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Assessment of the bioaccessibility of phenolic compounds and antioxidant activity in raw and pickled white cabbage and gherkins

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PAPER

Abstract

White cabbage and gherkin are vegetables that are widely consumed as pickles as well as raw vegetables. In this research, we explored the effect of pickling on the bioaccessibility of phenolics and flavonoids and changes in antioxidant activity after *in vitro* digestion. In general, the pickling process enhances the bioaccessibility of phenolics and flavonoids in white cabbage and gherkin. The bioaccessibility of total phenolics (TP) in cabbages, pickled cabbages, gherkins, and pickled gherkins is determined as 125.2%, 185.1%, 369.2%, and 462%, respectively. In contrast, after *in vitro* digestion of raw and pickled vegetables, total antioxidant activity is reduced. So it can be concluded that both raw and pickled gherkins are good sources of bioaccessible phenolics and flavonoids. The consumption of these vegetables and their pickles is suggested to promote the reduction of diseases plagued by free radicals.

Keywords: antioxidant; bioaccessibility; cabbage; gherkin; phenolics; pickle

Introduction

White cabbage and gherkin are consumed substantially throughout the world. White cabbage and gherkin are the most popular pickles and are consumed in raw form. In the United States, 245.85 million Americans consumed pickles in 2020. It is expected to increase to 251.03 million in 2023 (Statistica Research Department, 2022). The size of the global market for packed pickles, which was 7.9 billion in 2018, is expected to increase at a compound annual growth rate (CAGR) of 3.5% until 2025 (Grand View Research, 2019). Global consumption of cabbages and other brassicas, both raw and pickled, was 70.7 million tonnes in 2015 (Indexbox, 2016a). In 2015, 78.5 million tons of gherkins and cucumbers, both raw and pickled, were consumed globally (Indexbox, 2016b). In 2015, import and export volumes of pickled gherkins and cucumbers were 557.000 and 554.300 tonnes, respectively (Indexbox, 2016c).

Oxidative stress causes the formation of free radicals and other reactive oxygen species, which are involved in many diseases, particularly chronic degenerative diseases such as cancer, diabetes, cardiovascular disease, and obesity. As a result, reactive compounds must be quenched by antioxidants. Phenolic compounds are secondary metabolites of plants and have antioxidant properties. Phenolic compounds have several groups such as flavonoids, lignans, and phenolic acids. Flavonoids is comprised of quercetin, kaempferol, lutein, and naringenin. Some of phenolic acids are gallic acid, chlorogenic acid, and syringic acid (Tapia-Hernández *et al.*, 2018; Del-Toro-Sánchez *et al.*, 2021; Maribel Perez-Perez *et al.*, 2018). Gherkins and white cabbages have several antioxidant compounds, which can be categorized into phenolic compounds and non-phenolic compounds. As shown in Figure 1, the main antioxidant compounds in gherkin are flavonoids, tannins, triterpenes, alkoloids, and saponins (Mohamed *et al.*, 2022; Omokhua-Uyi *et al.*, 2020;

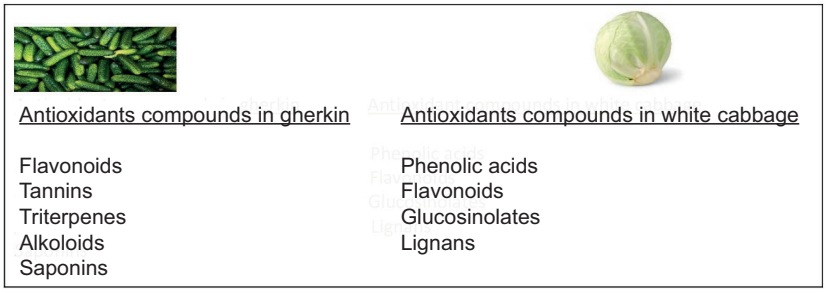

Figure 1. Antioxidant compounds in gherkin and white cabbage.

Dimitry *et al.*, 2022; Murthy *et al.*, 2022). The main antioxidant compounds in white cabbage are phenolic acids, flavonoids, lignans, and glucosinolates (Kuljarachanan *et al.*, 2021; Demir *et al.*, 2023; Tao *et al.*, 2019; Zhou *et al.*, 2022; Cvetković *et al.*, 2019).

