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Therapeutic and nutraceutical potential of bioactive compounds extracted from fruit residues

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The growing interest in the substitution of synthetic food antioxidants by natural ones has fostered research in identifying new low cost antioxidants having commercial potential. Fruits, such as mango, banana and those belonging to the citrus family leave behind a substantial amount of residues in the form of peels, pulp, seeds and stones. Due to lack of infrastructure to handle a huge quantity of available biomass, lack of processing facilities and high processing cost, these residues represent a major disposal problem, especially in developing countries. Because of the presence of phenolic compounds which impart nutraceutical properties to fruit residues, such residues hold tremendous potential in food, pharmaceutical and cosmetic industry. The biological properties such as anticarcinogenicity, antimutagenicity, antiallergenicity and antiageing activity have been reported for both natural as well as synthetic antioxidants. Special attention is focused on extraction of bioactive compounds from inexpensive or residual sources. The purpose of this review is to characterize different phenolics present in the fruit residues; discuss the antioxidant potential of such residues and the assays used in determination of anti-oxidant properties; discuss various methods for efficient extraction of the bioactive compounds and highlight the importance of fruit residues as potential nutraceutial resources and biopreservatives

Keywords: Anticarcinogenicity, antioxidants, biopreservatives, fruit residues, nutraceuticals, phenolic compounds

INTRODUCTION

The most important class of bioactive compounds found in plants are polyphenols, which are a diversified group of secondary plant metabolites that are derived through pentose phosphate, shikimate and phenylpropanoid pathways. Phenolic compounds are found predominantly in the by-products than in the edible portions as they tend to accumulate in the dermal tissues of plant body because of their potential role in the protection against UV rays, as attractants in fruit dispersal, and also as defense chemicals against pathogens (Haslam, 1988). Soong and Barlow (2004) reported that the total phenolic content (TPC) of seeds of several fruits, i.e., mango, longan and avocado was higher than that of the edible flesh. Li et al. (2009) reported that *p*-Coumaric acid was found to repress the expression of T3SS genes of the plant pathogen *Dickeya dadanti*, suggesting that the plants defend against the bacterial pathogens by manipulating the expression of T3SS gene.

In food and beverages, phenolic compounds are associated with sensory attributes such as colour, bitterness and astringency (Shi et al., 2003). Several reports have convincingly shown that the phenolic compounds have strong antioxidant properties as oxygen scavengers, peroxide decomposers, metal chelating agents and free radical inhibitors (Duan et al., 2007; Sreeramulu and Raghunath, 2010). Antioxidants are substances that delay or prevent the oxidation of cellular oxidizable substrates. Natural antioxidants present in foods and other biological materials have attracted considerable interest because of their presumed safety and potential nutritional and therapeutic value.

The fruit processing industry generates large volumes of solid waste in the form of peels, kernels and pulp following the industrial processing of fruit juices. Fruit residues found in the

household kitchens, hotel and restaurant trash bins also contribute significantly to the municipal solid waste. The disposal of residues in open spaces or in municipal bins leads to environmental pollution problems. One of the most effective options for management of fruit residues is the recovery of phytochemicals/ bioactive compounds from the fruit residues which could be used in food, cosmetic, and pharmaceutical industry. Far from claiming completeness, this review aims to examine the nature and chemistry of phenolics, *the presence of phenolic compounds in fruit residues*, assays for determination of antioxidant ability, role of phenolics in imparting antioxidant potential, different methods in extraction of bioactive compounds and potential application of these compounds in food and pharmaceutical industry.

CHEMISTRY AND CLASSIFICATION OF POLYPHENOLIC COMPOUNDS

Polyphenolic compounds are divided into several classes based on their structural diversity (Fig. 1). Of these, flavonoids, phenolic acids, tannins (hydrolyzable and condensed) are regarded as the main dietary phenolic compounds (D archivio et al., 2007). The chemical structure of the main classes of phenolic compounds is presented in Fig. 2.

Flavonoids: Flavonoids are important antioxidants due to their high redox potential which allows them to act as reducing agents, hydrogen donors, and singlet oxygen quenchers. The structure consists of two benzene rings, A and B on either side of a 3-carbon ring which forms heterocyclic ring, C. The aromatic ring A is derived from the acetate/malonate pathway, while ring B is derived from phenylalanine through the shikimate pathway (Merken and Beecher, 2000). Multiple combinations of hydroxyl groups, sugars, oxygen and methyl groups to these structures create various classes of flavonoids i.e. flavonols, flavones, flavanones, isoflavones,

flavanonols, and anthocyanidins (Hollman and Katan, 1999), of which flavones and flavonols are the most widely occurring (Harborne et al., 1999). The chemical structures of the main classes of flavonoids are presented in Fig. 3. Substitutions to rings A and B give rise to different compounds within each class of flavonoids (Pietta, 2000). Both flavonols and flavanones are important class of flavonoids. Flavanones are characterized by the presence of a saturated three-carbon chain and an oxygen atom in the C4 position. Flavanones are present in high concentrations in citrus fruits. Apart from citrus fruits, flavanones are also present in tomatoes and certain aromatic plants, such as mint. Isoflavones are phytochemicals found in many plants and plant-derived foods which impart health benefits. Some physiological effects are attributed to their structural similarities to β-estradiols, and thus, they are occasionally referred to as 'phytoestrogens' (D archivio et al., 2007; Klejdus et al., 2007).

Anthocyanins are water-soluble vacuolar pigments that may appear as red, purple, or blue depending on pH and are synthesized *via* the phenyl propanoid pathway. Anthocyanins occur in all plant tissues, including leaves, stems, roots, flowers, and fruits. The anthocyanidins are the basic structures of the anthocyanins which consist of an aromatic ring A bonded to a heterocyclic ring C that contains oxygen, which is also bonded by a carbon-carbon bond to a third aromatic ring B (Konczak and Zhang, 2004). The structures of six important anthocyanidins i.e. pelargonidin, cyanidin, peonidin, delphinidin, petunidin and malvidin are shown in Fig.4. Several researchers have investigated the antioxidant activity of flavonoid compounds and have attempted to define the structural characteristics of flavonoids that contribute to their activity. For example, the presence of o-dihydroxy groups in the B ring and C_2-double bond in

conjunction with the 4-oxo function in the A and C rings are associated with antioxidant activity (Foti et al., 1996; Neito et al., 1993).

Phenolic acids: Phenolic acids constitute about one-third of the dietary phenols, which may be present in plants in free and bound forms (Robbins, 2003). Bound phenolics may be linked to various plant components through ester, ether or acetal bonds (Zadernowski et al., 2009). Phenolic acids largely consist of two sub-groups; the hydroxybenzoic acid and the hydroxycinnamic acid. Previous studies have shown that hydroxycinnamic acids are generally more abundant than hydroxybenzoic acids in fruits and that they differ in the pattern of their aromatic rings (Herrmann, 1989; Shahidi and Naczk, 1995). Hydroxycinnamic acids are aromatic compounds with a three-carbon side chain (C_6– C_3) with caffeic, ferulic, p-coumaric and sinapic acids being the most common representatives (Bravo, 1998). The most well known bound hydroxycinnamic acid is cholorogenic acid, which is a combination of caffeic and quinic acids. Unlike hydroxycinnamates, hydroxybenzoic acid derivatives are mainly present in foods in the form of glucosides, such as p-hydroxybenzoic acid, vanilic and protocatechuic acid (Herrmann, 1989; Clifford, 1999; Manach et al., 2004; Shahidi and Naczk, 1995). Ferulic acid is covalently conjugated to polysaccharides present in the cell wall, lignin, glycoproteins, and insoluble carbohydrate biopolymers.

Among the variety of phenolic compounds, phenolic acids have attracted considerable interest in the past few years due to their potential health benefits. Caffeic acid, chlorogenic acid, ferulic acid, sinapic acid and p-coumaric acid have higher antioxidant ability than the hydroxy derivatives of benzoic acid viz., p-hydroxybenzoic acid, vanillic acid and syringic acid (Dziedzic 1981). Phenolic acids have been reported to demonstrate antibacterial, antiviral,

anticarcinogenic, anti-inflammatory and vasodilatory actions (Duthie et al., 2000; Shahidi and Naczk, 1995).

Tannins: Tannins can be subdivided into hydrolyzable and condensed tannins (Porter, 1989). The most widely studied condensed tannins are (-) epicatechin and (+) catechin. Epigallocatechin formed by addition of gallic acid to epicatechin showed higher antioxidant ability than epicatechin (Porter, 1989). Hydrolyzable tannins are derivatives of gallic acid (3, 4, 5 trihydroxyl benzoic acid) isolated from several genera of brown algae (Porter, 1989), but these do not contribute significantly to the human diet (Bravo, 1998).

***Stilbenes and lignans*:** Stilbenes are phytolexins which are induced in response to infection by pathogens or to a variety of stress conditions (Bavaresco, 2003). Resveratrol (3,5,4'-trans-trihydroxystilbene) is one of the important stilbenes present in the human diet (Delmas et al., 2006). It was first isolated from the roots of hellebore (*Veratrum grandiflorum*) in 1940 (Takaoka, 1940). The interest in this compound began when it was detected in wine and it showed some cardioprotective effects (Siemann and Creasy, 1992). It was only after the report of Jang et al. (1997) on anticancer potential of resveratrol that the scientific community became really interested in this compound and the number of scientific reports on the effects and properties of this compound increased exponentially. The interest in lignans and their synthetic derivatives is growing because of their potential applications in cancer chemotherapy and various other pharmacological effects (Saleem et al., 2005).

