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Physicochemical Study for Manna (Gazo) Collected from Different Places of Sulaimani Governorate

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ABSTRACT

Three samples of partial purified Manna from three locations at Penjween in Sulaymaniyah governorate/ Iraq were prepared. Locations were Ahmadklwan (A), Bnawaswta (B), and Kanimang (K). HPLC has been used to determined type and rates of sugars within the Manna. Results showed that all samples A, B, and K contained high amounts of fructose (22.3%, 21.9%, 22.6%) respectively. samples showed less glucose than fructose in their content which was (A 13.3, B 13.4, K 11.2%). Manna contained a considerable amount of sucrose and trehalose, for sucrose was 26.8%, in A, 26.9% in B, 26.0% in K. Likewise the rate of trehalose within sample A, B, and K was (36.8, 20.4, 24.2%) respectively. The existence of alcoholic sugars was very low, for instance, the quantity of sorbitol was (0.5%, 0.9%, 1.2%) for samples A, B, and K respectively, and for mannitol was 0.1% in all the samples. ICPE used to determine the rate of minerals, Calcium rate showed a significant difference among the Manna samples, which was A (25.200), B (11.000), K (16.450). As well as for iron (Fe) rate a mass variation was noticed through the samples (A 4600, B 3.785, and K 3.965). In general, magnesium (Mg) content was relatively high with the rate (4.410) in A, (3.005) in B, (3.365) in K. results confirmed that Manna no content chromium (Cr) and cadmium (Cd). Although, there was no lead (Pb) in B and K, but a very low amount appeared in A (8.55). Results are calculated in mg/kg.

Keywords: Manna, monosaccharide, disaccharide, trehalose, minerals.

INTRODUCTION

In some areas of the Middle East especially, Iraqi Kurdistan, Iran, Sanandaj, Turkey and another little area of the world, a fallen gummy material which is a mixture of insect and plant secretions is locally collected to use as candy or for herbal therapy. Locally this material called Gazo (in Sulaymaniya) or Man-alsma (in Arabic culture) or Manna (Internationally). Although this material or maybe similar has a special position among the other foods since it was mentioned in the three holy books, Taura, Bible, and Quran, the pay attention to this food is very rare. The term "Manna" broadens to include all the plant secretions either it takes please naturally without human interference or by making injury in the different species of plants. This widening of this term causes big differences in values of the quality and quantity of Manna; therefore, it must name the Manna by its local name to reduce confusion among the Manna types. In Iraqi Kurdistan especially in Benjween, the sweet collected Manna from oak trees especially genus *Fraxinus ornus* ("Manna Ash"). The leaves of this Manna produce sticky secretions when attacked by insects, and it is likely that exudates from the insects are also included in the mass. Fallen leaves are collected and boiled in water to extract the mixture of sugars on their surface, the resultant solution being 'mixed with eggs to make a popular dessert (Wotton, 2010).

On the other hand, (Takavar & Mohamadi, 2008) reported that Gaz-Alafi also called "Gazu" or "Kurdish Gaz" is considered as a byproduct of oak forests in the west of Iran and east of Iraq. It is a hard, brilliant resinous sweet natural product that appears on the leaves of some Quercus species including Q. brantii Lindi. And Q. infectoria Oliv. (Fagaceae). This Manna is the excretion of two insects known as *Thelaxes suberi* Del. and *Tuberculoides annulatus* Hart *Calaphidae.*

Manna is produced by nutrition–secretion activity of the larva feeds on the host plants. At first, the larva secretion is like a watery and fluent liquid that gradually gets hard and changes into a solid white cocoon with a rough surface. It seems that the metabolic interaction between the larva and plant depends also on climate and geographical conditions (Nasirzadeh *et al*., 2005).

Folklore books took cares with Manna especially Taranjebin Manna which was considered an effective drug for some diseases, that leading to achieve some researches about the functionality of this food. Several hundreds of tons of Manna are produced in the world especially in Iran, Iraqi Kurdistan, Turkish, Palestine, Egypt, Afghanistan, India, Italy and others (Hamedi *et al*., 2015).

This research aimed to study the quality and quantity of the type of Manna types from different three sites of Penjween Sulaymaniyah that are Ahmadklwan, Bnawaswta, and Kanimang, and to study the content of some minerals content.

