Chapter

The Role of Major Phenolics in Apple to Total Antioxidant Capacity

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Abstract

The naturally occurring phenolic compounds have received major attention in recent years as huge amounts of phenolic compounds can be extracted from fruits, vegetables and beverages that have substantial health benefits. From a physiological and metabolic aspect, phenolic compounds are vital in defence responses, such as anti-ageing, anti-inflammatory, anti-oxidant and anti-proliferative, anti-bacterial, anti-hyperlipidemic, anti-cancer, anti-diabetic, neuroprotective, cardioprotective activities. Among the fruits having a higher content of phenolic compounds, the apple (*Malus Domestica*) is the most widely consumed fruit in the world. Apples have a high nutritional value as it is a rich source of ascorbic acid, polyphenols and pectin. Apple peel forms a small percentage (6–8%) of the total fruit weight and contains the highest content of phenolic compounds, particularly chlorogenic acid. There are five major groups of polyphenolic compounds found in apples namely flavanols (Catechin, Epicatechin and Pyrocyanidins), phenolic compounds, phenolic acids (mainly Chlorogenic acids), dihydrochalcones (Phloretin glycosides), flavonols (Quercetin glycosides) and anthocyanins (Cyanidin). This chapter reviews the chemical properties, mode of action, types, extraction of phenolics in apples and the contribution and role of major phenolics in apples to the total antioxidant capacity.

Keywords: phenolic compound, flavanols, flavonols, dihydrochalcones, antioxidant capacity, anti-hyperlipidemic, contribution

1. Introduction

Metabolic functions are one of the important characteristics of living organisms. From a simple prokaryotic cell to a highly specialised eukaryotic organism, proper functioning of metabolism is essential for the survival of the organism. These metabolic processes are important for the survival, growth and dispersal of plants as well. In simple terms, metabolism refers to all the chemical processes in the body that convert food into energy. This energy is made available to all other cellular processes essential to sustaining life. Metabolism is further of two types-primary metabolism and secondary metabolism. Primary metabolism is responsible for the proper functioning of all major physiological processes of plants and animals while secondary metabolism includes all other metabolic pathways that are not essential for survival but plays various other important roles. Both types of metabolic processes result in the formation of certain chemical compounds known as metabolites. Primary metabolites are formed as a result of primary metabolic processes while secondary metabolism results in the formation of secondary metabolites.

Secondary plant metabolites are specialised chemical compounds produced by plants and do not possess any role in primary metabolic processes but are essential for the survival of plants in their environment. Earlier it was believed that secondary metabolites are formed as a by-product of primary metabolic reactions that are of no significance to plant growth. However, researchers have revealed various important functions of secondary plant metabolites. Though they are not directly involved in essential physiological processes, affect and regulate these processes by acting as intermediates in these processes. Secondary metabolic compounds in plants can be broadly grouped into 4 groups (**Figure 1**). Terpenes, Phenolics, nitrogen-containing compounds and sulphur-containing compounds. Each secondary metabolite has a specific role to perform (**Figure 2**). They act as structural components of plants in the form of lignins. They also act as a defence against pathogens and herbivores. Secondary metabolites provide better tolerance to stress conditions and protect against UV rays. Certain secondary metabolite act as an attracting agents for pollination and seed dispersal. They also inhibit the growth of microbes and check the competition by inhibiting the growth of nearby plants. Various research has established the fact that secondary metabolites act as bioactive compounds in fruits and vegetables.

Phenolics are one of the most significant phytochemicals which are naturally produced as a secondary metabolite in plants. Plant phenolics are bioactive compounds that have been reported to exhibit various biochemical properties such as antioxidant, structural polymer (lignin), attractants (flavonoids and carotenoids), UV

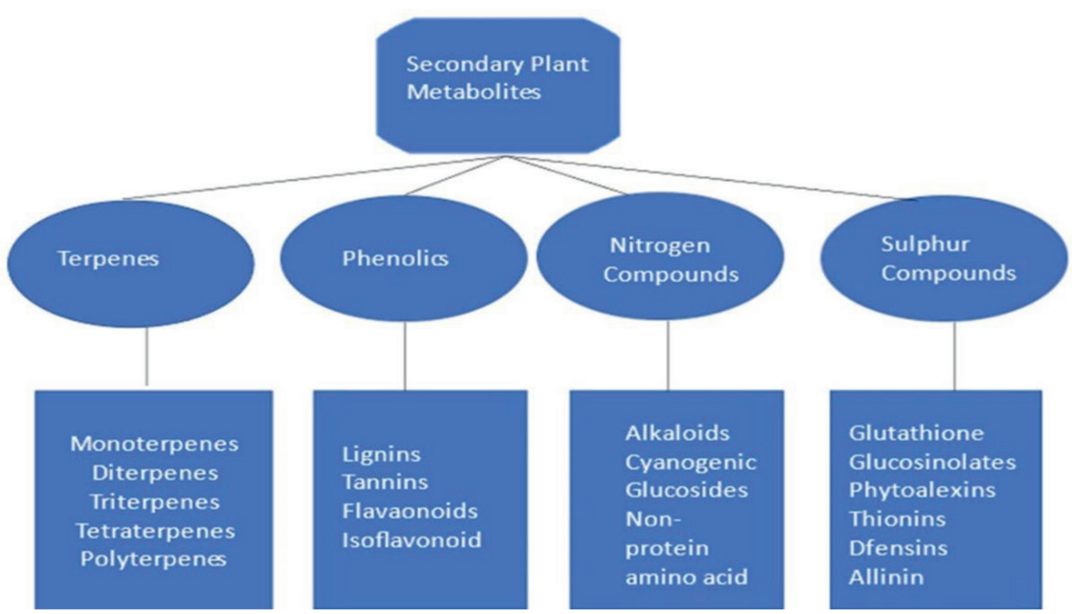

Figure 1.
Types of metabolites.