IMPORTANCE OF NUTRACEUTICAL COMPOUNDS IN HUMAN HEALTH

During the last decade, natural antioxidants, particularly phenolics have been under very close scrutiny as potential therapeutic agents against a wide range of ailments, including

neurodegenerative diseases, cancer, diabetes, cardiovascular dysfunctions, inflammatory diseases and also ageing. The concerns associated with the use of artificial antioxidants and the potential applications of the natural phenolics in treating various ailments are discussed in the following sections. The role of phenolic compounds in treating various disorders is also summarized in Table 1.

1. ***Toxicity caused by artificial antioxidants***

In food industry, synthetic antioxidants are used to prevent lipid peroxidation and oxidation of food constituents. Tert-butyl hydroxyanisole (BHA), tert-butyl hydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ) and propyl gallate (PG) are the commonest synthetic phenolic antioxidants used in edible oils or lipid based foods in order to prevent oxidative rancidity. However, the safety and toxicity of synthetic antioxidants have raised important concerns because such materials may cause liver swelling and influence liver enzyme activities and carcinogenicity (Jayaprakasha et al., 2003; Martin and Gilbert, 1968; Namiki, 1990). Reports have also revealed that BHA and BHT could be toxic (Sherwin, 1990). Moreover, the synthetic antioxidants show low solubility and moderate antioxidant activity and therefore strong restrictions have been placed on their applications (Barlow, 1990). Hence, considerable interest has been shown in the use of natural antioxidants which are likely to have properties that can be exploited by food and pharmaceutical industry. The replacement of synthetic antioxidants by natural ones may have benefits due to health implications and functionality, such as solubility in both oil and water.

2. ***Natural phenolic compounds as cancer preventive agents***

The interest in antioxidants has been increasing because of their high capacity in scavenging free radicals which are responsible for causing diseases, such as cancer. It is therefore important to understand the reasons for oxidative stress.

Oxidative stress

Oxidative stress may be defined as an imbalance between pro-oxidant and antioxidant agents. This imbalance may be due to an excess of pro-oxidant agents; a deficiency of antioxidant agents or both factors simultaneously. The origin of the oxidative stress is an alteration of the redox status in cells leading to a cellular response to counteract the oxidizing action (Sies, 1986). The most important pro-oxidant agents in biological systems are those derived from oxygen, more commonly known as reactive oxygen species ($ROS^{\cdot}$), although there are also reactive species derived from nitrogen ($RNS^{\cdot}$) and sulphur ($RSS^{\cdot}$) [Halliwell, 1994]. Some of these molecules exhibit great reactivity and the biological importance of such reactive molecules relies on their capacity to be easily transformed into the hydroxyl radical, especially in the presence of iron as is the case with superoxide radicals ($O_2^{\cdot}$) or hydrogen peroxide (H_2O_2) [Fenton, 1894].

A free radical is a chemical species with unpaired electron in an atom or molecule that provides greater reactivity thereby shortening its half life (Simic and Taylor, 1988). Some of these reactive species are generated during undesired secondary reactions between biomolecules. Other reactive species, however are generated *in-vivo* for a specific aim such as in the case of activated phagocytes which produce $O_2^{\cdot}$ and H_2O_2 (Halliwell, 1996). The production of these reactive species *via* exogenous sources is due to ionizing radiations, situations such as hyperoxia,

through the use of farm chemicals (fertilizers and pesticides), many prescription drugs, processed foods, cigarette smoke, environmental pollution, alcohol, electromagnetic radiation, and stress.

Many of the sources of free radicals are under our control, because they result from lifestyle choices which in most cases can be controlled. The endogenous sources of free radicals are mitochondrial and endoplasmic reticulum electronic transport chain, enzymatic system of xanthine oxidase, peroxisomes or microsomes and cytosolic enzymes (Davies, 1995). The attack of the reactive oxygen species on DNA and lipids causes mutagenesis and lipid peroxidation, respectively (Sawa et al., 1999). One of the most interesting parameters to determine oxidative stress is the glutathione redox status. The free radicals and other activated oxygen species are continuously formed in our body. Living organisms have developed a number of defense systems against the free radicals by preventing the production of reactive oxygen species and repair the damage caused by such molecules. These defense molecules may be enzymes like catalases, superoxide dismutases, glutathione peroxidases and the non enzymatic systems like antioxidants including polyphenols, vitamin C and vitamin E (Davies, 1995; Halliwell, 1994; Halliwell, 1996).

Recent scientific studies have proved that the antioxidants are capable of protecting cells from free radical damage by inhibiting mutation and cancer because they have a scavenging role against reactive oxygen species, i.e, superoxide anion, hydroxyl radicals and peroxy radicals (Hochstein and Atallah, 1988). Antioxidants act in various ways, which include forming complexes of redox-catalytic metal ions, scavenging of free radicals, and decomposition of peroxides. There is a considerable amount of evidence revealing an association between individuals who have a diet rich in fresh fruits and vegetables and decreased risk of certain forms

of cancer and a longer life expectancy. Mantena et al. (2006) studied the effect of grape seed proanthocyanidins in inducing apoptosis and inhibition of metastasis in both cultured breast and colon cancer cells. Pomegranate peel extracts have been shown to retard proliferation of cells in several different human cancer cell lines (Kawaii and Lansky, 2004; Mavlyanov et al., 1997; Settheetham and Ishida, 1995). Pomegranate peel contains substantial amounts of polyphenols such as ellagic acid and gallic acid (Nasr et al., 1996). The presence of these polyphenols in the pomegranate peel may be responsible for antimutagenicity of peel extracts (Gil et al., 2000). Another study conducted by Jang et al. (1997) illustrated that resveratrol, a natural product derived from grapes, inhibited tumor initiation, promotion, and progression.

3. ***Natural phenolic compounds as cardiovascular therapeutics***

Low density lipoproteins (LDL) transport cholesterol to extra hepatic tissues and high density lipoproteins (HDL) are responsible for the reverse transport of cholesterol. Strong evidence exists that oxidation of LDL is a risk factor for atherosclerosis and coronary heart disease (Diaz et al., 1997). Following oxidation, LDL is accumulated in sub-endothelial cells, the reverse transport of cholesterol is blocked and the adhesion of platelets to endothelial is promoted. In this situation, phenolics that bind LDL are good candidates for preventing lipid peroxidation and atherosclerotic process. The decline in LDL oxidation observed after consumption of foods rich in phenolic compounds provides indirect evidence of a binding of phenols to LDL (Meyer et al., 1998; Nakagawa et al., 1999).

Several studies have shown that phenolic compounds reduce *in-vitro* oxidation of low density lipoprotein. Of them, phenolics with multiple hydroxyl groups are generally the most

efficient for preventing lipid and low density lipoproteins (LDL) oxidation and therefore reduce the risk of atherogenesis (Meyer et al., 1998; Nakagawa et al., 1999). An anthocyanin rich extract from black rice decreased serum levels of triglycerides, total cholesterol and non-HDL cholesterol and reduced the area of atherosclerotic plaques in apolipoprotein E-deficient mice (Xia et al., 2006). Administration of a single dose of a mixture of anthocyanins decreased the size of infarct area in a rat model of myocardial injury (Kim et al., 2006). Grape seed extracts have shown a number of beneficial effects in humans (Kar et al., 2006), including the increase in plasma antioxidant capacity (Vinson et al., 2001) and prevention of plasma postprandial oxidative stress (Natella et al., 2002).

Furthermore, other physiological activities of natural antioxidants have been described, such as antibacterial, antiviral, antimutagenic (Ikken et al., 1999), antiallergic (Noguchi et al., 1999), antimetastasis activity (Maeda et al., 1999), platelet aggregation inhibition (Ito et al., 1998) and antiulcer activity (Saito et al., 1998; Vilegas et al., 1999). Furiga et al. (2009) evaluated grape seed extract activity on oral anaerobes and observed that the biofilm formation was significantly decreased at a concentration of 2000 µg/ml.

PHENOLIC COMPOUNDS IN IMPORTANT FRUIT RESIDUES

Increased awareness about the nutritional properties of fruits and vegetables has led to an upsurge both in acreage and production of horticultural commodities. The full utilization of horticultural produce is a requirement and a demand that needs to be met by countries wishing to implement low-waste technology in their agribusiness. In many cases, the raw fruit is not

consumed directly by humans but it first undergoes processing to separate the desired value product from other constituents and therefore generates large quantity of residues. These by-products or residues usually have significant value, which has not been realized in developing countries like India.

The inability to capture the unrealized value of by-products in developing countries could be attributed to three major factors. First and foremost is the lack of information about market opportunities for by-product uses. Secondly, there may be very few ancillary industries that are able to make use of specific by-products. Third factor influencing by-products utilization in developing countries is the low level of market development. Although, comprehensive information about the quantity of residues generated from different fruits is not available, previous studies have indicated that banana peel accounts for about 30-40% of the banana fruit weight (Hammond et al 1996, Oberoi et al., 2011). Kinnow peel, pulp and seeds account for more than 50% of the total fruit weight (Kalra et al., 1999). Major wastes of mango processing industry are peels and stones, amounting for about 35–60% of the total fruit weight (Larrauri et al., 1996). Litchi seeds and pericarp account for about 19% and 13%, respectively of the fresh fruit weight. Table 2 summarizes the contents of total phenolics found in the extracts of different fruit residues.

