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Utilization, valorization and functional properties of wild apricot kernels

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Abstract
Apricot is an outstanding source of natural acids, vitamins, carbohydrates, phenolic compounds and minerals. Apricot kernels have been used in folk medicine as a remedy for various diseases. It can hence be utilized for edible purpose in different forms in food industry. Besides being high in nutrition apricot kernels also contains cyanogenic glucoside 'Amygdalin' which on hydrolysis generates hydrogen cyanide and can be toxic to human beings. So, in order to make them feasible for edible purpose it is required to detoxify them first. Detoxification can be looked at from two perspectives. First is when a toxin is consumed or toxins have been released in the meal, which is detoxification of the body, and second is when toxins are removed from the food itself, which is detoxification of food. Various researchers have studied on apricot kernel detoxification and its use in various forms. Present review deals with the explanation of phenomenon of Amygdalin biosynthesis, catabolism, detoxification of kernels and their utilization in food and other areas.

Keywords: Apricot kernels, amygdalin, detoxification, utilization, functional properties

Introduction
Fruits are one of the essential parts of human diet and a healthier way to maintain the wellness. Apricot (*Prunus armeniaca* L) is a major fruit crop in the world that belongs to family *Rosaceae*, of around 100 genera and 2830-3100 species [1]. It is commonly known as Chullu or Chulli but it also has many local names in different languages Khubani, Zardalu (Hindi), Urumana, Zardalu (Sanskrit), Malhoi (Assamese), Khubanifal (Bengali), Jardalu (Gujarati), Apricot (Kannada), Jardaloo (Marathi), Apricot (Malayalam), Khubanibadam (Oriya), Apricot (Tamil), Pandlu (Telugu), Khurmani (Punjabi) and in Urdu it is named as Khubaani [2]. The roots of apricot seem to be strongly embedded in three interconnected regions in Asia [3, 4], the first being China, where certain wild form of apricot varieties are still growing in nature[5].Apricot is one of the most exquisite fruits of its kind. The fruit is an outstanding source of natural acids, vitamins, carbohydrates, phenolic compounds and minerals.It is a temperate fruit that requires a comparatively cold winter and moderately high temperature in the spring and early summer. Subtropical climate is not favorable for the cultivation of apricots. These are drupes like plump and peach. It is cultivated in several parts of the world with Turkey as the largest producer, followed by Uzbekistan, Iran, Algeria, Italy, Spain, Pakistan and France [6]. In India the fruit is majorly grown in Himachal Pradesh, Jammu and Kashmir, Uttarakhand and some extent north eastern hilly region [7].
Apricots in any form augment the quality of meals, whether it is fresh, dried or processed form on account having ample amount of bioactive components apart from basic nutrients, such as polyphenols, free radical scavengers, carotenoids, malonic, fumaric, succinic, tartaric, quinic oxalic, acetic and galacturonic acid [8].

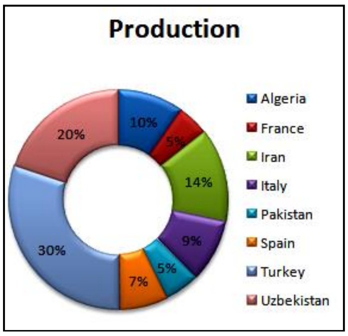

Fig 1: Leading share of different countries in apricot production

Apart from the pulpy edible portion, seeds also play a significant role in to maintain the fitness. The remaining part of the fruit is the stone which contains two types of kernels; with sweet kernel known as *Nyarmo* and bitter kernel known as *Khante* [9]. Kernels of apricot is superabundant in oil (40-56%), protein (22-29%), sugars (5-20%), fibers (6-9%), potassium (560-600 mg/100 g), phosphorus (90-107 mg/100 g) magnesium (191-204 mg/100 g), calcium (138-149 mg/100g), zinc (5-3.3 mg/100 g) and 2.5-2.9 mg/100 g iron **[10]**. As co-factors of antioxidant enzymes, a variety of trace elements protect the cell in the tissue from oxidative stress **[11, 12]** and apricot kernels are reported to contain vital macro and micronutrients that are important from dietary point of view **[13]**.Physico-chemical characteristics of apricot kernels are listed in Table 1.

