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Analysis of volatile compounds, betaine, and antioxidant effect in goji berry (*Lycium barbarum* L.) powder extracted by various drying methods and extraction solvents

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ABSTRACT

Goji berry (*Lycium barbarum* L.), a deciduous solanaceous shrub, were subjected to extraction using five solvents (water, 50% and 70% ethanol, and 50% and 70% methanol) and dried using two methods: freeze drying (FD) and spray drying (SD). To investigate the chemical properties of these various goji berry powders, an examination was conducted on the content of volatile compounds, betaine, antioxidant effect, total phenolic content (TPC), and total flavonoid compounds (TFC) ($p < 0.05$). The total volatile compound content was highest in SD powder with 50% ethanol extract, showing a 66.7% increase over the control. The betaine content was in the range of 9.25–31.9 mg/g dry weight, and it exhibited a significant increase with higher water concentration in the extraction solvent. Betaine, total phenolic compounds and total flavonoid compounds showed a significant increase in the sequence of SD followed by FD ($p < 0.05$). Overall, the SD sample showed superior benefits when evaluating volatile compounds, betaine, and antioxidant effect. SD was more suitable for drying goji berry, as it retains its appearance and biological activity.

1. Introduction

Goji berry (*Lycium barbarum* L.) is a deciduous solanaceous shrub and is known to inhabit mainly Tibet, China, and several Asian countries. The fruit is called wolfberry or goji berry. In various Asian regions, it serves as conventional medicine and functional material for food (Skenderidis et al., 2019). Goji berry is gaining popularity due to its health advantages, such as enhancing kidney and liver function, providing cytoprotective and antioxidant effects, and regulating the immune system (Chang and So, 2008). Previous studies have shown that goji berries are rich in vitamins, minerals, and betaine, in addition to bioactive compounds, including polysaccharides, carotenoids, and phenolic compounds (Benchennouf et al., 2017). These compounds are responsible for fruity flavor, and their concentration can affect sensory properties. In addition, comprehension of the health advantages of goji berries has been enhanced through antioxidant assays, clinical trials, and in vivo studies (Jiang et al., 2021).

Betaine is one of the significant functional alkaloids in goji berries. It has a variety of biological effects, such as neuroprotective activity, and anti-inflammatory activity (Chiu et al., 2010). Additionally, betaine content is related to the sweetness of goji berries (Qian et al., 2017). Betaine serves as an indicator for quality assessment of *Lycium* species in the Korean Pharmacopoeia (KP) and Chinese Pharmacopoeia (ChP). To date, a number of analytical techniques have been devised for the quantification of betaine in goji berries, including high-performance liquid chromatography-ultra-violet (HPLC-UV), liquid chromatography-mass spectrometry/mass spectrometry (LC-MS/MS), gas chromatography-mass spectrometry (GC-MS), and thin layer chromatography (TLC) scanning (Liu et al., 2020). However, the complicated extraction process of ChP makes it difficult to achieve effective recovery, and TLC scanning with low resolution and sensitivity, is not acceptable for the quantitative analysis of betaine (Liu et al., 2020). Consequently, it is crucial to devise an effective and simple method for analyzing the betaine content in goji berries.

Fresh goji is sold as dried or powdered fruits because of the short period of harvesting and storage. Drying enhances the stability of vegetables and fruits by decreasing the moisture content and inhibiting microbial growth and physicochemical changes. The drying process not only reduces transportation and storage costs but also extends the shelf life of food (Önal et al., 2019). Freeze drying (FD) and spray drying (SD)

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are commonly used in the food industry, among the various drying techniques developed to date. Each drying method has advantages and disadvantages and has its own unique characteristics. FD (freeze drying) dehydration operates through the process of ice sublimation at low pressure. It can assist in preserving product quality, such as color, flavor, and nutrition. However, it comes with drawbacks, including high production cost, long processing time, and high energy consumption. SD (spray drying) is a technique that provides a dry powder by quickly evaporating moisture at high temperatures. SD is cost-effective due to its high yield and fast drying speed (Zhao et al., 2015). Despite these positive aspects, high inlet temperatures can result in thermal breakdown of materials sensitive to heat and considerable loss of volatile compounds.

Flavor and functionality are important factors that affect the quality of products using goji berries and have a significant impact on consumers' product preference. Several existing studies are mainly on the characteristics of goji berry according to various cultivars and origins, as well as the characteristics of fermented wolfberry (Jiang et al., 2021; Liu et al., 2020). Unlike previous studies, this study focused on the flavor and antioxidant capacity of goji berry depending on the extraction solvent and drying method.

In the study, goji berry powder was dissolved in five solvents (water, 50% and 70% ethanol, and 50% and 70% methanol) for extraction, and then dried using two drying methods (FD and SD). To investigate the chemical properties of these various goji berry powders, an examination was conducted on the content of volatile compounds, betaine, antioxidant effect, total phenolic content (TPC), and total flavonoid compounds (TFC). This study provides practical information on the changes in volatile compounds, betaines, and antioxidant activity of dry powders with different extraction solvents and drying methods.

2. Materials and methods

2.1. Chemical reagents and materials

Goji berry (*Lycium barbarum* L.) harvested in 2022 was obtained from Jindo Nonghyup in Korea. It was grounded for 30 s with a commercially available food grinder and stored at −80 °C until analysis. For the analysis of volatile compounds, C7–C40 n-alkane standard, 1,2-dichlorobenzene, and divinylbenzene/carboxen/polydimethylsiloxane (50 μm DVB/CAR/PDMS) solid-phase microextraction (SPME) fiber were obtained from Supelco Inc. (Bellefonte, PA, USA).

Deionized water, methanol, ethanol, acetonitrile, and dichloromethane (HPLC-grade) were obtained from J.T. Baker (Philipsburg, NJ, USA). Betaine, Folin–Ciocalteu reagent, antioxidant activity reagents such as 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2′-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). All chemicals and reagents used in the study were of analytical grade.

2.2. Extraction process

The extraction process was performed following a previous study (Park et al., 2022). Ground goji berries (20 g) were extracted with 600 mL of extraction solvent (water, 50% and 70% ethanol, and 50% and 70% methanol) at 80 °C for 120 min. The supernatant of the extract was collected by centrifugation (6500 g, 10 min). It was filtered through a Whatman filter paper (0.45 μm). The concentration of the filtrate was performed under reduced pressure using a rotary evaporator (60 °C) to vaporize extraction solvent (ethanol or methanol).

2.3. Drying process

2.3.1. FD

The FD process was followed by the previous study (Park et al., 2022). The sample extract was frozen at −80 °C using a deep freezer (ZABA, Ilsinbiobase, Seoul, Korea) for more than 1 h. The frozen extract was dried using a freeze dryer (FD-8508, Ilsin Lab Co., Seoul, Korea) at −75 °C for 4 d. The dried goji berry powders were then stored in a deep freezer until analysis.

2.3.2. SD

The SD process was followed by the previous reference (Zhao et al., 2015). SD was conducted using a spray dryer (SD-1010, Buchi, Flawil, Switzerland) with a sample flow rate of 5 mL/min and an air speed of 5.8 m^3/min. The inlet air temperature was set at 170 °C. The dried goji berry powders were then stored in a deep freezer until analysis.

2.4. Analysis of volatile compounds in goji berry powder

The analysis of volatile compounds in goji berry powders was conducted using the headspace solid-phase microextraction coupled with a gas chromatography-mass detector (HS-SPME-GC/MS) method published previously (Han et al., 2022). Prior to analysis, the fibers were conditioned by heating to 270 °C in the GC injection port for 25 min. A total of 1.5 g of each sample and 1 g of NaCl were added into a 20 mL headspace vial. Additionally, 10 μL of 1,2-dichlorobenzene (10 μg/mL) was used as an internal standard. Following the equilibrium step (70 °C, 40 min, 400 rpm), a needle of preconditioned SPME fiber was exposed into the headspace of the vials (2.0 cm deep) above the sample at 70 °C for 45 min. After that, the fiber needle was inserted into the GC injection port for thermal desorption of the volatile compounds at 250 °C for 5 min.