These vegetables are healthy due to their phenolic content and antioxidant properties (Sayın *et al.*, 2015; Song *et al.*, 2010; Bahorun *et al.*, 2004). Phenolic compounds have antiviral, anti-allergic, antiplatelet, anti-inflammatory, antitumor, and antioxidant properties (Yao *et al.*, 2004). To exploit these benefits for humans, phenolic compounds should be bioaccessible and bioavailable. Bioaccessibility is the fraction of a compound that can reach the intestine by passing through the intestinal barrier.

Although the bioaccessibility of phenolics in different cabbage species has been studied previously (Kaulmann *et al.*, 2016; Tomas *et al.*, 2021), no studies about the bioaccessibility of phenolics and changes in antioxidant activity during simulated gastrointestinal digestion for white cabbages, pickled white cabbages, gherkins, and pickled gherkins have been reported in the literature. Our hypothesis is that the fermentation process loosens other molecules in the food matrix and allows the bound phenolics to be released from the cell wall, as depicted in Figure 2. On the other hand, fermentation can degrade vulnerable phenolics, and the bioaccessible fraction can be decreased.

Therefore, the objective of this research was to assess the effect of the pickling process on the bioaccessibility of phenolics and antioxidant activity in cabbage and gherkin. For achieving this objective, the total phenolic content (TPC), total flavonoid content (TFC), and antioxidant activity (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt [ABTS], 2,2-diphenyl-1-picrylhydrazyl [DPPH], and ferric reducing antioxidant power [FRAP]) were determined before and after *in vitro* digestion.

Materials and Methods

Chemicals

Phenolphtalein, sodium carbonate, catechin, 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ), iron(II) sulphate, 2,2-diphenyl-1-picrylhydrazyl (DPPH), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), potassium persulfate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, haemoglobin, Tris (hydroxymethyl) aminomethane (Trizma base), p-toluene sulfonyl-L-arginine methyl ester (TAME), pepsin, pancreatin, bile salt, methanol (≥%99.9), hyperoside and 4-hydroxybenzoic acid (4-HBA) standards were purchased from Sigma

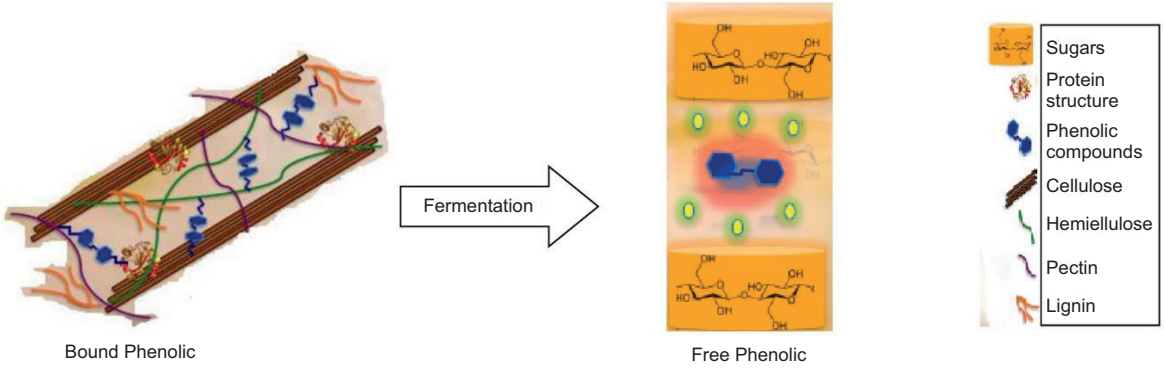

Figure 2. Conversion of bound phenolics to free phenolics by fermentation (Maribel Perez-Perez *et al.*, 2018).

Aldrich (USA). Sodium hydroxide, potassium chromate, silver nitrate, sodium chloride, De Man Rogosa and Sharpe (MRS) agar, formic acid, Folin-Ciocelteau, gallic acid, sodium nitrite, aluminium chloride, sodium hydroxide, sodium acetate trihydrate, glacial acetic acid, hydrochloric acid, iron(III) chloride, and calcium chloride dihydrate were obtained from Merck. Potassium chloride and ammonium carbonate were acquired from Riedel-de Haen (Germany). Sodium bicarbonate, magnesium chloride dihydrate, and acetonitrile (≥99.9%) were purchased from Carlo Elba (France). Pefabloc was obtained from Acros (USA). SM-199 *Lactobacillus plantarum* culture was purchased from Chris Hansen (Germany).

Cabbages and gherkins

Cabbage and gherkin samples were purchased from a local market in Manisa, Turkey. Small and firm cabbages and gherkins ranging in length from 3 to 6 cm were selected.