Table 1: Physicochemical characteristics of apricot kernels

Parameter	Value	References
Weight	0.28 – 0.72 g	[14, 15]
Length	14.0 - 19.17 mm	
Width	9.99 - 10.20 mm	
Thickness	3.3 - 6.27 mm	
Geometric mean diameter	9.89 – 10.72 mm	
Sphericity	56.1 – 73.7%	[14]
Stone/Kernel	1.70 – 6.03	
100 kernel weight	48 -65 g	[10]
Moisture	4.0-8.8%	[10]
Crude protein	14.1 to 45.3%	[10, 19]
Crude fat	25.0- 56.0%	[10, 65]
Carbohydrates	17.5-35.6%	[10, 65]
Amygdalin	1.39 - 6.35 g/100 g	[46]
HCN	30.20 to 317.7 mg/100 g	[46, 50]

Functional properties of apricot kernels

Apricot kernels used for various purposes such as cosmetics, oils, active carbon, perfume, appetizer and also in bakery products [14, 15]. Apricot and its kernel have been used in folk medicine as a remedy for various diseases. Apricot kernel has protein content is in the range of 14.1 to 45.3%. From a PAGE study, it was reported that it contain albumin, globulin, prolamin, and glutelin [10, 16-22]. Of the total amino acids, 32-34% is the essential amino acids present in apricot kernel. Arginine and leucine are the main essential amino acid whereas glutamic acid is the chief non-essential amino acid reported in apricot kernel [10, 16]. Some studies found high antioxidant activity and oil content in sweet apricot kernels than bitter ones. Apricot kernels contain 27.7 – 66.7% oil, major portion contributed by unsaturated fatty acid (91.5 – 91.8%) [23]. It comprises of following fatty acids - palmitic, palmitoleic, stearic, oleic, linoleic and linolenic [24, 25] which is used in pharmaceutical, snacks as well as cosmetic industries [26, 27]. Kernels of apricot also consist of vitamin B1 (thiamine), vitamin B2 (riboflavin), vitamin B3 (Niacin), vitamin C (ascorbic acid) and vitamin E (tocopherol) along with some minerals (Na, K, Ca, Mg, Fe, Zn, Mn, Ni and Co) [28]. It was reported that apricot kernel consist of high amount of natural antioxidant than its fleshy part [29]. Researchers observed that apricot kernel contain phenolic compounds i.e. epigallocatechin, caffeic acid, gallate, chlorogenic, p-coumaric, syringic, sinapic, quercetin and ferulic acid [30]. Epigallocatechin reported to have antioxidant properties and associated in the prevention of cancer, diabetes, tooth decay, obesity, viral disease and cardiovascular diseases in humans [31, 32]. Caffeic acid is known for its antioxidant and antibacterial activity that helps in the prevention of early aging, skin diseases and cardiovascular diseases such as atherosclerosis [33]. Quercetin shows numerous health benefit properties such as anti-inflammatory, anti-microbial, anti-diabetic, anti-oxidant, anti-Alzheimer and anti-arthritic characteristics [34]. It lowers the risk of cardiovascular diseases in human and also prevents the prostate and lung cancer [35].

