Research Progress in the Processing and Exploitation of Hawthorn
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Abstract. The planting area of Crataegus spp. is wide in China, and it has high edible and medicinal value. These fruit represent a highly renewable and cheap source of nutrients. The medicinal value, the processing technology of hawthorn, active substances extraction technology of hawthorn and the comprehensive utilization of hawthorn were summarized in this paper, and the prospect and direction of research on hawthorn processing was discussed. Moreover, the promising results of their nutritional value in health protection suggest the opportunity to take advantage of the large availability of this fruit to be used in functional foods and nutraceutical products.

Introduction

Hawthorn, the common name of the plants in the genus Crataegus of the Rosaceae family, which are widely distributed in the Northern Hemisphere mostly in China, Europe and North America [1]. Hawthorn is commonly called crabapple, rouge fruit, crataegus pinnatifida, and so on. It was traditionally used in food to improve digestion and increase appetite. In China, hawthorns have been planted since 1700 years ago, and the planting area is broad no matter in the mountains, plains, hills, the areas, acidic or alkaline soil [2]. People utilized the hawthorn for food, while the leaves and seeds were used for medicinal applications. Hawthorn became commercially important in 21th century in China, following the development of the food processing. Hawthorn is commercially important fruit, which represent a plentiful and inexpensive source of nutrients. In China, the utilization of hawthorn as a food is wide, as they are used in people’s daily meals. Industrial procedures of preparing different hawthorn products satisfy the exigency of convenience products for families.

According to hawthorn’s taste, it was divided into acid hawthorn and sweet hawthorn. The most popular hawthorn is acid hawthorn. There are several varieties of hawthorn, such as Big Venus, Big Cotton ball, Tilt Red, and so on. Hawthorn is a kind of high nutritional value fruit trees, which contains carbohydrates, protein, 18 kinds of amino acids, fat, carbohydrate, iron, calcium, flavonoids, triterpenoid, carotene, riboflavin, Vitamin (Vitamin C, Vitamin A, Vitamin B₁ and vitamin B₂) and other beneficial ingredients [3]. Among them, the content of calcium, iron and flavonoids was on the top fresh fruit [4]. Hawthorn polysaccharides and hawthorn fruit acid play an important role in promoting digestion, anti-hemorrhoids, anti-inflammatory, and so on. What’s more, hawthorn is a rich source of flavonoids and triterpenoids. Interestingly, hawthorn leaves are rich in flavonoids and hawthorn seeds are rich in triterpenoids. Therefore, both hawthorn fruit and its leaves have high nutrition value. This review focuses on the medicinal value of hawthorn, processing and utilization as well as on the problems and measures during the processing.
The Medicinal Value of Hawthorn

Hawthorn fruit has been used for a long time for their beneficial health effects, mainly consisting in curing scurvy, constipation and digestive disorders. Moreover, hawthorn flowers and leaves are often used against mild cardiac disorders [5]. In modern pharmacology, polyphenols, flavonoids and triterpenoid have been the most studied hawthorn health protective molecules. They have been linked to protection against oxidative stress, disorder digestion, high blood lipid and cancer. Modern pharmacologists also addressed the importance of bioactive molecules from hawthorn extracts and demonstrated their promoting digestion, antioxidant activity, reducing blood lipid, antihypertensive and anticancer activities.

Promoting Digestion

The Vitamin C, Vitamin B_2_, carotene and organic acid of hawthorn could increase the secretion of digestive enzymes in the stomach and enhance the activity of the enzyme, which is advantageous to the digestion. In addition, the ethanol extract of hawthorn has obvious effect to gastric dysfunction, and it plays the important role in invigorating spleen to promote digestion. Hawthorn fruit can also be used in the treatment of acute diarrhea, enteritis, and so on.