Pickling procedure

Cabbages and gherkins were placed into 660 mL jars with brine composed of 6% salt and 0.05% vinegar. Cabbage and gherkin brine were adjusted to 10^5 and 10^6 cfu/mL lactic acid bacteria (LAB), respectively, by using Chris Hansen SM-199 *Lactobacillus plantarum* culture, respectively. The weights of the vegetables and composition of the brine in the jar is shown in Table 1. Titratable acidity, pH, salt analyses, and total LAB counts were performed in brines and pickles.

Extraction of phenolic compounds

The extraction procedure reported by (Bovy *et al.*, 2002) was used with slight modifications. Samples were ground in a Waring blender, and 4 g of each sample was then homogenized in 10 mL of 75% methanol and incubated for 15 min in an ultrasonic water bath. Afterward, samples were subjected to a 2000 g, 10 min, 4°C centrifugation procedure. The extraction procedure was repeated three times, with the second and third extractions that included the addition 5 mL of 75% methanol. The supernatants were transferred to a plastic container, resulting in a final volume of 20 mL by adding 75% methanol. For further analysis, extracts were stored at −86 °C.

Table 1. Formulation of pickles in a jar.

	Cabbage pickle	Gherkin pickle
Weight of the vegetables (g)	245 ± 2	310 ± 2
Volume of brine (mL)	295	250
Volume of the culture solution (mL)	10	10
Total volume of brine (mL)	305	260
Volume of the jar (mL)	660	660

In vitro gastrointestinal digestion

The *in vitro* gastrointestinal digestion of samples was performed following the method described by (Minekus *et al.*, 2014), which involves oral, gastric, and intestinal phases. The only difference is that no salivary α-amylase was used in our protocol. Pepsin and pancreatin activity analyses were performed according to (Minekus *et al.*, 2014).

Note that 5 g of each sample were grounded in a Waring blender to mimic chewing process and mixed with 3.5 mL simulated saliva fluid (SSF), which was composed of 15.1 mmol/L KCl, 3.7 mmol/L KH_2PO_4, 13.6 mmol/L $NaHCO_3$, 0.15 mmol/L $MgCl_2(H_2O)_6$, and 0.06 mmol/L $(NH_4)_2CO_3$. The mixture was then mixed with 25 µL of 0.3 M $CaCl_2(H_2O)_2$. Afterward, the pH was adjusted to 7, and distilled water was added to make a total volume of 10 mL. In order to complete oral digestion, the mixture was shaken for 2 min at 100 rpm in a 37°C shaking incubator.

Following oral digestion, gastric digestion procedures were carried out immediately. To the oral bolus, 7.5 mL of simulated gastric fluid (SGF), containing 6.9 mmol/L KCl, 0.9 mmol/L KH_2PO_4, 25 mmol/L $NaHCO_3$, 47.2 mmol/L NaCl, 0.1 mmol/L $MgCl_2(H_2O)_6$, and 0.5 mmol/L $(NH_4)_2CO_3$ was added. Then, pepsin enzyme of 2000 U/mL activity and 5 µL of 0.3 M $CaCl_2(H_2O)_2$ were added, and the pH was adjusted to 3 with 6 M HCl. Then 20 mL of total volume was obtained by adding distilled water. Samples are kept in a shaking incubator at 100 rpm, 37˚C for 2 h to mimic gastric conditions.

Intestinal digestion was performed immediately after gastric digestion. 11 mL simulated intestinal fluid (SIF), which was composed of 6.8 mmol/L KCl, 0.8 mmol/L KH_2PO_4, 85 mmol/L $NaHCO_3$, and 38.4 mmol/L NaCl, and 0.33 mmol/L $MgCl_2(H_2O)_6$ was added to the gastric bolus. Then, pancreatin enzyme (100 U/mL tripsin activity), 10 mM bile extract, and 40 µL of 0.3 M $CaCl_2(H_2O)_2$ were added to gastric bolus and pH was adjusted to 7 with 1 M NaOH. Then, distilled water was added to make a total volume of 40 mL. Finally, samples were incubated for 2 h in a shaking incubator at 100 rpm and 37˚C to simulate intestinal conditions.

After all digestion procedures were completed, the enzyme reactions were halted by adding 150 mM Pefabloc enzyme inhibitor to the digested samples. The digested samples were subjected to 4000 rpm, 10 min, 4°C centrifugation procedure. The supernatant that remains on top was transferred to sample tubes and stored at –86˚C until further analysis.

