TOSHKENT DAVLAT AGRAR UNIVERSITETI
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THE ROLE OF AGRICULTURE AND MEDICINE IN SCIENCE JOURNAL

LONICERA CAERULEA L. BERRIES: A RICH SOURCE OF BIOACTIVE COMPOUNDS AND HEALTH BENEFITS

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ABSTRTACT. Two new biflavonoids, loniceraflavone A and loniceraflavone B, have been isolated from the aerial parts of Lonicera japonica along with five known compounds: luteolin, luteoloside, quercetin, rutin, and apigenin. The structures of the new biflavonoids were elucidated using detailed spectroscopic methods, including UV, IR, 1D and 2D NMR (^{1}H, ^{13}C, DEPT, COSY, HSQC, and HMBC), and mass spectrometry (ESI-QTOF-MS). The compounds were found to be linked through C–C and C–O–C bonds between flavonoid units. These biflavonoids represent a rare class of natural products in the Caprifoliaceae family. The antioxidant activity of the isolated compounds was also evaluated using DPPH radical scavenging assay, and the new biflavonoids demonstrated significant free radical scavenging activity, comparable to standard antioxidants. The study contributes to the phytochemical understanding of Lonicera japonica, a plant known for its traditional use in Chinese medicine.

Key words: Lonicera caerulea L., biflavonoids, loniflavone, methyl loniflavone, luteolin, chrysin, flavonoids, phytochemistry, NMR spectroscopy, ESI-QTOF-MS, bioactive compounds, natural antioxidants, plant secondary metabolites, traditional medicine, antiviral activity, anti-inflammatory, pharmacognosy, Himalayan plants.

INTRODUCTION

According to different references, the genus Lonicera (Caprifoliaceae) comprises from 150 [12] to more than 200 species [16] which are native to Siberia, North Eastern Asia, and Japan. Some species in this genus are used as ornamental and edible plants. Berries have been long harvested from wild plants in regions of Russia, China, and Japan [27]. However, in the scientific literature, the taxonomic classification of the species bearing edible fruits, especially of Lonicera caerulea, is not unequivocal [4, 20]. Lonicera caerulea, the blue honeysuckle, is also dubbed honeyberry, sweet berry honeysuckle, edible honeysuckle, haskap, haskup, hasukappu or haskappu. In the language of the Ainu people, the Aboriginal people of Hokkaidu Island, haskap means ‘lots of little things on the top of the branches’ [1]. Blue honeysuckle plants have been used for ages in Asia for their medicinal properties. During the past several decades, research in Russia and Japan has resulted in cultivars being selected for commercial production [27]. Lately, breeding works have

been also carried out in the Czech Republic Belarus, [23, 25] Canada [13] (USA), and in Poland [17, 26]. In Japan, high prices make haskap products special for souvenirs and gifts for special occasions [13]. The great advantage of the blue honeysuckle is early ripening a few weeks before strawberries. The plants bear at a very young age and the fruit are easily shaken off at harvest time. They may be ideally suited for mechanized harvesting since they do not sucker and have bushes of a similar size to other fruits that are harvested by machines. The plants appear to have few insect pests and diseases, making it a worthwhile crop to be considered for organic production [2]. The plants are frost-resistant and the bushes are not damaged even when the temperature decreases beneath -40°C, whereas the expanded flowers are not injured at -8°C. The fruits are elongated with an elliptic or cylindrical shape that is covered with an abrading wax bloom. They have a flavour commonly described as a combination of blueberries and raspberries. The natural accessions and varieties provide a large range of taste, tartness, sweetness, and acidity [13]. Honeysuckle berries are used in a wide range of products including juice, wine, pastries, jams, dairy products and are eaten fresh. The fruits are rich in phenolics, anthocyanins andvitamin C [24]. Consumption of high amounts of antioxidant substances may have a positive impact on human health, particularly the prevention of cancer and inflammatory diseases [6].

