Chemical Composition And Natural Antioxidant Content Of Dried Broccoli And Cauliflower By-Products

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الملخص العربي

هدف البحث إلى دراسة كيميائية لكل من مخلفات البروتكلي في القنبيط (الأوراق والسيقان) والمتعرف على محتواها فمن المركبات المضادة للأكسدة والمركبات الفينولية والفلافونويدات ، الكسريات والعناصر المعدنية .

دلت النتائج على ما يلي:

- يعتبر مخلفات البروكلي والقنبيط كمصدر جيد للبروتين ، الكربوهيدرات ، المعادن والألياف والعناصر المعدنية (الكالسيوم والفوسفور ، البوتاسيوم ، الصوديوم ، الماغنسيوم ، الحديد ، الزنك)
- كما أن هذه المخلفات غنية بالمركبات الفينوكيميائية ومضادات الأكسدة مثل فيتامين C ، الكاروتينات والكلورفيل والفينولات والفلافونويدات .
- يعتبر هذه المخلفات عينة بالمركبات الفينولية والفلافونويدات والتي أمكن التعرف عليها بواسطة جهاز التحليل الكروماتوجرافى HPL.

ABSTRACT

Both dried broccoli (DBBP) and cauliflower by-products (DCBP) are considered as a good sources of protein, ash, crude fibers, carbohydrates and minerals (K, Ca, P, Na, Mg, Fe and Zn). Also , they are rich sources of phytochemicals such as polyphenols, flavonoids, vitamin C, chlorophylls (A and B), carotenoids and also has an antioxidant activity. HPLC analysis of aqueous extracts of both DBBP and DCBP showed 20 compounds could be identified, the major compounds are pyrogallol, protocatchui acid, catechin, chlorogenic acid,

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catechol and benzoic acids. In addition, the major compounds are lueo-7-gucose, Apig-6-arabinose-8-gulactose, A pig-6-rhmainose-8-galactose and rutin. Also, they are a good source of sugars, especially glucoronic, stachyose and sucrose.

INTRODUCTION

Cauliflower leaves which are generally thrown away as waste are rich source of iron and beta carotene and can contribute these nutrient to the diet **(Singh et al., 2005).** The dehydrated cauliflower leaves can be used for development of various recipes. These products if incorporated in the diet, can help to reduce the incidence of iron and vitamin A deficiency **(Keith, 1997).** Cauliflower is rich Source of minerals, vitamins, dietary fibers, protein and carbohydrates **(Bose et al., 1993)**.

Green leafy vegetables occupy and Important place among the food crops as they provide adequate amounts of vitamins and minerals for human. These are rich source of minerals auch as iron, calcium and phosphorus. Also the main source of vitamins like as corbic acid, riboflavin and carotene **(Emebu and Anyika, 2011).** Cruciferous vegetables are a good source of many health promoting and potentially protective phytochemicals including selenium, folic acid vitamin c, carotenoids and phenolics **(Kumar and Andy, 2012).** Also, broccoli and cabbage Juice mix showed a significant reduction in blood levels of low- density lipoprotein **(Don, 2011)**.

Broccoli is a good natural sources of antioxidants like vitamins, phenolic acids, flavonoids and carotenoids. The major compounds are B-carotene and vitamin c, selenium, crude fibers and phytochemicals can act bydiffered mechanisms in order to inhibit free radicals and increase natural antioxidant status **(Eyre et al., 2004 and Nihal et al., 2005)**

Cruciferous vegetables were an excellent dietary source of phytochemicals including glucosinolates phenolics and vitamins as well as dietary essential minerals (Ca, K, Na, Fe, Zn) Dietary antioxidants such as vitamins and flavonoids present in broccoli may decrease the risk of certain cancers **(Finley et al., 2001)**.

Broccoli contains the amount of health-promoting compounds such as glucosinolates, phenolic compounds and essential minerals, thus, it benefits health be yond providing just basic nutrition, and consumption of broccoli has been increasing over the years **(Ana et al., 2013) .**

Dietary antioxidants, such as water – soluble vitamin C as well as soluble vitamin E, phenolic compounds and carotenoids, present in vegetables which contribute both to the first and second defense lines against oxidative damage, and may therefore prevent chroic diseases, such as cancer, diabetes and cardiovascular disease **(Anna, 2007)**.