Total phenolic content (TPC)

TPCs were assessed using the Folin-Ciocelteau technique with some modifications as described by (Miceli *et al.*, 2009). Then, 100 mL of appropriately diluted sample extract was combined with 200 mL of 0.2 N Folin-Ciocelteau reagent. Then, 1 mL of 6% $NaCo_3$ solution and 2 mL of pure deionized water were added and vortexed. The mixture was incubated at room temperature for 2 h before the absorbance at a wavelength of 765 nm was measured with a Multiskan GO UV/Vis Microplate Spectrophotometer (Thermo Fisher Scientific, USA). The results are given as milligrams of gallic acid equivalents (GAE) per 100 g of fresh weight (FW).

Total flavonoid content (TFC)

TFCs were determined using the method provided by (Dewanto *et al.*, 2002) with some changes. A total of 250 µL of appropriately diluted sample extract was combined with 1.25 mL of pure deionized water. After adding 75 µL of sodium nitrite and letting it sit for 6 min, 150 µL of aluminium chloride was then added. After 5 min, a total mixture amount of 2.5 mL was obtained by adding 0.5 mL NaOH and pure deionized water. Prior to the measurement of the absorbance at 510 nm with a Multiskan GO UV/Vis Microplate Spectrophotometer (Thermo Fisher Scientific, USA), the mixture was vortexed. The results are presented as milligrams of catechin equivalents (CEs) per 100 g of FW.

Total antioxidant activity (TAA)

Three different methods, ABTS, DPPH, and FRAP, were used to measure the total TAA.

The ABTS method was applied (Miller *et al.*, 1997) with various adjustments. Different extract volumes (1–20 µL) were combined with pure deionized water to create a final volume of 20 µL. Following the addition of 180 µL of ABTS, the absorbance at 734 nm was measured after 30 s. The identical procedure was carried out for the control using 20 µL of pure deionized water. Using 20 µL Trolox standards, the same procedure was also carried out.

This is how the percentage inhibition of ABTS was determined:

$$\text{Inhibition of ABTS } (\%) = \frac{(A_{control} - A_{sample})}{A_{control}} \times 100$$

where $A_{control}$ = absorbance of the control solution and A_{sample} = absorbance of the sample solution.

A graph showing the inhibition of the ABTS (%)-amount of sample (mg) was created for each sample. The inbition of the ABTS (%)-amount of Trolox (µg) plot was also created. The ABTS antioxidant activity was estimated by dividing the slope of the sample graph by the slope of the Trolox graph. The results were expressed as Mg Trolox equivalents/100 g of sample.

With some adjustments, the DPPH method was assayed in accordance with (Brand-Williams *et al.*, 1995; Singh *et al.*, 2002). A final volume of 200 µL was created by mixing different extract volumes (1, 10, 25, and 50 µL) with 75% methanol. Then, 3.8 mL DPPH solution was added. After 30 min of incubation, the absorbance of the mixtures was measured at a wavelength of 515 nm. The identical procedure was carried out for the control using 200 µL of pure deionized water. The same procedure was also carried out by using 200 µL Trolox standards.

The percent inhibition of DPPH was calculated as follows:

$$\text{Inhibition of DPPH } (\%) = \frac{(A_{control} - A_{sample})}{A_{control}} \times 100$$

where $A_{control}$ = absorbance of control, A_{sample} = absorbance of sample

A graph of inhibition of DPPH (%) versus amount of sample (mg) was drawn for each sample. The inhibition of DPPH (%) versus the amount of Trolox (µg) was also plotted. The DPPH antioxidant activity was calculated by dividing the slope of the sample graph by the slope of the Trolox graph. The results were expressed as mg Trolox equivalents/100 g of sample.

The ferric reducing antioxidant power (FRAP) method was used according to (Liu *et al.*, 2008; Wang *et al.*, 2012).

Statistical analysis

The statistical software SPSS 16.0 was used to conduct the statistical analysis. The results are expressed as the mean ± standard deviation. The paired sample *t*-test was used to analyze the differences in the mean values between two paired comparisons. Differences between the means were considered significant at $P < 0.05$. Correlation coefficients (R^2) between different methods were calculated.

Table 2. Physical and chemical properties of the raw vegetables.