Antioxidant Activity

Hawthorn extracts have been widely studied for their antioxidant activity. It is potential source of phytochemicals particularly phenolic and flavonoid compounds, which are major bioactive compounds and natural antioxidants. Shanlihong variety was studied by Lingrong Wen [6]. Procyanidin B2 was the most abundant phenolic compound in all samples, followed by epicatechin, chlorogenic acid, hyperoside, and isoquercitrin. The free ORAC values, and free hydro-PSC values were 398.3-555.8 µmol TE/g DW, and 299.1-370.9 µmol VCE/g DW, respectively. Importantly, the differential antioxidant effects of phenolic extracts between hawthorn fruit peels (HPP) and fleshes (HFP) were different. Xiao Han [7] found that polyphenols of hawthorn contents in hawthorn fruit peels were all higher than those in hawthorn fruit flash. Meanwhile, HPP was also more effective than HFP to mitigate liver inflammation and oxidative stress. In general, hawthorn has promising potential in the development of functional foods and nutritional supplements.

Antihypertensive Activity

Preparations from hawthorn leaves with flowers have a long history in the treatment of cardiovascular disorders. WS® 1442 was a special extract of hawthorn leaves with flowers used for the treatment of mild cardiac failure, which was found by Eva Rieckeheer [8]. Many cardiovascular disorders are associated with reduced NO bioactivity. WS® 1442 is one of the few interventions that have been demonstrated to increase red blood cell NO formation. This effect could contribute to improved microcirculation in situations of hypoxia and intravascular shear stress, e.g., the capillary bed of skeleton and cardiac muscle during exercise. What’s more, the extracts of hawthorn prepared were effective in the experimental rats to prevent the formation of high blood lipid level [9]. It can be developed into the Chinese drugs preparation of low-dose and stable-effect.

Anticancer Activity

Hawthorn fruit and leaf extracts are beneficial for human health. The anticancer effects of the peel polyphenolic extract (HPP) and flesh poly-phenolic extract (HFP) from hawthorn fruit in human MCF-7 breast cancer cells was investigated by Ting Li [10]. He found that the polyphenol and flavonoid contents of HPP were obvious higher than that of HFP. At the same time, both HPP and HFP inhibited cell growth in a dose-dependent manner with the IC₅₀ of 88.6 µg/mL and 175.5 µg/mL, respectively. What’s more, hawthorn extracts could prevent esophagus cancer and papillary
stomach carcinoma of mouse, which were caused due to the feeding of sodium nitrite and methyl benzyl amine solution [11]. All these findings indicate that hawthorn fruit, especially its peel, is an excellent source of natural chemopreventive agents in the treatment of cancer.

**Processing Technique of Hawthorn**

**Brewing Processing**

The utilization rate of hawthorn is low because of its small consumption volume, big nuclear and sour taste, which causes big wasting. In recent years, the economic and social benefits have greatly increased because of the development of hawthorn brewing technology, which mainly contains hawthorn wine and hawthorn vinegar. Using apple and hawthorn as materials, the brewing technology of apple-hawthorn wine is studied by Lihui Yun [12]. The optimal conditions were confirmed by orthogonal test as follows: initial sugar content 24%, pH value 4.0, yeast 0.015% and temperature 25°C. What’s more, hawthorn vinegar produced traditionally only in Bolu (Turkey) is believed to cure some diseases such as cold, flu and cardiovascular diseases by local people [13]. In order to investigate the metabolic effects of hawthorn vinegar, 37 patients who were diabetic, hypertensive, overweight and taking related medications with high cardiovascular risk group were selected and without changing their diet habits and exercise program. Hawthorn vinegar was added into each meal during four-week. The results showed that there was a significant change on the weight loss, body mass index change, blood pressure decrease, glucose, cholesterol and triglyceride. Total phenolic substance concentration (mg/mL) and total monomeric anthocyanin content (mg/L) and total antioxidant capacity (%) of the Hawthorn vinegar were measured as 0.51, 0.25 and 77, respectively. In a conclusion, hawthorn wine and vinegar have positive effects on people’s health.

**Canned Processing**

Canned processing is one of the main technologies of food processing and storage. The canned processing was determined by Bangan Zhang [14]: cleanout, classification, denucleation, color-protecting, precook, decking, exsufflation, can sealing, sterilization, refrigeration and finished products. The reason of long-time preservation of hawthorn canned was that pumping air into vacuum state, pasteurization and maintaining the sealing state. One of the main problems in hawthorn canned processing is color fading problem. Protecting color process is a critical step in hawthorn canned processing technology, and further research is needed to prolong the shelf life.