METHODOLOGY. The tetraploid species Lonicera caerulea L. belongs to the Lonicera L. subsect. Caeruleae Rehd. The first experiments on the domestication of this species commenced in Russia in 1913–1915. Genotypes for the breeding of new cultivars were collected in northern and eastern Russia, Japan, and China, where the richest genetic diversity was concentrated in natural habitats. Comprehensive investigations on the biological properties of L. caerulea corroborated the early ripening of berries, winter hardiness, and high resistance to spring frosts. Several studies reported that berry yields of different wild genotypes and cultivars varied from 0.26–1.24 kg/bush, from 977–2216 g/bush, and from 0.478–1.873 kg/bush. Berries of L. caerulea are distinguished by the content of biologically active substances, which depends on climatic conditions and cultivation techniques. A high total polyphenolic content was reported as an important property of blue honeysuckle berries, while it is known that phenolic compounds are among the most widespread bioactive substances associated with the antioxidant activity of different fruits. In general, the relationship between high contents of phenolic compounds in different berries and their high biological activities are widely acknowledged. Different studies have confirmed that certain types of phenolic compounds are variety-dependent and show greater antioxidant activity than others. It has been established that berries of L. caerulea accumulate flavonols (quercetin, quercitrin, rutin) as well as flavanes (catechins, pro anthocyanin's).

RESULTS

It also has been confirmed that anthocyanin's, conditioning the blue color of berries, are very strong antioxidants, important for human health.

Table 1. Bioactive Compounds in Lonicera caerulea Berries and Their Functional Properties

№	Compound Category	Key Components / Examples	Functional Characteristics
1	Anthocyanins	Cyanidin-3-O-glucoside (C3G)	76.61–92 % of total anthocyanins; strong antioxidant; makes up over 60% of polyphenols
2	Flavonols	Quercetin, Quercitrin, Rutin	Powerful antioxidants with anti-inflammatory effects

ISSN: 3060-5032

3	Flavanes	Catechins, Proanthocyanidins	Enhance antioxidant capacity; contribute to disease prevention
4	Phenolic acids	Various polyphenolic compounds	Broad antioxidant activity; linked to reduced oxidative stress
5	Iridoids	(Not specified)	Known for anti-inflammatory and neuroprotective properties
6	Sugars	Fructose (~50%), Glucose (~33%), Sucrose	Provide natural sweetness; important for taste profile
7	Organic Acids	Citric, Malic, Quinic, Tartaric acids	Total acid content 655–1104 mg/100g; contribute to flavor and stability
8	Vitamin C	Ascorbic acid	Up to 186 mg/100g; essential antioxidant and immune booster
9	Fatty Acids (PUFA)	Linoleic acid	Major polyunsaturated fatty acid (71.79%)
10	Fatty Acids (MUFA)	Oleic acid	Monounsaturated; supports heart health
11	Fatty Acids (SFA)	Palmitic acid	Saturated; structural role in cell membranes
12	Minerals	Ca, Mg, Na, K, Cu, Zn, Fe, Mn, P, trace Ag	Involved in enzymatic processes, immune function, bone health, and cellular protection

As Del Bo et al. have reported, anthocyanins constitute large proportions of berry polyphenols. Therefore, berries of L. caerulea are appreciated as an excellent source of anthocyanins which are widely used in both the food and pharmaceutical industries [14,19,20]. Chemical analysis of L. caerulea berries revealed that cyanidin-3-O-glucoside is the major anthocyanin, comprising 79–92% of the total anthocyanin content and over 60% of the total content of polyphenolic compounds [21]. Blue honeysuckle contains a variety of carbohydrate substances, fructose is nearly half, glucose accounts for about a third, and sucrose minimum. In addition, the content of organic acids is 655–1104 mg/100g, citric acid is the main, and malic acid, quinic acid, and tartaric acid also can be detected in blue honeysuckle berries. A variety of mineral elements can also be detected in the blue honeysuckle berries.