	Humidity (%)	pH	Acidity (%)	Salt (%)
Cabbage	92.44 ± 0.93	6.74 ± 0.20	0.14 ± 0.00	0.31 ± 0.03
Gherkin	95.12 ± 1.25	6.55 ± 0.17	0.14 ± 0.00	0.19 ± 0.04
Pickled cabbage	92.80 ± 0.92	3.55 ± 0.02	0.73 ± 0.02	2.85 ± 0.09
Pickled gherkin	94.10 ± 0.49	3.73 ± 0.09	0.57 ± 0.02	2.55 ± 0.03

Results and Discussion

Physical and chemical properties of raw vegetables and their pickles

The results of humidity (%), pH, acidity (%), and salt (%) analyses are shown in Table 2. The humidity (%) of the cabbage, gherkin, pickled cabbage, and pickled gherkin is determined as 92.44% ± 0.93, 95.12% ± 1.25, 92.8 ± 0.92, and 94.1 ± 0.49, respectively. The pH values for cabbage and gherkin are 6.74 and 6.55, respectively, and the pickling process reduces the pH values to 3.55 and 3.73 for pickled cabbage and pickled gherkin, respectively. The salt content (%) for pickled cabbage and pickled gherkin is balanced at 2.85% and 2.55%, respectively. The total LAB for pickled cabbage and pickled gherkin is 5.60×10^6 cfu/g and 2.67×10^7 cfu/g, respectively.

Total phenolic content (TPC)

The TPCs of cabbages before and after *in vitro* digestion and the bioaccessibility values are shown in Table 3. The TPC of cabbages and pickled cabbages is 104.3 ± 6.5 and 107.3 ± 1.5 mg GAE/100 g, respectively. Fermentation with *Lactobacillus plantarum* does not change the TPC of the cabbage ($P > 0.05$).

In a previous study (Sayın *et al.*, 2015), the fermentation process was found to increase TPC initially and then decrease the TPC of white cabbage. In another spontaneous fermentation study, fermentation decreased the TPC of white cabbage (Parada *et al.*, 2022). Sauerkraut production was found to increase TPC and some individual phenolics (Ciska *et al.*, 2005a; Tlais *et al.*, 2022). In these studies, except a study (Tlais *et al.*, 2022), bacterial culture was not used in brine processing, but *Lactobacillus plantarum* was used in our study. Different fermentation conditions, such as temperature, time, microorganisms, acidity and pH, are probably responsible for the variation in the TPC after the brining process (Sayın *et al.*, 2015; Ciska *et al.*, 2005b).

After *in vitro* digestion, the TPC of cabbage and pickled cabbage is increased to 130.2 ± 2.9 and 198.6 ± 8.5 mg GAE/100 g, respectively. The bioaccessibility of TPC is higher for pickled cabbage (185.1%) than cabbage (125.2%) ($P < 0.05$). The increase in TPC values after *in vitro* digestion is probably related to the release of bound phenolic compounds in the matrix of the cabbage. In the literature, no study has investigated the bioaccessibility values for total phenolics (TP) for white cabbage. In a study of red cabbage (Vanhoutte, 2014), alkaline hydrolysis was applied to red cabbage, and it was found that the alkaline extract contained a total phenolic content of more than 3 times that of the methanolic extract of red cabbage. This indicates that the majority of phenolics in red cabbage consist of nonextractable phenolics. Alkali hydolysis can break ether and ester bonds (Vanhoutte, 2014; Acosta-Estrada *et al.*, 2014; Rashmi *et al.*, 2020). Similarly, sodium hydroxide (NaOH) is used in the intestinal digestion part of our study, as in alkaline hydrolysis. The TPC of white cabbage is increased after *in vitro* digestion in our study, indicating that some of the phenolics in white cabbage are composed of nonextractable phenolics and that the alkali application leads to the release of phenolics via the breaking of ether and ester bonds.

The higher bioaccessibility of TP in pickled cabbages compared to cabbages can be explained by the protective effect of fermentation. Although the protective mechanism for fermentation has not yet been fully explained, it is thought that lactic acid produced by fermentation can alleviate the negative effect of pH on phenolic compounds by providing hydrogen ions and creating a buffer environment (Zhao *et al.*, 2016).

Fermentation decreases the TPC for gherkins from 40.3 ± 0.2 to 29.4 ± 1.4 mg GAE/100 g ($P < 0.05$); this value is similar with (Kiczorowski *et al.*, 2022), but is lower than that found in another literature (Ciniviz *et al.*, 2020). After the *in vitro* digestion process, TPC values for gherkins and pickled gherkins are increased to 149.1 ± 7.3 and 136.2 ± 11.2 mg GAE/100 g, respectively. The bioaccessibility values for gherkin and pickled gherkin are determined to be 369.2% and 462.0%, respectively ($P < 0.05$). Higher bioaccessibility values in pickled gherkins are probably related to the protective effect of fermentation (Zhao *et al.*, 2016; Leonard *et al.*, 2021; Ed Nignpense *et al.*, 2022).

