Analysis of Ash and Trace Metals in Korean Native Bee Honey

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Trace metals in honey have an influence on the taste of honey along with pollens. Western bee honeys, which are mostly collected from acacia, have less than 0.1% of ash. Savor of Korean native-bee honey is thought to be due to the difference of the contents of trace metals. Korean native-bee honeys collected from Jirisan District, which is the greatest producing area of native-bee honey in Korea, showed high contents of ash. Korean native-bee honeys from the districts other than Jirisan District also showed similar results (0.44–0.83% of ash) to those from Jirisan District. Potassium was found to be the principal factor of high content of ash with over 85% of trace metals in ash.

Key words: Native-bee honey, ash, trace metals, potassium

In recent years, honey have attracted lots of scientists' interest because of its biological actions showing various effects such as antibacterial activities¹⁾, enzyme activities^{2,3)}, and sugar⁴⁾ and lipid metabolism⁵⁾. With much regret, most scientists are interested in the honey produced by foreign bees, but not by oriental bees. Studies, in fact, on the native-bee honey produced by oriental bees in Korea are much limited due to the small-scaled business.

The authorities of food, in fact, have not been stern in the quality control of native-bee honey, which has poor market circumstances because its production and marketing are led by small-scale producers. Much higher price of native-bee honey in comparison to foreign-bee honey led people to producing counterfeit native-bee honey, resulting in consumers' distrust in native-bee honey. Therefore, it is very important to restore the consumers' trust in native-bee honey through stern and proper quality control for the sake of prosperity of its business.

Trace metals in honey have an influence on the taste of honey along with pollens. Foreign-bee honey generally gives a much stronger sweetness than native-bee in spite of the same amount of invert sugars. In addition, native-bee honey usually gives not only its specific savor but also weak bitterness due to high percentage of trace metals. Korea Food Code⁶ prescribed that the ash content of honey should be below 0.6% but the clause on ash was eliminated in 2005 because lots of samples of native-bee honey did not meet the criteria. These studies were performed to examine which component is related to the high ash content in native-bee honey.

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Materials and Methods

Sample collection. Native-bee honey samples were collected from various districts to determine the contents of ash. Native-bee honey, produced in 2004 in the vicinity of Mount Jirisan, was collected by two branches of National Agricultural Cooperative Association at Namwon and Jirisan from producers in Jirisan District to sell to Korea Ginseng Corporation (KGC). The samples of the districts other than Jirisan were purchased or provided free of cost directly from producers. Western bee honey samples were purchased from markets.

Analysis of ash. Ash was analyzed by the method described in Korea Food Code⁶⁾. Samples of honey were weighed to 0.1 mg by around 2.0 g (S) into crucibles (W0), which had been weighed after heating for 2 h at 550°C in a furnace and cooling down in a desiccator. They were heated for complete dryness at 150°C for 3 h in a dry oven. The dried samples were placed in a furnace to burn to ashes. The temperature of the furnace was set up to rise to 550°C for 3 h and then keep the temperature for 6 h further. When the furnace was cooled down to 200°C after burning the samples, they were put into a desicator. After cooling down to room temperature for 40 min. they were weighed to calculate the contents of ash using the following equation.

Ash (%) =
$$\frac{W_1 - W_0}{S} \times 100$$

W₀: weight of a crucible (g)

W₁: weight of a crucible and ash after burning the sample (g) S: amount of a sample (g)

Analysis of trace metals. Five grams of a native-bee honey sample was burned at 550°C for 6 h to attain ash. It was

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Table 1. The conditions for the analysis of trace metals using ICP-AES

Spectrophotometer:	Jobin-Yvon JY 38 plus monochromator Focal length 0.75 m
Generator:	RF output 1.4 kW, Torch type fixed
Argon flow:	Coolant gas 12 L/min Carrier gas 0.4 L/min
Torch observation height:	8 mm
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soaked in a small amount of water and then dissolved in 5 ml of conc-HCl. The sample solution was transferred into 50 ml volumetric flask and adjusted to 50 ml with water. Ten trace metals in the sample solution were determined using ICP-AES.

The conditions for the analysis of trace metals are described in Table 1.

Results and Discussion

Mount Jiri is the widest area in Korea prohibiting the breeding of western bee in order to insure the production of native-bee honey. Namwon and Jirisan Regional Nonghyups (National Agricultural Cooperative Federation) collect nativebee honey produced within their districts to sell it in place of farmers. They collected about 25 tons of native honey from farmers only to deliver 17 tons to KGC. Eight tons of honey remains to be delivered to the corporation owing to higher contents of ash than prescribed (below 0.6%) in Korea Food Code. Table 2 shows the ash contents of native-bee honeys containing over 0.6% of ash which are stored in the two Nonghyups because of high contents of ash in the first test by KGC. All the samples presented over 0.6% of ash also in the second analysis of ash. Among 34 samples, not one was below 0.6% of ash and eight samples contained higher than 0.9% of ash.

Total ash content and 10 trace metals were determined in 10 native-bee honeys produced in Jirisan District to elucidate the reason why they contained large amount of ash. As seen in Table 4, native-bee honeys selected at random among those in Jirisan district contained large amount of total ash and trace

Table 3. Distribution of ash contents in native-bee honeys

Range	No of samples				
below 0.60%	0				
0.60~0.69%	5				
0.70~0.79%	8				
0.80~0.89%	13				
0.90~ 0.99%	5				
over 1.00%	3				
Total	34				

metals, especially potassium.