Apricot kernels contain amygdalin, a cyanogenic glycoside, which is known for its anti carcinogenic properties [36]. This compound is also found in peaches, apples, almond and cherries kernels [37]. Laetrile®, artificially prepared from natural amygdalin, is the patented form of amygdalin that can be orally taken or injected (intramuscular or intravenous) to humans [38]. One of the hypothesis suggests that cancer occurs because of the deficiency of vitamin B-17, which was the name given by E.T. Krebs to laetrile. In amygdalin, cyanide group is present between glycoside and benzene ring which is liberated after hydrolysis [39]. Amygdalin release HCN and benzaldehyde on enzymatic hydrolysis (beta-glucosidase in human body) [40]. If amygdalin is taken orally, it can cause toxicity by hindering the cytochrome oxidase of the electron transport chain in the mitochondria [41-43]. The highest amygdalin dose in the human body is approximately 0.07 g/kg when given intravenously [44]. Amygdalin can be toxic to human if consumed in high amount. On the other hand, it is used as anticancerous agent in the form of laetrile/vitamin B-17 [45]. Traditionally, amygdalin is used in several diseases such as asthma, diabetes, bronchitis. Paste of apricot kernel used as a remedy in vaginal infection [46]. Small amount of toxic HCN is prescribed in asthma, constipation and cough.

Amygdalin and HCN chemistry

Amygdalin is a substance present in apricots and other stone fruits as well as kernels. The existence of this cyanogenic di-glucoside, in various levels, causes bitterness in the seeds of fruits such as cherry, peach, plum, apricot, and apple. Besides the bitterness, amygdalin is also responsible for the toxicity of these fruit kernels, as enzymatic breakdown releases hydrocyanic acid (HCN). As a result, the presence of amygdalin makes it difficult for processors to use it for culinary purposes. Amygdalin (D-mandelonitrile-D-gentiobioside; also known as D-mandelonitrile-D-glucosido-6-D-glucoside) is found in nature in the dextrorotatory configuration (R-amygdalin), which is thought to be its active form. The inactive form, the S-isomer, is not found in nature [47]. When nuts or seeds are macerated or crushed, enzymatic breakdown of amygdalin can result in the generation of cyanide [48]. Amygdalin's chemical formula is $C_{20}H_{27}NO_{11}$, with a molecular mass of 457.4 gmol-1 and a melting point of 213 degrees Celsius. It is highly soluble in ethanol, slightly soluble in water (83 gL-1 at 25 °C), and insoluble in non-polar solvents such as benzene, chloroform, and ether, with a powdered form that is white, crystalline, and odourless [49].

Cyanides are a class of complex and dangerous chemical compounds with a CN moiety that can be developed from a variety of natural sources. Bitter almonds, plum seeds, cherry laurel leaves, peach pits and cassava as plant sources of cyanides, have been employed as poison for thousands of years. Hydrogen cyanide (HCN) is a colourless gas with a bitter almond odour that is also described as prussic acid, formonitrile, and methanenitrile [49]. The molecular mass of HCN is 27.03 gmol-1, and its melting point is -14 °C. It exists as a colourless liquid with a boiling point of 25.6 °C in its purest form. At 20 °C, it has a density of 0.687 gmL-1 as well as a vapour pressure of 630 mmHg. With a pKa of 9.22, this is a very weak acid that is water soluble at 25 °C and evaporates beyond room temperature. In alkaline solutions (pH > 9), about 60% of cyanide remains in solution as CN-, whereas at physiological pH 7.4, 99 percent of it exists in volatile HCN form. Stone fruit kernels, such as apricot, plum, peach, and cherry, have been shown to contain different quantities of HCN, which could induce toxicity if consumed [50]. The amount of HCN in apricot seeds varies depending on the cultivar/variety, the growth conditions and the maturity. HCN levels in apricot kernels range from 290 to 292 mg/100g [51]. HCN levels were found to be 72 mg/100g throughout the kernels of Himachal Pradesh in the apricot varieties like Chuli and New Castle [50]. The HCN content of kernels from diverse apricot cultivars (bitter and sweet) ranged from 30.20 to 317.7 mg/100g, with bitter varieties having greater HCN concentrations of 220.55 to 317.7 mg/100g versus sweet types with 30.20 - 79.20 mg/100g [46].