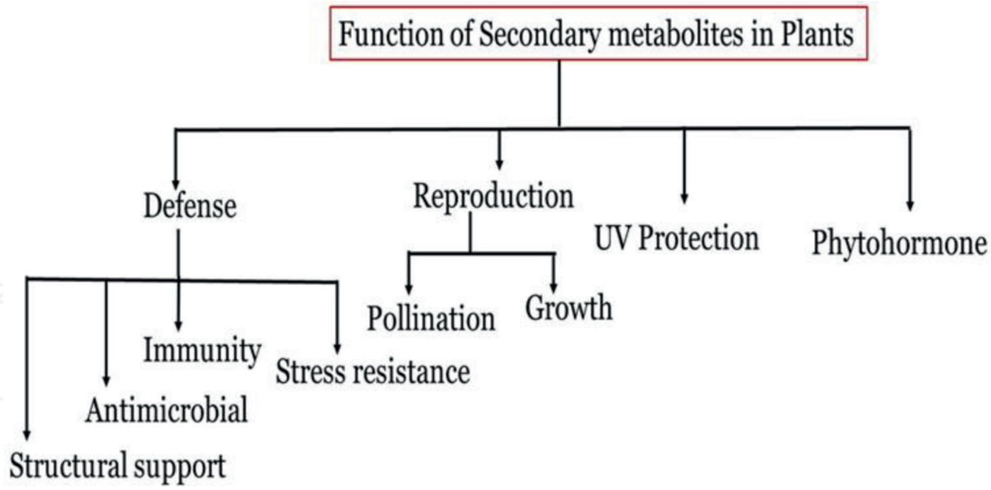

Figure 2.
Functions of secondary metabolites.

screens(flavonoids), signal compounds (salicylic acid and flavonoids) and defence response chemicals (tannins and phytoalexins) [1].

Chemically, phenolics are compounds that have an aromatic ring or a benzene ring with one or more hydroxide groups. They may be in the form of simple phenols or polyphenols based on the number of phenol or hydroxide groups present on them and also possess variation in the number of attached carbon atoms (**Table 1**). They may also possess functional derivatives such as esters, methyl esters, glycosides *etc.* attached to them.

In plants, they are found in conjugated form and may be joined to carboxylic acids, organic acids, amines, lipids and other phenolic compounds. Phenolics play important roles in plants as they protect plants from harmful ultraviolet radiation, pathogen and parasite infection as well as from predators. A phenolic compound such as Anthocyanin provides red, orange, blue or purple colour to fruits.

1.1 Mechanism of action of phenolic compounds

Phenolic compounds are bioactive in nature and act as anti-oxidant by reacting with a variety of free radicals. The mechanism of anti-oxidant actions involves either hydrogen atom transfer or transfer of a single electron or sequential proton loss electron transfer or by chelation of transition metals [2].

No. of C atoms	Basic structure	Class
6	C_6	Simple Phenols; Benzoquinones
7	C_6-C_1	Phenolic acids
8	C_6-C_2	Acetophenone; Phenylacetic acid
9	C_6-C_3	Hdroxycinnamic acid; Coumarin; Isocoumarin
10	C_6-C_4	Napthoquinone
15	C_6-C_3-C_6	Flavonoids; Isoflavonoids
30	$(C_6$-C_3-$C_6)_2$	Biflavonoids
n	$(C_6$-$C_3)_n$ $(C_6)_n$ $(C_6$-C_3-$C_6)_n$	Lignins; Catecholmelamine;

Table 1.
Types of phenolics based on number of carbon atoms.

1.2 Antioxidant

One of the most important properties of phenolics is their antioxidant property which has become a matter of interest for the scientific community in recent years. *Antioxidants* are substances that inhibit the process of oxidation and thus prevent or delay the damage to the cells caused due to free radicals [3] or unstable molecules that are produced in the body as a response to biological, metabolic, environmental or other factors. Free radicals are waste substances produced by cells as the body processes food and reacts to the environment. Antioxidants are supposed to be" free radical scavengers" as they help in neutralising free radicals in our bodies and in this way benefit our health. Several factors influence the activity or effectiveness of antioxidants. These factors include the chemical structure of the antioxidant, its concentration, temperature and its location in the system.

Fruits and vegetables are rich sources of antioxidants that enhance the nutritional quality of fruits and vegetables. The antioxidant property of phenols present in fruits and vegetables is beneficial to human health as researchers have suggested that antioxidants can lower the risk of various chronic diseases such as cancer, heart stroke and age-related macular degeneration [4].

2. Apple

Apple (*Malus Domestica*) is the fruit of a domesticated tree belonging to the genus Malus and the family Rosaceae. Apples are one of the most widely cultivated tree fruits. Apples originated in central Asia and have been grown for thousands of years in Asia and Europe and were brought to North America by Europeans. From sweet red varieties like Red Delicious, Fuji or Gala to tangy green ones like Granny Smith, over 7500 different cultivars of apples are available worldwide that makes apples also the most widely consumed fruit globally [5].