These native-bee honeys show much higher contents of ash than imported bee honeys collected from various flowers except honeydew⁷⁾. According to Popek⁷⁾, honeys from acacia, lindon, floral, buckwheat heather and rape contain a small amount of ash from 0.08% to 0.3%, while that collected from honeydew contains a large amount of ash from 0.4% to 0.73%, which is similar to Korean native-bee honey.

Potassium was the primary cause of high content (2,218~4,328 ppm) of ash in native-bee honey, holding over 85% in total trace metals. These results are in agreement with Terrab's report⁸⁾ suggesting that several honeys contain over 2,000 ppm of K among the 98 honeys tested.

Plant inhales CO_2 in air and releases water through stoma. Opening or closing of stoma is closely related to the concentration of K^+ in guard cell. In other word, stoma opens with the concentration of K^+ in guard cell increased to inhale CO_2 in air. Accordingly, potassium in native-bee honey is thought to come from plant while bees are collecting nectar from flowers.

Seven native-bee honeys were purchased through the Internet or obtained from local producers to compare ash contents with honey produced in Jirisan. Native-bee honeys from the districts other than Jirisan also show the same result as the honey from Jirisan District (Table 5). In other words, ash contents were higher than 0.6% in 4 of 7 honeys. All three honey samples also had high contents of trace metals. The content of potassium was the highest with around 80% of K in total trace metals.

Table 2. Ash contents of native-bee honeys with over 0.6% of ash in the vicinity of Jiri mountain

	Namwon N	onghyup		Jirisan Nonghyup					
No	No Content(%)		No Content(%)		Content(%)	No	Content(%)		
1	0.87	11	0.94	1	0.89	11	0.71		
2	0.65	12	0.84	2	1.00	12	0.73		
3	0.85	13	0.82	3.	0.87	13	0.69		
4	0.85	14	0.68	4	0.90	14	1.24		
5	0.94	15	0.82	5	0.89	15	0.76		
6	0.84	16	0.69	6	0.77				
7	0.73	17	0.79	7	0.75				
8	0.96	18	0.94	8	1.13				
9	1.04	19	0.74	9	0.86				
10	0.66			10	0.88				

Table 4. Contents of trace metals in Korean native-bee honeys of Jirisan District

No	Contents of inorganic components (mg/kg, ppm)										Ash content	
NO	Al	Fe	Mg	P	Cu	Zn	Si	Na	Ca	K	Total	(%)
1	84.7	7.4	101.9	134.4	1.7	1.5	58.4	8.8	126.1	3,154	3,678.9	0,66
2	76.4	5.2	115.1	126.0	1.5	1.1	1.3	10.8	. 113.3	2,931	3,381.7	0.71
3	37.9	6.6	89.8	99.6	1.2	1.0	31.1	5.0	88.1	2,417	2,777.3	0.55
4	59.6	8.7	74.4	87.7	1.2	0.8	42.3	6.2	114.0	2,278	2,672.9	0.49
5	38.4	9.9	99.0	97.9	1.3	1.1	25.6	5.6	112.5	3,060	3,451.3	0.63
6	62.1	8.6	113.3	139.3	1.2	1.5	25.9	7.7	117.1	3,474	3,950.7	0.59
7	79.8	13.5	156.4	219.1	1.8	2.0	78.9	9.2	143.7	3,140	3,844.4	0.69
8	107.4	10.4	148.8	208.6	1.8	2.0	99.6	12.6	142.9	3,040	3,774.1	0.65
9	90.9	11.8	118.0	151.4	1.8	1.7	77.1	12.2	116.6	2,309	2,890.5	0.84
10	37.6	6.7	142.9	248.6	1.3	2.2	27.3	8.1	179.4	4,328	4,982.1	0.95

Table 5. Contents of trace metals in Korean native-bee honeys of other districts than Jirisan

No -	Contents of inorganic components (mg/kg, ppm)									Total	Ash content	
	Al	Fe	Mg	P	Mn	Zn	Si	Ca	Na	K	(ppm)	(%)
CC	89	8.2	67	71	5.3	1.6	100	150	174	2,350	3,016.1	0.44
KI	22	4.8	96	105	3.1	1.6	48	164	240	3,967	4,651.5	0.78
JК	16	5.3	95	101	17	2.1	39	160	180	3,250	3,865.4	0.54
JS1	-	-	-	-	-	-	-	-	-	-	-	0.48
JS2	-	-	-	-	-	-	-	-	-	<u>.</u> '	-	0.83
JS3	-			-	-	-	-	-	-	-	-	0.81
JS4	-	-	-	-	-	-	-	-	-	-	-	0.83
FH	5.6	10	7.9	28	0.32	<1	14	18	46	19	149.8	0.03

CC: Produced in Chungwon of Chungbuk Province, KI: Produced in Inje of Kangwon Province, JK: Produced in Kwangyang of Jeonnam Province, JS: Soonchang of Jeonbuk Province, FH: Foreign-bee honey produced by Jeonbuk Nonghyup and purchased in a supermarket.

These results suggest that Korean native-bee honeys contain high percentages of ash, especially K, compared with foreign-bee honey and potassium plays the most principle role in high contents of ash in native-bee honey.

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