Biosynthesis and catabolism of amygdalin

Araceae, Euphorbiaceae, Asteraceae (Compositae), Flacourtiaceae, Malesherbiaceae, Fabaceae (Leguminosae), Papaveraceae, Proteaceae, Passifloraceae, Poaceae (Gramineae), Rosaceae, Ranunculaceae, Turneraceae, Sapindaceae and *Turneraceae* are among the plant families wherein cyanogenesis is usual [52]. All six amino acids, L-isoleucine, L-valine, L-leucine, L-tyrosine, L-phenylalanine and cyclopentenyl-glycine, are thought to be biosynthesized into cyanogenic glycosides [48, 53]. Plants produce these chemicals for protection as well as for use in the primary metabolism. The synthesis of cyanogenic glycosides in plants occurs in three stages. (I) Aldoximes are made up of two consecutive N-hydroxylations of the amino group of the parent amino acid by a cytochrome-P450 enzyme; (ii) Aldoximes are transformed to cyanohydrins by some other cytochrome-P450 enzyme; and (iii) cyanohydrins are glycosylated by a soluble enzyme Uridine diphosphate (UDP)-glucosyltransferase, resulting in formation of cyanogenic glycosides [53].

The cleavage of the carbohydrate moiety by β-glycosidases initiates the metabolism of cyanogenic glycosides, resulting in the formation of respective α -hydroxynitrile [54, 55]. By the action of -hydroxynitrile lyase, this intermediate can disintegrate spontaneously or enzymatically to give HCN along with an aldehyde and ketone [55]. β-glucosidases, which degrade cyanogenic chemicals, exhibit a high selectivity for the aglycone component of these compounds [56]. Mandelonitrile lyase (a kind of hydroxynitrile lyase) catalyses the conversion of (R)-mandelonitrile to benzaldehyde and HCN in *Rosaceae* species (Genus: Prunus) [57]. Mandelonitrile lyases are found in the seeds of the *Prunoideae* and *Maloideae* subfamilies [58, 59]. As in the case of wild apricot kernels, cyanogenic glycosides such as amygdalin are not hazardous in and of themselves, but their hydrolysis products are [48].The rate of cyanide liberation against cyanide detoxification determines the toxicity of cyanogenic glycosides, including amygdalin [49].

