Journal of Apiculture 31(4) : 367~371 (2016)
DOI: 10.17519/apiculture.2016.11.31.4.367

Free Sugar and Organic Acid Content of the Unripe and Ripe Jujube (*Zyziphus jujuba*) as Honey Plant

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(Received 7 November 2016; Revised 26 November 2016; Accepted 27 November 2016)

Abstract

The fruit of five cultivars (Mudeung, Geumseong, Wolchul, Bokjo and Boeun) of jujube (*Zyziphus jujuba*) were analyzed to estimate free sugar and organic acid content in unripe and ripe jujube cultivars. Glucose, galactose, fructose and sucrose were the major sugar components of jujube. In this study, we observed that sucrose, glucose and fructose content increased during fruit ripening. The highest sucrose content of jujube fruit was 20.54g/100g in ripe Wolchul cultivar. The sweetness index, which plays important role of taste, was also calculated from the content of sucrose, glucose and fructose. The sweetness of jujube fruit increased with fruit growth and development. The highest sweetness of jujube fruit was 116.32 in ripe Geumseong cultivar. Main organic acid detected in jujube were citric acid, malic acid and fumaric acid. As the weight, diameter and soluble solids of *Zyziphus jujuba* fruit were increased with the progress of ripening, organic acids were also increased. The highest citric acid and malic acid content in jujube fruit were 14.64g/100g (Boeun, ripe) and 19.33g/100g (Geumseong, ripe), respectively.

Key words: Citric acid, Fruit ripening, Fumaric acid, Jujube, Malic acid, Sucrose

INTRODUCTION

Jujube (*Ziziphus jujuba* Mill.), Rhamnaceae plant, is widely distributed in the subtropical and tropical regions of southern Asia. Five main jujube cultivars such as Mudeung, Geumseong, Wolchul, Bokjo and Boeun were available in Korea (Park and Kim, 2016). It can be used for fruit tree and honey plants (Ryu, 2003).

Jujube is known for its high nutritional and functional values, containing high amount of sugars, polysaccharides, minerals, proteins, organic acids, vitamin C, and polyphenols (Wu *et al*., 2012). The fruit of jujube has also been used as a traditional medicine in Korea and China for thousands of years as it possesses numerous medicinal properties for human health. According to recent study, jujube fruits have many bioactive compounds having activities such as anti-inflammatory, antioxidant and antiinsomnia effects (Guo *et al*., 2015). From the fruit of jujube, guanosine 3', 5'-monophosphate was isolated and identified (Cyong and Takahashi, 1982). It is also found that some useful constituents such as triterpenic acids, flavonids, nucleosides, phenolic acids, cerebrosides, and sugars were isolated from the jujube fruit (Lee *et al*., 2003). From the jujube flower, the honey, a natural product produced by *Apis mellifera* from the nectar, usually obtained in June and July and consumed as food and medicine (Chen *et al*., 2012).

In *et al*. (1999) studied the seasonal variations in chemical compositions of jujube leaf by analyzing general composition such as sugar, amino acid, fatty acid, mineral

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and flavonoid content. From the results, it was found that the contents of fructose and glucose in jujube leaf increased during growth, while the content of sucrose and maltose in leaf decreased. Because the free sugars (glucose, fructose and sucrose) and organic acids (citric acid, malic acid and fumaric acid) mainly contribute to the taste of jujube fruit, the knowledge of the composition and concentration in unripe and ripe jujube cultivars will benefit consumers. It is also important to know the composition of free sugars and organic acid in jujube fruit for maintaining fruit quality and determining nutritive value (Ashoor and Knox, 1982).

Zozio *et al*. (2014) studied changes in antioxidant activity during the ripening of jujube (*Ziziphus mauritiana* Lamk) and Park and Kim (2016) also studied antioxidant activity, total phenolics, vitamin C and sugar content during fruit ripening of jujube. While there are some data on the constituents and biological activities of jujube, there are no studies of the free sugar and organic acid content of five main jujube cultivars during ripening.

Thus, in this study, we report changes in the overall free sugar and organic acid content of unripe and ripe jujube fruit. We aim to increase the understanding knowledge of fruit ripening process, which may be useful for optimal harvest timing and the processing and utilization of jujube fruit, especially unripe jujube fruit.

MATERIALS AND METHODS

Sample collection and preparation

Z. jujuba fruits of five cultivars (Mudeung, Geumseong, Wolchul, Bokjo and Boeun), grown in the National Institute of Forest Science in Suwon were obtained. A voucher specimen was deposited at the National Institute of Forest Science, Suwon, Korea. From each cultivar of two kind samples were collected according to their maturity (unripe and ripe stages). Unripe jujube fruit (white) sample was collected at September 1st and the ripe jujube fruit (red) which can be used for commercial food was collected at October 1st when the fruit were fully matured.