Apple pomace is the main by-product of apple juice processing plant and has been found to be a good source of polyphenols (Peschel et al., 2006; Chodak and Tarko, 2007). Among all the known fruit residues, grape residues probably have been most extensively studied for their therapeutic potential. Grape seed extract has been found to decrease thiobarbituric acid reactive substances (TBARS) value but showed no effect on HDL-cholesterol, (Vigna et al., 2003).

Authors however reported a significant reduction in the LDL-cholesterol, triglycerides and total cholesterol values. Grape seed extract has also been found to reduce chronic pancreatic problems, vomiting and pain (Banerjee and Bagachi, 2001).

Litchi (*Litchi chinensis Sonn*.) is a tropical fruit originating from China, with a bright red attractive pericarp surrounding a white aril (Nakasone and Paul, 1998). Litchi pericarp contains large amount of anthocyanins which are responsible for the red colour and possess anti-oxidant characteristics. Some recently published reports have highlighted the importance of litchi seeds. Xu et al. (2010a, 2010b, 2011a, 2011b) isolated principal compounds from litchi seeds and evaluated them for different biological activities. They isolated two sesquiterpenoid glucosides and three flavonoid glycosides which showed potent *in-vitro* cytotoxicity against human carcinoma cell lines. They further reported that seven proanthocyanidins exhibited *in-vitro* antiviral activity against coxsachie virus and herpes simplex virus, c-AMP phosphodiesterase inhibitory and antioxidant activities. The structures of some of the new compounds isolated by Xu et al., (2010a, 2010b, 2011a, 2011b) are presented in Figure 5.

Citrus fruits consist of oranges, Kinnow, khatta, lime, lemon, grapefruit, malta, sweet orange etc. Citrus by-products are major sources of phenolic compounds. Citrus peels in particular are an abundant source of natural flavonoids and contain higher amount of phenolics compared to the edible portions. Flavonoids present in citrus by-products have been extensively studied for antioxidative, anti-cancer, anti-viral, and anti- inflammatory activities, effects on capillary fragility, and an observed inhibition of human platelet aggregation (Braddock, 1995). Recent research suggests that citrus fruits possess another group of health benefit phytochemicals called limonoids, which are highly oxygenated triterpenoids. Citrus limonoids appear in large

amounts in citrus juice and citrus tissues as water soluble limonoid glucosides or in seeds as water insoluble limonoid aglycones. Limonin, nomilin and nomilinic acid are the major limonoids in citrus fruits, while both neem seeds and leaves contain the limonoid azadirachtin (Jayaprakasha et al., 2008). Currently, limonoids are under investigation for a wide variety of therapeutic effects, which include antiviral, antifungal, antibacterial, antineoplastic and antimalarial effects (Bentley et al., 1990).

Mango (*Mangifera indica*) is one of the most important tropical fruits. India ranks first in production of mangoes in the world. Mango peels and stones generated in large quantities during processing of mangoes may also be used as a source of natural antioxidants.

Papaya (*Carica papaya*) is a tree-like herbaceous plant, a member of the small family Caricaceae and widely cultivated for its edible fruits. Phenolic compounds from papaya waste are considered as powerful antioxidants which help in reducing oxidative stress.

Banana (*Musa paradisiaca*) represents one of the most important fruit crops with a global annual production of more than 50 million tons. Attempts at utilization of banana waste include the biotechnological production of ethanol, α-amylase, hemicellulases and cellulases (Oberoi et al., 2011). Banana peel has also been studied for antioxidant and antimicrobial properties (Matook et al., 2005). Furthermore, carotenoids, such as β-carotene, α-carotene and different xanthophylls have been identified in banana peel in the range of 300–400 μg lutein equivalents/100 g (Subagio et al., 1996) as well as sterols and triterpenes, such as β-sitosterol, stigmasterol, campesterol, cycloeucalenol, cycloartenol, and 24-methylene cycloartanol (Knapp and Nicholas, 1969). Pazmino et al. (2001) concluded that the banana waste is a good and abundant source of anthocyanins and a useful tool in anthocyanins identification since all the six

most common anthocyanidins (delphinidin, cyanidin, pelargonidin, peonidin, petunidin and malvidin) are present in banana peels.

Pomegranate peel, a nutritive-rich by-product accounts for a significant portion of the pomegranate fruit is also available in large quantities, owing to the increased production of pomegranate. Pomegranate peel yields double the amount of antioxidants than the pulp. Pomegranate peel has been used in the preparation of tinctures, cosmetics, therapeutic formulae and food recipes. The phenolic constituents of some of the important fruit residues are summarized in Table 3.

METHODS FOR DETERMINING ANTIOXIDANT ACTIVITY

A desirable method for evaluating the antioxidant activity should be rapid, reproducible, should require small amounts of chemicals, and should not be influenced by the physical properties of the matrix. Depending on the action of antioxidants, most of the chemical methods are based on their ability to scavenge different free radicals. However, UV-absorption and chelation ability are also responsible for the antioxidant activity in oily systems (Chen and Ahn, 1998). Methods like ABTS + (radical cation of 2,2-azinobis-3-ethylbenzothiozoline-6-sulphonate), DPPH (2,2-diphenil-1- picryl hydrazyl) radical have been developed for determining the scavenging activity with different challengers, such as superoxide radical ($O_2^{\cdot -}$), hydroxyl ($OH^{\cdot}$), nitric oxide ($NO^{\cdot}$) and alkylperoxyl radicals. Two methods commonly used to evaluate antioxidant activities are DPPH and ABTS assays, which use DPPH and ABTS as free radical generators, respectively. The mechanism involved in both the methods is similar as the absorption spectra of the free radical changes when molecule is reduced by an antioxidant or free

radical species (Arnao, 2000). Some findings have suggested that the ABTS assay is better than DPPH as ABTS is soluble in water and organic solvents and it reacts relatively rapidly compared to DPPH (Teow, et al. 2007). Trolox (a water-soluble vitamin E analog) equivalent antioxidant capacity (TEAC) has been used to determine the hierarchy of radical scavenging abilities of flavonoids as electron- or H donating agents through determination of their ability to scavenge ABTS radical/ DPPH radical (Rice-Evans and Miller, 1998). Colour interference of the DPPH assay with samples that contain anthocyanins leads to under estimation of the antioxidant activity. However, this problem does not occur with ABTS assay (Arnao, 2000).

Oxygen radical absorbance capacity (ORAC) is another method used to measure antioxidant capacity *in-vitro*. This method is based on inhibition of peroxyl radical induced oxidation initiated by thermal decomposition of azo-compounds, such as 2, 2- azobis (2- amidino propane) dihydrochloride (AAPH). The antioxidants react with peroxyl radicals and delay the degradation of fluorescein, a fluorescent probe. The ORAC method uses biologically relevant free radicals, integrates both time and degree of antioxidant activity into one data value and it is readily adaptable to a high throughput assay system. The advantage of ORAC method is its ability to assay both hydrophilic and lipophillic antioxidants, which results in better measurements of total antioxidant activity (Prior et al., 2003).

Ferric reducing antioxidant power (FRAP) method has also been widely used to measure the antioxidant capacity. However, the disadvantage of this method is that it is time consuming and not very reliable as the continuous release of ferrous ions alter the absorbance values, leading to erroneous results. Other drawbacks of this method are interference with the extracts containing coloured pigments, reaction kinetics and quantification method (Prior et al., 2005).

Previous studies have reported correlations among antioxidant activities measured by different methods (Awika et al., 2005; Babbar et al., 2011). In a previous study we observed a significant correlation between DPPH and ABTS (r^2-0.91) for different fruit residues (Babbar et al., 2011). In another study, the r^2 values for correlation between ORAC and ABTS, and ORAC and DPPH were 0.99 and 0.98 respectively, for the antioxidant capacity of sorghum grains (Awika et al., 2003). Although, it is not possible to arrive at a single most efficient assay method which is simple, cheap, accurate and precise, we feel that the antioxidant capacity should be determined by at least two methods so that more of the types of antioxidants measured by different methods provide a reliable antioxidant profile and precise and accurate values are reported for the compound.

METHODS FOR EXTRACTION OF POLYPHENOLIC COMPOUNDS:

The antioxidant activity of extracts is also strongly dependent on the solvent used for extraction of the phytochemicals due to the different antioxidant potential of compounds with different polarity (Julkunen, 1985; Marinova and Yanishlieva, 1997). Since, the antioxidant activity depends on the concentration of polyphenols and the antioxidant assay, comparative studies on selection of a solvent for extraction of polyphenolic compounds that impart antioxidant activity are also required for each substrate.