The analysis was conducted using an Agilent 7820 A gas chromatography-mass spectrometry detector 5977 E (Agilent, Santa Clara, CA, USA) and a DB-WAX UI column (60 m × 0.25 mm x 0.25 μm, J&W Scientific, Folsom, CA, USA) was used for separating the volatile compounds. Helium was used as the carrier gas at a constant flow of 1.0 mL/min. Sample injection into the GC column was carried out in splitless mode. The oven temperature was set at 40 °C for 3 min, and then increased to 100 °C at 3 °C/min and held for 3 min. Then the temperature was raised to 160 °C at 2 °C/min and held for 5 min, and finally increased to 240 °C at a rate of 6 °C/min, where it was maintained for 5 min before being cooled back to 40 °C. The scan range of the mass spectrometer detector was 35–550 m/z. The temperatures of the detector and MS ion source were 250 °C and 230 °C, respectively.

The amount of volatiles was calculated by peak area ratio (PAR: relative ratio of each volatile with internal standard) and qualitative analysis of the volatile compounds was performed using two identification methods (Choi et al., 2023). (Skenderidis et al., 2019) Comparison of the compound mass spectrum and its respective RI with the reference value and the RI from the NIST spectra library (MassHunter Workstation Software, NIST08, Wiley) (Chang and So, 2008). The retention index (RI) was determined by using a series of n-alkanes ranging from C7 to C40 as reference values in the DB-WAX UI method. The approximate amount of each volatile compound in the samples was estimated by comparing each peak area with that of the internal standard obtained from the total-ion chromatograms. For precision and accuracy, all experiments were performed thrice by the same analyst using uniform equipment and reagents. Results are presented as the mean ± standard deviation.

2.5. Analysis of betaine in goji berry powder by HPLC-UV

2.5.1. Preparation of sample solutions

Sample preparation for betaine analysis was performed following the methodology outlined in a previous study conducted by Liu et al. (2020). A total of 25 mL of dichloromethane was added to 0.5 g of goji berry powder and refluxed using a water bath (60 °C, 30 min). The extract was cooled and filtered through filter paper. The filtrate was removed, and the residue was extracted with 25 mL of 80% methanol (pH 1.0, adjusted with hydrochloric acid) by refluxing in a water bath (80 °C, 30 min). The extract was cooled and filtered using a Whatman filter paper.

Concentration of the filtrate was carried out using a rotary evaporator (75 °C), and the residue was dissolved in 2 mL of 80% methanol. The supernatant was filtered using a solid phase extraction cartridge (Bond Elut Al, Agilent technology) and 40 mL of ethanol with 5% NH_4OH was added. The solution was evaporated and then mixed with 10 mL of ethanol. Filtration of the supernatant was performed using a 0.45 μm PTFE-O syringe filter.

2.5.2. Instrumentation and chromatographic conditions

The analysis of betaine content in goji berries was conducted using a HPLC 1200 series system of Agilent Technologies (Santa Clara, Ca, USA) equipped with a UV–visible detector. The chromatography was performed using a Poroshell 120 HILIC column (4.6 × 150 mm, 4 μm). The column was thermostated at 40 °C. The mobile phase was composed of acetonitrile/water (70:30, v/v) at a flow rate of 1.3 mL/min. The injection volume was 20 μL, and the detection wavelength was 195 nm.

2.6. Total phenolic content (TPC) and total flavonoid content (TFC)

Sample extraction was performed as described by (Park et al., 2022). A total of 0.1 g of goji berry powder was added with 10 mL of a solution of methanol/water (80:20) and mixed for more than 12 h. The extract was then re-extracted by dissolving in the same extraction solvent and filtered using a 0.45 μm PTFE-O syringe filter.

TPC was determined using the Folin-Ciocalteu assay (Ratseewo et al., 2019) with a slight modification. A total of 0.3 mL of sample extract was mixed with 2.25 mL of 10% Folin-Ciocalteu reagent and reacted for 5 min. Subsequently, 2.25 mL of 6% Na_2CO_3 solution was added. The mixture was reacted for 90 min, after which measurement of the absorbance was performed at 725 nm. Calibration curves were constructed using gallic acid solutions ranging from 1 to 200 mg/L. The TPC was expressed as milligrams of gallic acid equivalents (GAE) per gram of dry weight (DW) (mg GAE/g DW).

TFC was determined using the aluminum chloride colorimetric method described by (Siriamornpun et al., 2012). A total of 0.5 mL of sample extract was mixed with 150 μL of 5% $NaNO_3$ solution and 2.25 mL of water. After reaction for 6 min, 300 μL of 10% $AlCl_3 \cdot 6H_2O$ solution was added and incubated for 5 min, and 100 μL of NaOH solution was added. The measurement of the absorbance was performed at 510 nm. The results were expressed as mg of quercetin equivalents (QCE) per g of dry weight (DW) (mg QCE/g DW).

2.7. Antioxidant effect of goji berry powder

Sample extraction, as well as DPPH and ABTS radical scavenging assays, were conducted following the method outlined by (Komonsing et al., 2022) with slight modifications. A total of 0.1 g of dried goji berry powder was combined with 10 mL of methanol using a shaker for 10 s. Subsequently, the mixture was subjected to ultrasonic treatment in a bath for 15 min at 35 °C. Following ultrasonication, the mixture was centrifuged at 4500 g for 10 min, and the resulting supernatant was collected. The residue was subjected to two additional extraction cycles, and the resulting extract was filtered using a 0.45 μm PTFE-O syringe filter.

For the DPPH radical scavenging assay, 0.1 mL of the sample was combined with 3.9 mL of 0.1 mM DPPH reagent. The aliquots were allowed to incubate for 30 min in the dark. The absorbance was then measured at 517 nm.

For the ABTS radical scavenging assay, a 7 mM ABTS reagent was mixed with 2.6 mM $Na_2S_2O_8$ solution in equal volume and reacted for 12 h in the dark. The ABTS solution was diluted with methanol to adjust an absorbance of 1.000 ± 0.020. The 980 μL of ABTS solution was mixed with 20 μL of each sample and reacted for 2 h in the dark. The absorbance was then measured at 734 nm.

2.8. Color measurement

The color value of goji berry powder was measured with a colorimeter (Nipon Denshoku Industries Co., Ltd., Tokyo, Japan). A total of 5 g of each sample was placed on the Petri dish and read in three replicates. The L* value [light (L* = 100) and dark (L* = 0)], a* value [red (+) and green (−)], and b* value [yellow (+) and blue (−)] were measured. The total color change (Δ*E*), Chroma (*C**), Hue (H*) and browning index (BI) were calculated using Equations (Skenderidis et al., 2019; Chang and So, 2008; Benchennouf et al., 2017; Jiang et al., 2021), respectively (Abd El-Baset W and Almoselhy, 2023):

$$\Delta E = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2} \quad (1)$$

$$C^* = \sqrt{(\Delta a*)^2 + (\Delta b*)^2} \quad (2)$$

$$H^* = \tan^{-1}\,[b^*/a^*] \quad (3)$$

$$BI = 100/0.17\ ((a^*+1.75L^*)/(5.645\ L^*+a^*-0.012\ b^*)-0.31) \quad (4)$$

2.9. Statistical analysis

All experiments were carried out in triplicate (n = 3) and all quantitative data were expressed as mean ± standard deviation. To compare significant differences between data, the data were analyzed using one-way ANOVA and Duncan's multiple range test ($P < 0.05$) using IBM SPSS statistics 27 (IBM, Armonk, NY, USA). The principal component analysis (PCA) was performed using XLSTAT (v.2021, Addinsoft, Paris, France), and the distribution of the samples was visualized according to the various extraction and drying methods. A hierarchical cluster heatmap analysis was performed to express the similarities and differences between the samples.

