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A Study on the Formation and Safety of HMF in Honey

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ABSTRACT

Honey is a natural sweet substances produced by honey bees from the nectar of flowers or blossoms or secretions of living parts of plants. Despite having abundant nutritional value of honey, some of toxic contaminants be formed during improper thermal processing and preservation such as hydroxymethylfurfural(HMF). Significant correlation has been identified between HMF and thermal process and preservation time and temperature. HMF is a furanic compound produced as a result of Maillard reaction or from direct dehydration of sugar under acidic conditions. Apart from process condition, HMF content of honey is influenced by several factors such as pH, acidity, water activity, diastase and invertase activity and divalent cations concentration. HMF content is an indicator of the freshness and quality of honey and use a reliable method to diagnosis adulteration. In this article, mechanism of HMF formation, its toxicity and affecting factors on its content, have been surveyed.

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INTRODUCTION

Honey, as defined by the Codex Alimentarius is the natural sweet substance produced by honey bees from the nectar of plants or secretions of living parts of plants.It has been collected by the bees and transform by combining with specific substances of their own, deposit, dehydrate, store and leave in the honey comb to ripen and mature [10]. Honey is a complex mixture of sugars, water, vitamins, enzymes, minerals and etc. The properties and composition of honey is related toitsorigin, season, varietyof bee, plantsource of nectar, time duration of its storage in honey combs and harvest condition [25,17]. There are numerous nutritional and medicinal properties of honey but as a result of inappropriateheat treatment or storage condition, some non-nutrition compounds are formed in that. Among various contaminants introduced during recent years, hydroxymethylfurfural (HMF) in honey have gained much attention as a high toxicologicaland carcinogenesis potential. So determination of HMF is important to assess the quality of honey [7]. Maximum limit of HMF in honey has been determined 40 mg/kg by international standardcommissions [4]. It could be more up to 80 mg/kg; in thehoneyswhich are produced in the countries with tropical temperatures [13,16] According to increasing demand to consume safe foods in recent decades; this article, review new findings about risk of HMFand influencing factors onthe formation of this compound in honey.

2- Hydroxymethylfurfural formation mechanism:

HMF is a furanic compound produced as a result of Mailard reaction or from direct dehydration of sugarunder acidic conditions [16]. Formation of HMFin the honey isas a result of monosaccharide's degradation in acidic conditions, especially fructose, whichhas been done in beehiveduringnectar aging [24]. HMF production reaction in honey occurs via Maillard reaction orcaramelizationand which is the main pathway to introducespecial color, taste and flavor to that [6]. The mechanism of HMF formation during dehydration of glucose is shown in Figure 1. As seen in Fig1; 3-deoxyglucosone has been formed as a result of glucose dehydration through 2,3enolization. Further dehydration of 3-deoxyglucosone has been lead to an aromatic compound named hydroxymethylfurfural which has high tendency to polymerization [11].

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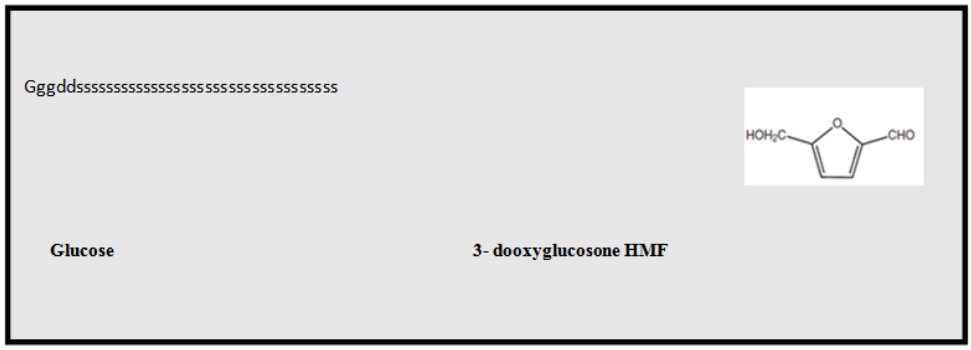

Fig. 1: The mechanism of HMF formation during dehydration under acidic condition

Hydroxymethylfurfuralcould be found in the wide range of food stuffs such as coffee, bakery, cereals, malt, fruit juice, vinegar but its presence and amount of that in honey is a freshness and quality indicator which determine the extent of thermal damage to it [16,22]. We should note that HMF content alone is not a suitable factor to determine thermal damage of honeybecause of existence of HMF in fresh honey and HMF increase dependence to floral origin. It should also be noted that the increase in HMF content istoo slow and often is not detectable when honey has been keptin low temperature [6].