Apolar solvents are among the most commonly employed solvents for extracting polyphenols from different sources. Ethyl acetate and diethyl ether have been used for extraction of low molecular weight phenols from oak wood (Fernandez et al., 1996). Table 5 shows the

efficiency of different solvents in extraction of polyphenolic compounds. The extraction efficiency for extracting the phenolic compounds from tamarind seeds was better with less polar solvents such as, ethyl acetate than with the mixtures of ethanol and methanol, or methanol alone. Lower IC_{50} values for the DPPH radical (amount of antioxidant required for causing a 50% reduction in the absorbance of DPPH) were observed for butanol extracts followed by ethyl acetate extracts (Tsuda et al., 1994). Julkunen (1985) found a different behaviour in the extraction of different compounds and total extractable polyphenols (TEP). The author further reported that the maximum TEP yields were attained with methanol, whereas 50% acetone extracted more selectively leucoanthocyanins, but no significant effect was observed in the extraction of glycosides using either of the solvents. Azizah et al. (1999) reported maximum antioxidant activity from cocoa by-products (cocoa powder, cocoa nib, cocoa shell) extracted with methanol, followed by mixtures of chloroform, ether and dichloroethane or chloroform, methanol and dichloroethane. Maximum yield of phenolic compounds was obtained using methanol containing 0.1% HCl (v/v) ; methanol containing water; and a mixture of ethanol and water (3:1 v/v), respectively, whereas pure ethanol resulted in poor polyphenol extraction from grape seeds (Maier et al., 2009). The highest content of total phenolics was found in the extracts obtained with water from residues of different oilseeds followed by methanol while acetone gave the lowest yield (Matthaus, 2002).

Water as an environmental friendly extraction medium has been found to be very effective in antioxidant extraction from pomegranate marc (Qu et al., 2009; Singh et al., 2002). A combination of ethanol/methanol with water was effective in extraction of polar compounds such as flavonoids, phenolic acids and sugars from litchi seeds depending upon their polarity

(Jayaprakasha et al., 2008). As discussed in this section, solvents with different polarities work well with different residues. The concentration of active compounds, their bonding with the other cells/ tissues and other constituents like cellulose, lignin, pectin etc. determine their extraction efficiency. Although, no single solvent can be termed as the most ideal solvent for recovery of the bioactive compounds, available literature suggests that the solvents like methanol and ethanol are effective in extraction of phenolic compounds from the fruit residues. Some of the common solvents successfully employed for extraction of specific phenolic compounds are mentioned in Table 4.

The above mentioned solvents are usually employed for extraction of free phenolics from the fruit residues. The bound phenolics such as ferulic acid and p-coumaric acid are ester-linked to the cell wall polysaccharides in most plants. Acidified and alkaline solvents are generally used for extraction of bound phenolics from the plant material. Bound phenolics are extracted from the residues from which the free phenolics have already been extracted. Kumar et al. (2006) treated the residual material after extraction of free phenolics from amla and turmeric with sodium hydroxide containing sodium borohydride under nitrogen atmosphere and the supernatant obtained after centrifugation was acidified with hydrochloric acid and the extracted phenolics were determined colorometrically. Bocco et al (1998) treated the citrus peel and seeds from which the free phenolics had already been extracted with 2M NaOH under nitrogen. The clear supernatant was acidified with 6 N HCl at pH 1 and was then extracted three times with ethyl acetate. The organic phase was evaporated to dryness under vacuum at 40 °C, and the residue was dissolved in dimethylformamide (DMF) for determination of bound phenolics. Nara et al. (2006) also employed the procedure of Bocco et al. (1998) for extraction of bound

phenolics from potato peels except that methanol was used instead of DMF for subsequent determinations.

Supercritical fluid extraction (SFE) technology is also being used extensively to extract target compounds from a variety of matrices at laboratory and commercial scale. Supercritical Fluid extraction (SFE) is based on the fact that, close to the critical point, the solvent changes its properties rapidly with only slight variations of pressure (Palenzuela et al., 2004). In supercritical fluid extraction, carbon dioxide is the main solvent used especially when the target molecule is apolar. However, supercritical water systems have also been used to extract polar compounds (Henry and Yonker, 2006). The critical point of water is very high (374 °C, 22.064 MPa), therefore superheated water cannot be used to extract heat-labile compounds (Lang and Wai, 2001). Carbon dioxide on the other hand, has a relatively low critical temperature of 31.1 °C and a low critical pressure of 7.4 MPa (CRC, 2008).Other advantages of using CO_2 are its safety, food grade nature and easy availability at a relatively low cost and high purity (Diaz et al., 2006). In the critical region, there is only one phase, which possesses properties of both a gas and a liquid (Taylor, 1996).

The main disadvantage of using CO_2 as a solvent is that it is relatively apolar and thus for extraction of polar molecules, a co-solvent such as ethanol has to be added to CO_2 (Diaz et al., 2006). Pinelo et al. (2007) compared phenolic content and the antiradical activity of extracts obtained from grape pomace by using solid-liquid and supercritical fluid extraction. The extracts obtained from SFE showed a higher phenolic concentration and antiradical activity than those obtained using solid–liquid extraction, corroborating the efficiency of SFE for the recovery of phenolic compounds. The extraction conditions with SFE can vary depending on the nature of

the analyte (total phenolics, specific phenolic classes or individual compounds) and type of matrices. In a study by Castro et al (2010), the yield of phenolic compounds in guava seeds by SFE was lower than that of combined solvent system i.e. CO_2 and ethanol. Some of the conditions used for the extraction, recovery and characterization of phenolic compounds from food and plants using supercritical fluid extraction are summarized in Table 5**.** Although, SFE appears to be a promising method for extraction of phenolic compounds, the techno-economic feasibility studies need to be carried out for commercial exploitation of such a process.

RELATIONSHIP BETWEEN ANTIOXIDANT ACTIVITY AND TOTAL PHENOLIC CONTENT

Some authors have reported a high degree of correlation between total phenolic content (TPC) and antioxidant activity (AOA), while the others have reported a moderate to low degree of correlation. The antioxidant activity of phenolic compounds is due to their ability to scavenge free radicals, donate hydrogen atoms or electrons, or chelate metal cations. The structure of phenolic compounds is a key determinant of their radical scavenging and metal chelating activity. The antioxidant activity of phenolic acids increases with increasing degree of hydroxylation. However, substitution of the hydroxyl groups at 3 and 5 position with methoxyl groups as in syringic acid reduces the activity (Rice-Evans, 1996). Variations in the correlations could be due to the possible interaction (either synergistic or antagonistic) of diverse types and

relative amounts of phytochemicals in the extracts that might lead to different responses in different antioxidant assays (Sreeramulu and Raghunath, 2010).

The correlation between TPC and AOA has been widely studied in different foodstuffs, such as fruits and vegetables (Klimczak et al., 2007; Jayaprakasha et al., 2008). Some studies have demonstrated a linear correlation between phenolic content and antioxidant ability in fruits and vegetables (Kaur and Kapoor, 2000; Maier et al., 2009). A positive and strong correlation (R^2=0.807) between TPC and AOA of kale waste was shown by Ahmed (2009). Reddy et al. (2010) evaluated fourteen fresh fruits and ten dry fruits for TPC and AOA. They reported that the correlation analysis between the TPC and AOA as assessed by two methods showed that phenolics may contribute maximally to ABTS (r-0.84) and to a lesser extent to DPPH (r-0.77) in fresh fruits, whereas in dry fruits they correlated well to DPPH activity (r-0.97) and to lesser extent to ABTS (r-0.87). However, this was not true for all the fruit residues analyzed for phenolic concentration and antioxidant activity. Kinnow peel extract with low TPC in comparison with extracts from litchi seeds, litchi pericarp, and grape seeds exhibited higher ABTS and DPPH radical scavenging ability as well as higher reducing power than the extracts obtained from other residues (Babbar et al., 2011).

Anagnostopoulou et al. (2006) reported a low r^2 value of 0.42 between TPC and DPPH for extract obtained from sweet orange peel. Significant negative correlation (r^2 -0.542) was observed between total phenolic content and the EC_{50} values (amount of either extract or trolox necessary to decrease the 50% initial concentration of DPPH in a steady state) for DPPH radical scavenging activity by Rowena et al. (2009). Matthaus (2002) did not find any correlation between TPC and the AOA of the extracts obtained from residues of different oilseeds. It is clear

from the above discussion that phenolic compounds contribute significantly to the antioxidant ability, but some of the studies reported a low degree of correlation between TPC and AOA, suggesting that sugars, reducing agents, ascorbates and tocopherols etc also contribute significantly to the antioxidant ability of the fruit residues (Babbar et al., 2011).

It is felt that more research is needed to ascertain the role of the characterized phenolic compounds in imparting AOA to the fruit residues. At this point in time it is important to evaluate different reliable methods and arrive at either the most efficient method for each residue or a group of residues for assaying the antioxidant potential of different fruit residues. Similarly, future research should also be directed towards establishing the role of non-phenolic compounds in imparting antioxidant ability to some of the fruit residues.

PRACTICAL APPLICATIONS

1. *Antimicrobial properties of fruit residues*

Natural antimicrobial compounds are a re-emerging alternative to food preservation. Some of the molecules consist of a single substituted phenolic ring with some hydroxyl groups like cinnamic and caffeic acids (Dorman and Deans, 2000). Others like flavonoids have three phenolic rings with several hydroxyl groups. The site(s) and number of hydroxyl groups on the phenol group are thought to be related to their antioxidant and antimicrobial capacity and relative toxicity to microorganisms with evidence that increased hydroxylation results in increased microbial toxicity (Cowan, 1999). Some published literature describing the antimicrobial activity of phenolic extract from fruit residues is presented in Table 6. Xia et al. (2011) investigated the phenolic compounds and antimicrobial activity of ethanolic extract from seeds of *P. mume*.

Three chlorogenic acid isomers, namely, 3-O-caffeoylquinic acid, 4-O-caffeoylquinic acid and 5-O-caffeoylquinic acid were identified from *P. mume* seeds. The ethanolic extract exhibited inhibition against bacteria and fungi.