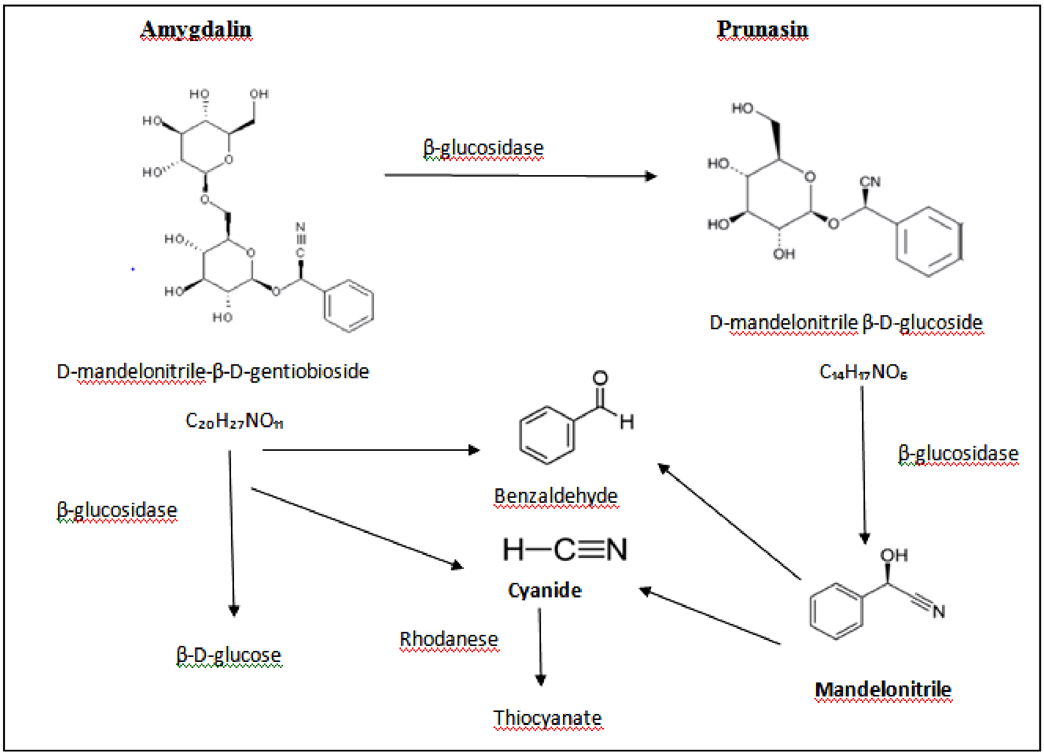

Fig 2: Route of amygdalin metabolism [47]

Detoxification of apricot kernels

Detoxification can be looked at from two perspectives. First is when a toxin is consumed or toxins have been released in the meal, which is detoxification of the body, and second is when toxins are removed from the food itself, which is detoxification of food. Crushing, grating, grinding, soaking, fermenting, and drying plant material comprising cyanogenic glycosides lowers cyanide toxicity either by removing some water-soluble glycosides or by producing cyanide via the action of certain plant or microbial enzymes and then losing it through evaporation prior to consumption [48]. Enzymatic hydrolysis of amygdalin to mandelonitrile occurs in somewhat acidic conditions (pH 5.0 - 5.8), whereas alkaline hydrolysis of mandelonitrile to benzaldehyde and HCN occurs rapidly (pH 10). Sulfuration converts cyanide to thiocyanate (SCN-), which is mostly eliminated in the urine, with a minor quantity exhaled as formate (HCOO-) and CO2. Rhodanese (thiosulfate sulphur transferase) and 3-

mercaptopyruvate sulphur transferase catalyse the sulfuration of cyanide to thiocyanate [47]. In addition to the use of enzymes, amygdalin breakdown can proceed in a heated aqueous solution via the isomerisation process. After 3 minutes in boiling water, D-amygdalin can be changed to neoamygdalin which is an epimer of amygdalin [48].Within 29 hours of fermentation, *Lactobacillus plantarum* LP1 (originally isolated from fermented cassava) was able to totally breakdown the cyanogenic glycosides linamarin, amygdalin, and the linseed cyanogens [60].

A number of cyanide toxicity instances have been recorded, some of which were fatal, as a result of the consumption of amygdalin formulations and bitter apricot kernels. Between 2000 and 2004, there were roughly 260 cases of paediatric apricot kernel poisoning in Turkey, according to statistics from the National Poison Centre [61]. The fatal oral dose of HCN in humans has been estimated to be between 0.5 and 3.5 mg/kg body weight. In humans, a toxicity threshold of 0.5 mg/L of cyanide in the blood is recorded [49]. As a result, if the average weight of a common man is 50 kg, the deadly dose is 25 - 175 mg, and consumption of less than 25 mg HCN should not be poisonous.The permissible limitations for HCN in food and beverages are: (a) 50 mg/kg (50 ppm) in nougat, marzipan or its replacements, or similar goods; (b) 35 mg/kg (35 ppm) in alcoholic beverages; and (c) 5 mg/kg (5 ppm) in canned stone fruit, according to European laws [62]. FSSAI allows 5 ppm (0.5 mg/kg) of HCN in nougat, marzipan or its equivalents or similar products, alcoholic drinks, confectionary, canned stone fruit, and stone fruit juices [63].