According to data from Food and Agriculture Organisation Corporate Statistical Database, total apple production in 2017 was 83,139,326 metric tonnes and in 2020, it was 87,236,221 metric tonnes. China tops the list of the highest apple-producing countries in the world followed by the United States and Turkey [6]. Based on a comparison of 161 countries in 2019, Hungary ranked first in apple consumption per capita with 33.3 kg followed by the Netherlands and Albania [7].

Apart from higher production, several other factors make apples the most widely consumed fruit. These factors include easy market availability, cost affordability, long shelf life, variety of processed apple products such as Jams, pies, canned apples, apple juice, smoothies etc.

There is nothing new to talk about the health benefits of eating apples as the whole world is familiar with a very popular saying "An apple a day keeps the doctor away." Apples are incredibly nutritious fruits [8] (**Table 2**). Apples are low in sodium, fat and cholesterol. They are a very good source of Vitamin C, fibre and antioxidants.

2.1 Antioxidant capacity of apples

The antioxidant activity of apples is mainly attributed to the phenolic compounds present in apples. There is a correlation between the phenolic content of apples and antioxidant activity. The apple varieties with higher phenolics tend to have higher antioxidant activity. Various phenolic compounds are present in different parts of

Amount per 100 grams	
Calories	52 cal.
Total Carbohydrate	14 g
Total Fat	0.2 g
Protein	0.3 g
Cholesterol	0 mg
Calcium	0%
Magnesium	1%
Sodium	1 mg
Potassium	107 mg
Dietary Fibre	2.4 g
Sugar	10 g
Vitamin C	7%
Vitamin B6	0%
Vitamin D	0%

Sources: United States Department of Agriculture (per cent daily values are based on a 2000 calorie diet) [6].

Table 2.
Nutrition value of apple.

apples such as peels, pulp, core, and seeds in different concentrations (**Figure 3**). Generally, apple peel is rich in the concentration of phenolic compounds as compared to flesh or pulp part. Apples had the highest portion of free phenolics when compared to other fruits which makes them easily absorbable into the bloodstream.

In the United States, 22 per cent of the phenolics consumed from fruits are from apples making them the largest source of phenolics [9]. When compared to many fruits in the United States, apples had the second highest level of antioxidant capacity [10].

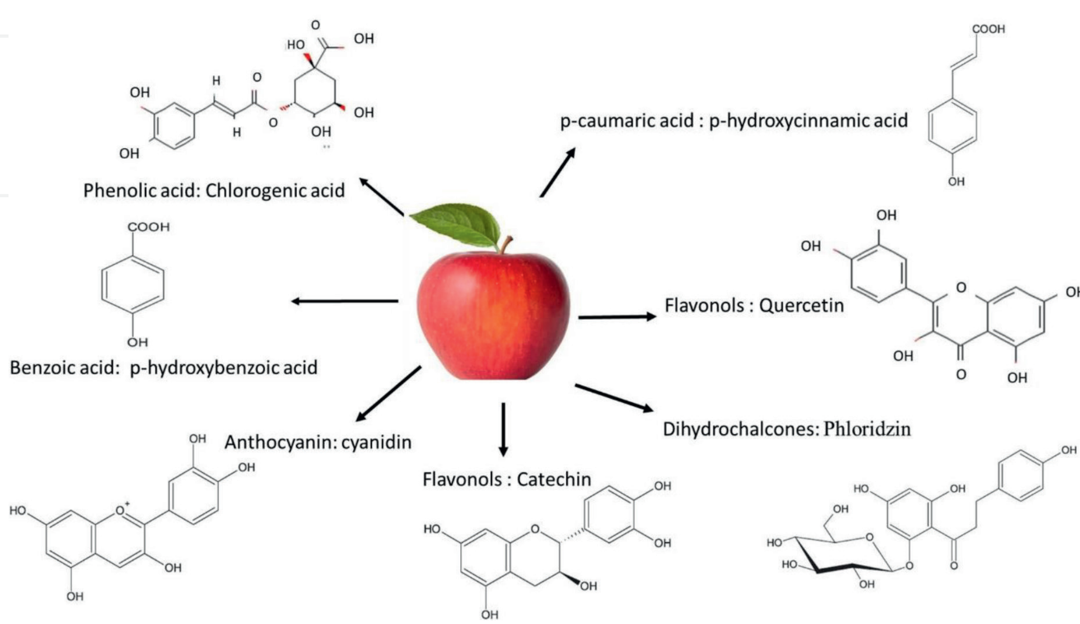

Figure 3.
Enriched phenolic compounds in apples.