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MATERIALS AND METHODS

Materials

Manna

The partial purified Manna (prepared to use in candy process) was purchased from three sites of Penjween Sulaymaniyah that are Ahmadklwan, Bnawaswta, and Kanimang which again sieved by 125 μm sieve to discard the large pieces of Manna.

Methods

This study was done to analyze both sugars and minerals content in Gazo (Manna) based on (Fakhri *et al*., 2017)

1 proximate chemical composition of Manna types:

The moisture, ash, crude protein, crude lipids, total carbohydrate, total sugars, reducing and non-reducing sugars content were determined and calculated in Manna samples for three different varieties [Ahmadklwan (A), Bnawaswta (B), and Kanimang (K)] according to the method described by AOAC (2016).

2 Determination of Manna sugar types by HPLC:

Samples for three different varieties [Ahmadklwan (A), Bnawaswta (B), and Kanimang (K)] of Manna were collected and stored in glass jars. They were then weighed out and dissolved in water in order to obtain 30 mg/ml solution of each. 30 μL of each sample was injected onto Agilent hi-plex ca, 7.7* 300 mm, 8 μm columns at 85c with a flow rate of 0.6 ml/min. pure water was used as eluent, and detection carried out on an Agilent RI detector according to Ouchemoukh *et al*., (2010).

3 Determination of minerals content in Manna types:

The instrument ICPE-9800 Series was used to determine the minerals of the studied Manna types. They also feature user-friendly software that makes analysis easy. Furthermore, we used 0.1g of gazo with 50ml of HNO_3 this instrument is multi microwave and do the digestion in 20 minutes in 200ºC according to van Franeker & van Oyen (2015). The minerals from mg/L to mg/kg were calculated from the following equation:

Metal (mg/kg) = [concentration of metals (mg/L) X volume of sample (mL)] / [sample weight (kg) x 1000]

OR

Metal (mg/kg) = [concentration of metals (mg/L) X volume of sample (L)] / [sample weight (kg)]

RESULTS AND DISCUSSION

1 Chemical Composition of Manna

Chemical analysis of Manna (Table 1) showed that Manna samples were differed in their content of moisture which ranged from 9.96 for K to 14.66% for B. This result is agreed with (Caligiani *et al*., 2013) who found that the range of moisture in some collected manna was between 8.6 and 10.8%. These percentages of moisture are suitable to store manna powder for a long time especially, in the presence of a relatively high percentage of total sugar which may decrease the water activity that is necessary for microorganism activity. The results also showed that the Manna content of protein was low in all Manna samples which ranged from 1.42 for K to 2.12 for B. This result is agreed with (Hamedi, *et al*., 2015) who found that Trehalose Manna contained 2.4% protein. However, the same researchers found that the water-soluble of Manna hadn't contained a considerable amount of protein. On the other hand, (Caligiani *et al*., 2013) found that the amount of protein was very low ranged between 0.01- 0.05% in some types of Manna exudates. It is important to know that Manna is not considered as a resource of protein.

The studied Manna contained a little amount of crude fat which was ranged from 1.16 for K to 2.91 for B. This result isn't agreed with (Caligiani *et al*., 2013) who found that some types of Manna contain about 0.1- 0.4% of crude fat. Oleic acid (58.45- 67.95%) palmitic acid (17-32.49%) and Stearic acid 3.77- 4.07% of the total fat was the main fatty acids, in addition to little amount of odd number of fatty acids, not exceeded than 1% were identified also in samples of Manna by (Caligiani *et al*., 2013). The total ash content of Manna showed a major significant difference among studied samples which ranged between 2.61 for B to 10.10% for K. This wide difference may reflect the difference of cleaning efficiency among the resources of the Manna samples.

Table 1. Proximate chemical composition of different studied samples of Manna.

Gazo sample	Moisture %	Ash %		Protein %	Lipids %	Total Carbohydrate
		Total	Insoluble			
A	13.28	8.52	4.28	1.74	1.83	70.35
B	14.66	2.61	1.30	2.12	2.90	76.41
K	9.10	10.10	5.05	1.42	1.17	73.16
LSD	1.03	1.55	0.54	0.62	0.08	0.15