Different antimicrobial packaging systems including lemon extracts have been used to preserve mozzarella cheese. Results showed an increase in the shelf life of all active packaged mozzarella cheeses, confirming that lemon peel extract may exert an inhibitory effect on the microorganisms responsible for spoilage phenomena without affecting the functional microbiota of the product (Conte et al., 2007).

The flavonoid rich extract from the peel of bergamot citrus fruit, an important by-product of the processing industry was successfully assessed against different bacteria and yeast (Mandalari et al., 2007).

Petroleum ether, methanolic and ethyl acetate extract of the jamun leaf showed antibacterial effects on *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Salmonella typhimurium* and *Enterobacter aerogenes*. The *in-vitro* studies showed that the aqueous extract of the Jamun leaves was effective in inhibiting the replication of the buffalopox virus (Bhanuprakash et al., 2007) and goatpox virus (Bhanuprakash et al., 2008). The results showed that the extract caused 98.52% inhibition of the buffalopox virus at its maximum concentration of approximately 2000 µg/ml, and that the EC_{50} was 134 µg/ml (Bhanuprakash et al., 2007). In this context, the fruits and their by-products are promising new sources of phenolic antimicrobial compounds offering new commercial opportunities to food industry.

2. *Inhibition of lipid peroxidation*

One of the principal causes of food quality deterioration is lipid peroxidation. Lipid peroxidation results in the formation of reactive oxygen species and free radicals, which are associated with carcinogenesis, mutagenesis, inflammation, DNA changes, ageing and cardiovascular diseases. There has been a growing interest in natural antioxidants because they have greater application in food industry for increasing the stability and shelf life of the fruit products. The antioxidant compounds from residual sources could be used for increasing the stability of foods by preventing lipid peroxidation and also for protecting oxidative damage in living systems by scavenging oxygen radicals. Polyphenols responsible for this protective effect are most commonly flavonoids and cinnamic acid derivatives that occur abundantly throughout the plant kingdom.

The ability of compounds to act as antioxidants is based on the fact that they are able to form delocalized unpaired electrons and stabilize the formed phenoxyl radical after reaction with lipid radicals. These properties allow the molecule to act as reducing agent, hydrogen donor and singlet oxygen quencher (Gordon, 1990). Shui and Leong (2006) reported that antioxidants obtained from star fruit residues slowed the rancidity process of oil to a greater extent than did BHT. Devatkal and Naveena (2010) reported the effects of pomegranate seed powder (PSP), Kinnow rind powder (KRP) and pomegranate rind powder (PRP) on color and oxidative stability of raw ground goat meat stored at 4 ± 1 ^{o}C. Percent reduction of TBARS values was highest in PSP (443%) followed by PRP (227%) and KRP (123%). Therefore, these powders have the potential to be used as natural antioxidants to minimize the auto-oxidation and salt induced lipid oxidation in raw ground goat meat.

The shelf life of sunflower oil was enhanced by incorporating tomato peel, cucumber peel and water melon peel extract (Zeyada et al., 2008). Lipid oxidation was significantly lowered in cooked beef containing the cocoa shell and roselle seeds compared to BHT (Ismail and Yee., 2006). Both synthetic and natural phenols enhanced the oxidative stability of freeze dried, ground extruded corn starch and soybean oil mixtures (Camire and Dougherty, 1998). Zandi and Gordon (1999) evaluated the methanolic extracts of old tea leaves (OTL) and rosemary extract during deep-fat frying of potato crisps at 180 ^{o}C and reported that the OTL extracts had relatively higher antioxidant ability than the rosemary extract during the frying stages. Benherlal and Arumughan (2007) evaluated the inhibition of lipid peroxidation of the ethanolic extract of the fruit pulp, kernel and seed coat *in-vitro* and observed that the kernel extract was better than the seed coat and pulp extract.

Ahn et al. (2008) demonstrated the effect of natural plants extract (NPE) such as rosemary, broccoli sprout and citrus on inhibition of lipid oxidation of microencapsulated high oleic sunflower oil (MEHS). Similar to that of high oleic sunflower oil (HS) in liquid state, lipid oxidation of MEHS was remarkably reduced under the accelerated storage condition in the presence of a mixture of NPEs rather than a single component of NPE. Specifically, induction period of MEHS was significantly enhanced in the presence of NPE when tested through the rancimat method. Peroxide value (POV) and p-anisidine value (ASV) were also significantly lowered by addition of NPE during storage for 30 days at 60 ^{o}C.

Grape seed and peel extract was effective in inhibiting the lipid oxidation of raw and cooked chicken meat with results (Selani et al., 2011). Luther et al. (2007) reported that the ethanol extract of grape seed flour not only suppressed overall lipid peroxidation in fish oil, but

also protected eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), the longer bioactive *n-3* fatty acids against oxidative loss.

IN-VIVO TRIALS

A large number of phytochemicals containing nutraceuticals with various compositions and health claims are now widely distributed and available in the market. However, the scientific evidence supporting their health benefits is still insufficient and it is mostly based on the *in-vitro* or animal model assays. Clinical trials that evaluate the actual physiological effects in humans are scarce and results are controversial. There are many confounding factors that may have an impact on the final outcome of the trials, i.e., the stability of the bioactive compounds in different pharmacological forms and in the gastrointestinal tract. Any chemical alteration of the original bioactive compound that may take place during storage or digestion may modify the bioavailability and bioactivity of the compounds severely. Another important factor is the inter-individual variability for bioavailability and metabolism as well as for the biological response.

Many of the human age-related degenerative diseases are associated to oxidative processes. It has been well established that many of the phytochemicals present in plant derived foods have antioxidant capacity, i.e., they are able to remove free radical species which are responsible for various diseases. The measurement of antioxidant capacity using *in-vitro* tests is extensively used to claim a benefit for some of these nutraceutical products. The word 'antioxidant' on a label sells the product and is now well accepted amongst producers and

consumers. The values provided by these tests may however be misinterpreted by both producers and consumers. Scientists have now agreed that the *in-vitro* antioxidant activity of a certain compound may not reflect its activity *in-vivo*, especially in view of its *in-vivo* transformation into metabolites and (or) other derivatives which are the true bioactive compounds (Cerda et al., 2004). Antioxidant activity assessed through *in-vitro* trials may be used as a quality indicator of its nutritional benefit to the humans.

CONCLUSIONS

In this review we have tried to demonstrate the importance of fruit residues which are generated in large quantities during processing. Because of the non-availability of commercially feasible technologies for utilization of such residues, their disposal leads to environmental pollution problems. Therefore, it becomes important to evaluate the potential of these fruit residues for finding a significant use for them. The review comprehensively describes the classification and structure of different phenolic compounds; nutraceutical and therapeutic potential of phenolic compounds obtained from natural sources and nature and concentration of the phenolic compounds present in various fruit residues. Among the phenolic compounds, flavonoids, phenolic acids and tannins are the most important compounds which have shown potential for their use in food and pharmaceutical industry. Although, the residues obtained from most of the fruits contain phenolic compounds that have strong anti-oxidant potential, there are only a few residues, such as seeds and peels from grapes and litchi that have been extensively studied. Grape seeds and peels have been extensively studied for their total phenolic content,

nature and concentration of phenolic compounds, their anti-oxidant potential and their therapeutic potential.

We feel that a lot of work still needs to be done in appraising the potential of Kinnow peels and seeds, pomegranate peels, jamun seeds and banana peels as potential biopreservative or nutraceutical resources. It is also important to characterize the phenolic compounds present in such residues and ascertain the role of each compound in imparting antioxidant potential to these residues. Although, antioxidant assay methods have been described in literature, it is important to determine the antioxidant potential of the extracts from fruit residues by at least two methods for precise and reliable estimations. Antioxidant determination assays like DPPH, FRAP, TEAC and ORAC discussed in the paper are considered to be reliable methods for determination of antioxidant potential of compounds derived from different sources.

Because of the presence of different anti-oxidant constituents in various fruit residues and the nature of bonding between the constituents of the fruit residues, different solvents are required for effective extraction of such compounds. As discussed previously, there cannot be a single solvent that can be used for effective extraction of phenolics from all the fruit residues. Besides conventional extraction with solvents such as ethanol, methanol, ethyl acetate, other methods such as supercritical extraction alone and in combination with solvents must be evaluated for extraction of bioactive compounds from fruit residues because they offer a good yield and preserve the properties of the antioxidants.

It is evident from this review that the fruit residues offer a tremendous potential for their applications in food and pharmaceutical industry as food stabilizers, biopreservatives, therapeutic and nutraceutical agents. The growing awareness about the role of organic compounds in

imparting health benefits has led to research in evaluating the worth of fruit residues for the benefit of mankind. Once, the nutraceutical and therapeutic potential of residues obtained from important fruits is established, a detailed economic analysis will help setting up commercial units, thereby establishing a commercial use for such residues. This will help in complete utilization of the fruits thereby fetching extra remuneration to the growers by the sale of residues and also in mitigating the environmental pollution problems caused by the poor disposal of fruit residues.