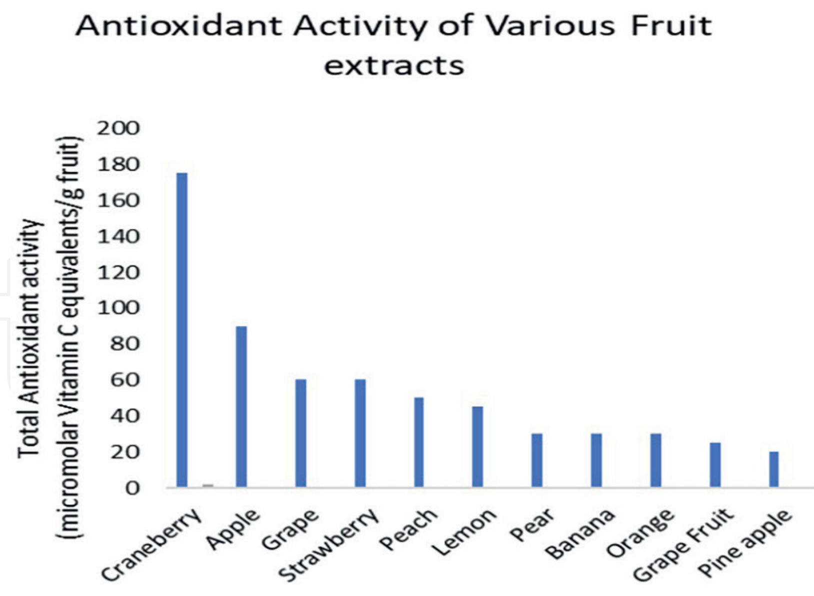

Figure 4.
Chart depicting the antioxidant activity of different fruits.

According to available literature and research, antioxidant activities and total phenolic content of 62 fruits (**Figure 4**) were evaluated using ferric reducing anti-oxidant power (FRAP) and Trolox equivalent antioxidant capacity (TEAC) assay and the Folin-Ciocalteu methods. The experiment revealed statistical data related to different varieties of apples which showed that apples belonging to the cultivars of Green-delicious, Red-delicious and Rose-red had intermediate values of 68.29, 73.96 and 70.57 mg GAE/100 g of wet weight respectively [11].

2.2 Flesh vs. peel

Certain individual phenolic compounds may also be found in higher concentrations in flesh as compared to peel. "Chlorogenic acid" is a type of phenolic compound found in apples that were found in peel in higher concentration as compared to flesh in apple varieties of Elstar, Fuji, McIntosh Pinova, Red Delicious, but Idared, Golden Delicious, Granny Smith, Reineta possessed higher concentration of chlorogenic acid in flesh than peel [12]. Another type of phenolic compound known as Anthocyanin which is responsible for the bright red skin colouration of apples is highly concentrated in the peel. The peel of Granny Smith, Golden Delicious, and McIntosh is richer in p-coumaroylquinic acid content while in Gala, the flesh has a higher content of the same phenolic compound [12].

2.3 Phenolic content in apple seeds

Apple seeds are also a good source of polyphenols particularly phloridzin. Apart from phloridzin, other phenolic compounds are also found in apple seeds such as dihydrochalcones, hydroxycinnamic acid, hyperin, chlorogenic acid, quercetin, caffeic acid, protocatechuic acid, and flavan-3-ols which are found in monomeric and oligomeric forms as well as polymeric forms. Monomeric forms include Catechin and Epicatechin while oligomeric forms such as proanthocyanin are present. Flavonols are also found in apple seeds.

HPLC analysis has proved phloridzin as the chief phenolic compound found in seeds as phloridzin content was found to be 240.45–864.42 mg/100gDW which was measured by the Folin-Ciocalieu assay of apple seeds of seven cultivars. The seven apple cultivars included varieties of Gale Gala, Starking, Honeycrisp, Fuji, Qinguan, Golden Delicious, and Qinyang. Among the seven cultivars, Honeycrisp showed the highest phenolic content while Qinyang showed the lowest value of phenolic compounds [13].

3. Factors affecting phenolic content of apples

The difference in the content of individual phenolic compounds in apples of different varieties can be attributed to different biosynthesis pathways of phenolic compounds. Other factors affecting the phenolic concentration in apples include cultivar, maturity of the fruit, conditions of cultivation, growing season, harvest, storage, and environmental factors. Comparative study of antioxidant activity and phenolic content of apples is difficult to evaluate due to different extraction methods, different cultivars of apples, geographical region, soil type, and light hours. It is also supposed that organically grown apples have higher phenolic content as compared to the apples grown by integrated farming. The genetic constitution of the different cultivars of apples majorly affects the phenolic content in apples. One important factor that affects the phenolic content of apples is the ripening or maturation condition of apples. Researchers have found that the amount of dihydrochalcones in very young apples is very high but after 14 weeks the number of dihydrochalcones, flavonols, and chlorogenic acid decreased in both the peel as well as the flesh. Various studies regarding the apple varieties and factors affecting the phenolic content have revealed a general trend in the phenolic content and its concentration in different parts of apples. The antioxidant properties of different parts of apples follow the order: peel>core>flesh. This has also been revealed that the apple peel contains two to six times more phenolic compounds as compared to the flesh of the apple [12].