3. Results and discussion

3.1. Analysis of volatile compounds in goji berry powder by GC-MS

Tables 1–3 and Fig. S1 show the types and concentrations of the identified volatile compounds. Fig. S2 is a total ion chromatogram of volatiles in the control isolated using headspace SPME (solid-phase microextraction); red arrows indicate internal standards (1,2-dichlorobenzene). A total of 45 volatile compounds were identified in a total of 11 samples. These include six acids, five alcohols, eight aldehydes, three esters, four furans, eleven terpenes, and eight others. However, the control group consisted of 20 compound combinations, including three acids, five alcohols, four aldehydes, one ester, six terpenes, and one other. The dried goji berry powder consisted of combinations of 18–29 volatile compounds. These results indicate that the choice of drying method and extraction solvent influence the type of volatile compounds in goji berries.

It is known that d-limonene has significant biological effects, including antioxidant properties, anti-cancer and anti-inflammatory activity (Miller et al., 2011). Safranal (2,6,6-trimethyl cyclohexane-1, 3-dien-1-carboxaldehyde) is the main distinctive compounds in the dried stigmas of *Crocussatibus* L. and has been shown to possess antioxidant and immunomodulatory properties (Chen et al., 2015). These volatile compounds are essential for improving the storage safety and nutritional value of goji berries, as well as providing the necessary sensory cues for humans. Previous studies have shown that 2-pentylfuran, linalool, ethyl octanoate, methyl salicylate, hexyl acetate, nonanal, (E)-2-hexenal, hexanal, 1-hexanol, isoamylol, 1-octen-3-ol, beta-elemene,beta-cyclocitral, d-limonene, and o-cymene were aromatic volatiles characteristic of Ningxia goji fruit (Lu et al., 2017).

The FD process reduced the content of total volatile compounds by

Table 1
Volatile compounds in the goji berry samples.

No.	Volatile compounds	KI	KI (Ref.)	Odor description	Identification method
Acids					
1	Acetic acid	1450	1450	Sour, vinegar	MS, KI, Co
2	Propanoic acid	1537	1537	Rancid	MS, KI
3	2-Methylbutanoic acid	1678	1677	Sweet, fruity	MS, KI
4	Hexanoic acid	1847	1847	Goat	MS, KI
5	Crotonic acid	1992	1991	Dairy	MS, KI
6	Octanoic acid	2074	2073	Fruity acid,	MS, KI
Alcohols					
7	3-Methyl butanol	1216.9	1216.9	Disagreeable	MS, KI
8	1-Octen-3-ol	1458	1458	Mushroom	MS, KI, Co
9	2-Nonanol	1527	1528	Cucumber	MS, KI
10	Benzenemethanol	1888	1888	Roasted bread	MS, KI
11	Benzeneethanol	1919	1919	Rose	MS, KI
Aldehydes					
12	Butanal, 3-methyl-	926	926	Apple	MS, KI
13	Hexanal	1091	1091	Green leaves	MS, KI, Co
14	Nonanal	1400	1400	Orange-rose	MS, KI
15	2-Octenal	1435	1435	Green-leafy	MS, KI
16	Methional	1462	1462	Onion, meat	MS, KI
17	Furfural	1469	1469	Almond	MS, KI
18	Benzaldehyde	1532	1532	Almond	MS, KI, Co
19	2-Phenyl-2-butenal	1964	1964	Cocoa, roast	MS, KI
Esters					
20	Butanoic acid, methyl ester	1126	1126	Apple	MS, KI
21	Hexanoic acid, hexyl ester	1543	1543	Apple peel	MS, KI
22	Butanoic acid, butyl ester	1864	1864	Floral	MS, KI
Furans					
23	2-Acetylfuran	1543	1536	Cocoa	MS, KI, Co
24	5-Methylfurfural	1574	1574	Caramellike	MS, KI
25	Furfuryl alcohol	1679	1679	Faint burning	MS, KI
26	Furaneol	2049	2049	Pineapple	MS, KI
Terpenes					
27	beta-Pinene	1119	1118	Piney	MS, KI
28	Limonene	1202	1202	Pleasant lemon	MS, KI, Co
29	1,8-Cineole	1223	1223	Camphor	MS, KI
30	Nerol oxide	1476	1473	Flower	MS, KI
31	Linalool	1549	1549	Floral, wood	MS, KI
32	Safranal	1658	1648	Herb	MS, KI
33	alpha-Terpineol	1707	1707	Peach, sweet	MS, KI
34	Zingiberene	1769	1769	Spicy	MS, KI
35	Ar-curcumene	1784	1784	Clove, curry	MS, KI
36	p-Cymen-8-ol	1852	1852	Celery	MS, KI
37	beta-Turmerone	2210	2210	Clove, curry	MS, KI
Others					
38	Tetramethylpyrazine	1483	1483	Cocoa, coffee	MS, KI, Co
39	Methyl nicotinate	1792	1793	Heat	MS, KI
40	Methyl salicylate	1804	1804	Almond	MS, KI
41	Guaiacol	1891	1891	Sweet, smoke	MS, KI
42	2-Acetylpyrrole	1977	1977	Nutty, cherry	MS, KI
43	p-Vinylguaiacol	2203	2203	Clove, curry	MS, KI
44	2-Methoxy-4-vinylphenol	2201	2201	Woody, peanut	MS, KI
45	2,3-Dihydro-3,5-dihydroxy-6-methyl-4h-pyran-4-one	2223	2225	Burnt sugar	MS, KI

1) Kovats retention index on DB-WAX UI in NIST database.
2) Odor description was obtained from the literature.
3) Identification methods: MS = Comparison with mass spectrum (MS) in Wiley Library; KI = Kovats Retention Index obtained from NIST database on DB-WAX UI; Co=Co-injection with authentic chemicals.

16.2% on average. A previous study (Krokida and Philippopoulos, 2006) showed that the volatiles in goji berry extract were reduced in FD mainly due to ice sublimation. During this phase, volatile compounds with vapor pressures greater than that of water molecules are removed from the frozen material and evaporated when the sample matrix exceeds the glass transition temperature (Chin et al., 2008).

SD decreased the total volatile compounds by 0.3% on average compared to the control group, while 50 ESD increased them by 60% in comparison with the control. This result contrasts with the previous studies of coffee extract (Ishwarya and Anandharamakrishnan, 2015) and durian pulp (Chin et al., 2008), where FD retained more volatile compounds than SD. 2-Acetylfuran, furaneol, and butanoic acid methyl esters are characteristic volatile compounds found only in SD. This suggests that in the SD process, these compounds may be formed under the influence of in-process heating.

The concentration of volatile compounds according to the extraction solvent was the highest in the order of water > methanol > ethanol. Beta-pinene was detected only in the control. Furfuryl alcohol, furaneol, 5-methyl furfural, and 2-acetyl furan were detected only in the methanol extracts (50 MFD, 70 MFD, 50MSD, and 70MSD). Terpenes such as limonene and ar-curcumene decreased or disappeared in the FD and SD samples, and aldehydes and others such as 3-methylbutanal and 2-acetylpyrrole increased compared to the control. Tetramethylpyrazine, methyl nicotinate, and guaiacol were found only in the FD samples. Regarding the type and change in the content of these volatile compounds, it seems that the difference between the presence or absence of drying and the drying method changes the characteristic flavor of goji berry powders.

Table 2
Peak area ratio (PAR) of volatile compounds in goji berry powder according to the various extraction solvents and freeze-drying.

