruits grown in the organic and conventional system is composed of UFA. Among the UFA identified, linoleic acid (C18:2*n*6c), known as omega 6 (ω-6), was predominant (52.47 and 49.85%), followed by oleic acid (C18:1*n*9c), 20, 61, and 19.58% (Table 4). Endes et al. [42], Kulczyński and Gramza-Michałowska [47] studied different species of goji berry, and also identified linoleic acid as the main UFA, with a proportion of 50 to 70% of the total lipids.

Linoleic acid (ω-6) plays important physiological roles in the human body, as does linolenic acid (ω-3). These FA are called essential, as they are not synthesized by the body, being acquired in the diet. However, studies have shown that the intake levels of the ω-6/ω-3 ratio are more important than the levels of these individual FAs. Balance is

essential for the proper functioning of the human body's physiological functions, such as blood pressure regulation, platelet and cardiovascular function, inflammatory processes, and tumor cell inhibition [48, 49]. Coklar and Akbulut [50] compared individuals with diets based on canola and sunflower oil with the ω-6/ω-3 ratio of 2.8 and 28, respectively. The diet rich in sunflower oil increases platelet aggregation and the risk of cardiovascular diseases, suggesting that high ω-6/ω-3 ratios may cause a physiological imbalance in the human body.

Skenderidis et al. [44] showed goji fruits grown in Mongolia had a ω-6/ω-3 ratio ranging from 4.48–7.82. A ω-6/ω-3 ratio of 8.26 was determined in goji fruits grown in Northern Italy by Zorzi et al. [51]. In our study, the ω-6/ω-3 ratio was 0.13 and 0.12 (Table 4) for organic and conventional oils, indicating a balance between linoleic and linoleic essential FA. Genetic factors, soil composition, degree of ripeness and cultivation techniques can also explain the differences in FA composition determined for goji berry fruits (Table 4). Skenderidis et al. [44] demonstrated that fruits grown in August (high temperatures) in the Thessaly area (Greece) had a higher content of bioactive substances compared to fruits grown in December (low temperatures). According to the authors, the thermal stress caused by the high temperatures in August induced the fruits to produce high concentrations of bioactive compounds. In addition, according to Macoris et al. [52], organic vegetables are strongly attacked by insects and pathogens, and in response to stress, conditions synthesize a large amount of bioactive compounds, such as the FA.

Thermal stability

Oils from new plant sources, such as those obtained from organic and conventional goji fruits have shown interest in industry and cuisine. However, these products must have a certain stability in processing, storage, and preparation steps [53].

Therefore, studies related to the thermal stability of vegetable oils are critical to offer a quality product, define the processing and storage conditions, and determine the most viable application [54].

During heating under controlled temperature and oxidative atmosphere of organic and conventional goji berry oil, 4 mass losses were identified, and similar thermal decomposition behavior was found. As the temperature rises, small molecules and weak chemical bonds are gradually decomposed [55]. The temperatures for each stage are shown in Table 5.

The first mass loss stage may be related to the loss of volatile compounds that remain adhered to the oil after solvent extraction, such as chloroform. Losses close to 100 ºC can also be associated with water volatilization, as Santos et al. [56] reported. Subsequently, degradation in successive stages was observed for both samples, and the presence and chemical structure of fatty acids in these stages are decisive for thermal decomposition and oil stability. The higher degree of fatty acid unsaturation is negatively correlated with its stability in the presence of extrinsic factors, such as oxygen and temperature, which induce oxidation [57]. Consequently, estimating the maximum temperature of oil use from the thermogravimetric analysis is possible to avoid its degradation (Table 5). The degradation temperature (ΔT) for conventional oil was higher than organic oil, starting at 174 and 130 °C, respectively. These results can be explained by the higher content of monounsaturated and polyunsaturated fatty acids in the organic sample, which are easily degraded at temperatures above 100 °C.