After *in vitro* digestion, it was shown that the TPC value in both the cabbage and cucumber samples is increased. There is no study in the literature that investigates the TPC after *in vitro* digestion of white cabbage and gherkin samples, but there are many studies that show an increase in the TPC after the *in vitro* digestion process in various foods. The release of phenolic compounds from the food matrix due to a change in pH values, digestive fluids and enzymes during digestion is thought to be the underlying cause for this increase in TP value after digestion. The activities of enzymes can lead to hydrolysis of phenolics bound to other food components. Enzymes can disintegrate high molecular weight compounds such as proteins and carbohydrates, thus enabling the release of phenolics attached to these macromolecules (Bouayed *et al.*, 2012; Thomas-Valdés *et al.*, 2018; Celep *et al.*, 2017; Ti *et al.*, 2015; Tomas *et al.*, 2018; da Silva Fernandes *et al.*, 2017; Ed Nignpense *et al.*, 2022). The Folin-Ciocelteau method is a simple and useful method for determining TP. Nonphenolic compounds such as ascorbic acid, sugars, aromatic amines, organic acids, and proteins are also likely to react with Folin reagent, leading to an overestimation of the amount of phenolic compounds. Despite the fact that many different compounds reduce the Folin reagent, these interfering compounds remain in the food matrix prior to digestion. As a result, although the Folin method is not selective enough, it can be used to demonstrate an increase in the concentration of Folin reagent reducing compounds when compared to the control sample (Fernandes *et al.*, 2017; Prior, 2005).

Total flavonoid content (TFC)

The TFC of cabbages and gherkins before and after *in vitro* digestion is shown in Tables 3 and 4. The TF values for cabbages (1.85 ± 0.31 mg CE/100 g) and pickled cabbages (1.89 ± 0.36 mg CE/100 g) are similar ($P > 0.05$). *In vitro digestion* increases the TFC of raw and pickled cabbage. The TF bioaccessibility of raw and pickled cabbages is 124.3% and 161.2%, respectively ($P > 0.05$). Similar to the bioaccessibility of TPC, the bioaccessibility of TFC is also higher in pickled cabbages, probably due to the protective effect of fermentation (Zhao *et al.*, 2016).

The TFC of gherkin and pickled gherkin is 0.34 and 0.23 mg CE/100 g, respectively ($P > 0.05$). After *in vitro* digestion, the TFC for gherkin and pickled gherkin is increased to 1.19 and 0.78 mg CE/100 g, respectively. The TF bioaccessibility for raw (347.7%) and pickled gherkins (348.2%) is similar.

After *in vitro* digestion, the TF values for both cabbages and gherkins are increased, which show a similar trend to that observed for the TP values.

ABTS, DPPH, and FRAP antioxidant activity

The TAA of gherkins and cabbages was determined by measuring their free radical scavenging activities using the ABTS, DPPH, and FRAP methods. The values and

Table 3. Total phenolic content (TPC) and total flavonoid content (TFC) of cabbages.

	Total Phenolic Content (TPC) (mg GAE/100 g)			Total Flavonoid Content (TFC) (mg CE/100 g)		
	Before *in vitro* digestion	After *in vitro* digestion	BA (%)	Before *in vitro* digestion	After *in vitro* digestion	BA (%)
Cabbage	$104.3 \pm 6.5^{A, b}$	$130.2 \pm 2.9^{B, a}$	125.2 ± 9.4^{B}	$1.85 \pm 0.31^{A, b}$	$2.30 \pm 0.42^{A, a}$	124.3 ± 12.4^{B}
Pickled cabbage	$107.3 \pm 1.5^{A, b}$	$198.6 \pm 8.5^{A, a}$	185.1 ± 10.0^{A}	$1.89 \pm 0.36^{A, b}$	$3.07 \pm 0.78^{A, a}$	161.2 ± 17.0^{A}

Values are the mean ± standard deviation. A-B different letters indicate that the difference between the values in the same column is significant at the $P < 0.05$ level. a-b different letters indicate that the difference between the values in the same row is significant at the $P < 0.05$ level.

Table 4. Total phenolic content (TPC) and total flavonoid content (TFC) of gherkins.