No.	Compounds	Control	Freeze drying				
			WFD	50 EFD	70 EFD	50 MFD	70 MFD
Acids							
1	Acetic acid	N.D	N.D	0.122 ± 0.007 ^{a}	0.15 ± 0.01 ^{a}	0.35 ± 0.02 ^{c}	0.44 ± 0.02 ^{d}
2	Propanoic acid	N.D	N.D	N.D	N.D	0.080 ± 0.008 ^{a}	0.12 ± 0.01 ^{b}
3	2-Methylbutanoic acid	0.20 ± 0.01 ^{d}	0.13 ± 0.01 ^{bc}	0.12 ± 0.01 ^{b}	0.099 ± 0.005 ^{a}	N.D	0.23 ± 0.02 ^{e}
4	Hexanoic acid	0.12 ± 0.01 ^{b}	0.19 ± 0.02 ^{c}	0.13 ± 0.01 ^{b}	0.130 ± 0.006 ^{b}	0.50 ± 0.03 ^{d}	0.42 ± 0.04 ^{d}
5	Crotonic acid	N.D	0.034 ± 0.003 ^{a}	N.D	N.D	N.D	N.D
6	Octanoic acid	0.050 ± 0.003 ^{ab}	0.24 ± 0.01 ^{f}	0.13 ± 0.01 ^{de}	0.101 ± 0.003 ^{cd}	0.51 ± 0.02 ^{h}	0.47 ± 0.04 ^{g}
Total acids	0.37 ± 0.02	0.60 ± 0.01	0.51 ± 0.02	0.482 ± 0.005	1.43 ± 0.02	1.67 ± 0.03	
Alcohols							
7	3-Methyl butanol	0.31 ± 0.02 ^{b}	0.09 ± 0.01 ^{a}	N.D	N.D	N.D	N.D
8	1-Octen-3-ol	0.33 ± 0.01 ^{a}	1.77 ± 0.06 ^{b}	N.D	N.D	N.D	N.D
9	2-Nonanol	0.096 ± 0.006 ^{a}	0.130 ± 0.002 ^{b}	N.D	N.D	N.D	N.D
10	Benzenemethanol	0.142 ± 0.007 ^{bc}	0.163 ± 0.006 ^{c}	0.121 ± 0.008 ^{b}	N.D	0.44 ± 0.03 ^{d}	0.28 ± 0.02 ^{d}
11	Benzeneethanol	0.71 ± 0.06 ^{d}	0.41 ± 0.03 ^{c}	0.26 ± 0.02 ^{b}	0.204 ± 0.004 ^{b}	1.27 ± 0.05 ^{e}	1.28 ± 0.08 ^{e}
Total alcohols	1.59 ± 0.02	2.55 ± 0.02	0.38 ± 0.01	0.204 ± 0.004	1.71 ± 0.04	1.56 ± 0.05	
Aldehydes							
12	3-methyl-Butanal	0.22 ± 0.02 ^{a}	0.81 ± 0.06 ^{cd}	0.59 ± 0.02 ^{bc}	2.74 ± 0.06 ^{e}	0.41 ± 0.03 ^{ab}	0.33 ± 0.03 ^{a}
13	Hexanal	0.053 ± 0.006 ^{b}	0.114 ± 0.009 ^{f}			0.07 ± 0.01 ^{c}	0.070 ± 0.005 ^{de}
14	Nonanal	0.22 ± 0.03 ^{e}	0.149 ± 0.009 ^{d}	0.019 ± 0.002 ^{a}	0.100 ± 0.005 ^{c}	0.234 ± 0.009 ^{e}	0.083 ± 0.008 ^{bc}
15	2-Octenal	N.D	N.D	N.D	N.D	0.039 ± 0.002 ^{b}	0.062 ± 0.003 ^{c}
16	Methional	N.D	N.D	N.D	N.D	0.042 ± 0.003 ^{b}	0.029 ± 0.002 ^{a}
17	Furfural	N.D	N.D	0.047 ± 0.003 ^{ab}	0.031 ± 0.003 ^{ab}	0.66 ± 0.02 ^{d}	0.66 ± 0.06 ^{d}
18	Benzaldehyde	0.053 ± 0.005 ^{b}	0.39 ± 0.03 ^{f}	0.029 ± 0.002 ^{a}	0.024 ± 0.002 ^{a}	0.10 ± 0.01 ^{c}	0.127 ± 0.008 ^{d}
19	2-Phenyl-2-butenal	N.D	0.174 ± 0.009 ^{e}	N.D	N.D	N.D	N.D
Total aldehydes	0.54 ± 0.02	1.63 ± 0.06	0.683 ± 0.004	2.897 ± 0.004	1.55 ± 0.06	1.36 ± 0.05	
Esters							
20	Methyl butyrate	N.D	N.D	N.D	N.D	N.D	N.D
21	Hexyl hexanoate	0.34 ± 0.03 ^{c}	0.45 ± 0.03 ^{e}	0.49 ± 0.03 ^{e}	0.24 ± 0.02 ^{b}	N.D	N.D
22	Butyl butyrate	N.D	N.D	N.D	0.091 ± 0.002 ^{b}	N.D	N.D
Total esters	0.33 ± 0.03	0.45 ± 0.03	0.49 ± 0.03	0.32 ± 0.01	N.D	N.D	
Furans							
23	2-Acetylfuran	N.D	N.D	N.D	N.D	N.D	N.D
24	5-Methylfurfural	N.D	N.D	N.D	N.D	0.031 ± 0.002 ^{a}	0.033 ± 0.003 ^{a}
25	Furfuryl alcohol	N.D	N.D	N.D	N.D	0.23 ± 0.02 ^{b}	0.10 ± 0.01 ^{a}
26	Furaneol	N.D	N.D	N.D	N.D	N.D	N.D
Total furans	N.D	N.D	N.D	N.D	0.23 ± 0.01	0.103 ± 0.007	
Terpenes							
27	beta-Pinene	0.127 ± 0.005 ^{a}	N.D	N.D	N.D	N.D	N.D
28	Limonene	0.59 ± 0.07 ^{b}	N.D	N.D	N.D	0.080 ± 0.005 ^{a}	0.061 ± 0.003 ^{a}
29	1,8-Cineole	0.70 ± 0.06 ^{b}	0.40 ± 0.01 ^{a}	N.D	N.D	N.D	N.D
30	Nerol oxide	N.D	N.D	N.D	N.D	0.038 ± 0.004 ^{a}	0.054 ± 0.002 ^{b}
31	Linalool	N.D	0.049 ± 0.001 ^{b}	N.D	N.D	0.074 ± 0.004 ^{c}	0.088 ± 0.007 ^{d}
32	Safranal	N.D	0.241 ± 0.009 ^{a}	0.24 ± 0.02 ^{a}	0.50 ± 0.02 ^{d}	N.D	N.D
33	alpha-Terpineol	N.D	0.20 ± 0.06 ^{c}	0.018 ± 0.001 ^{a}	N.D	N.D	0.046 ± 0.004 ^{b}

(*continued on next page*)

Table 2 (*continued*)