4. Biosynthesis pathway of phenolics in apples

Biosynthesis of phenolic compounds may occur via various pathways (**Figure 5.**) i.e., the Shikimate pathway, Phenylpropanoid pathway, and Flavonoid pathways. The

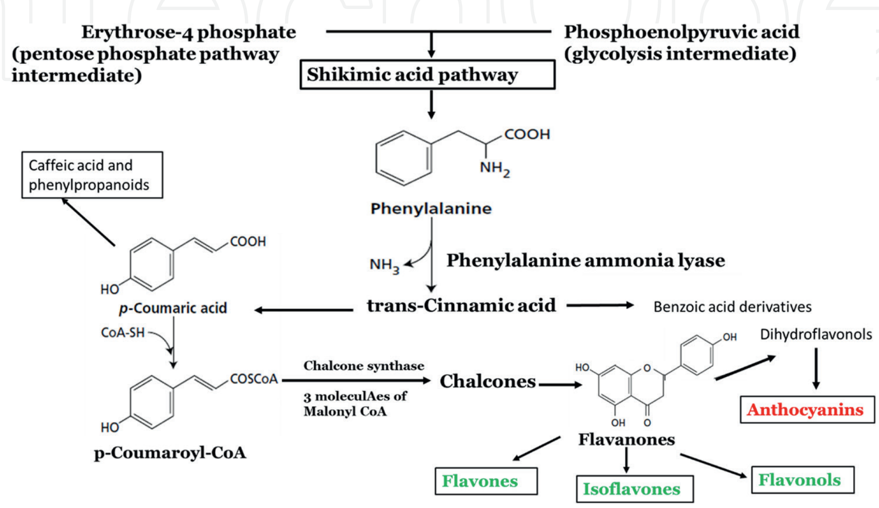

Figure 5.
Biosynthesis pathway of phenolics in apple.

first step in the synthesis of phenolic compounds is the involvement of glucose in the Pentose Phosphate Pathway (PPP) and the transformation of glucose-6-phosphate into ribulose-5-phosphate. The first step in conversion to ribulose-5-phosphate is catalysed by the enzyme glucose-6-dehydrogenase. The conversion to ribulose-5-phosphate produces an equivalent amount of nicotinamide adenine dinucleotide phosphate (NADPH) which acts as a reducing agent for cellular anabolic reactions.

PPP also produces erythrose-4-phosphate along with phosphoenolpyruvate from glycolysis. This phosphoenolpyruvate is used in the Phenylpropanoid pathway to produce phenolic compounds after going through the Shikimic pathway in which phenylalanine is produced.

5. Extraction of phenolic compounds from apples

The extraction of phenolic compounds from apples is a very crucial step in the study and characterisation of chemical and nutraceutical properties of phenolic compounds as only after proper extraction the phenolic compound could be studied and used as a dietary supplement, cosmetic product or pharmaceutical. Earlier Conventional methods such as maceration, decoction, and soxhlet were used for the extraction of phenolic compounds from apples. These days, non-conventional methods have overtaken conventional methods and are being extensively used for the extraction of phenolics. The non-conventional methods include UAE or ultrasound-assisted extraction, MAE or microwave-assisted extraction, SFE or supercritical fluid extraction, PLE or pressurised liquid extraction, and ASE or accelerated solvent extraction. The non-conventional techniques are better than conventional methods concerning yield, time, cost, solvent saving and other factors. Generally, before extraction, the samples have to go through various procedures such as milling, grinding, homogenisation etc. other procedures include air drying or freeze drying. Freeze drying is prefered over air drying because it retains the phenolic content of the sample to the maximum extent. The most commonly used method is extracting phenolic compounds using a suitable solvent. The generally used solvents for extraction procedures are methanol, ethanol, acetone, and ethyl acetate. The yield of the phenolic compound using the chemical method varies with the type of solvent used. Usually, phenolic compounds having low molecular weight give better yield in methanol while the polyphenols having higher molecular weight such as flavanols give better yield with acetone.

5.1 Introduction to different non-conventional methods of extraction

Ultrasound-assisted extraction or UAE is a non-conventional extraction technique where the extraction procedure is assisted by ultrasound waves. The efficiency of this technique greatly depends on cell disruption and effective mass transfer.

In *Microwave assisted extraction or MAE*, solvents in contact with the samples are heated using microwave energy. This feature of fastly heating the sample solvent is the main advantage of using this technique. MAE technique takes about 15 to 30 minutes but uses a very small amount of sample volume as compared to conventional methods of techniques.

In the *Supercritical fluid extraction or SFE* technique, the extractant that is the phenolic compound is separated from the matrix using supercritical fluids as extracting solvents. The main advantages of using this technique are its selectivity and high speed as the extraction process is based on the diffusion of the solvent into the matrix. The matrix used for extraction is generally solid but also may be in liquid form. One disadvantage of the SFE technique is the requirement of high pressure for extraction which makes this technique costlier as compared to other conventional methods of extraction.

Accelerated Solvent extraction and Pressurised liquid extraction or PLE techniques are quite similar to the supercritical fluid extraction technique in the respect that it also uses a solid or semi-solid matrix for extraction and also require a high degree of temperature and pressure.

5.2 Antioxidant activity measurement assay

Nowadays sophisticated methods are available for the antioxidant activity measurement assay. Chemical methods with sensitive and automated detection features are being used for the assay of antioxidant activity. The experiment for assay of the antioxidant activity was performed on two cultivars of apple namely the Idared and the Sampion. The antioxidant activity was estimated using ABTS and DPPH assays. The polyphenol profile was determined by the HPLC method. Seeds of the sample apple cultivars showed higher antioxidant capacity and also a higher content of phenolic compounds found as compared to their peel and flesh. The two phenolic compounds found in abundance in seed and peel respectively were Phloridzin and Quercetin glycoside. The result of the assay may be seen in **Table 3** [14].