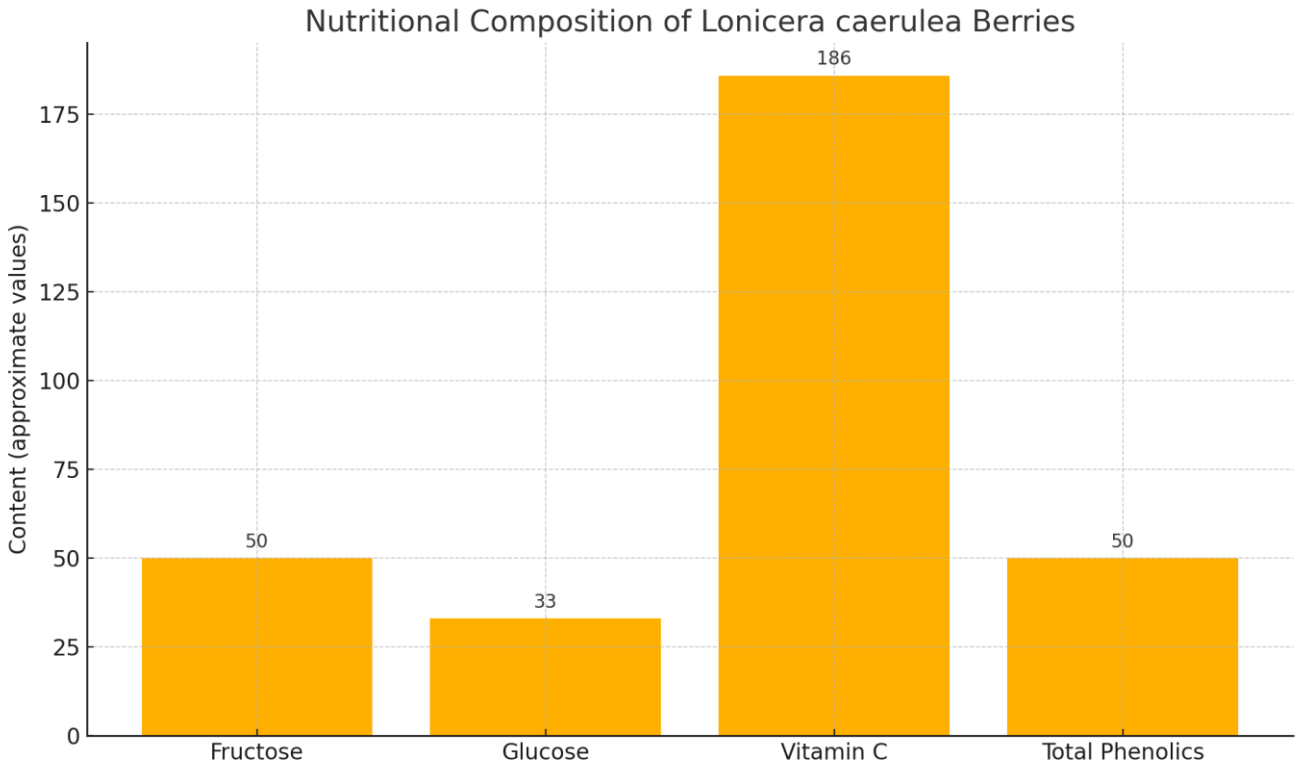

Figure 1. Nutritional composition of Lonicera caerulea berries.

ISSN: 3060-5032

The content of vitamin C reaches 186 mg/100g in blue honeysuckle berries. Anthocyanins make up nearly half of all phenols in blue honeysuckle berries (Fig. 1). Blue honeysuckle has been used in food processing, berries of blue honeysuckle can be used to make many kinds of foods, such as blue honeysuckle mud and blue honeysuckle canned, etc. Food made from blue honeysuckle berries is usually purple, because the color of anthocyanin is purple, and blue honeysuckle contains many anthocyanins with high antioxidant capacity [11]. Blue honeysuckle contains multiple anthocyanins [7] the major anthocyanin in blue honeysuckle berry was identified as cyanidin-3 glucoside(C3G), which accounted for 76.61–92% of total anthocyanins [7,14] (Fig. 1). C3G has been verified to have preventive and therapeutic effects on cerebral ischemia in the central nervous system, and other diseases [22]. It is reported that C3G extracted from blue honeysuckle berries is a food-functional raw material, because of its functions [23]. Haskap berries are rich sources of various fatty acids (FA)