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Table 1 Phenolic compounds reported in various pathophysiological conditions

Phenolic compounds	Pathology	References
Quercetin, kaempferol, genistein, resveratrol	Colon cancer	Lee et al., 1998
Catechins	Neurogenerative diseases	Levites et al., 2003
Proanthocyanidin	Cardiovascular disorders	Bagchi et al., 2003
Ferulic acid	Diabetes	Balasubashini et al., 2004
Caffeic acid	Anti-inflammatory	Da Cunha et al., 2004
Proanthocyanidins	Inhibition of metastasis	Mantena et al., 2006
Resveratrol	Inhibition of tumor	Jang et al., 1997
Epicatechin	Inhibition of xanthine oxidase thus interfering with free radical generation	Cos et al., 1998
Baicalein, cinnamic acid, oleuropein, rutin, quercetin and tephrosin	Reduction of gastric ulcer	Mohd et al., 2011

Table 2 Total phenolic content (TPC) of important fruit residues

Residues	TPC	References
Apple pomace, peel	52.2 [a], 17.90 [b], 33 [a]	Peschel et al., 2006; Chodak and Tarko, 2007;Wolfe and Liu, 2003
Strawberry waste	59.8 [a]	Peschel et al., 2006
Pear waste	18.4 [a]	Peschel et al.,2006
Litchi seed, pericarp	17.9 [a], 24.6 [a]	Babbar et al., 2011
Grape seed	37.4 [a], 47.3 [c]	Babbar et al., 2011; Velioglu et al., 1998
Banana peel	9 -30 [a]	Nguyen et al., 2003; Someya et al., 2002; Babbar et al., 2011
Mango kernel, peel	117 [a],109.70 [a]	Soong and Barlow, 2004; Larrauri et al.,1996; Ajila et al., 2007
Kinnow seed, peel	3.68 [a],17.5 [a]	Babbar et al., 2011
Other citrus fruit peel	66-222[d]	Ghasemi et al., 2009
Guava peel	58.70 [a]	Lim et al., 2007
Watermelon seeds	9.69 [b]	Chodak and Tarko, 2007
Plum seeds, peels	43.68 [b], 33.40 [b]	Chodak and Tarko, 2007
Lemon peel	96.62 [b]	Chodak and Tarko, 2007
Orange peel and seeds	10.1 [a]- 8.49 [b], 2.12 [b]	Anagnostopoulou et al., 2006; Chodak and Tarko 2007
Star fruit residue	33.2[a]	Shui and Leong, (2006)
Kiwi seeds and peel	1.02 [b], 11.61 [b]	Chodak and Tarko, 2007
Red grapefruit seeds and peel	2.22 [b],5.57 [b]	Chodak and Tarko, 2007

[a] mg/g GAE [b]mg/g Catechin

[c] mg/g ferulic acid [d]mg/g quercetin

Table 3 Phenolic constituents of different fruit residues

Fruit	Residue	Phenolic constituent	References
Apple	Peel and pomace	Epicatechin, catechins, hydroxycinnamates, phloretin glycosides, quercitin glycosides, procyanidins, chlorogenic acid, anthocyanins	Lu and Foo, 1997; Foo and Lu, 1999; Wolfe and Liu, 2003
Grapes	Seed and skin	Cinnamic acid, coumaric acid, caffeic acid, ferulic acid, chlorogenic acid, neochlorogenic acid, p-hydroxybenzoic acid, protocatechuic acid, vanillic acid, gallic acid, proanthocyanidins, quercetin 3-O-gluuronide, quercetin, resvaratrol	Shrikhande, 2000; Negro et al. , 2003; Maier, et al. 2009.
Citrus	Peel	Hesperidin, naringin, eriocitrin, narirutin	Coll et al., 1998
Mango	Kernel	Gallic acid, ellagic acid, gallates, gallotannins, condensed tannins	Arogba, 2000; Puravankara et al.,2000
Banana	Peel	Gallocatechin, anthocyanins, delphindin, cyaniding, catecholamine	Someya et al., 2002; Kanazawa and Sakakibara, 2000; Monelongo et al., 2010
Litchi	Pericarp, seeds	Cyanidin-3-glucosides, cyanidin-3-rutonoside, malvidin-3-glucoside, gallic acid, epicatechin-3-gallate	Lee and Wicker, 1991; Duan et al., 2007

Chia (*Salvia hispanica*) Seeds	Caffeic acid, chlorogenic acid, myricetin, quercitin, kaempferol, caffeic acid	Taga et al., 1984

Table 4: Published literature on different solvents used for extraction of polyphenolic compounds from different fruit residues

Polyphenolic compounds	Solvent	References
Phenolic acids, flavonols, anthocyanins	Ethyl acetate	Pinelo et al, 2005; Russell et al, 2008
Anthocyanins, phenolic acids, catechins, flavanones, flavones, flavonols, procyanidins, ellagic acids, rutin, chlorogenic acids	Methanol (50-90%, v/v)	Bleve et al, 2008; Caridi et al, 2007; Ross et al, 2009
Anthocyanins, flavonols, free phenolic acids	Ethanol (10-90 %, v/v)	Balas and Popa, 2007; Wang et al., 2009; Ross et al., 2009
Gallic acid, gallocatechin, procyanidin, epicatechin	50% Ethyl acetate	Pelillo et al., 2004; Osman and Wong, 2007; Prasad et al., 2009
Flavonols, free phenolic acids	Chloroform	Sharififar et al., 2009
Proanthocyanidins	Hot water (80-100 ^{o}C)	Diouf et al., 2009
Tannins, bound phenolic acids	NaOH (2N-10 N)	Nardini et al., 2002, Ross et al., 2009

Table 5 Extraction, recovery and characterization of phenolic compounds from using supercritical fluid extraction

Sample	Temperture (°C)	Pressure (Bar)	Co-solvent (%)	Target Compounds	References
Red grape pomace	45	100-250	Methanol (5)	Proanthocyanidins	Louli et al., 2004
Spearmint leaves	40-50-60	100-300	Ethanol (10)	Flavonoids	Bimakr et al., 2009
Green tea leaves	60	310	Ethanol (10)	Catechins	Chang et al., 2000
Tomato paste waste	880	300	Ethanol (5)	Carotenoids	Nobre et al., 2009
Tomato skin	75	350	Ethanol (10)	Carotenoids	Shi et al., 2009
Grape seed	30-40	130	Ethanol (30)	Anthocyanins	Bleve et al., 2008

Table 6 Effect of extracts obtained from different fruit residues on inhibition of food-borne pathogens

Fruit extract	Pathogens	References
Pomegranate peel and seed	*Leuconostoc monocytogenes*, *Staphylococcus aureus* and *Bacillus cereus*	Kanatt et al., 2010; Hayrapetyan et al., 2011; Zoreky, 2009
Grape seed extract	*Aeromonas hydrophila*, *Bacillus amyloliquefaciens*, *B. brevis*, *B. cereus*, *B. megaterium*, *B. subtilis*, *Enterobacter aerogenes*, *Enterococcus feacalis*, *E. coli*, *Klebsiella pneumoniae*, *L. monocytogenes*, *M smegmatis*, *Proteuss vulgaris*, *Pseudomonas aeruginosa* and *S aureus*	Baydar et al., 2004
Grape pomace	*Penicillium chrysogenum*, *P. expansum*, *Aspergillus niger* and *Trichoderma viride, Zygosaccharomyces rouxi*i and *Z. bailii*	Corrales et al 2010; Sagdic et al., 2011
Mango kernel	Gram +ve and Gram –ve bacteria	Kabuki et al., 2000
Jamun leaf	*E. feacalis*, *E*scherichia *coli*, *K. rhizophila*, *Neiserria gonorrhoeae*, *P. aeruginosa*, *S. flexneri*, *S. aureus* and the multi-resistant *K. pneumoniae*, *P. aeruginosa* and *S. aureus*	De Oliveira et al., 2007