**Drinks Processing**

Now the beverage processing technology has rapid development, and beverage products are becoming one of the most popular food. Hawthorn beverage products mainly include hawthorn juice, hawthorn concentrate juice, hawthorn soda, hawthorn fruit tea and hawthorn fruit-vegetable juice. The composite health drink could overcome the disadvantage of nutritional imbalance. Recent research demonstrates that the main antioxidant capacities of the hawthorn drinks come from total polyphenolics rather than total anthocyanins or total flavonoids [15]. The effect of microwave and heat pretreatment on the content and composition of anthocyanins, phenolics, and the antioxidant capacity of hawthorn drink were investigated. Heat and microwave pretreatments had a significant impact on the relative contents of hawthorn anthocyanins, such as cyanidin-3-galactoside (82.9% and 76.9%, respectively) and cyanidin-3-glucoside (9.2% and 11.5%, respectively). The technological process and stability of compound fruit-vegetable juice of apple, hawthorn and carrot was evaluated by Zhiming Zhou [16]. The best recipe was the ratio of hawthorn, apple and carrot 1:4:3, granulated sugar 7%, sodium carboxymethyl cellulose 0.1% and xanthan gum 0.05%. The compound juice had
attractive color and good flavor. At the same time, it was rich in organic acid, vitamin and mineral substance. Further research was assessed by Yan Liu [17]. The fruit juice quality produced by different raw material (the fresh fruit, dry piece, dry powder) was compared through determining soluble solids content and sensory evaluation. The results showed that the technique of hawthorn juice produced by dry piece is simple and the flavor is fuller.

Pickled Processing

With the development of the increasing of food varieties, people put forward new requirements to nutritional food. As a traditional snack food, though candied hawthorn is fruity, sweet, rich in nutritional ingredients, but the production has been limited to its old processing technology. Recently a new product has appeared, which solves the problem of high-sugar. With hawthorn and sweet potato as materials, the process and formula for production of low-sugar jam were studied [18]. The optimal formula of the jam was that the ratio of sweet potato slurry and hawthorn slurry was 4:1 (w/w), and the content of sugar, CMC-Na and citric acid were 20% (w/w), 0.6% (w/w), and 0.15% (w/w), respectively. Under these conditions, the jam was orange and tasty with light natural hawthorn flavor and particular fragrance of sweet potato. The produce soluble solids were 32% with homogeneous texture. Besides, the making of low-sugar preserved hawthorns with fresh hawthorn also made great progress. The optimum of vacuum preserving was studied by Jin Kong [19]: vacuum degree 0.06 Mpa, filling time 30 minutes, the temperature difference between sugar solution and material was over 55 °C, impregnation time 4-6 h. On the basis of this study, he found that sodium benzoate could make preserved hawthorn intact.

Others Processing

In addition to the above processing technologies of hawthorn, convective drying of hawthorn fruit, hawthorn jelly, hawthorn cake and hawthorn roll also have important position in the hawthorn processing technology. Thin layer drying characteristics and physicochemical properties of hawthorn were investigated by Serdar Aral [20]. The drying process of hawthorn took place in the falling rate period, and the drying time decreased with increasing air temperature and velocity. Effective moisture diffusion coefficients were calculated by Fick’s diffusion model and their values varied from $2.34 \times 10^{-10}$ m$^2$/s to $2.09 \times 10^{-9}$ m$^2$/s. The types of hawthorn rolls have shifted from single hawthorn rolls to composite hawthorn rolls. The new types are appearing, such as kelp-hawthorn rolls, jujube-hawthorn rolls and mushroom-hawthorn rolls. The pigment content has an effect on the processing of hawthorn cake, which is a serious problem to be solved. It can be speculated that the food processing technology has been widely applied in hawthorn.