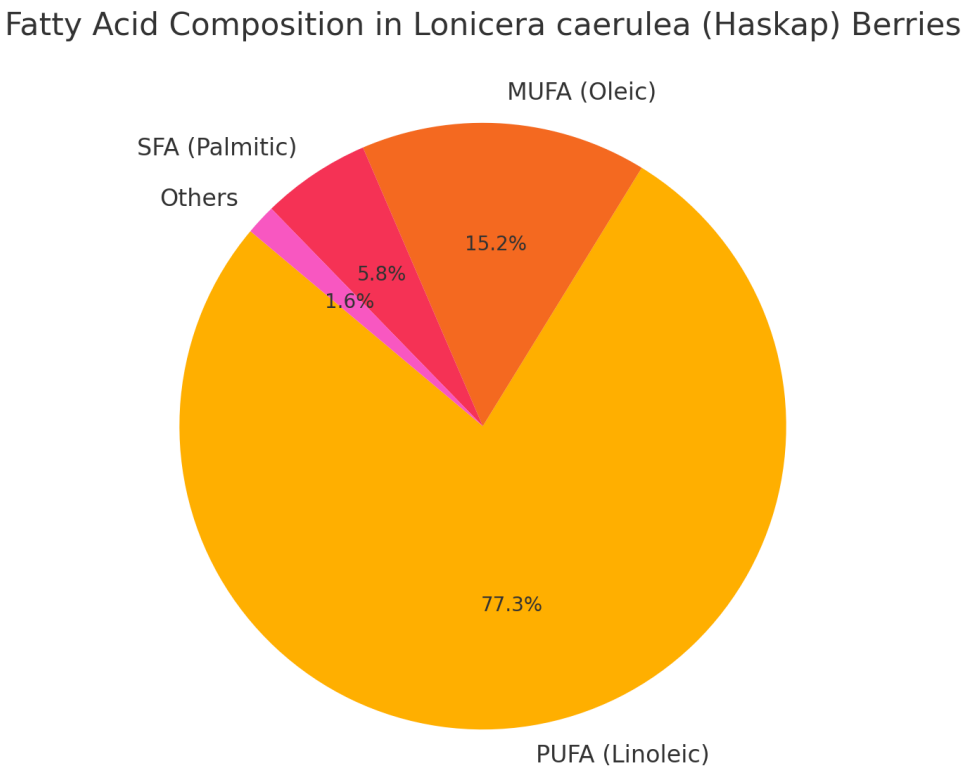

Figure 2. Fatty acid composition in Lonicera caerulea (Haskap) berries.

The percent fraction of polyunsaturated FA (PUFA), monounsaturated FA (MUFA), and saturated FA (SFA) was 77.69%, 14.4%, and 7.91%, respectively. Among 20 fatty acids, the FA composition of haskap berries was dominated by noleic acid (71.79%), oleic acid (180) (14.15%), and palmitic acid (181) (5.39%) [15]. Furthermore, eicosenoic acid (171) (0.20%) and a cis isomer of vaccenic acid (1.30%) were identified in a Canadian and a Russian variety of haskap, respectively [3]. Honeysuckle berries also contain mineral elements, including calcium (1030 mg/kg), magnesium (1020 mg/kg), sodium (863 mg/kg), potassium (324 mg/kg), copper (124 mg/kg), zinc (203 mg/kg), iron (128 mg/kg), manganese (1.4 mg/kg), and phosphorus (151 mg/kg). Furthermore, traces of silver were also found [3]. These minerals play an essential role in many biological events, including enzymatic reactions, proper fluid balance, formation of haemoglobin, cofactors in electron transfer chain, bioelectrical signals, and

ISSN: 3060-5032

protection of cells, and is also essential for healthy teeth and bones [8].

CONCLUSIONS

Lonicera caerulea L. shows high health potential and is a promising source of numerous bioactive compounds, mainly anthocyanins, phenolic acids and flavonols. A unique feature of honeysuckle berries is the presence of iridoids, which are a great anti-inflammatory and antioxidant agent. The rich content of berries corresponds to numerous health benefits. Both in vitro and in vivo studies confirm efficient free radical scavenging of honeysuckle extracts. Reduction of reactive oxygen species is the main reason for properties such as antitumor activity, minimizing insulin resistance and neurocognition improvement. Recent studies emphasize the positive impact on the prevention of diabetes mellitus and decreasing the negative effects. Analysis of the exact content and mechanism of action of the extracts has attracted the attention of many researchers. Therefore, it has been confirmed that a daily intake of honeysuckle berries is able to improve physiological and cognitive functions. Developing honeysuckle-based products, a valuable source of health-promoting compounds which could serve as nutraceuticals, is an important aspect of current research. Definitely, the knowledge about the fruit is broadening, and it is worth continuously updating the topic.

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ISSN: 3060-5032