No.	Compounds	Control	Freeze drying				
			WFD	50 EFD	70 EFD	50 MFD	70 MFD
34	Zingiberene	0.108 ± 0.008 [b]	0.058 ± 0.002 [a]	0.098 ± 0.009 [b]	N.D	N.D	N.D
35	ar-Curcumene	3.1 ± 0.2 [b]	N.D	N.D	N.D	N.D	N.D
36	p-Cymen-8-ol	0.101 ± 0.007 [a]	N.D	N.D	N.D	0.29 ± 0.02 [c]	0.25 ± 0.01 [b]
37	beta-Turmerone	N.D	0.093 ± 0.007 [a]	0.090 ± 0.002 [a]	0.266 ± 0.007 [c]	N.D	0.161 ± 0.008 [b]
	Total terpenes	4.68 ± 0.06	1.03 ± 0.01	0.442 ± 0.008	0.77 ± 0.01	0.478 ± 0.008	0.659 ± 0.006
Others							
38	Tetramethylpyrazine	N.D	N.D	N.D	N.D	0.32 ± 0.03 [b]	0.024 ± 0.002 [a]
39	Methyl nicotinate	N.D	N.D	N.D	N.D	0.111 ± 0.006 [a]	0.147 ± 0.005 [b]
40	Methyl salicylate	N.D	1.07 ± 0.03 [e]	0.9 ± 0.1 [d]	0.58 ± 0.01 [c]	0.29 ± 0.02 [a]	0.199 ± 0.005 [a]
41	Guaiacol	N.D	N.D	N.D	N.D	0.048 ± 0.004 [a]	0.059 ± 0.005 [b]
42	2-Acetylpyrrole	0.028 ± 0.003 [a]	0.19 ± 0.02 [c]	0.13 ± 0.01	0.115 ± 0.004 [b]	0.127 ± 0.004 [b]	0.134 ± 0.007 [b]
42	2-Acetylpyrrole	0.028 ± 0.003 [a]	0.19 ± 0.02 [c]	0.13 ± 0.01	0.115 ± 0.004 [b]	0.127 ± 0.004 [b]	0.134 ± 0.007 [b]
43	p-Vinylguaiacol	N.D	N.D	0.28 ± 0.02 [d]	0.20 ± 0.02 [b]	N.D	N.D
44	2-Methoxy-4-vinylphenol	N.D	0.28 ± 0.02 [b]	0.31 ± 0.03 [b]	N.D	0.46 ± 0.04 [c]	0.43 ± 0.03 [c]
45	2,3-Dihydro-3,5-dihydroxy-6-methyl-4h-pyran-4-one	N.D	N.D	N.D	N.D	0.12 ± 0.02 [a]	0.19 ± 0.01 [b]
	Total others		0.028 ± 0.003	1.55 ± 0.02	1.58 ± 0.04	0.89 ± 0.07	1.47 ± 0.02
	Total		7.6 ± 0.4 [de]	7.8 ± 0.3 [ef]	4.14 ± 0.05 [a]	6.13 ± 0.08 [b]	7.0 ± 0.2 [cd]

1) All values are shown as mean ± S.D. (standard deviation) (n = 3).
2) Lowercase letters (series "a-h") indicate significant (Duncan's range test, $p < 0.05$) differences in the same row.
3) N.D: Not detection.

The content of volatile compounds changed both qualitatively and quantitatively after FD and SD. SD can improve the characteristic flavor of dried goji berries more than FD. For example, it increases the content and number of aldehydes and other total aroma components. This suggests that, from an aroma point of view, SD is a superior drying method for goji berries. The reason for the difference in volatile content between the control and manufactured samples is largely due to the extraction and drying method. Because it was extracted and dried at a high temperature, oxidation of fatty acids and Maillard reaction occurred during the extraction process. Due to this reaction, most of the volatile components in the dried sample after extraction would have developed a sweeter flavor compared to the control group. This is also the reason why there are more furans in dried samples after extraction with organic solvents than in hot water. The second is the drying method. Spray drying is a method of spraying and drying extracts at high temperatures. It is presumed that the high temperature during the drying process promotes the Maillard reaction, which is why the volatile content of furans is higher in SD than in FD.

Heat maps and dendrograms were used to visualize differences and similarities between samples for 45 volatile compounds. Heat maps and dendrograms of the volatile compounds are shown in Fig. S3. In the dendrogram, volatile compounds and samples were grouped respectively in terms of similarity or proximity. WFD had the highest similarity to the control, and samples with the same drying method had the highest similarity.

A PCA was performed on the data set to analyze the influence of the drying method on the grouping of the goji berry samples. The two-dimensional bi-plots of the loading and scoring of the dried samples are shown in Fig. 1. The first two principal components (PCs) accounted for 30.28% and 22.34% of the total variance, respectively. The cumulative contribution of PC1 and PC2 accounted for 52.62%, which explained most of the variation in the data set. Sample grouping can be found in the PCA bi-plot. The control samples were found on the upper left of the X-axis, whereas most of the FD and SD samples were found on the lower left of the X-axis, suggesting that there may be significant differences in volatile compounds between control and dried goji berries. The fact that the extracts are grouped shows that there may be differences in volatile compounds depending on the type of extract. Most likely, alcohols contributed more to the control samples, while aldehydes and furans were associated with the FD and SD samples.

3.2. Analysis of betaine in goji berry powder by HPLC-UV

This study investigated the betaine content of dried goji berry powder. The retention time for betaine was found to be 2.9 min. The analytes showed linearity ($R^2 = 0.9999$) at a concentration range of 1–5000 μg/mL (Fig. 2). The findings of this study revealed that the betaine content in dried goji berry powders was influenced by various extraction solvents and drying methods.

The betaine content ranged from 9.25 to 31.9 mg/g DW. The highest betaine content was observed in the WSD sample with 31.9 mg/g DW, while the control sample exhibited the lowest content with 9.25 mg/g DW. The betaine content increased significantly as the water content in the extraction solvent increased with the same drying method ($p < 0.05$). The reason why the betaine content in goji berry powder extracted with water is higher than that extracted with organic solvent can be explained as follows. At the same extraction temperature, betaine is known to have a high solubility in the order of 2-propanol < n-butanol < n-propanol < ethanol < methanol < water. The solubility of betaine in binary mixtures, either water or ethanol + methanol, increases with the content of water or methanol at a given temperature. These results could stem from the polarity of the pure and mixed solvents, or from the intermolecular hydrogen bonding between water or alcohol and betaine (Wang et al., 2012).

3.3. Analysis of antioxidant effect

Antioxidants are crucial for the body's defense against free radicals,

Table 3
Peak area ratio (PAR) of volatile compounds in goji berry powder according to the various extraction solvents and spray drying.