Broccoli has been reported as the one of main sources of natural antioxidants i.e., phenolic compounds and vitamins and chemopreventive compounds i.e., glucosinolates and their degradation products, isothiocyanates **(Olga et al., 2009).**

MATERIALS AND METHODS

Materials

Broccoli (*Brassica Olearacea* L) and cauliflower (*Brassica Olearacea*. L. spp. Botrytis) such as stems and leaves were obtained from local market in Giza, Egypt. The products were washed with tap water , dried with solar energy and ground into fine powder.

Methods

Chemical analysis (Moisture, fat, protein, ash and crude fibers of dried broccoli and cauliflower by-products was determined as the methods of **A.O.A.C.; (2005).** Carbohydrates were calculated by difference. Caloric values were calculated as (**FAO/WHO, (1989).**

Mineral contents , mg/100 g DW (Ca, Na, K, Mg P, Fe and Zn) were determined using a Pye Unicum SP1900 Atomic

Absorption Spectroscopy Instrument (Perkin Elmer, Model 4100 ZL as the method of **AOAC (2005)** in Agriculture Research Institute.

Extraction of antioxidant compounds as the method of **Batista et al., (2011).** Total phenols and flavonoids (mg/100g DW) were determined as the method of **Batista et al., (2011).** Chlorophylls (A and B) and Carotenoids (mg/100 g DW) were determined according to **Lichtenthaler and Wellburn (1983).** Vitamin C (mg/100g DW) was determined by HPLC as described by **Romeu-Nadal et al., (2006),** DPPH radical assay was determined as **Hanato et al., (1988)**.

Fractionation of phenolic compounds (PPm) , flavonoide compounds (were determined by using HPLC according to the method described by **Goupy et al., (1999) and Mattila., et al., (2000),** respectively in Food Technology Research Institute Fractionation of sugars (ppm) were determined befor and after acid hydrolysis as the methods of **Zielimski et al., (2014) and Randall et al., (1989)** by using HPLC.

RESULTS AND DISCUSSIONS

Chemical analysis

Chemical composition

Table (1) shows gross chemical composition of dried broccoli and cauliflower by-products (g/100 g on dry weight basis). Dried broccoli by-products (DBL) consists of 21.33% protein; 44.8% carbohydrates; 17.36% crude fibers, 11.65% ash content and 4.86% fat. Meanwhile, total energy was 308 k. calories/ 100g on dry weight basis. These results are inagreement with those obtained by **Campas Bay Poli et al., (2009) Madhu and Kochhar, (2014) and Ayed, Najlh, (2018)**.

On the other hand, dried cauliflower by-products consists of 22.81% crude protein, 44.0% total carbohydrates, 16.73% ash content, 12.43% crude fibers and 4.03% fat. In addition, total energy was

304 K.calories/ 100g on dry weight basis. These results are confirmed by **Al-Ajmi, Naglaa, (2018)**.

Table (1): Chemical composition of dried broccoli and cauliflower by-products.

Vegetables Constituents	Dried broccoli by-products	Dried cauliflower by-products
Moisture (%)	9.79	8.60
Protein (%)	21.33	22.81
Fat (%)	4.86	4.03
Ash (%)	11.65	16.73
Fiber (%)	17.36	12.43
Carbohydrates (%)	44.80	44.00
Energy (Kcal /100g)	308	304

* **g/100g on dry weight basis**

Mineral contents

Table (2) illustrates mineral contents (K, Na, P, Na, Mg, Fe and Zn) of dried broccoli and cauliflower leaves. Results showed that dried broccoli by-products consists of K(426.3) (mg/100g); Na (1002.1 mg/100g), Ca (2635.9 mg/100g), P(441.4 mg /100g), Mg (354.5 mg/100g), Fe (48.5 mg /100g) and Zn (5.32 mg/100g). These results are in agreement with those found by **Bhandari and Kwak 2015, and Ayed, Najlah, (2018).**

Also , the obtained results indicated that dried cauliflower by-products consists of K (388.7mg/100g); Na(1542.3 mg/100g); Ca (6845.5 mg/100g); Mg (664.2 mg/100g); p(316.71 mg/100g), Fe (79.2 mg/100g) and Zn (3.98 mg/100g), these results are in agreement with those obtained by **Al-Ajmi, Naglaa, (2018).** On the other hand, dried broccoli and cauliflower by-products contained 9.09 and 13.15 pb (ppm).