5.3 Antioxidant activity assay techniques

Radical scavenging method (ROS) requires no lipids and uses a chemical system containing an oxidant, an oxidizable probe and antioxidants under assay. The mechanism followed may be either hydrogen atom transfer or electron transfer.

Oxygen radical absorbance capacity (ORAC) assay works by monitoring inhibition of peroxyl radical-induced oxidation.ORAC can detect both lipophilic as well as hydrophilic antioxidants.

Chemiluminiescence method of antioxidant assay requires a chemiluminescence species, an oxidant generally used is hydrogen peroxide and the extract to be detected. It is a very sensitive and low-cost tool used for the antioxidant assay.

DPPH radical scavenging is a commonly used antioxidant assay tool frequently used for the antioxidant assay of apples. Chemically, DPPH is 2,2-Diphenyl-1-picrylhydrazyl and a stable chromogen and deep purple in colour. DPPH method of assay is based on an electron transfer mechanism also hydrogen atom transfer being an intermediate reaction pathway.

Trolox equivalent antioxidant capacity (TEAC) assay measures the total antioxidant capacity by the ability of antioxidants to scavenge ABTS which is a stable radical. Chemically ABTS is (2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonic acid)). TEAC

Cultivar	Part	Phenolic compound	Percentage of compound
Idared	Seed	Phloridzin	84
Sampion	Seed	Phloridzin	72
Idared	Peel	Quercetin glycoside	54
Sampion	Peel	Quercetin glycoside	38

Table 3.
Phenolic content: part vs. variety.

also employs electron transfer and hydrogen atom transfer mechanisms. When combined with HPLC, it provides an efficient rapid and accurate method for the detection of individual compounds.

Ferric reducing antioxidant power (FRAP) is an electron transfer-based method which uses ferric trivalent cation as an oxidant. It is a very simple and low-cost method of antioxidant assay.

Total phenolic content (TPC) is an important tool for measuring total antioxidant activity, particularly in the case of apples. The Folin-Ciocalteu assay is generally used for the estimation of Total phenolic content. The assay uses the Folin-Ciocalteu reagent which is reduced by phenolic compounds under alkaline conditions. It is a very simple and reliable method for the assay of total antioxidant capacity but has a few drawbacks also. Folin-Ciocalteu assay is sensitive to ph, and temperature changes, therefore proper care must be taken for the accurate assay of antioxidant capacity while using this technique.

5.4 Estimation protocol of phenolic compounds

The commonly used methods for the estimation of different phenolic compounds are HPLC combined with Folin-Ciocalteu assay and chromatography analysis. Samples extracted from different varieties of fruits are collected with a mixture of acetone/water to achieve a good yield of polyphenol content. The polyphenols are analysed by normal phase HPLC and LC-MS. The total phenolic content of the sample is measured using the Folin-Ciocalteu assay. The different phenolic compounds present in the sample are detected by chromatographic analysis.

6. Phytochemical profile of apples and their bioavailability

The apple is a very nutritious food and has a very rich phytochemical profile, particularly that of phenolic compounds. Various types of phenolic compounds are found in all parts of the apple including the seeds and core. The phytochemical profile of different varieties of apples differs in terms of the content of phenolic compound and its amount also varies in different parts of apples. Phenolics are the most significant phytochemical found in apples. The phenolic content of apples includes many flavonoid compounds, phenolic acids, majorly chlorogenic acid and also hydroxycinnamic acid in small quantities, quercetin glycosides, phloretin glycosides and anthocyanins. The phenolic content of apples may vary from 0.1 g/Kg fresh weight to 10 g/Kg in certain Cider apples [15]. The apple cultivar Honeycrisp shows the highest phenolic content while the Qinyang variety showed the least content of phenolic compounds. The apple cultivar Granny Smith showed higher content of p-coumaroylquinic acid in the peel while the same phenolic content was higher in the flesh of the Gala cultivar.

Any chemical compound that is a part of our diet and beneficial to our body benefits only when it is absorbed to the highest extent in our systemic circulation. The term "*Bioavailability*" refers to the rate and extent of absorption of a particular chemical compound by the body of the organism consuming that compound. The higher the bioavailability of a compound, the greater its effectiveness. Apples have a very rich content of beneficial chemical compounds and possess high bioavailability of various phenolic compounds.

6.1 Factors affecting the bioavailability of phenolic compounds in apples

The bioavailability of different phenolic compounds found in apples is not the same. Many factors affect the bioavailability of different phenolics in apples. These factors may be Environmental factors, Food processing techniques, Chemical composition of food and Type of phenolic compound.

Environmental factors include sunlight duration, ripening stage of apple, rainfall, fruit yield etc. food processing techniques may affect the bioavailability of apple phenolics by increasing or decreasing the phenolic content of food. The different food processing techniques include Thermal treatment, Homogenisation, cooking method and method of storage. Raw apples have a higher content of phenolic compounds while cooked apples show lower phenolic content because excessive heating of apples during cooking reduces phenolic content. Homogenisation may cause alteration of the apple matrix thereby increasing the bioavailability of its phenolic content. Food processing techniques are also an important factor affecting apples' bioavailability of phenolic content. It is generally found that apple puree and apple juice have higher bioavailability as compared to unprocessed apples. That is because the phenolic content is easily and quickly absorbed from the processed apple. The method and duration of storage of apples and their products also affect the bioavailability of apple phenolics. The presence and absence of positive or negative effects in our diet may also affect the bioavailability of phenolic content from apples. The storage of apple juices for 11 months resulted in a decrease in phenolic content in apple juice [16].