Legends to the Figures

Figure. 1. The general breakdown of plant based phenols

Figure. 2. Chemical structures of some important phenolic compounds

Figure. 3. Chemical structures of some important flavonoids

Figure.4. Chemical structures of some important anthocyanidins

Figure.5. Important compounds isolated from litchi seeds

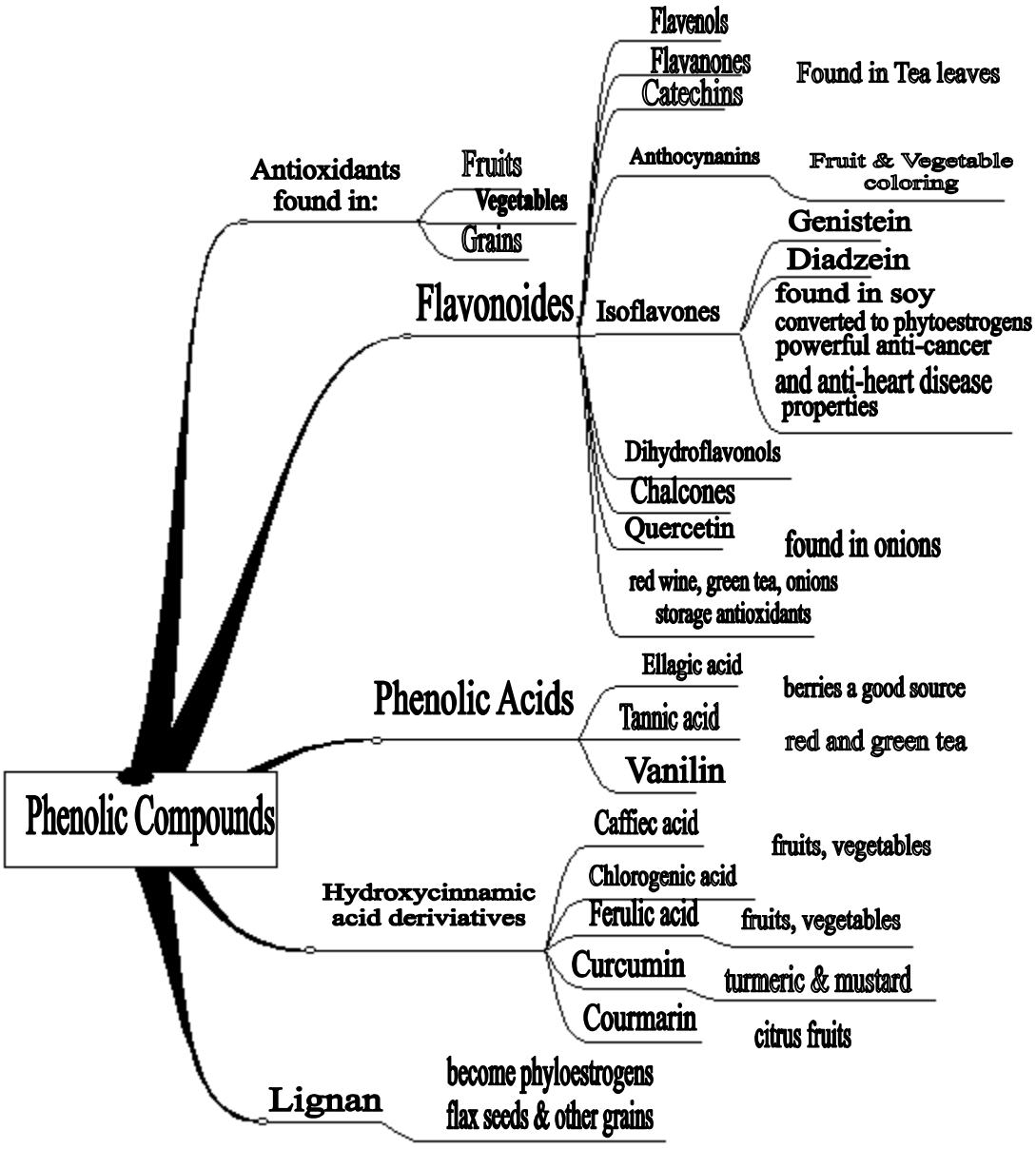


Figure. 1. The general breakdown of plant based phenols

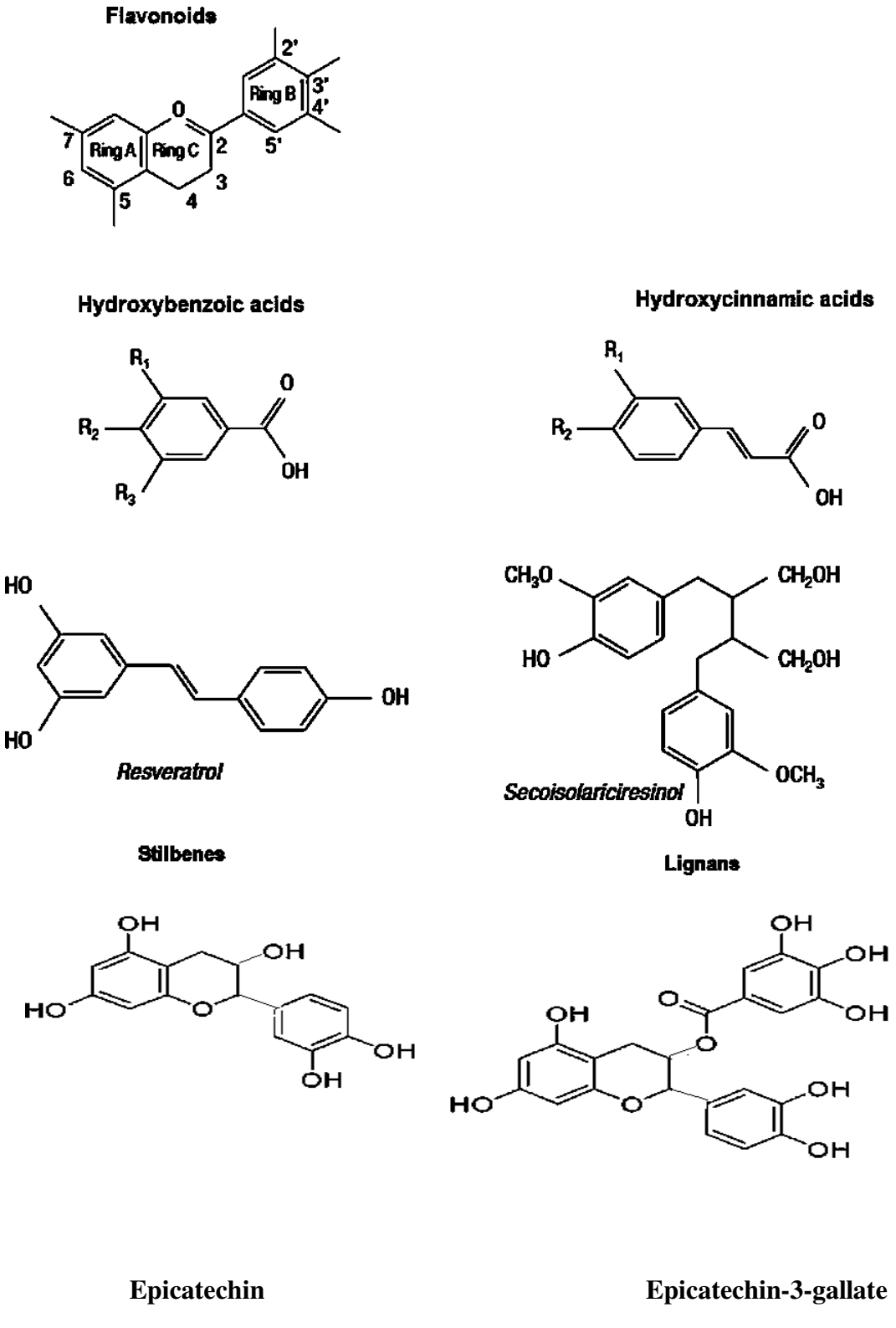
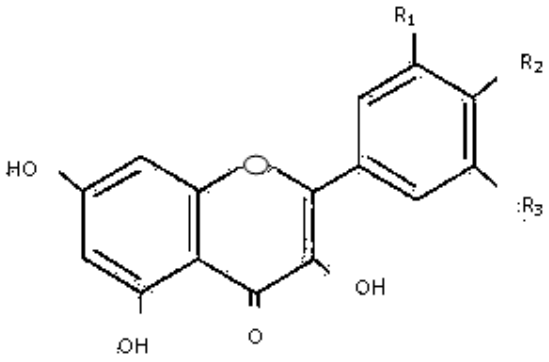