The results also showed that the percentage of the total, reducing and non-reducing sugar were differed among the tested samples (Table 2). Total sugar ranged from 14.02% for B to 17.01% for K while reducing sugar ranged between 11.07% for K to 13.23% for A. The results also showed that sample B contained a low percentage of 5.02% of non-reducing sugar. However, it is difficult to say, this result is agreed with some researchers since there is a wide difference among the researchers' results about the percentage of sugar which may due to the differences of secretion resources. (Nicknejad, 1976) Analyzed Manna, collected from desert trees, and reported that it contained about 40% sucrose and 10% fructose. (Caligiani *et al*., 2013) reported that the quantitative sugar profile of the Manna samples is mannitol (41–48 g/100 g), mannotriose (13–22 g/100 g), fructose (9–16 g/100 g), stachyose (1–11 g/100 g) and glucose (2–3,7 g/100 g) being the most abundant saccharides in genuine Fraxinus Manna samples which emphasized that this type of Manna didn't contain nonreducing sugar especially sucrose and trehalose. This finding doesn't agree with the results of this research which found that studied Manna contains at least 5.04% to 8.62% of non-reducing sugars for sample B and K, respectively, which emphasized by HPLC results.

Table 2. Total, reducing and non-reducing sugars.

Gazo samples	Total sugars	Reducing sugars	Non-reducing sugars
A	16.955	13.238	6.965
B	14.029	11.835	5.024
K	17.014	11.070	8.624
LSD	2.1	1.116	1.2

2 The type of Manna sugar types identified by HPLC:

Table (3) shows the results of HPLC for Manna samples compared with some standard solutions of mono and disaccharides. The results showed that in general, the three examined Manna contained the same types of mono and disaccharide. However, the results showed that there was difference among Manna samples in their content of trehalose which was 36.83% for A, 20.43% for B and 24.28% for K of Manna samples. This result was agreed with (Tawfiq, 2012) who emphasized that Manna sugars, which is collected in the north of Iraq (Kurdistan) contains about 23- 30% of trehalose. (Hamedi *et al*., 2015) also reported that Manna sugars contain about 25% of trehalose. On the other hand, (O'Brien-Nabors, 2016) reported that Manna contains 45-65% of its dry matter as trehalose.

Also, results showed that there were different in Manna samples content of other identified sugars. Manna content of sucrose ranged between 26.05% for K of Manna sample and 26.97% for the B sample. This results were less than that reported by (Nicknejad, 1976) who analyzed Gaz-alafi, collected from desert trees, and reported that Manna contained about 40% sucrose. On the other hand, there were no differences between A (13.37%) and B (13.40%). While, sample K recorded (11.28%) of glucose.

In the same table, the results also cleared that the studied samples of manna contained very little amount of alcoholic sugars especially sorbitol and mannitol. Manna content of sorbitol ranged between 0.5 for sample A and 1.23% for sample K. This result was in agreed with (Caligiani *et al*., 2013) and (Guarcello *et al*., 2019) who found that Manna contains about 0.5–0.6 % of sorbitol. On the other hand, the results showed that the studied Manna contains a considerable amount of fructose which slightly differs among the samples of Manna. Fructose content ranged between 21.92% for the B sample and 22.66% for the K Manna sample. These values of fructose percentage were somewhat higher than (Caligiani *et al*., 2013) report who found it was about 9–16%. But they were agreed with (Guarcello *et al*., 2019) who found that the 22 -23% of fructose were included with the values of 35 types of Manna which their fructose contents were 4.41- 33.0% of total sugar.

Mannitol percentage was the lowest value of sugar percentage compared with the other identified sugars, as the results showed. Most types of Manna, as the articles reported, contain a higher content of mannitol 28- 60% (Guarcello *et al*., 2019). This result of mannitol may attribute to the difference in the resources of tree exudations (Caligiani *et al*., 2013) and (Guarcello *et al*., 2019).

Table 3. Manna sugar types.

Sugar types	Sample A	Sample B	Sample K
Unknown	--------	16.225	14.35
Trehalose	36.835	20.435	24.28
Sucrose	26.81	26.975	26.055
Glucose	13.37	13.4	11.285
Sorbitol	0.525	0.9	1.23
Fructose	22.335	21.92	22.66
Mannitol	0.125	0.14	0.13

3. Manna minerals content:

Table (4) showed the results of Manna samples content of minerals included heavy metals.

Calcium content in Manna samples were ranged between 11.000 ppm for B to 25.200 ppm for A samples. The Recommended Daily Allowance (RAD) and Tolerable Upper Intake Limit (TUIL) for calcium are 1000 mg and 2500 mg, respectively (Edori & Marcus, 2017) which means it can consider Manna as a suitable resource of calcium.