In addition, organic goji berry oil showed lower thermal decomposition Tonset than conventional fruit. However, peak temperatures were similar for the two samples, where there was a maximum loss rate. These results may be related to the high

concentration of linoleic acids (present in higher concentration), oleic and palmitic acids in the oils of organic and conventional goji fruits.

Kapusniaki and Siemion [58] found an approximate temperature of 150 ºC for the decomposition of linoleic acid (heating ratio 5 ºC). For oleic acid, Niu et al. [55] identified an initial decomposition temperature (10 ºC/min) of 198.17 ºC. Palmitic acid (smaller carbon chain) exhibited decomposition temperatures above 137 ºC, and after 190 ºC evaporated rapidly, presenting up to 80% of mass loss at a temperature of 261 ºC, at a heating rate of 20 ºC/min [59]. Increases in the heating rate can shift the degradation temperature to higher values due to the decreased heat distribution in molecular and weakened heat transfer efficiency at higher sample temperature heated rate [55].

As explained, oils with most fatty acids with a higher degree of unsaturation have less thermal stability. In addition, another factor must also be considered, such as the size of the carbon chain. Longer chains contribute to more excellent oil stability, as noted by Silva et al. [60] for soybean oil (rich in unsaturated longer-chain components), compared to *Scheelea phalerata* oil (rich in saturated short-chain components), conferring the greatest stability for soybean oil.

In the second loss, other components of the oil are also being decomposed, such as antioxidants. As shown in this study, organic and conventional goji berry oil samples, in addition to the high concentration of unsaturated fatty acids, also have important concentrations of phenolic compounds and carotenoids [9, 61].

The study by Juhász et al. [62] showed that ascorbic acid had a degradation temperature of 190 ºC (heating ratio 20 ºC/min) [63] and 188 ºC (heating ratio 4 ºC/min). Decomposition temperature above 200 ºC was found for raspberry (*Rubus idaeus* L.) and blackberry (*R. fruticosus* L.) oils, berries with significant amounts of linoleic acid, and antioxidants such as tocopherol [64].

Muruci oil (*Byrsonima crassifolia* L.) extracted with supercritical CO_2 showed stability up to 200 °C, with a fatty acid profile formed mainly by oleic acid (44.4%), palmitic acid (32.9%), and linoleic acid (16.3%), in addition to the presence of a high concentration of carotenoids. A high mass loss was observed at around 250 °C, with the loss continually increasing with increasing temperature. However, these temperatures already exceed the operational values involved in food preparation [62].

The third loss started at temperatures close to both oils (~ 400 ºC). Santos et al. [56] determined sharp peaks between 400–500 ºC for the oil of Patauá (*Oenocarpus bataua*), which correspond to the oxidation and final degradation of the fatty material with subsequent release of energy in the form of heat.

The decomposition of the oils was completed at 646 and 620 ºC, leaving only inorganic matter. A value of 2.7 and 1.3% were identified for conventional and organic oil, respectively. Minerals such as zinc, selenium, and iron found in the fruit may be present in this fraction. In our previous studies, minerals such as potassium, sodium, phosphorus, calcium, magnesium, iron, zinc, copper, and manganese have been identified. In addition, heavy metals such as cadmium, mercury, and lead have also been identified in the fruit when grown by the conventional method [65].

Therefore, according to the results presented, organic goji berry oil should be used at lower temperatures (about 130 °C decomposition starts) when compared to conventional goji berry oil (about 170 °C) to avoid its degradation (Table 5).

Conclusion

Compared to conventional shaker shaking, the ultrasound method was the most effective in extracting TPC with high AA from organic and conventional goji fruits. The Fast Blue BB method proved to be the most suitable for quantifying TPC in goji berries.