Figure. 2. Chemical structures of some important phenolic compounds

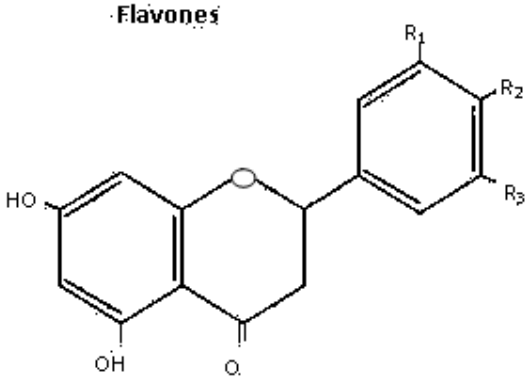
Flavonols



R_2=OH; R_1=R_3=H. : Kaempherol

R_1=R_2=OH; R_3=H. : Quercetin

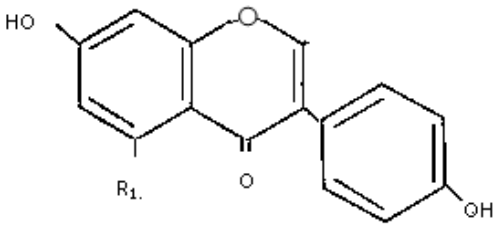
Flavones



R_1=H; R_2=OH : Apigenin

R_1=R_2=OH. : Luteolin

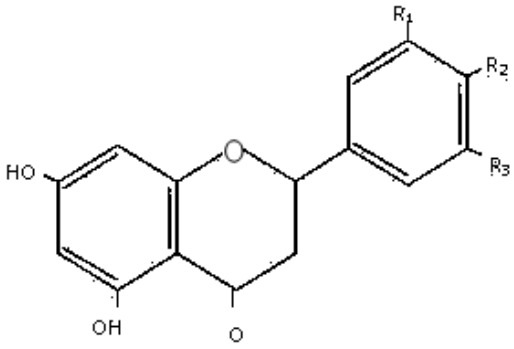
Isoflavonoes



R_1=H: Daidzein

R_1=OH: Genistein

Flavanones



R_1=H; R_2=OH; Naringenin

R_1=R2=OH: Eriodictyol

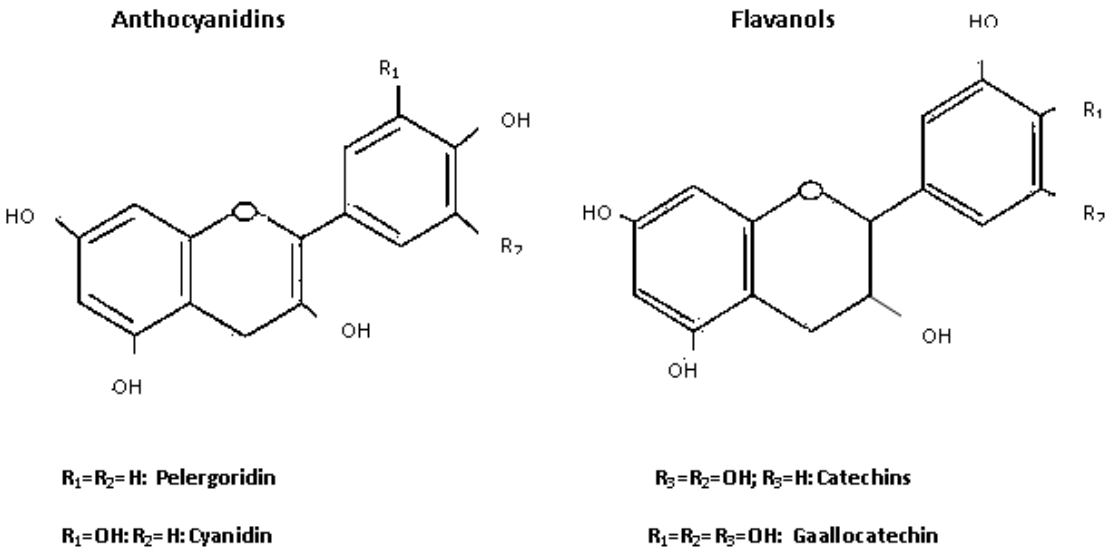


Figure. 3. Chemical structures of some important flavonoids

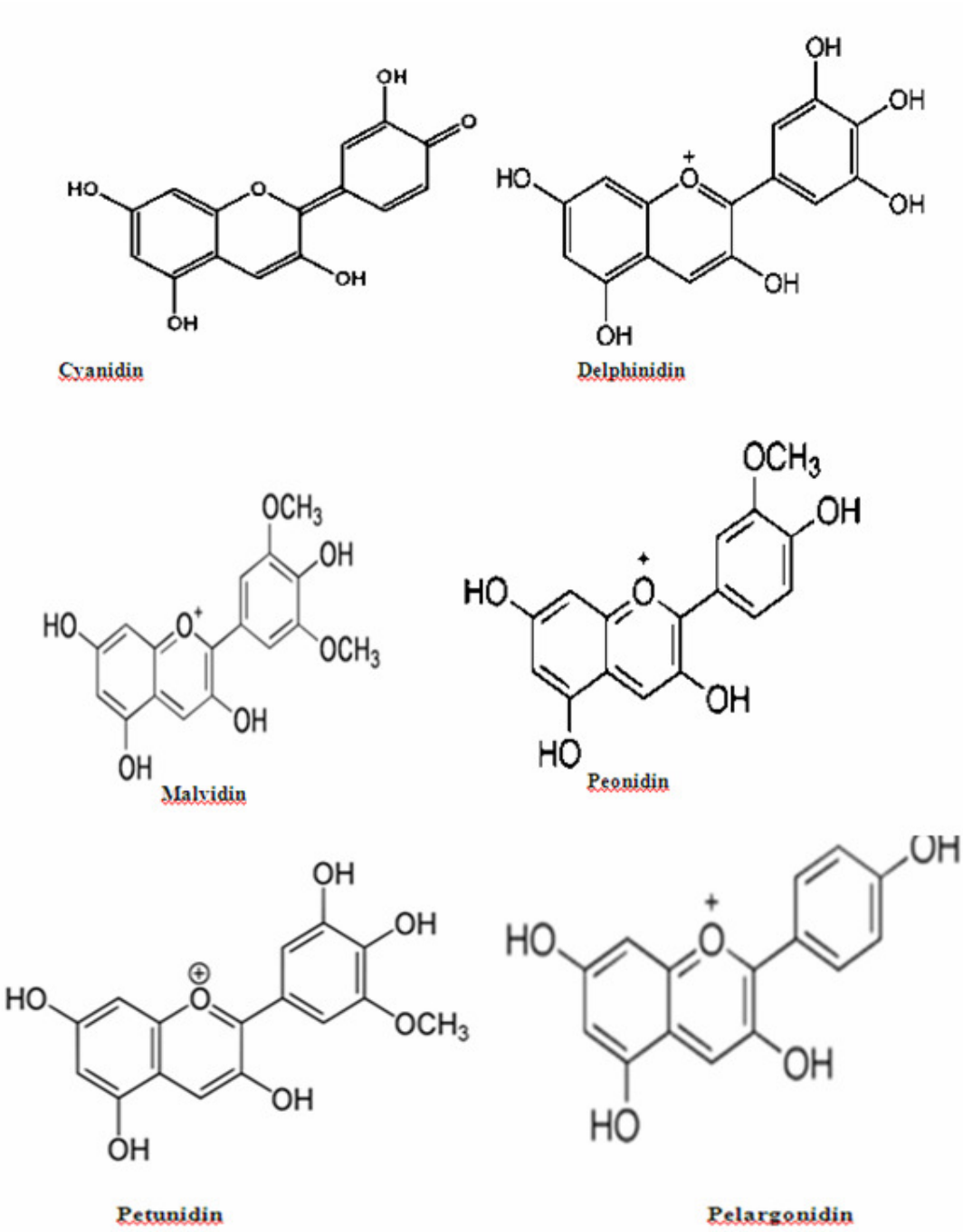


Figure.4. Chemical structure of some important anthocyanidins

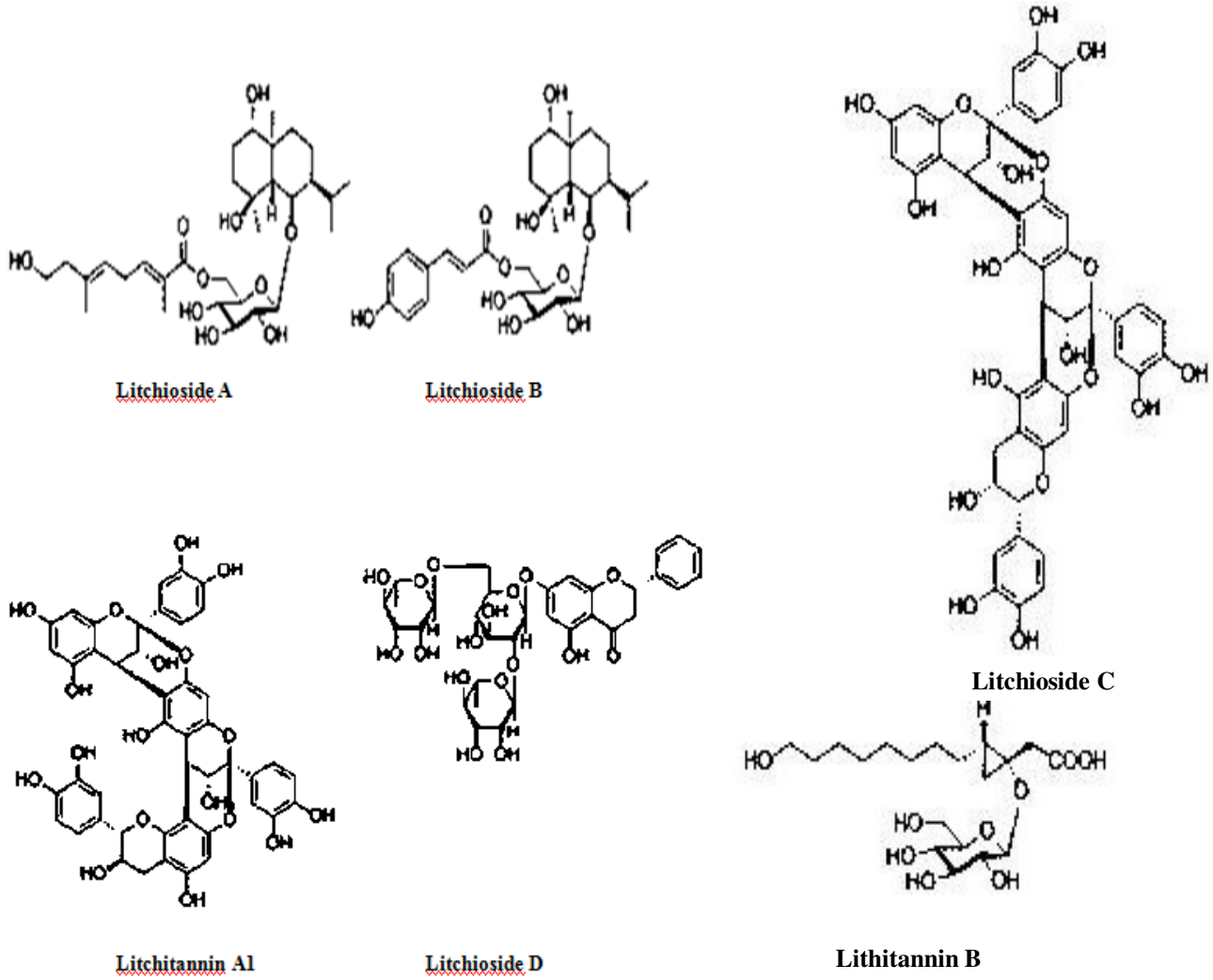


Figure.5. Important compounds isolated from litchi seeds (Xu et al., 2010a, 2010b, 2011a, 2011b)