The results showed that iron content for samples A, B and K were 4.600, 3.785 and 3.965 ppm, respectively. Yazdanparats *et al*., (2014) found that Manna contained 1730.0396 ppm of iron in Gaz-Alafi (Oak Manna), 781.5932 ppm in Taranjebin (camel's thorn Manna), 138.7188 ppm in Bid-Khesht (willow Manna) and 99.7218 ppm in Shir-Khesht (pocks pray Manna). These differences may attribute to the kind and quantity of adjunct materials that presence with Manna, in addition to the type of cleaning for these Manna samples which were brought from the local market. (Edori & Marcus, 2017) reported that RDA and TUIL for iron are 8 mg and 45mg, respectively that emphasize the Manna as a superior resource of iron metal.

In general, magnesium content was relatively high in the studied Manna samples which ranged between 3.005 ppm for B and 4.410 ppm for K of Manna samples. (Edori & Marcus, 2017) also reported that RDA and TUIL for Mg are 310 and 400 mg, respectively.

The results also showed that investigated Manna samples were free from chromium and cadmium. As for Lead only detected in the sample A as a trace element in concentration of (0.017 ppm).

Even though, Manna samples contained a high amount of minerals, it could be eaten in a little amount not exceed 5-10 mg as a minerals supplement.

Table 4. Manna minerals content.

Mineral	Sample A (ppm)	Sample B (ppm)	Sample K (ppm)
Calcium	25.200	11.000	16.450
Iron	4.600	3.785	3.965
Magnesium	4.410	3.005	3.365
Chromium	N.D.	N.D.	N.D.
Cadmium	N.D.	N.D.	N.D.
Lead	0.017	N.D.	N.D.

CONCLUSION

In this research, this Manna collected in different areas in the Penjween governorate contains many sugars in different proportions determined by HPLC, also Manna contains different types of minerals determined by ICPE. All these results show Manna a good source of sugars and minerals.

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دراسة فيزوكيميائية للمن (الكزو) المجموع من مناطق مختلفة من محافظة السليمانية

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تم الحصول على ثلاثة عينات من مادة (من السما) الخام المنقاة جزئيا وذلك من ثلاثة مناطق في قضاء بنجوين محافظة السليمانية/العراق وهي احمد كلوان و بناواسوتا وكاني مانك. تم تحديد نوعية وكمية السكريات الأحادية والثنائية باستخدام جهاز HPLC وبينت النتائج احتواء عينات المن على نسب عالية من الفركتوز فكانت ٢٢,٣ و٢١,٩ و٢٢,٦٪ من نسبة السكر الكلي لكل من A وB وK على التوالي. كما احتوت العينات على نسب جلوكوز اقل من الفركتوز وهي ١٣,٣ و١٣,٤ و١١,٢٪ لكل من A و B وK على التوالي. اما السكروز والتريهالوز فقد كانت كمياتهما كبيرة نسبيا فكانت للسكروز ٢٦,٨٪ Aو ٢٦,٩٪ Bو ٢٦,٠٪ K وكانت نتائج التريهالوز ٣٦,٨٪ A و ٢٠,٤٪ B و٢٤,٢٪ K على التوالي. وأوضحت النتائج ان المن احتوت على نسب قليلة جدا من السكريات الكحولية فكان السوربتول ٠,٥٪ A و٠,٩٪ B و١,٢٪ K. اما المانيتول فكانت نسبته ٠,١٪ للعينات الثلاث من المن. واستخدم جهازICPE لتقدير كميات بعض العناصر المعدنية، فقد كان هنالك ملحوظة بين العينات في محتواها من الكالسيوم فكان ٢٥,٢٠ في A و ١١,٠٠ في B و ١٦,٤٥ في K. وبينت النتائج عدم وجود فرق في محتوى عينات المن من عنصر الحديد فقد كانت نسبته ٤,٦٠٠ و ٣,٧٨٥ و ٣,٩٦٥ لكل من A و B و K على التوالي. وبصورة عامة كانت كمية المغنيسيوم كبيرة نسبيا فهي ٤,٤١ A و٣,٠٠ B و٣,٣٦ K. وكذلك بينت النتائج ان عينات المن تحت الدراسة لم تحتوي على بعض العناصر الثقيلة مثل الكروميوم والكادميوم اما بالنسبة للرصاص فلم يعثر عليه الا بنسبة قليلة جدا في عينة A والتي كانت 0.017جزء في المليون.