	Total Phenolic Content (TPC) (mg GAE/100 g)			Total Flavonoid Content (TFC) (mg CE/100 g)		
	Before *in vitro* digestion	After *in vitro* digestion	BA (%)	Before *in vitro* digestion	After *in vitro* digestion	BA (%)
Gherkin	$40.4 \pm 0.2^{A, b}$	$149.1 \pm 7.3^{A, a}$	369.2 ± 17.2^{B}	$0.34 \pm 0.12^{A,b}$	$1.19 \pm 0.45^{A,a}$	347.7 ± 5.6^{A}
Pickled gherkin	$29.4 \pm 1.4^{B, b}$	$136.2 \pm 11.2^{A, a}$	462.0 ± 17.1^{A}	$0.23 \pm 0.04^{A,b}$	$0.78 \pm 0.12^{A,a}$	348.2 ± 3.2^{A}

Values are the mean ± standard deviation. A-B different letters indicate that the difference between the values in the same column is significant at the $P < 0.05$ level. a-b different letters indicate that the difference between the values in the same row is significant at the $P < 0.05$ level.

Table 5. ABTS, DPPH, and FRAP antioxidant activity values for cabbage.

	ABTS (mg TE/100 g)			DPPH (mg TE/100 g)			FRAP (mmol Fe/100 g)		
	Before *in vitro* digestion	After *in vitro* digestion	DF (%)	Before *in vitro* digestion	After *in vitro* digestion	DF (%)	Before *in vitro* digestion	After *in vitro* digestion	DF (%)
Cabbage	25.1 ± 0.9^{A,a}	13.8 ± 2.4^{A,b}	(−) 45.1	9.7 ± 0.7^{A,a}	9.8 ± 1.1^{A,a}	(+) 1.4	0.30 ± 0.02^{A,a}	0.29 ± 0.04^{A,a}	(−) 1.42
Pickled cabbage	24.3 ± 0.9^{A,a}	13.8 ± 2.8^{A,b}	(−) 43.6	9.3 ± 0.5^{A,a}	9.1 ± 1,2^{A,a}	(−) 2.8	0.32 ± 0.01^{A,a}	0.34 ± 0.02^{A,a}	(−) 6.32

Values are the mean ± standard deviation. A-B different letters indicate that the difference between the values in the same column is significant at the P < 0.05 level. a-b different letters indicate that the difference between the values in the same row is significant at the P < 0.05 level. DF: Difference.

Table 6. ABTS, DPPH, and FRAP antioxidant activity values for gherkins.

	ABTS (mg TE/100 g)			DPPH (mg TE/100 g)			FRAP (mmol Fe/100 g)		
	Before *in vitro* digestion	After *in vitro* digestion	DF (%)	Before *in vitro* digestion	After *in vitro* digestion	DF (%)	Before *in vitro* digestion	After *in vitro* digestion	DF (%)
Gherkin	16.1 ± 0.8^{A,a}	12.2 ± 0.7^{A,b}	(−) 24.2^{A}	8.06 ± 0.10^{A,a}	6.06 ± 0.34^{A,b}	(−) 24.8^{A}	0.35 ± 0.02^{A,a}	0.40 ± 0.0^{B,a}	(+) 14.7^{B}
Pickled gherkin	15.2 ± 1.0^{A,a}	10.5 ± 1.6^{A,b}	(−) 30.9^{A}	7.03 ± 0.2^{B,a}	5.23 ± 0,22^{B,b}	(−) 25.6^{A}	0.40 ± 0.04^{A,b}	0.55 ± 0.0^{A,a}	(+) 36.8^{A}

Values are the mean ± standard deviation. A-B different letters indicate that the difference between the values in the same column is significant at the P < 0.05 level. a-b different letters indicate that the difference between the values in the same row is significant at the P < 0.05 level. DF: Difference.

changes after *in vitro* digestion are shown in Tables 5 and 6.

Raw cabbages (25.11 mg TE/100 g) and pickled cabbages (24.33 mg TE/100 g) show comparable ABTS antioxidant activity values (P > 0.05). (Sayın *et al.*, 2015) found that fermentation first increases and then decreases ABTS antioxidant activity. ABTS antioxidant activity was found to remain unchanged by brining in another study, similar to our study (Girgin *et al.*, 2015). *In vitro* digestion decreases the ABTS antioxidant activity values for raw and pickled cabbage by 45.1% and 43.6%, respectively.