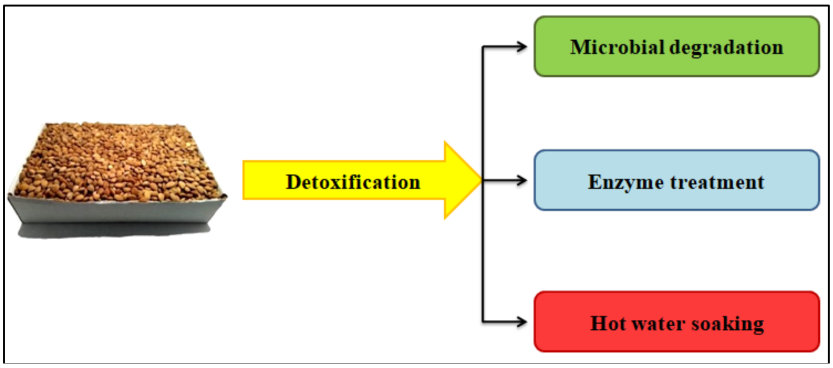

Fig 3: Detoxification methods for apricot kernels

Utilization of Apricot Kernel

Application of Apricot kernel Oil

Stone recovery from the wild apricot fruits range from 12.7-22.2%. Kernels of wild apricot are usually considered as waste. Pits of most of the stone fruits can be utilized for extraction of kernel oil [64]. Hence, an experiment was conducted at semi- pilot scale to check the potential of wild apricot kernel oil application as edible oil and in pharmaceuticals. Oil was extracted with the help of table oil expeller. Oil yield was obtained up to 38-40% in wild apricot kernels Oil had good nutritional and pharmaceutical potential. Method of oil extraction was efficient and economical. Hence, can be feasible for semi-commercial scale. However, it was also observed that oil extracted by solvent extraction was free from HCN while oil extracted using portable power ghani and table oil expeller contained different proportion of HCN [65].A study was done to enhance recovery and quality of cold pressed wild apricot kernels using various enzymes. Wild apricots were ground into powder form and then mixed with different enzymes with different concentrations (Pectazyme, Mashzyme and Pectazyme + Mashzyme). This mix was then kept for 2 hr. at a temperature of 50°C prior to oil extraction. This indicated that application of enzymes enhanced oil recovery by 9.00–14.22% with maximum oil recovered at 0.3–0.4% concentration of enzyme concentration used individually or in combination. It was observed that combination of 0.3% pectazyme and mashzyme showed synergistic effect in extraction and gave maximum yield of about 47.33% in comparison to 33.11% in the control. However, as per the quality of the oil is concerned it was seen unaffected even with enzymatic treatment and can be commercially used in markets as other oils [66]. It was revealed in a study that during enzymatic hydrolysis incubation period is the most important factor to affect oil yield. Other factors included are enzyme concentration, enzyme ratio and moisture content [67]. In another study extraction of oil was also done using hexane as solvent and applying ultrasound technology. Results were compared with the traditional methods of mechanical extraction and Soxhlet extraction. It was concluded that ultrasound technology application led to more yield 44.72% with less consumption of solvent in less time period i.e., 44 minutes [68].The apricot kernels oil has been used as fixed oil, in macaroon paste and for enrichment of noodles [10].

Application of apricot kernel oil press cake

Wild apricot kernels are used for extraction of oil. After extraction of oil, press cake so obtained was used to make protein isolate for its utilization in food supplements. These protein isolates have low hypoglycaemic index, wonderful bioactive properties, good functional properties and good protein digestibility. Press cake contained 34.5% crude protein and hence could be used to make protein isolate. Press cake was boiled in water at a ratio of 1:20 (w/v) for 1 hr. followed by increasing pH up- to 8, stirring few minutes, filtration, coagulating at pH 4, sieving, pressing for overnight, drying and then grinding. About 71.3% of total protein present in press cake was extracted successfully. Protein isolate so prepared contained about 68.8% protein, 12% carbohydrates and 6.4% crude fat [69]. In a study, apricot kernel protein isolate at a level of 5% and 10% was added along with isolates from soy bean and wheat germ to fortify wheat flour (72%) for preparing macaroni. Protein digestibility was increased in the fortified macaroni in comparison to control. Wild apricot kernel oil has been used to check its potential in production of biodiesel. Wild apricot oil contained less than 2% free fatty acids, so *Prunus armeniaca* methyl ester (PAME) was produced by single stage alkali catalysed (potassium hydroxide) transesterification process. This transesterification process yielded 96.5% by wt. of *Prunus armeniaca* biodiesel. It was concluded that PAME can be used to substitute petro diesel which can be used in diesel engine without doing any major amendments in the engine [70].