The contents of TPC and AA were 3 to 20 times higher in solid samples (Quencher) than extracts. (All-*E*)-zeaxanthin was the main carotenoid present in the extracts of goji berry. The high values of vitamin C obtained can contribute considerably to daily ingestion. Linoleic acid (ω-6) was identified as the main UFA in goji berry samples. The ω-6/ω-3 ratio for goji fruits showed a favorable equilibrium relationship for different physiological functions in the human organism. The thermogravimetric analysis showed that oils obtained from organic goji berry showed a degradation temperature below conventional goji oils. Organic fruit extracts had a higher TPC content (all-E)-zeaxanthin, vitamin C and PFA, and high AA than traditional fruit extracts. These results show that extracts and oils from goji fruits have the potential for applications in different industrial segments, especially fruits grown in the organic system. These fruits have better functional properties and provide the development of products with higher quality and security.

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Conflict of interest

The authors declare no conflict of interest.

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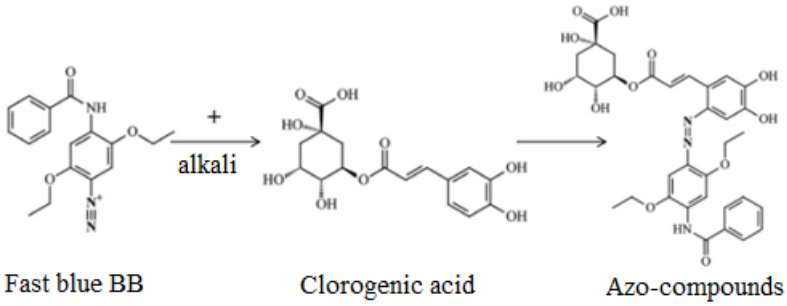

Figure 1 Reaction between the diazonium salt (Fast Blue BB) and chlorogenic acid.
Source: Medina (2011).

List of tables

Table 1 TPC and AA of extracts obtained by different methods and solid samples of organic and conventional dried goji berries.

Methods	Extracts[1]		Solid samples (Quencher)[1]	
	Organic	Conventional	Organic	Conventional
Shaker				
Fast Blue[2]	$740.34^{Bc} \pm 10.69$	$712.88^{Bd} \pm 12.53$	$5074.03^{Aa} \pm 231.57$	$2265.95^{Bb} \pm 337.16$
Folin[2]	$1059.18^{Ac} \pm 20.93$	$912.42^{Ad} \pm 10.11$	$5952.43^{Aa} \pm 302.88$	$4566.06^{Ab} \pm 200.02$
Ultrasound				
Fast Blue[2]	$803.34^{Bd} \pm 10.12$	$763.01^{Bc} \pm 6.75$	$7076.43^{Aa} \pm 342.54$	$6366.30^{Bb} \pm 257.41$
Folin[2]	$1094.92^{Ab} \pm 22.05$	$973.17^{Ac} \pm 12.14$	$6350.54^{Ba} \pm 147.15$	$5987.15^{Ba} \pm 342.24$
(FRAP)				
Shaker[3]	$10.72^{Bc} \pm 0.15$	$10{,}09^{Ac} \pm 0{,}68$	$46.53^{Aa} \pm 2.54$	$38.78^{Bb} \pm 2.19$
Ultrasound[3]	$11.45^{Acd} \pm 0.09$	$10{,}27^{Ac} \pm 0{,}56$	$234.11^{Aa} \pm 22.66$	$117.12^{Ab} \pm 18.20$

[1]Values expressed as means (n = 3). [2]mgGAE/100 g. [3]mmolTE/100 g. In each line, different capital letters indicate significant differences ($p \leq 0.05$, *t-student*). In each column, different lowercase letters indicate significant differences ($p \leq 0.05$, *t-student*).

Table 2 Content of unsaponified and saponified carotenoids in organic and conventional dried goji fruits.