Extracting Technique of Bioactive Substances

Flavonoids

At present, semi-bionic extraction, microwave-assisted extraction, accelerated solvent extraction, supercritical fluid extraction, diacolation extraction, cold-soaked extraction, ionic-liquid aqueous two phase extraction, reflux extraction, ultrahigh pressure extraction and ultrasonic-assisted extraction have been used for the extraction of flavonoids from vegetal materials [21,22]. Compared with soxhlet extraction method and ultrasonic-assisted extraction [21], ultrahigh pressure extraction had obvious advantage at extracting time and extracting efficiency. And the suitable conditions were that ethyl alcohol volume percentage 90%, liquid/solid 24:1 mL/g, ultrahigh pressure 500 MPa, retention time 12 min. What’s more, hawthorn is an important by-product of the hawthorn processing industry. Flavonoids compounds could be extracted from its seed. Guangyan Pan [22] confirmed that the significant parameters of ultrasound-assisted extraction from hawthorn’s seed were ultrasound temperature 65 °C, ultrasonic time 37 min, extraction temperature 91 °C, extraction
time 1.5 h, solid-liquid ratio of 1:18 and 72% ethanol. In addition, pressurized solvent extraction technology is a new bioactive components extraction technology. Huikai Cao [23] set up the new technology of hawthorn flavonoids extraction by comparing with supercritical fluid extraction and microwave extraction: extraction temperature 80 °C, extraction time 5 min, cycle index of 3 and 50% ethanol. Under these conditions, the extraction rate can be as high as 4.99%, which was significantly higher than the supercritical fluid extraction and microwave extraction. Pressurized solvent extraction technology will become a new way to extract natural products.

Flavan

Related research about flavan composition mainly focused on the extraction, separation and enrichment of anthocyanins, which are mainly spectrophotometric method and high performance liquid chromatography (HPLC) method. Through stoving, crushing, drying, hot reflux extraction, filtration, vacuum distillation and constant volume, hawthorn extraction was obtained [24]. The optimal conditions of ethanol reflux extraction were: 70% ethanol, extraction temperature 80 °C, solid-liquid ratio 1:15, extraction time 2 h and recycle 2 times. Under these conditions, the extraction rate can be 3.14%.

Triterpenoid

The extraction methods of triterpenoid (oleanolic acid and ursolic acid) include soxhlet extraction, reflux extraction, ultrasonic extraction, microwave assisted extraction and ultrahigh pressure extraction, and so on. 95% ethanol reflux extraction, 60% ethanol hot-reflux extraction, ultrasonic-assisted extraction and alkali-alcohol extraction were compared by Baolong Chen [25]. The extraction process were: ethanol-assisted extraction, filtration, neutralization, drying, hot reflux extraction, secondary filtration, neutralization, rotary evaporation, filtration and merging the filtrate. Alkali-alcohol extraction was efficient, simple, easy to large scale. They were suitable for extraction and purification process of triterpenoid acids from hawthorn. Furthermore, in order to investigate triterpenic acid content in hawthorn, ultrahigh pressure extraction method was optimized by Xuejun Sun [26], which was high efficiency and low energy consumption. The total yield of oleanolic acid and ursolic acid was used as indicators, ethanol volume percentage, liquid/solid ratio, power and retention time were investigated in this experiment. The results showed that the optimal conditions were that ethanol volume percentage 73%, liquid/solid ratio 33 mL/g, ultrahigh pressure 383 MPa, retention time 11 min. Under these conditions, the yield of total triterpene acid was 2.81 mg/g.

Polysaccharide

As a ubiquitous component of fruits and vegetables, polysaccharide is a major contributor to textural quality of fruit products. Extraction and analysis of polysaccharide are more difficult because of its complicated structure. Solvent extraction, ultrafiltration extraction, enzymatic hydrolysis method, flash type extraction, ultrasonic-assisted extraction, microwave-assisted extraction, high pressure cooking method and supercritical fluid extraction are popular in the extraction of polysaccharide. The hawthorn polysaccharide was extracted with the method of hot bath by Yuanchen Dai [27]. The main process were: washing and slicing, drying, pulping, hot water bath for extraction of 6 h, pectinase was added in it, enzyme deactivation, centrifugation and suction filter, enrichment, centrifugation, washing and drying. It was found that with the optimized conditions, that solid/liquid of 1:20, time of 6 h, the temperature at 90 °C, the polysaccharide yield was up to 3.92%. At the same time, the growth-promoting effect of hawthorn polysaccharide on Lactobacillus bulgaricus was most obviously when polysaccharide ratio of 2%, pH value 6.5, temperature of 42 °C.
Existing Problems and Solutions