Table (2): Mineral contents of dried broccoli and cauliflower by-products

Vegetables Minerals	Dried broccoli by-products	Dried cauliflower by-products
Minerals	Broccoli	Cauliflower
K (mg /100g)	426.3	388.7
Na (mg /100g)	1002.1	1542.3
Ca (mg /100g)	2635.9	6854.5
P (mg /100g)	441.4	316.71
Fe (mg /100g)	48.5	79.2
Mg (mg /100g)	354.5	664.2
Zn (mg /100g)	5.32	3.98
Pb (ppm)	9.09	13.15

* Results expressed as mg/100g on dry weight basis

Antioxidant contents

Phytochemicals

Table (3) shows antioxidant contents of dried broccoli and cauliflower by-products (as mg /100 g on dry weight basis). Results showed that dried broccoli consists of total phenols, 10426.5 mg/100g;total flavonoids, 24.42mg/100g vitamin C.; 1.58 mg/100g chlorophyll A; 0.93mg/100 g; chlorophyll B; 2.51 mg/100g, total chlorphylls and 1.23 mg/100g; total carotenoids. This results of vitamin C are in agreement with those mentioned by **Munyaka et al., 2010; Kumar and Andy, (2002).**

Table (3): Phytochemicals of dried broccoli and cauliflower leaves:

Vegetables Antioxidants	Dried broccoli by-products	Dried cauliflower by-products
Vitamin C (mg/100g)	24.42	56.70
Total phenols (mg/100g)	10426.5	14117.7
Total flavonoids (mg/100g)		
DPPH (%)	86.56	74.32
Chlorophyll A (mg/100g)	1.58	2.85
Chlorophyll B (mg/100g)	0.93	1.77
Total chlorophyll (mg/100g)	2.51	4.62
Total carotenoids (mg/100g)	1.23	2.24

* Total phenols as gallic acid and total flavonoids as quercetin

Broccoli is also a good source of polyphenolic compounds with high antioxidant activity **(Dominguez-Perles et al., 2010)**.

In addition, broccoli by-prducts and broccoli florets are rich source of polyphenols, dietary fibers and other nutrients **(Campas – Baypoli et al., 2009 and Dominguez-Perles et al., 2010)**.

On the other hand, dried cauliflower by-products contained 14117.7 total phenols, (mg/100 g), total flavonoids; (2.85 mg/100g) chlorophyll A; 1.77 (mg/100g), chlorophyll B; 4.62 mg/100g total chlorophylls, 2.24 (mg/100g), total carotenoids and 56.7 (mg/100g) vitamin C. Results are in agreement with those found by **Kumar and Andy, (2012)** likewise, polyphenols are a large group of antioxidant compounds in considerable amounts of Brassica vegetables **(Munyaka et al., 2010).** Also there are several reports revealed that broccoli and cauliflower contained phenolics and flavonoid contents **(Aires et al., 2011, Cartea et al., 2011 and Lee et al, 2012).**

Brassica family is a rich source of antioxidant content such as phenolics, vitamins C and A **(Finely et al., 2001, Kumar and Andy 2012).** Also Brassica vegetables are rich sources of polyphenols and flavonoids **(Ferres et al., 2005 and Jaiswal et al., 2012).**

Phytochemicals such as glucosinolate were higher in florets as compared with by-products in both broccoli and cauliflower cultivars **(Bhandari and Kwak, 2015)**.

It is evident from the results that DPPH of dried broccoli and cauliflower by-products were 86.56% and 74.32% .i.e broccoli has high antioxidant activity than cauliflower. Broccoli is also a good source of polyphenolic compounds with high antioxidant activity **(Dominguez – Perles et al., 2010)**. In addition, the antioxidant potential of Brassica vegetables is high as compared to other vegetables **(Traka and Mithen , 2009 and Verkerk et al., 2009) .**

Phenolic compounds

Table (4) shows HPLC analysis of phenolic compounds in aqueous extract of dried broccoli and cauliflower by-products were identified. It could be separated and identified of nineteen compounds in dried broccoli by-products and twenty phenolics compounds in dried cauliflower leaves.

The major compounds of dried broccoli by-products are pyrogallol 1235. 69 ppm, followed by chlorogenic acid 477.14 ppm, protocatchuic acid 438.31 ppm, catechein 178.63 ppm and benzoic acid 128.8 ppm (on dry weight basis), respectively. These results are in agreement with those found by **Kumar and Andy, (2012)** who found that cruciferous vegetables are a good source of phenolics.