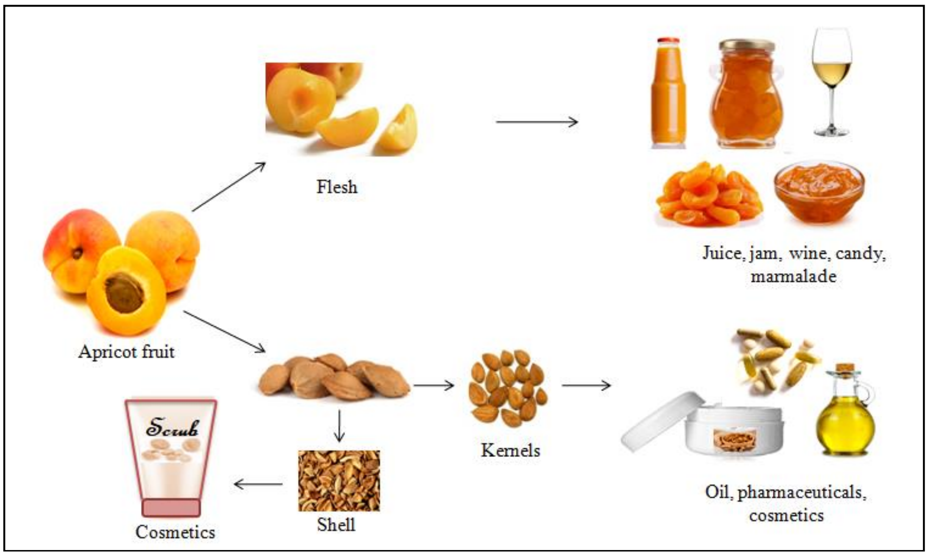

Fig 4: Different products from flesh and kernels of apricot fruit

Application of apricot kernel oil in cosmetics

Apricot kernel oil being rich in vitamin E and fatty acids can also be applied in cosmetic product manufacturing. An abrasive skin cleansing substance has been developed using apricot kernels [71]. In a study apricot kernel oil has been used as base material in preparing a massage cream. Different concentrations of apricot oil were used and compared for quality characteristics with the apricot cream available in the market. Massage cream containing 10-15% of apricot kernel oil was found efficient on the basis of qualitative characteristics such as viscosity, total fatty matter and vitamin E. Also, the cream had good spread ability, medium emollient, thermal stability (as per the BIS standards). Hence, its application in cosmetics was justified by the study [72].

Application of apricot kernels can also be done in soap industry as they contain higher amount of fatty acids such as oleic acid (81.73%). A study was done to use apricot kernel oil with palm stearin in making toilet soap. It was suggested that apricot kernel can be used at ratio of 50% in fatty blend for toilet soap making [73]. Wild apricot oil kernel contains both saturated and unsaturated fatty acids. Wild apricot kernel oil is also reported to have antimicrobial activity against some of the pathogenic bacteria like*Salmonella typhimurium, Serratia marcescens, Staphylococcus aureus, E. coli* and *Streptococcus pyogenes* [74].

Application of apricot kernel oil in Pharmaceuticals

Apricot kernels and kernel oil have been utilized in pharmaceuticals for vaginal infections, ulcers, tumors and various diseases [75]. Apricot oil when utilized in different types of cakes and biscuits are reported to have excellent properties which are comparable to corn oil at the same level [19]. Apricot kernel oil can be used to in alteration to almond oil as they both contain similar fatty acid composition [76].