Flesh Browning

Hawthorn fruit belongs to respiration climacteric fruit and the most common problem in processing is flesh browning, which is divided into enzymatic browning and non-enzymatic browning. The reason of former is that hawthorn contains some oxidases or their substrates, which react with oxygen during processing. The latter easily happened at high temperatures. Now solutions about hawthorn browning mainly include: hot water scald, keeping product of low water content, the SO\(_2\) treatment, adding antioxidants, and so on. Modified atmosphere packaging (MAP) in polyvinyl chloride (PVC) or high carbon dioxide permeable bags combined with ethylene absorbent (EA) treatment before low temperature storage could inhibit the browning [28]. The results showed that at (0±0.5) °C, hawthorn fruits displayed climacticer characteristics. PVC film with a thickness of 30 µm was beneficial for maintaining the hardness of fruits and restraining the decreases in titratable acid (TA) and VC, but accelerated the increase in malondiadehyde (MDA) and flesh browning at the later period of storage. High carbon dioxide permeable film with a thickness of 15 µm restricted the release of ethylene and the increase in MDA content at the later period of storage, and reduced the browning rate.

Acidity Problems

Hawthorn fruit is rich in nutrition and fresh colour with special aroma. But too much acidity in it has been always the factor that influences its production and consumption. Reducing acidity has become a serious problem about hawthorn products. Traditional acidity reduction method was to add plentiful sugar, but high sugar was bad for human health. Now acidity reduction method is mainly divided into biological reducing acidity, chemical reducing acidity and physical reducing acidity. Biological reducing acidity removes organic acid by microbial fermentation, which is difficult in screening of suitable strains; chemical reducing acidity neutralize organic acid by alkaline substances, which is easy to weaken the nutrients; physical reducing acidity is popular because of less energy consumption and better effect. Ion exchange resins were used by Jiping Song [29] to reduce the acidity of hawthorn juice due to this situation. Weakly basic anion exchange resin D301G was selected to be the best resin which can effectively reduce the acidity of hawthorn juice by comparing with D370 and D382. Thus ion exchange resin separation provides a wider field for hawthorn processing.

Preservation Problems

In order to prolong fresh-keeping period of hawthorn fruits and improve storage quality of the fruits, hawthorn storage technologies achieve rapid development. Refrigeration preservation and gas adjusting preservation has become a hotspot in research of food preservation. Liang Wang [30] found that under the condition of (0±0.5) °C, PVC bag with 30 µm thickness was beneficial to lessen fruit hardness and titratable acid content. However, in the late period of storage, it promoted rise of MDA content and browning rate. Comparatively, fresh-keeping bag effectively penetrating CO\(_2\) with 15 µm thickness had insignificant effect on restriction of hardness decline and retard of titratable acid decomposition, but possessed active effect on lessen the rise of MDA content and browning rate. In a word, fresh-keeping bag effectively penetrating CO\(_2\) with 15 µm thickness had the best storage effect and was suitable for long-period fresh-keeping of hawthorn fruits. What’s more, the preservation effects of compound coating antistaling agent of polysaccharide on hawthorn with temperature 28-32 °C and relative humidity 68%-86% were assessed by Lei Shi [31]. The method can restrain the senescence process and extend the shelf life.
Conclusions

Hawthorn is a rich source of active polysaccharide, polyphenols, flavonoids, triterpenoid and vitamins. In fact, hawthorn leaves and seeds represent a cheap and edible material, which makes large-scale purification industrially possible, with little environmental harm. By using the leaves as starting material, the purification process can provide a mixture of polyphenols, flavonoids and triterpenoid. Further studies are needed to scale-up the purification to obtain sufficient amount of these flavonoids for in vivo studies of their biochemical properties. Hawthorns show therapeutic potential owing to their antioxidant capacity, low toxicity and anti-hypertensive activity on tumor cells, for further investigation as cancer inhibitors agents. Consumers may benefit from regular consumption of hawthorn-related products. These products show interesting properties, such as detoxification and blood lipid lowering effect. Moreover, it is necessary to deeply understand how hawthorns changes their properties when added to foods, as in some cases the food matrix can positively affect the bioactivity of the products.

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