Free sugar content analysis

The content levels of sugars (sucrose, glucose, and fructose) in the samples were analysed by a modified procedure of a reported LC method (Godin *et al*., 2011). A total of 2g of freeze-dried jujube powders was extracted with 100mL of water in a cooled ultrasonic bath (40kHz) for 60 min. Then the extract was centrifuged (15,000 rpm, 4°C, 10 min) and the supernatant was separated with membrane filter (0.45um) and transferred to vials. Samples were analysed on a Dionex Ultimate 300 HPLC system. A Sugar-pak (waters, 300×6.5mm) column with deionised water as the mobile phase was used for separation of the sugars. The flow rate were optimized as 0.5mL/min and a Shodex RI-101 Detector was used for identification. Quantification was performed on the basis of linear calibration plots of the logarithm of peak areas versus the logarithm of concentrations. The concentrations were expressed in grams per 100g of DW. The summary of HPLC conditions for free sugar analysis in this study were listed in Table 1.

Organic acid analysis

3g of freeze-dried jujube powders were transferred to Eppendorf tube with 5ml of distilled water. Then the extract was centrifuged (15,000 rpm, 4°C, 10 min) and the supernatant was separated with membrane filter (0.45um) and transferred to vials. Organic acids in jujube fruit were analyzed by a Dionex Ultimate 300 HPLC system. The chromatographic separation used for organic acid detection

Table 1. The operating conditions of HPLC for analysis of free sugars

Instrument	Dionex ultimate 3000 shodex RI-101 detector
Column	Sugar-pak (waters, 300×6.5mm)
Solvent	Distilled water
Flow rate	0.5ml/min
Injection volume	10uL

employed 0.01 N H_2SO_4 as the mobile phase, with a flow rate of 0.5 ml/min, and the samples were injected into an Aminex 87H (300×10mm) column (Bio-Rad, USA). Organic acids were detected with a RI detector (ERC, RefractoMax, Japan).

Estimation of jujube taste parameters

Sweetness index in this study was calculated based on the amount and sweetness properties of individual carbohydrate in fruit (Keutgen and Pawelzik, 2007). The contribution of each carbohydrate was calculated, based on the fact that fructose is 2.30 and sucrose 1.35 times sweeter than glucose. Accordingly, sweetness index = [1.0 (glucose) + 2.30 (fructose) + 1.35 (sucrose)].

Statistical analysis

All experiments were performed at least three times and the results were reported as mean±SD. Data were statistically evaluated by one-way ANOVA analysis and Duncan's multiple range test. Results of tables and figure were presented as mean±SD.

RESULTS AND DISCUSSION

Free sugars analysis

The HPLC quantitative analytical data of the free sugars in unripe and ripe jujube fruit are listed in Table 2. The fruit of five different jujube cultivars were used in this study for comparing the difference among cultivars. As shown in Table 2, increasing trends were found for the contents of glucose and fructose during fruit ripening except Wolchul cultivar. Although the sucrose was very small at unripe stage, its content continued to increase and reached as high as 20.54g/100g. These results are due to the fact that the sweetness of jujube fruits rapidly increased after ripe period, which confirmed that accumulation of mono- and disaccharides in jujube fruit occurs mainly in the last stages of ripening (Guo *et al*., 2015). Although the relationship between fructose and glucose content was about 1:1, which is typical for berry fruit, fructose content in jujube fruit has more high than glucose content (Keutgen and Pawelzik, 2007). It is well known that fruit sweetness depends not only on the content of each sugar,

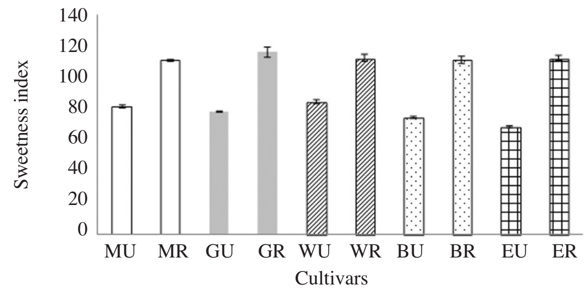

Fig. 1. Sweetness index of the unripe and ripe jujube cultivars (MU: Mudeung unripe, MR: Mudeung ripe, GU: Geumseong unripe, GR: Geumseong ripe, WU: Wolchul unripe, WR: Wolchul ripe, BU: Bokjo unripe, BR: Bokjo ripe, EU: Boeun unripe, ER: Boeun ripe).