No.	Compounds	Control	Spray drying				
			WSD	50 ESD	70 ESD	50MSD	70MSD
Acidsrowhead							
1	Acetic acid	N.D	0.207 ± 0.001 [b]	0.59 ± 0.06 [e]	0.24 ± 0.02 [b]	0.25 ± 0.02 [b]	0.22 ± 0.02 [b]
2	Propanoic acid	N.D	N.D	N.D	N.D	0.075 ± 0.006 [a]	0.11 ± 0.01 [b]
3	2-Methylbutanoic acid	0.20 ± 0.01 [d]	0.092 ± 0.001 [a]	0.15 ± 0.01 [c]	N.D	N.D	0.092 ± 0.005 [a]
4	Hexanoic acid	0.12 ± 0.01 [b]	0.205 ± 0.007 [c]	N.D	0.046 ± 0.003 [a]	0.202 ± 0.008 [c]	N.D
5	Crotonic acid	N.D	0.086 ± 0.002 [b]	0.12 ± 0.01 [c]	0.027 ± 0.003 [a]	N.D	0.09 ± 0.01 [b]
6	Octanoic acid	0.050 ± 0.003 [ab]	0.146 ± 0.005 [e]	0.072 ± 0.007 [bc]	0.029 ± 0.004 [a]	0.11 ± 0.01 [cd]	0.15 ± 0.02 [e]
Total acids		0.37 ± 0.02	0.736 ± 0.004	0.92 ± 0.04	0.338 ± 0.003	0.63 ± 0.01	0.648 ± 0.003
Alcoholsrowhead							
7	3-Methyl butanol	0.31 ± 0.02 [b]	N.D	N.D	N.D	N.D	N.D
8	1-Octen-3-ol	0.33 ± 0.01 [a]	N.D	N.D	N.D	N.D	N.D
9	2-Nonanol	0.096 ± 0.006 [a]	N.D	N.D	N.D	N.D	N.D
10	Benzenemethanol	0.142 ± 0.007 [bc]	0.12 ± 0.01 [b]	N.D	N.D	N.D	0.054 ± 0.006 [a]
11	Benzeneethanol	0.71 ± 0.06 [d]	N.D	N.D	N.D	0.075 ± 0.002 [a]	0.24 ± 0.03 [b]
Total alcohols		1.59 ± 0.02	0.12 ± 0.01	N.D	N.D	0.075 ± 0.002	0.29 ± 0.02
Aldehydesrowhead							
12	Butanal, 3-methyl-	0.22 ± 0.02 [a]	3.1 ± 0.1 [f]	6.4 ± 0.1 [i]	0.87 ± 0.02 [d]	4.6 ± 0.2 [h]	3.8 ± 0.3 [g]
13	Hexanal	0.053 ± 0.006 [b]	0.08 ± 0.09 [e]	N.D	N.D	0.026 ± 0.001 [a]	0.028 ± 0.006 [a]
14	Nonanal	0.22 ± 0.03 [e]	0.074 ± 0.001 [b]	0.066 ± 0.003 [b]	0.156 ± 0.007 [d]	N.D	N.D
15	2-Octenal	N.D	N.D	N.D	0.060 ± 0.007 [c]	N.D	0.031 ± 0.003 [a]
16	Methional	N.D	0.050 ± 0.001 [c]	0.076 ± 0.003 [d]	0.051 ± 0.001 [c]	0.050 ± 0.005 [c]	0.038 ± 0.003 [b]
17	Furfural	N.D	0.095 ± 0.004 [b]	0.19 ± 0.01 [c]	0.063 ± 0.001 [ab]	1.17 ± 0.02 [f]	0.8 ± 0.1 [e]
18	Benzaldehyde	0.053 ± 0.005 [b]	0.058 ± 0.001 [b]	0.074 ± 0.006 [b]	0.069 ± 0.002 [b]	0.13 ± 0.01 [d]	0.17 ± 0.02 [e]
19	2-Phenyl-2-butenal	N.D	0.108 ± 0.001 [d]	0.20 ± 0.01 [f]	0.058 ± 0.003 [a]	0.017 ± 0.007 [b]	0.089 ± 0.008 [c]
	Total aldehydes	0.54 ± 0.02	3.56 ± 0.03	6.96 ± 0.02	1.326 ± 0.006	6.01 ± 0.04	4.995 ± 0.006
Estersrowhead							
20	Butanoic acid, methyl ester	N.D	N.D	N.D	N.D	0.155 ± 0.004 [b]	0.137 ± 0.008 [a]
21	Hexanoic acid, hexyl ester	0.34 ± 0.03 [c]	0.186 ± 0.009 [a]	0.38 ± 0.02 [d]	0.49 ± 0.01 [e]	N.D	N.D
22	Butanoic acid, butyl ester	N.D	0.134 ± 0.005 [c]	N.D	0.43 ± 0.03 [d]	N.D	0.046 ± 0.006 [a]
	Total esters	0.34 ± 0.03	0.319 ± 0.007	0.38 ± 0.02	0.92 ± 0.02	0.155 ± 0.004	0.183 ± 0.007
Furansrowhead							
23	2-Acetylfuran	0.141 ± 0.008 [a]	0.20 ± 0.01 [c]	N.D	0.262 ± 0.007 [d]	0.18 ± 0.02 [b]	0.141 ± 0.008 [a]
24	5-Methylfurfural	N.D	N.D	N.D	0.161 ± 0.006 [c]	0.13 ± 0.02 [b]	N.D
25	Furfuryl alcohol	N.D	N.D	N.D	N.D	0.12 ± 0.01 [a]	N.D
26	Furaneol	0.076 ± 0.006 [d]	0.087 ± 0.006 [e]	0.303 ± 0.002 [a]	0.059 ± 0.002 [d]	0.046 ± 0.001 [b]	0.076 ± 0.006 [d]
	Total furans	N.D	0.217 ± 0.007	0.285 ± 0.008	0.030 ± 0.002	0.321 ± 0.005	0.34 ± 0.01
Terpenesrowhead							
27	beta-Pinene	0.127 ± 0.005 [a]	N.D	N.D	N.D	N.D	N.D
28	Limonene	0.59 ± 0.07 [b]	N.D	N.D	N.D	N.D	0.07 ± 0.01 [a]
29	1,8-Cineole	0.70 ± 0.06 [b]	N.D	N.D	N.D	N.D	N.D
30	Nerol oxide	N.D	N.D	N.D	N.D	N.D	N.D
31	Linalool	N.D	N.D	N.D	N.D	0.029 ± 0.001 [a]	0.055 ± 0.007 [b]
32	Safranal	N.D	0.27 ± 0.02 [b]	0.330 ± 0.006 [c]	N.D	N.D	N.D
33	alpha-Terpineol	N.D	N.D	N.D	N.D	N.D	N.D
34	Zingiberene	0.108 ± 0.008 [b]	0.097 ± 0.001 [b]	N.D	0.23 ± 0.01 [c]	N.D	N.D
35	ar-Curcumene	3.1 ± 0.2 [b]	N.D	N.D	0.082 ± 0.006 [a]	N.D	0.041 ± 0.006 [a]
36	p-Cymen-8-ol	0.102 ± 0.007 [a]	N.D	N.D	N.D	N.D	N.D
37	beta-Turmerone	N.D	N.D	N.D	N.D	N.D	N.D
	Total terpenes	4.67 ± 0.06	0.36 ± 0.01	0.330 ± 0.006	0.315 ± 0.008	0.029 ± 0.001	0.162 ± 0.008
Othersrowhead							
38	Tetramethylpyrazine	N.D	N.D	N.D	N.D	N.D	N.D
39	Methyl nicotinate	N.D	N.D	N.D	N.D	N.D	N.D
40	Methyl salicylate	N.D	N.D	0.41 ± 0.03 [b]	N.D	N.D	N.D
41	Guaiacol	N.D	N.D	N.D	N.D	N.D	N.D
42	2-Acetylpyrrole	0.028 ± 0.003 [a]	0.73 ± 0.03 [f]	1.10 ± 0.06 [g]	0.141 ± 0.006 [bc]	0.61 ± 0.02 [e]	0.45 ± 0.05 [d]
43	p-Vinylguaiacol	N.D	0.25 ± 0.01 [c]	0.32 ± 0.02 [e]	0.114 ± 0.006 [a]	N.D	N.D

(*continued on next page*)

Table 3 (*continued*)

No.	Compounds	Control	Spray drying				
			WSD	50 ESD	70 ESD	50MSD	70MSD
44	2-Methoxy-4-vinylphenol	N.D	N.D	N.D	N.D	0.27 ± 0.03 [b]	0.19 ± 0.03 [a]
45	2,3-Dihydro-3,5-dihydroxy-6-methyl-4h-pyran-4-one	N.D	0.65 ± 0.04 [d]	0.75 ± 0.09 [e]	0.31 ± 0.02 [c]	N.D	N.D
	Total others	0.028 ± 0.003	1.62 ± 0.03	2.57 ± 0.05	0.56 ± 0.01	0.88 ± 0.03	0.64 ± 0.04
	Total	7.6 ± 0.4 [de]	6.97 ± 0.08 [cd]	11.4 ± 0.3 [g]	3.6 ± 0.1 [a]	8.3 ± 0.1 [f]	7.4 ± 0.6 [de]

1) All values are shown as mean ± S.D. (standard deviation) (n = 3).
2) Lowercase letters (series "a-h") indicate significant (Duncan's range test, $p < 0.05$) differences in the same row.
3) N.D: Not detection.