6.2 Major phenolics found in apples

The two broad groups of phenolic compounds found in apples are the Flavonoids and Phenolic acids with each group consisting of a large number of compounds (**Table 4**) with varying structures.

Flavonoids are a class of polyphenolic secondary metabolites found in plants and commonly consumed in the diet of humans. Chemically, flavonoids have a general structure of a 15-carbon skeleton which consists of two phenyl rings and a heterocyclic ring. The carbon structure can be abbreviated as C6-C3-C6.

Flavonoids may be further grouped into classes such as flavanols (Catechin, Epicatechin, Pyrocyanidins), dihydrochalcones (Phloridizin, Phloretin glycosides), flavonols (Quercetin glycosides), anthocyanins.

Flavanols are derivatives of flavans that possess a 2-phenyl-3,4-dihydro-2H-chromen-3-of skeleton. Flavan-3-ol has 2 chiral carbons. Catechin and Epicatechin are epicatechins, with (−) epicatechin and (+) catechin being the most optical isomers found in nature.

Dihydrochalcones or 1,3-Diphenylpropan-1-one are organic compounds with the formula C6H5C(CH2)2C6H5 and a molar mass of 210.27 g/mol. It is a white solid and soluble in many organic solvents. Phenolic compound Phloretin belongs to this group which occurs as glycosides in apples.

Anthocyanins are glycosides of anthocyanidins, that are water-soluble vacuolar pigments. In acidic conditions, anthocyanins appear as red pigments while in alkaline conditions, they appear as blue pigments. They are abundantly present in apple peels of red apples.

The term Phenolic acids refer to the phenolic compounds having one carboxylic acid group. They are generally found in bound form as amides, esters, and glycosides and rarely occur in free form. Phenolic acids are mainly divided into two subgroups

Phenolics types	Phytochemicals
Phenol	Chlorogenic acid Hydroxy benzoic acid Hydroxycinnamic acid
Flavanoids	
Anthocyanidins	Cyanidin 3-O-arabinose Cyanidin 3-O-galactoside Cyanidin 3-O-xyloside Cyanidin 3-O-xylgalactoside
Flavonols	Quercetin 3-arabinopyranoside Quercetin 3-arabinofuranoside Quercetin 3-galactoside Quercetin 3-glucoside Quercetin 3-rhamnoside Quercetin 3-rutinoside Quercetin 3-xyloside
Dihydrochalcones	Phloretin Phloretin-20-O-xyloglucoside Phloridzin 3-Hydroxyphloridzin
Flavan-3-ols	Monomeric; (+) – Catechin, Epicatechin Oligomeric (Procyanidins) Procyanidin B1 Procyanidin B2 Procyanidin B5 Procyanidin B7 Procyanidin C1

Table 4.
Potential phenolics in apple.

hydroxybenzoic and hydroxycinnamic acid. The most abundant soluble bound hydroxycinnamic acid present in apples is Chlorogenic acid.

Chlorogenic acid is the ester of caffeic acid and quinic acid functioning as an intermediate in lignin biosynthesis. The acid has the formula $C_{16}H_{18}O_9$ and a molar mass of 354.31 g/mol.

6.3 Role of phenolics

Phenolics play an important role in plant development as phenolic compounds are significant molecules for the biosynthesis of lignin and other plant pigments. In plants, phenolic compounds have anti-microbial activity and also resist pathogens.

7. Apple: eating an apple a day keeps the harmful radicals away!

The tremendous contribution of phenolics and flavonoids to antioxidant capacity provides a significant role as a scavenger and alleviates the harmful effect of reactive oxygen species in the cell. Research has suggested that the various polyphenol compounds of apples are effective in preventing several chronic diseases such as heart disease, cancer etc.

Polyphenols also exhibit anti-obesity effects. Flavanoids such as epicatechin may prevent heart disease by lowering blood pressure, reducing LDL cholesterol and reducing atherosclerosis [17].

Quercetin and phloridzin reduce type 2 diabetes risk. Quercetin's anti-inflammatory effects reduce insulin resistance while phloridzin cuts sugar uptake by the intestines [18].

Quercetin helps in regulating the immune system by reducing inflammation. It is also effective against bronchial asthma and sinusitis [19].

Proanthocyanidins have been reported to prevent and reduce allergic asthma airway inflammation [20].

Various researchers have also suggested that phenolic compounds have anti-cancer properties and are effective in preventing certain cancers, i.e., lung breast and digestive tract cancer [21].

Chlorogenic acid is supposed to inhibit weight gain, prevent liver steatosis and block insulin resistance [22].

Various researchers have reported that apple extracts also show antimicrobial properties. According to literature data, extracts of the peel of the Royal Gala variety and the Granny Smith variety showed inhibition of the growth of *Escherichia coli*, *Pseudomonas aeruginosa* and staphylococcus aureus strains.

8. The role of phenolics in apples to the total antioxidant capacity

Research that aimed to examine the average concentrations of the major phenolic compounds in six cultivars of apples. The average phenolic concentration detected among six cultivars is summarised in the table below and a pie chart (**Figure 6**) (derived from **Table 5**) showing percentages of different phenolics [23].

The results derived from high-performance liquid chromatography with diode array detection [24] performed on different varieties of apples are summarised in the chart (**Table 6**).