3-Hydroxymethylfurfural safety:

5-Hydroxymethylfurfural as a potent carcinogen metabolite has been considered in recent years. Two main metabolic pathway have been recognized for 5-HMF. The first one, include aldehyde function oxidation to 5-hydroxymethyl-2-furoic acid (HMFA) and then its conjugation to glycine, which ultimately, 5-hydroxymethyl-2-furoyl glycine (HMFG) is made. Because of their appearance in urine (HMFA & HMFG), toxicity of them is less. Another metabolic pathway which from the viewpoint of toxicity is more important than the previous one, is sulphonation of the allylic hydroxyl function of 5-HMF [14]. It has been demonstrated that, SMF is a potent genotoxic and has a mutagenic effects through a highly electrophilic allyl carbocation [1,12]. In the research which has been conducted by Pryor *et al*. [20], rats treated with C-labelled 5-HMF through injection and orally. Whole-body autoradiography found some radioactivity in the liver shortly after administration; however, there was a greater amount in the kidneys and bladder. High level of radioactivity has been observed in the intravenously treated rats. Further findings of these researchers revealed that liver, kidneys and small intestine have a relatively low level of non-extractable radioactivity which is a symptom of covalent binding. SMF has been identified in the 5-HMF treated rats but there is not any evidence about SMF formation from 5-HMF in humans [18]. Durling*et al.*, [12] have been proposed instability of SMF in humans as a result of lack of it in the urine of 5-HMF treated humans. In relation to carcinogenicity, the findings are confusing but in comparison with other carcinogenic compounds, 5-HMF has low carcinogenic potential [19]. In a longer-term study which has been conducted by Zhang *et al.* [28], rats were given 0, 40, 80 and 160mg/kg 5-HMF bw 6 days a week over a period of 11 months. According to their findings, there are not any significant differences between protein and lipid metabolism, ascorbic acid levels in the adrenal glands, the activity of the hepatic succinate dehydrogenase, organ morphology and body weight of treated rats with controls. However minor changes in the clinical chemical parameters have been observed at the 160 mg/kg bw received groups. Within the framework of the US National Toxicology Program (NTP), a 3-month period study on mice has been performed. The results showed that treated mice with 750 mg/kg bw (5 days per week) were a significantly lower weight increase compared with the controls. At 94 mg/kg bw (5 days per week) and below, no adverse effects were observed. Hence, the maximum dose observed with no adverse effects (NOAEL) regarding acute and sub acute toxicity in animal experiments is in the range of 80–100 mg/kg bw per day [1].

4- Influencing factors to theformation ofhydroxymethylfurfural:

4-1- Origin:

HMF content of honey is influenced by several factors such as itssugar content, pH,acidity, water activity, diastase and invertase activityand divalent cations concentration [27,2]. It has been noted that HMF content in honey is in association with the initial pH so that predicted HMF content for the samples with pH <4 and a pH >4 could be 40 mg/kg and 20–25 mg/kg, respectively [13]. Acidic conditionaccelerate HMF formation reactions so thatHMF content in the low pH honey, will be more [2]. It has been revealed that, HMF formation reaction so that in the formation of 1 mole HMF; is 3 moles of water have been produced [3].

4-2- Heat Processing and Storage Time:

Selection of best operation conditions including time and temperature is one of the main challenges in production and packaging of honey. Despite the advantages of thermal processing againstspoilage of honey

through fermentation with microorganisms; the quality of product could be destroyed during heat treatment. To overcome these problems, time and temperature must be carefully controlled and cooling of honey take place immediatelyafter heating [27]. Nowadays, honey is not a seasonal product and could be available throughout the year, so its storagecould be done locally before and after transporting and because of that; maintenance of good storage management is important [16]. The concentration of HMF in honey depends on temperature and time of heat treatment; so it's content is the main criteria to predict optimization of thermal processing.HMF is a harmful compound which isproduced due to honey heating; therefore, the use of thermal treatments for technological purposes, such as reduction of its tendency to crystallization or spoilage with microorganisms could be as short as possible [23]. Tosi*et al.* [23] found thattemperatures over than 130^{o}C, even for a short time, increase HMF content of honey to a levels higher than accepted standard limits. The survey ofChis and Purcarea(2011) about the effects of heat treatment and correlation between HMF formation and pH changes,showedthat heating at 60^{o}C in Chestnut honey did not cause any meaningful increase in HMF(lower than 40 mg kg^{-1}). Khalil *et al.* [16] reported that fresh Malaysian honey samples stored for longer periods (12months),had much higher HMF concentrations than control samples. Castro-Vazquez et al. [8] reported HMF increase over the limited level after 12 monthsstorage at 40 ^{o}C.Sahinlerand Gul [21] has stated that due to the continuing changes caused by temperature during storage, which leads to the production of HMF and weakening enzymes in honey, honey can be used to maintain low temperatures. They concluded thatthere is no significant differences between the fresh honeys with the samples stored for several years at very low temperatures. Karabournioti and Zervalaki [15] havementioned that heat treatment on honey shows a significant relationship between HMF accumulation and different temperatures; HMF increases reach significantly higher values at high temperatures. Visquert *et al.* [26] observed that during pasteurization processesof honey HMF increasesBut in none of the samples, HMF did not exceed more thanits maximum (40 mg/kg) amount. Turhan *et al.* [25] suggested that the excessive HMF content can be related to primitive storage conditions rather than overheating. Boonchiangma *et al.* [5] also confirmed this fact and assert that temperature and storage time strongly affects the occurrence of Maillardreaction. Khalil *et al.* [16] also have expressed the storage time isthe most important factor in the formation of HMF.

Conclusions:

According to the mentioned results, it seems that bycontrol of production conditions, we can reduce the risk of HMF formation in honey which is a toxic contaminant. Furthermore, by considering effect of plantsand climatic on HMF content of honey, it should be mentioned that comprehensive researches must be doneto identify compositions of locally produced honey and determine specific thermal condition to them. By identifying honey collected from different regions, perform of industrial operation under controlled condition, could be possible. By considering these remarks and increase safety level of honey; consumers could be achieved to the therapeutic and remedial properties of honey which has been mentioned in traditional medicine.

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