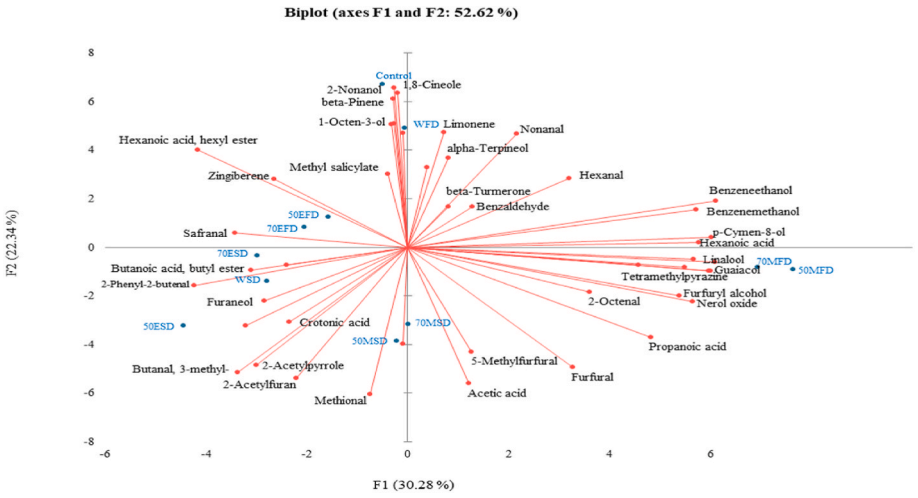
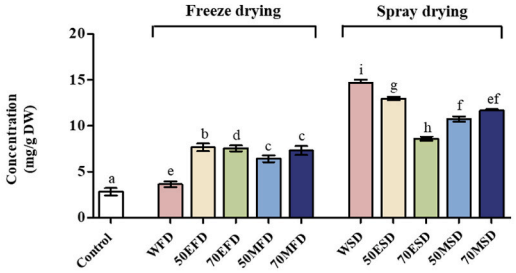


Fig. 1. Principle component analysis (Bi-plot) of the volatile compounds in goji berry powder according to the various extraction solvents and drying methods.1) Lowercase letters (series "a-i") indicate significantly (Duncan's range test, $p < 0.05$) differences in total volatile compounds. 2) WFD: water extraction and freeze drying, EFD: ethanol extraction and freeze drying, MFD: methanol extraction and freeze drying, WSD: water extraction and spray drying, ESD: ethanol extraction and spray drying, MSD: methanol extraction and spray drying.



1) Lowercase letters (series "a-i") indicate significantly (Duncan's range test, $p < 0.05$) differences in total volatile compounds.
2) WFD: water extraction and freeze drying, EFD: ethanol extraction and freeze drying, MFD: methanol extraction and freeze drying, WSD: water extraction and spray drying, ESD: ethanol extraction and spray drying, MSD: methanol extraction and spray drying

Fig. 2. The concentration of betaine from goji berry powder according to the various extraction solvents and drying methods.

and goji berries are well-known for their abundant antioxidant content (Yildiz et al., 2015). The antioxidant effect of the dried goji berry powder was assessed using DPPH and ABTS radical scavenging assays. Trolox was used as a standard for the analysis and exhibited a high degree of linearity ($R^2 = 0.9998$ and 0.9997) within the concentration ranges of 0–200 μg/mL and 0–400 μg/mL, respectively. The results of the DPPH and ABTS assays for the dried goji berry samples are shown in Table 4. It was observed that the DPPH and ABTS values of the dried goji berry powder were significantly influenced by the choice of extraction solvent and drying method.

DPPH is a stable free radical that forms a violet solution in ethanol at room temperature. The presence of antioxidant molecules leads to a reduction in absorbance at 517 nm, indicating a decrease in the DPPH radical and the formation of a colorless solution (Fernandes et al., 2014). Phenolic compounds, in general, contribute significantly to the antioxidant effect of many plants, and a higher TPC is associated with greater antioxidant capacity. The variations in the observed results may attributed to differences in the effectiveness of various phenolic compounds as antioxidants (Ismail et al., 2004).

The results of the DPPH and ABTS radical scavenging assay in this study were consistent with a previous study conducted on the control group (Song et al., 2018), with reported values of Trolox/DW 2.8 mg and Trolox/DW 14.6 mg, respectively. In the case of DPPH, the dried powder showed concentrations ranging from 3.64 to 14.7 mg Trolox/DW. Within each drying method, the organic solvent extracts exhibited higher values compared to the water extracts. This difference can be attributed to the varying polarities of the solvents used for extraction, leading to different amounts of dissolved phenolic compounds (Tepsongkroh et al., 2019). Furthermore, when comparing the drying methods, the SD goji berries exhibited higher antioxidant effect than the FD samples. These results may be due to the reaction of heat during drying with the various phenolic compounds present in goji berries (Saikia et al., 2015). In addition, high-temperature SD can increase antioxidant effect by forming high molecular weight brown peptide bonds known as melanoidin (Vashisth et al., 2011). Previous studies have shown that high-temperature processing, either alone or in combination with other natural phenolic compounds, can enhance antioxidant effect by promoting the Maillard reaction. In addition, drying can remove moisture and concentrate bioactive compounds. Similar results were reported for dried apricots through hot air drying at 55 °C and 75 °C, which showed increased antioxidant effect at higher temperatures (Madrau et al., 2009).

Table 4
DPPH, ABTS, TPC, and TFC contents in goji berry powder according to the various extraction solvents and drying methods.

Sample		DPPH (mg Trolox/g DW)	ABTS (mg Trolox/g DW)	Total phenolic content (mg GAE/g DW)	Total flavonoid content (mg QCE/g DW)
Control		2.8 ± 0.4 [a]	14.6 ± 0.3 [a]	8.3 ± 0.1 [a]	13.3 ± 0.3 [a]
Freeze drying	Water	3.64 ± 0.37 [b]	18.1 ± 0.2 [b]	13.6 ± 0.1 [b]	31 ± 2 [e]
	50% Ethanol	7.7 ± 0.4 [d]	32 ± 2 [e]	19.3 ± 0.2 [e]	25 ± 2 [c]
	70% Ethanol	7.6 ± 0.3 [d]	25 ± 1 [cd]	15.85 ± 0.04 [c]	20 ± 1 [b]
	50% Methanol	6.4 ± 0.4 [c]	23.3 ± 0.3 [c]	15.8 ± 0.3 [c]	26 ± 1 [c]
	70% Methanol	7.3 ± 0.5 [d]	25.8 ± 0.8 [d]	17.1 ± 0.3 [d]	29 ± 1 [de]
Spray drying	Water	14.7 ± 0.5 [i]	43.5 ± 0.8 [i]	27.9 ± 0.2 [j]	30 ± 1 [de]
	50% Ethanol	13.0 ± 0.2 [h]	41.4 ± 0.3 [h]	26.41 ± 0.02 [i]	27 ± 2 [cd]
	70% Ethanol	8.6 ± 0.2 [e]	31.6 ± 0.7 [e]	25.5 ± 0.1 [h]	31 ± 2 [e]
	50% Methanol	10.9 ± 0.5 [f]	34 ± 1 [f]	23.1 ± 0.3 [f]	26 ± 1 [c]
	70% Methanol	11.7 ± 0.2 [g]	36 ± 2 [g]	23.9 ± 0.1 [g]	26 ± 2 [c]

1) All values are represented as mean ± standard deviation (S.D.) (n = 3).
2) Different superscript letters in the same column denote significant differences (Duncan's range test, $p < 0.05$).

3.4. TPC and TFC

For the analysis of TPC and TFC, gallic acid (GAE) and quercetin (QCE) showed linearity ($R^2 = 0.9991$ and 0.9992, respectively) within the concentration ranges of 5–400 μg/mL and 1–400 μg/mL, respectively. The TPC and TFC contents of the dried goji berry samples are listed in Table 4. The drying method and extraction solvent has a significant effect on the TPC and TFC of the dried goji berry powder.