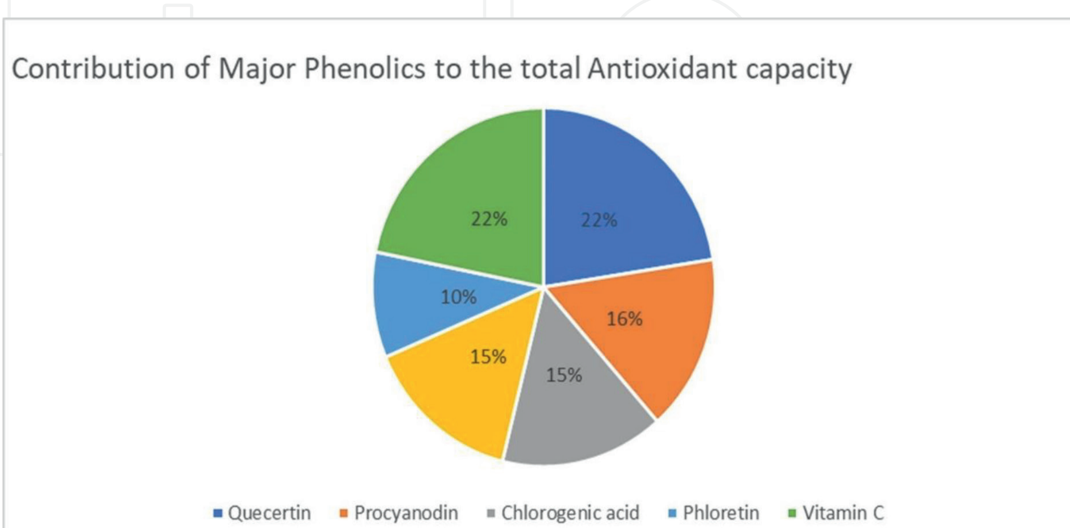

Figure 6.
Pie chart depicting the contribution of different phenolics to the total antioxidant capacity.

Compound detected	Amount present (mg/100 g)
Quercetin glycosides	13.2
Procyanidin B	9.35
Chlorogenic acid	9.02
Epicatechin	8.65
Phloretin glycosides	5.59
Vitamin C	12.8

Table 5.
Amount of different phenolic compounds in apples.

Apple variety	Part of apple	Content of major phenolic compound	Antioxidant contribution	Benefits	Reference
Golden delicious	Peel	Catechin	66–164	Prevent cell damage	[24]
Red delicious	Peel	Phloridzin	104–159	Anti-diabetic	[24]
Reineta	Peel	Epicatechin	283–439	Anti-hypertensive	[24]
Red delicious	peel	Chlorogenic acid	113–157	Anti-obesity	[24]

Table 6.
The major content of phenolic compounds with their antioxidant contribution (mg/kg fresh weight).

8.1 Phenolic compounds to the total antioxidant capacity of apples

According to available literature and experiments conducted by various researchers, we may conclude that flavanol content contributes most to the antioxidant capacity of apples. The table and pie chart also supports that the antioxidant activity of apples is majorly due to phenolic compounds which are flavanoids and phenolic acids and Vitamin C has an insignificant contribution to the antioxidant capacity of apple as compared to phenolic compounds.

9. Phenolics: emerging nutraceutical

Phenolic compounds obtained naturally from plants have lately become significant molecules. Scientists hold high aspirations as the research suggests phenolics to be a compound of high nutraceutical value which could be used in the diet, drugs cosmetics etc. many researchers have indicated the promising result of the use of phenolic compounds in the industrial sector. A very well-researched property of Phenolic compounds is their antioxidant property which has shown significant results in various health ailments. Phenolic compounds can be used in food as additives and preservatives; in cosmetics as UV protection and anti-ageing agents. Research has given hopes of using phenolic compounds as potential pharmaceuticals which may in future provide cures to many incurable and chronic diseases. However, there is still a lack of knowledge and awareness about the bioavailability and nutritional value of phenolic compounds and further research is being done. The potential use of phenolic compounds in different spheres of life may become a substitute for many artificially synthesised compounds and would prove to be a boon for the human race.

10. Conclusion

Apples have been praised for their health benefits for ages and now it is evident as per the research and experiments conducted on the quantitative and qualitative characterisation of apple phytochemicals. The different parts of apples such as peel, flesh and even seeds are enriched with several types of phenolic compounds. Comprehensive research is being done by the scientific community for the advancement of techniques used for the extraction and processing of phenolic compounds from apples so that the bioavailability of the phenolic compounds could be enhanced. The higher concentration of phenolic compounds in apples has drawn the attention of the health sector due to its potential to be used as a dietary supplement as well as an essential component of many industrial products such as drugs and cosmetics. Several phenolic compounds have been detected in the different parts and different cultivars of apples and each with specific health benefits. The amount of phenolic compounds present in apples is higher than the other phytochemicals in apples. The antioxidant activity of apples due to vitamin C and other phytochemicals is very low as compared to the antioxidant activity due to the concentration of the phenolic compound in apples. According to this review based on the available literature data, it is concluded that the antioxidant capacity of apples is significantly due to the phenolic compounds present in them. The apple is a very good source of antioxidants and should be consumed with peel as the peel shows a higher level of antioxidant activity.

Conflict of interest

The authors declare no conflict of interest.

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