Also, these results was confirmed by **Olga et al, (2009)**; **Ana et al., (2013) and Ayed, Najlah, (2018).** Broccoli is a rich source of polyphenolic compounds with high antioxidant activity **(Dominguez- Perles et al., 2010).**

It is obvious from the abovementioned results that, the major phenolic compounds of dried cauliflower by-products are chlorogenuic acid value 949.17 ppm on dry weight, followed by protocatchuic 791.3 ppm; catchein, 311.68ppm, pyrogallol 234.05 ppm and catechol 180.51 ppm, respectively, these results was confirmed by **Olga, et al., 2009; Ana et al., 2013 and Ayed, Naglah**

2018. Broccoli is a rich source of polyphenolic compounds with high antioxidant activity **(Dominguez-Perles et al., 2010)** respectively. These results are in agreement with those found by **(Anwar Sara, 2015 and –Al-Ajami, Naglaa, 2018).** Circiferous vegetables are a rich source of phenolics **(Olga et al., 2005 and Jaiswal et al., 2012).**

Brassica vegetables are contained a considerable amounts of polyphenols **(Munyaka et al., 2010)** and also it has rich source of polyphenols and flavonoids **(Ferreres et al., 2005 and Jais wall et al., 2012).**

Table (4): HPLC analysis of phenolic compounds of dried broccoli and cauliflower by-product.

Vegetables Phendic compounds	Dried broccoli by-products	Dried cauliflower by-products
Items	**Byproduct of broccoli**	**Byproduct of cauli-flower**
Gallic acid	4.92	--
Pyrogallol	1235.69	234.05
4-Amino-benzoic acid	2.79	41.42
Protocatchuic acid	438.31	791.30
Catechein	178.63	311.68
Chlorogenic acid	477.14	949.17
Catechol	126.75	180.51
Caffeine	28.22	32.35
P-oh-benzoic acid	102.58	147.18
Caffeic acid	12.10	20.86
Vanillic acid	38.93	17.77
P-Coumaric acid	49.30	95.92
Ferulic acid	18.72	39.60
Iso-ferulic acid	6.76	6.30
Alpha-coumaric acid	--	10.13
Ellagic acid	54.88	11.54
Benzoic acid	128.80	88.55
Coumarin	8.93	15.36
3.4.5methoxy Cinnamic acid	10.16	7.23

Salycilic acid	25.14	104.96
Cinnamic acid	4.95	1.61

* Results expressed as ppm on dry weigh basis.

Flavonoid compounds

Table (5) illustrates HPLC analysis of flavooids in aqueous extract of dried broccoli and cauliflower by-products. Results indicated that there are eighteen flavonoid compounds of both broccoli and cauliflower by-products as shown in the results . These compounds are a pig-6-arabinose-8-galactose, apig-6-rhaminose 8-glaactose, narengin, luteo-7-glucose, hespirdin, rutin, quercetrin-3-0-glucoside, Apig-3-0-neohespiroside, kamp 4,7-dirhamoside, quercetrin, apigenin -7- glucose, Acacetin-7-neohesperside, kamp 3, (2-P-comaroyl) glucose, acacetin neo-rutinoside, querecetin, narengenin, hespirdin, kampferol, rhamnetin and apigenin.

The major compounds of dried broccoli by-products are hespirdin 606.65 ppm on dry weight basis, followed by luteu-7-glucose 359.79 ppm, Apig-6-rhaminose-8-galactose 171.16 ppm, Apig-6-arabinose-8-galactose 107.7 ppm and Narengin 101.51 ppm, respectively. These results are inagreement with those mentioned by **Anwar, Sara, (2015).** Several authors reported that broccoli and cauliflower contained antioxidant contents such as flavonoids and phenolics **(Cartea et al., 2011, Aires et al., 2011; and Lee et al., 2012).**

It is evident from the results that the major flavonoid compounds of dried cauliflower by-products are hesperidin 1333.39 ppm, followed by luteo-7-glucose 453.8ppm a pig-6-arabinose-8-galactose 290 ppm, rutin 77.21 ppm and a pig -6- rhaminose-8-galactose 59.74 ppm, respectively. Broccoli and cauliflower are contained flavonoids **(Ferreres et al., 2005; Jaiswal et al., 2012 and Lee et al., 2012).** Brassica vegetables has high antioxidant potential as compared with the other vegetables **(Traka and Mithen, 2009 and Verkerk et al., 2009)**

Table (5): HPLC analysis of flavonoid fractions of broccoli and cauliflower by-products (ppm on dry weight basis).