Table 2. Free sugar content of the unripe and ripe jujube cultivars (g/100g)

Cultivar	State of fruit	Contents of analyte (mean±SD, n=3)				Total
		Glucose	Galactose	Fructose	Sucrose	
Mudeung	unripe	22.46±0.38e*	0.24±0.02ab	25.6±0.24cd	0.05±0.00f	48.44±13.88d
	ripe	26.83±0.41c	0.21±0.03b	29.42±0.22b	12.27±0.22c	68.72±13.60b
Geumseong	unripe	20.45±0.02f	0.22±0.03b	25.21±0.05d	0.02±0.01f	45.91±13.26e
	ripe	27.74±0.82b	0.23±0.02b	29.89±0.89b	14.70±0.39b	72.55±13.70a
Wolchul	unripe	24.04±0.36d	0.16±0.02c	26.38±0.37c	0.05±0.01f	50.64±14.52c
	ripe	24.75±0.54d	0.27±0.02a	26.15±0.61c	20.54±0.16a	71.71±12.01a
Bokjo	unripe	19.67±0.23g	0.15±0.02cd	23.43±0.17e	0.80±0.03e	44.04±1.27f
	ripe	27.08±0.60bc	0.22±0.02b	29.60±0.63b	12.14±0.27c	69.05±13.73b
Boeun	unripe	19.01±0.18g	0.11±0.01e	21.60±0.24f	0.06±0.01f	40.78±11.72g
	ripe	30.0±0.48a	0.1±0.01de	31.94±0.52a	6.72±0.05d	68.84±16.17b

*Different letters indicate Duncan's multiple range test (Significant at $p<0.01$).

Table 3. Organic acid content of the unripe and ripe jujube cultivars (g/100g)

Cultivar	State of fruit	Contents of analyte (mean±SD, n=3)		
		Citric acid	Malic acid	Fumaric acid
Mudeung	unripe	10.94±1.54abc*	15.32±2.33abcd	0.15±0.05ns**
	ripe	13.11±4.84ab	15.20±0.46abcd	-
Geumseong	unripe	6.76±0.68c	15.52±2.29abcd	0.25±0.02ns
	ripe	8.55±0.10bc	19.33±1.48a	0.15±0.03ns
Wolchul	unripe	11.86±4.74abc	12.42±4.05d	-
	ripe	10.94±2.21abc	14.00±0.36cd	-
Bokjo	unripe	7.01±0.08c	17.16±0.39abc	0.10±0.00ns
	ripe	8.72±0.15bc	18.68±2.25ab	-
Boeun	unripe	8.57±0.85bc	14.92±0.29bcd	0.18±0.00ns
	ripe	14.64±5.26a	17.25±3.58abc	-

*Different letters indicate Duncan's multiple range test (Significant at p<0.01).
**ns means not significant.

but also on the ratios of the main individual sugars (Zheng *et al*., 2016). It is also found that the sweetness index, which plays important role of taste, increased with fruit growth and development (Fig. 1). The highest sweetness of jujube fruit was 116.32 in ripe Geumseong cultivar while the lowest sweetness of jujube fruit was 68.77 in unripe Boeun cultivar.

Organic acid

Organic acids represent further compounds contributing to taste and flavour of jujube fruit. Three organic acids in jujube fruit, citric acid, malic acid, and fumaric acid, were detected by HPLC. The organic acids of unripe and ripe fruit of jujube cultivars during ripening are shown in Table 3. Malic acid showed the main organic acid in jujube fruit followed by citric acid and fumaric acid. Although citric acid dominated in lemons, limes and orange, the malic acid was the main organic acid in jujube fruit (Albertini *et al*., 2006). Citric acid content in Bouen ripe fruit were the highest as 14.64g/100g. Fumaric acid were the third-most common organic acids, and occupied 0.10~0.25g/100g according to cultivrs. A similar trend was reported for strawberry (Keutgen and Pawelzik, 2007). As shown in Table 3, increasing trends were also found for the contents of citric acid and malic acid during fruit ripening except Mudeung cultivar in malic acid. Malic acid contents in Mudeung ripe and unripe jujube were similar unlike other culivars.

In summary, to our knowledge, this is the first study investigating the content changes of free sugars and organic acids in unripe and ripe five different jujube cultivars. From the results of this study we found that the content levels of free sugars and organic acids were increasing with fruit ripening. The sweetness index were also calculated from the content of sucrose, glucose and fructose. The highest sweetness of jujube fruit was 116.32 in ripe Geumseong cultivar. Organic acid in jujube were mainly composed of citric acid, malic acid and fumaric acid. The highest citric acid and malic acid content in jujube fruit were 14.64g/100g (Boeun, ripe) and 19.33g/100g (Geumseong, ripe), respectively. The results would be helpful for the choice of suitable harvest time for jujube fruit, due to the beneficial effects of these compounds for human health.

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