The DPPH antioxidant activity of raw and pickled cabbages is 9.68 and 9.33 mg TE/100 g (P > 0.05), respectively, and no change is observed after the brining process, similar to results reported in the literature (Girgin *et al.*, 2015). Differently, in a previous research, the DPPH antioxidant activity of white cabbage increased on day 1 and then lowered through fermentation, probably due to the passage of antioxidant compounds to the brine (Parada *et al.*, 2022). After *in vitro* digestion, DPPH antioxidant activity is found to remain unaffected by *in vitro* digestion of raw and pickled cabbage.

The FRAP antioxidant activity values obtained for the cabbages were similar. The FRAP antioxidant activities of raw cabbage, pickled cabbage, digested raw cabbage, and digested pickled cabbage are determined to be 0.30, 0.32, 0.29, and 0.34 mmol Fe/100 g, respectively.

The ABTS antioxidant activity values for gherkin and pickled gherkin are determined as 16.11 and 15.19 mg TE/100, respectively (P > 0.05). After *in vitro* digestion, the ABTS antioxidant activity of gherkin and pickled gherkin is reduced by 24.2% and 30.9%, respectively (P > 0.05).

While the DPPH antioxidant activity value in gherkin is 8.06 mg/TE, this value is decreased to 7.03 mg TE/100 g for pickled gherkin. It is observed that DPPH antioxidant activity values are decreased after *in vitro* digestion of gherkin and pickled gherkin compared to before digestion. After the digestion of gherkins and pickled gherkins, the DPPH antioxidant values are decreased by 24.8% and 25.6%, respectively.

The FRAP antioxidant activity values for gherkin and pickled gherkin are determined as 0.35 and 0.40 mmol Fe/100 g, respectively (P > 0.05). The FRAP antioxidant activity value before digestion in gherkin, 0.35 mmol Fe/100 g, becomes 0.40 after *in vitro* digestion (P > 0.05). The FRAP antioxidant value of pickled gherkins (0.40 mmol Fe/100 g) is increased to 0.55 mmol Fe/100 g (P < 0.05).

Correlations between TP, TF, ABTS, DPPH, and FRAP

The correlation coefficients between TP, TF, ABTS, DPPH, and FRAP values were determined by only using the values obtained for the cabbage samples and are

Table 7. Correlation coefficients between TP, TF, ABTS, DPPH, and FRAP in cabbage.

	TF	ABTS	DPPH	FRAP
TP	0.768	−0.788	−0.279	0.577
TF	–	−0.538	0.048	0.663
ABTS	–	–	0.289	−0.193
DPPH	–	–	–	−0.211

Table 8. Correlation coefficients between TP, TF, ABTS, DPPH, and FRAP in gherkins.

	TF	ABTS	DPPH	FRAP
TP	0.841	−0.854	–0.835	0.524
TF	–	−0.710	−0.643	0.276
ABTS	–	–	0.939	−0.698
DPPH	–	–	–	−0.790

shown in Table 7. The strongest correlation is found to occur between the TP and TF in cabbage samples. TP and TF give the highest positive correlation coefficients for FRAP antioxidant activity among the antioxidant activity tests. It is also observed that there is no strong positive correlation between antioxidant activity values in cabbage samples. In the literature, while a very strong correlation has been found between ascorbic acid and ABTS, the TP-ABTS correlation is insignificant (Güleç *et al.*, 2013). In another study conducted using *Brassica* vegetables, including cabbage, the TP-FRAP and TF-FRAP correlation coefficients were determined to be 0.357 and –0.0737, respectively (Jaiswal *et al.*, 2011).

The correlation coefficients between TP, TF, ABTS, DPPH, and FRAP values were calculated using values obtained for the gherkin sample and are shown in Table 8. The strongest positive correlations were found to occur between ABTS-DPPH and TP-TF. According to the data obtained, the phenolic compounds in gherkins have little effect on antioxidant activity. However, FRAP antioxidant activity is found to have the highest positive correlation with TP and TF among antioxidant activity analyses.

Conclusion

White cabbages, gherkins, and their pickles are healthy foods due to their phenolic and flavonoid contents and antioxidant activity. Fermentation does not affect TPC, TFC, or antioxidant activity in white cabbage. For gherkin, TFC and antioxidant activity are also not affected by fermentation, but the TPC is decreased. The bioaccessibility of the TPC and TFC for raw vegetables is lower than that for pickled vegetables; fermentation probably leads to looser bonds between phenolic compounds and other molecules in the food matrix, and these compounds are easily released after *in vitro* digestion. Fermentation also has a protective effect on phenolics. Both raw and pickled white cabbages and gherkins contain highly bioaccessible phenolics.

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Disclosure Statement

The authors declare that they have no known competing interests to report.

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