Vegetables / Flavonoid compounds	Dried broccoli by-products	Dried cauliflower by-products
Items	**Byproduct of broccoli**	**Byproduct of cauliflower**
Apig.6arabinose 8-galactose	107.70	290.00
Apig.6rhamnose 8-galactose	171.16	59.74
Narengin	101.51	--
Luteo.7-glucose	359.79	453.80
Hespirdin	606.65	1333.39
Rutin	43.91	77.21
Querecetrin -3-0-galucoside	20.20	--
Apig. 7-0-neohespiroside	56.85	51.12
Kamp3,7-dirhamoside	23.82	24.70
Quercetrin	69.16	38.21
Apigenin-7-glucose	16.67	21.59
Acacetin 7 neo hespesperside	8.90	12.46
Kamp3,(2-p-comaroyl)glucose	--	--
Acacetin neo.rutinoside	--	30.15
Querecetin	16.85	10.81
Narengenin	5.57	3.79
Hesphirtin	5.52	33.55
Kampferol	1.98	7.86
Rhamnetin	29.34	22.20
Apigenin	6.80	1.58

* Results expressed as ppm on dry weigh basis.

Sugars Fractions

Table (6) shows sugar fractions by HPLC of both dried broccoli and cauliflower by-products before and after acid hydrolysis. Results indicated that HPLC analysis of sugars of broccoli by-products before hydrolysis showed that there are twelve fractions of sugars could be separated and identified. These sugars are glucoronic, galacturonic, stachyose, sucrose, maltose, glucose, xylose, galactose, rhaminose, fructose, arabinose and sorbitol.

The major sugars of broccoli-by-products glucoronic 2.72% (g/100 g on dry weight basis), followed by galacturonic 2.448%, stachyose 2.103% sucrose 0.541% and galactose 0.319%, respectively.

On the other hand, HPLC analysis of sugars of dried cauliflower by-products showed there are eight sugars fraction could be separated and identified before hydrolysis, these sugars are glucoronic, stachyose, sucrose, glucose, xylose, rhaminose, arabinose, sorbitol. The major sugars are glucoronic 2.104%, stachyose 1.314%, glucose 0.975%, rhaminose 0.480 and xylose 0.404%, respectively.

It is evident from the results that after hydrolysis of sugars of both dried broccoli and cauliflower by-products caused a decrease in the most of these sugars i.e hydrolysis process had affected on sugar in either dried broccoli or cauliflower by-products.

Total sugars of broccoli by-products was 9.422% (g/100 g on dry weight basis), meanwhile it was 5.903% in cauliflower by-product i.e had broccoli by-products the higher sugars than cauliflower by-products in either before or after acid hydrolysis. These results are in agreement with those obtained by **Madhu and Kochhar, (2014).** In addition Bhandari and Kwak, 2015 found that free sugars were found at higher levels in the leaf parts than flowerets in both broccoli and cauliflower by- products.

Finally it could be concluded that both dried broccoli and cauliflower by-products is considered as a good source of sugars especially, glucoronic, stachyose and sucrose.

Table (10): HPLC analysis of sugar fractions of dried broccoli and cauliflower by-products.

Vegetables / Sugars	Dried broccoli by-products		Dried cauliflower by-products	
	Before	**After**	**Before**	**After**
Glucoronic	2.720	1.231	2.104	0.638
Galacturonic	2.448	0.919	---	0.143
Stachyose	2.103	0.623	1.314	---
Sucrose	0.541	0.183	0.295	---
Maltose	0.189	0.133	---	0.136
Glucose	0.59	0.081	0.975	0.043
Xylose	0.272	---	0.404	0.018
Galactose	0.319	---	---	0.047
D- mannose	---	1.289	---	---
Rhaminose	0.138	0.794	0.480	0.014
Fructose	0.025	0.339	---	0.010
Arabinose	0.021	---	0.244	0.029
Manitol	---	0.022	---	0.011
Sorbitol	0.056	0.180	0.087	0.037
Total sugars	9.422	5.794	5.903	1.126

* Results expressed as ppm on dry weigh basis.

Conclusion:

It could be concluded that both broccoli and cauliflower by-products is as considered as a good sources of proteins, carbohydrates ash, crude fibers, mineral (K, Ca, P, Na, Mg Fe and Zn) and also antioxidant contents (Vitamin C, chlorphyl, coarotenoids, phenolic , flavonoid compounds and sugars.

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