Amygdalin present in apricot kernels has been used to prevent and treat cough, migraine, constipation, chronic inflammation, hypertension, asthma and to enhance cerebral functions [40, 45, 77]. Sweet apricot kernels were mixed with peach kernel and walnut kernels to cure upper respiratory tract infection, asthma, pulmonary tuberculosis, acute and chronic bronchitis [78]. A herbal tea for patients having anorexia, disturbed sleep, dry excrement, dry mouth and tongue has been prepared from the apricot kernels [79]. A liquor supressing thrombosis, delaying senility and relaxing cough and asthma was prepared from black plum apricot kernel [80].

Application of Apricot Kernel flour in food

The apricot kernel flour and protein isolates had good potential as protein sources in food products [19]. In some countries, apricot kernels have also been used to make marzipan [81]. The apricot kernel can be used in bakery product either as whole kernels or in the grounded form. Also, they can be used as appetizers [82]. Apricot kernel flour can also be used as a dietary supplement. Being high in nutrients apricot kernels can be used in different products if converted to flour form. Apricot kernel flour has been added in spaghetti making at different concentrations (4-16%) and compared with semolina spaghetti. It was observed that addition of apricot kernel flour enhanced the net protein utilization, digestibility, food efficiency ratio and biological value but deteriorated the quality attributes of spaghetti [83]. An experiment was conducted in which wheat flour was replaced with apricot kernels flour at different concentrations. Apricot kernel flour and resistant starch were used in cookies as fat replacers. Cookies supplemented with resistant starch and apricot kernel flour were showed increase in the spread ratio up to 20% level, hardness above 10% and total dietary fibre content. Also, sensory properties of the cookies were similar to the control ones [84]. Another study revealed that apricot kernel flour can be used for replacing shortening at the level of 10% and 20% [85]. It was incorporated in biscuits and it was observed that physical characteristics, texture, colour, protein, ash and fibre content of the biscuits were improved. Based on the sensory evaluation it was concluded that apricot kernel flour could be replaced up to a level of 15% [86].

Apricot kernels have been used to make yoghurt [87]. Apricot kernel powder was defatted and used as protein source in ice cream and yoghurt in the ratio of 10-50% and 10-40% for ice-cream and yoghurt respectively in replacement with some part of added skim milk powder. It was observed that addition of defatted apricot kernel powder reduced the over run of the ice cream and deteriorated the flavour of the product. However, protein stability was higher in the products and it was concluded that skim milk can be substituted with apricot kernel powder up to 30% in ice cream. As far as yoghurt is concerned, addition of apricot kernel powder led to decrease in the lactic acid bacteria count, pH and acetaldehyde value. It was concluded that skim milk could be substituted up to a level of 20% in the yoghurt [88]. In a study quality of stirred yoghurt was improved by adding apricot kernel powder. Cow's milk was supplemented with 1% of apricot kernel powder. It was observed that addition by apricot kernel powder increased protein content, total solid and ash content and decreased the titratable acidity [89].

Application of apricot kernel debittering water

Debittering of apricot kernel is done by using water. This water is usually drained as such and hence is a waste. This waste water contains various flavour and aromatic compounds like benzaldehyde and benzyl alcohol. So, a research was conducted to use water left after debittering of apricot kernels to develop a flavoured beverage. Debittering water was membrane ultrafiltered and then used in beverage manufacturing [90].

Conclusion

Apricot kernels thus can be detoxified and used in various ways. It will not only reduce the waste created after apricot fruit processing but will enlighten the diversified possibilities for utilization of this underutilized crops. Being rich in nutrition and bioactive compounds these kernels have immense potential. Though they contain cyanogenic glucoside 'Amygdalin' but this barrier can be overcome by using various detoxification methods facilitating application of apricot kernel utilization.

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