Carotenoids[1] (mg/100g)	Retention time (min)	Organic	Retention time (min)	Conventional
Unsaponified				
(all-*E*)-lutein	5.30	$0.16^{Ac} \pm 0.02$	5.42	$0.13^{Ac} \pm 0.03$
(all-*E*)-zeaxanthin	7.62	$0.28^{Ab} \pm 0.04$	7.69	$0.24^{Ab} \pm 0.06$
Saponified				
(all-*E*)-zeaxanthin	8.28	$8.36^{Aa} \pm 0.15$	8.05	$6.61^{Ba} \pm 0.03$

[1]Values expressed as means and standard deviation (n = 3). In each line, different capital letters indicate significant differences ($p \leq 0.05$, *t-student*). In each column, different lowercase letters indicate significant differences ($p \leq 0.05$, ANOVA).

853 **Table 3** Ascorbic acid content in organic and conventional goji fruits.

Ascorbic acid[1]	Goji berry	
(mg/100 g)	Organic	Conventional
Total ascorbic acid	$101.83^{Aa} \pm 2.24$	$80.46^{Ba} \pm 1.85$
L-ascorbic acid	$34.88^{Bc} \pm 1.99$	$40.87^{Ab} \pm 1.34$
L-dehidroascorbic acid	$66.95^{Ab} \pm 4.24$	$39.60^{Bb} \pm 0.52$

854 [1]Values expressed as means and standard deviation (n = 3). In each line, different capital letters indicate
855 significant differences ($p \leq 0.05$, *t-student*). In each column, different lowercase letters indicate significant
856 differences ($p \leq 0.05$, ANOVA).
857

Table 4 Fatty acid composition of organic and conventional goji berry[1].

Fatty acids	Organic (%)	Conventional (%)
Lauric acid (C12:0)	ND	ND
Myristic acid (C14:0)	0.12 ± 0.01	0.21 ± 0.01
Palmitic acid (C16:0)	13.47 ± 0.02	15.89 ± 0.03
Palmitoleic acid (C16:1)	0.39 ± 0.02	0.52 ± 0.02
Stearic acid (C18:0)	2.65 ± 0.01	2.94 ± 0.01
Oleic acid (C18:1*n*9c)	20.61 ± 0.02	19.58 ± 0.01
Linoleic acid (C18:2*n*6c)	52.47 ± 0.02	49.85 ± 0.01
Linolenic acid *n*-3 (C18:3*n*3)	1.90 ± 0.01	1.64 ± 0.03
Linolenic acid *n*-6 (C18:3*n*6)	5.20 ± 0.01	4.24 ± 0.08
Arachidic acid (C20:0)	0.49 ± 0.07	0.73 ± 0.02
Arachidonic acid (C20:4*n*6)	1.41 ± 0.08	1.12 ± 0.10
Behenic acid (C22:0)	0.72 ± 0.02	0.68 ± 0.08
Docosadienoic acid cis-13,16 (C22:2)	1.58 ± 0.09	1.29 ± 0.05
Lignoceric acid (C24:0)	0.98 ± 0.08	0.82 ± 0.05
SFA	18.43 ± 0.08	21.27 ± 0.05
MFA	21.01 ± 0.05	20.10 ± 0.09
PFA	62.56 ± 0.10	58.14 ± 0.06
UFA	83.57	78.24
PFA/SFA ratio	3.39	2.73
Ômega-6/ômega-3 ratio	0.13	0.12

858 SFA - satured fatty acids; MFA - monounsatured fatty acids; PFA polyunsatured fatty acids; UFA unsatured
859 fatty acids (MFA + PFA). ND - not detected.
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Table 5 Thermal stability data (TG/DTG) of the oil extracted from the goji berry

Goji berry	Step	Δm (%)	ΔT (ºC)	Tp (ºC)
Conventional	1st	6.4	30-174	82.9
	2nd	49.7	174-395	372.3
	3rd	31.0	395-500	428.6
	4th	10.2	500-646	544.5
Organic	1st	1.2	30-130	70.0
	2nd	57.1	130-403	370.0
	3rd	27.4	403-489	429.5
	4th	13.0	489-620	518.6

867 TG = thermogravimetry; DTG = derived from thermogravimetry; Δm (%) = mass variation; ΔT (ºC) =
868 temperature variation; Tp (ºC) = peak temperature.
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