The TPC and TFC of the sample without extraction and drying were 8.3 mg GAE/g DW and 13.3 mg QCE/g DW, respectively, which was consistent with the findings of (Song et al., 2018). The contents of TFC and TFC varied depending on the extraction solvent, with the organic solvent extract showing higher values compared to the water extract under the same drying methods. This disparity arises from the greater solubility of phenolic compounds in less polar solvents than in water (Pinelo et al., 2005).

The TPC content ranged from 8.3 to 27.9 mg GAE/DW, and the value obtained by SD was higher than that of FD ($p < 0.05$). The phenol content can be attributed to oxidation and the destruction of cell membranes and cell walls caused by heat treatment. FD, with lower oxygen exposure, is more prone to enzymatic oxidation by polyphenol oxidase and peroxidase. In addition, damage to cell structures due to ice crystal formation can promote the loss of phenolic compounds, and long drying times at low temperatures can lead to the decomposition of phenolic compounds (Nunes et al., 2016). Heat treatment results in a decrease in water content, leading to an alteration in the three-dimensional structure of the cell wall. This change reduces the affinity of polyphenols for the cell wall and disrupts the covalent or non-covalent interactions between the cell wall matrix and polyphenols. Ultimately, it leads to the destruction of plant cell wall polymers (Le et al., 2005).

The TFC exhibited a similar trend to the TPC, with values ranging from 13.3 to 31 mg QCE/g DW. The TFC significantly increased after drying, and SD had a higher average value than FD. Previous studies with orange juice have suggested that the increase in TFC is due to reactions or structural degradation of various phenolic compounds that occur during high-temperature SD (Saikia et al., 2015). It was reported that drying processes generally result in the decomposition of flavonoids. But, this study indicates that SD is a technique that can preserve flavonoids (Kim et al., 2021).

3.5. Color value

It is well known that high temperatures during the drying process can significantly degrade qualities such as color. The color measurement of dried goji berry powder was conducted in reflection mode with a colorimeter in triplicate. The results regarding the color of goji berry powder extracted using various solvents and drying methods are detailed in Table 5.

The L* value represents the brightness of the sample, while +a* indicates redness and –a* indicates greenness. Similarly, +b* represents yellowness and –b* represents blueness. In this study, the control group had L*, a*, and b* values of 38.06, 25.75, and 38.66, respectively. The L* values were significantly increased ($p < 0.05$) in the FD and SD powders compared to the control, indicating that the drying process lightens the color of the product appearance. The a* values of the FD and SD powders decreased significantly, and changes in the L* and a* values indicated that the samples darkened (Saxena et al., 2012). This may be related to the Maillard reaction, caramelization, or discoloration (Zou et al., 2013). This is because the pigment is decomposed by high-temperature heat during the SD process, resulting in a large loss of red pigment (Tuyen et al., 2010). Previous studies have shown that it is difficult to maintain the red color of carrots (Chen et al., 1995) and tomatoes (Shi et al., 1999) when the drying temperature is increased. The ΔE value was used to determine the overall color difference between samples, and the FD and SD powder values were higher than those of the control group. This is because, as mentioned above, the L* value increased and the a* value decreased. H* values in FD and SD powders were significantly higher than those in the control group ($p < 0.05$). This indicates a shift in the dominant wavelength of light defining the perceived color, resulting in a change in the color's appearance (Pridmore, 2011). The BI values of SD powder were significantly higher than those of FD powder, except in the cases of water and 50% methanol as extraction solvents. This can be attributed to various factors such as changes in drying temperature and air velocity that affect the drying rate of the sample (Ndukwu, 2009). The drying process significantly affects the color of the sample.

The drying process significantly affects the color of the sample.

4. Conclusions

In this study, goji berry powder prepared using drying methods (FD and SD) and five extraction solvents (water, 50% and 70% ethanol, and 50% and 70% methanol) were analyzed. The levels of volatile compounds, betaine, antioxidant effect, TPC, and TFC were confirmed in a total of 11 samples, including the control group. Antioxidant effect, TPC, and TFC rose significantly with increasing concentration of ethanol and methanol in the extraction solvent ($p < 0.05$). The betaine content, antioxidant effect, TPC, and TFC showed higher values in the SD powder than in the FD powder. In conclusion, SD powder after extraction with 50% ethanol is a processing method that can increase volatile compounds, betaine content, and antioxidant effect.

Ethics approval and consent to participate

Not applicable.

Table 5
Color values of goji berry powder according to the various extraction solvents and drying methods.

Sample		Color value						
		L*	a*	b*	ΔE*	C*	H*	BI
Control		38.06 ± 0.05 [a]	25.75 ± 0.05 [j]	38.66 ± 0.02 [f]	60.06 ± 0.01 [a]	46.45 ± 0.05 [k]	56.34 ± 0.06 a	43.87 ± 0.08 j
Freeze drying	Water	54.49 ± 0.03 [c]	10.30 ± 0.03 [a]	31.45 ± 0.03 [a]	63.75 ± 0.01 [b]	33.09 ± 0.04 [a]	71.86 ± 0.04 f	13.39 ± 0.05 d
	50% Ethanol	56.32 ± 0.03 [f]	11.61 ± 0.02 [d]	35.59 ± 0.02 [b]	67.63 ± 0.01 [c]	37.43 ± 0.08 [b]	71.94 ± 0.03 g	14.56 ± 0.03 e
	70% Ethanol	57.58 ± 0.01 [g]	12.06 ± 0.02 [f]	35.57 ± 0.01 [b]	68.75 ± 0.01 [e]	37.56 ± 0.01 [c]	71.27 ± 0.04 e	14.78 ± 0.03 f
	50% Methanol	56.03 ± 0.02 [e]	11.71 ± 0.03 [e]	36.16 ± 0.03 [c]	67.71 ± 0.02 [d]	38.01 ± 0.06 [d]	72.06 ± 0.04 h	14.76 ± 0.04 f
	70% Methanol	60.22 ± 0.01 [i]	10.60 ± 0.02 [b]	37.80 ± 0.02 [d]	71.89 ± 0.05 [i]	39.26 ± 0.02 [e]	74.34 ± 0.03 k	12.53 ± 0.02 b
Spray drying	Water	62.52 ± 0.01 [j]	11.72 ± 0.01 [d]	38.43 ± 0.01 [e]	74.29 ± 0.01 [j]	40.13 ± 0.03 [f]	73.24 ± 0.00 i	13.14 ± 0.00 c
	50% Ethanol	54.87 ± 0.01 [d]	14.09 ± 0.03 [h]	41.35 ± 0.03 [i]	70.93 ± 0.02 [f]	43.92 ± 0.06 [i]	70.32 ± 0.07 c	18.81 ± 0.06 h
	70% Ethanol	53.21 ± 0.02 [b]	16.45 ± 0.03 [i]	43.29 ± 0.03 [j]	70.55 ± 0.01 [g]	46.31 ± 0.03 [j]	69.20 ± 0.03 b	21.41 ± 0.01 i
	50% Methanol	67.39 ± 0.04 [k]	11.09 ± 0.03 [c]	38.96 ± 0.02 [h]	78.62 ± 0.01 [k]	40.50 ± 0.07 [g]	74.11 ± 0.01 j	11.73 ± 0.00 a
	70% Methanol	58.70 ± 0.01 [h]	13.82 ± 0.02 [g]	38.79 ± 0.02 [g]	71.70 ± 0.07 [h]	41.18 ± 0.06 [h]	70.40 ± 0.04 d	16.52 ± 0.02 g

1) All values are represented as mean ± standard deviation (S.D.) (n = 3).
2) Different superscript letters in the same column denote significant differences (Duncan's range test, $p < 0.05$).

Consent for publication

Not applicable.

Availability of data and material

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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CRediT authorship contribution statement

Subeen Do: Formal analysis, Investigation, Methodology. **Yuri Kim:** Methodology. **Jonggab Yim:** Methodology. **Kwang-Geun Lee:** Supervision, Validation, Investigation, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Not applicable.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2024.100798.

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