

Investigation of the advanced glycation end products precursors in dried fruits and nuts by HPLC using pre-column derivatization

JALE CATAK – MUSTAFA YAMAN – HALIME UGUR – ESRA YILDIRIM SERVI – ÖMER FARUK MIZRAK

Summary

Nuts and dried fruits are among the most popular foods consumed worldwide due to their many beneficial effects on health. Many harmful products, such as 1,2-dicarbonyl compounds, glyoxal (GO) or methylglyoxal (MGO), can be formed during thermal processing and long-term storage as precursors of advanced glycation end products (AGE) in foods. This study aimed to determine GO and MGO in nuts and dried fruits. In this study, 38 different raw and roasted nuts and 17 different dried fruits were purchased from various markets in Istanbul, Turkey. The contents of GO and MGO in these foods were determined by HPLC using 4-nitro-1,2-phenylenediamine as a pre-column derivatizing reagent. The determined contents of GO and MGO in the nuts ranged from 0.02 mg·kg⁻¹ to 8.77 mg·kg⁻¹ and from 0.04 mg·kg⁻¹ to 6.20 mg·kg⁻¹, respectively. Raw nuts contained lower levels of GO and MGO than processed nuts. The contents of GO and MGO in dried fruits ranged from 0.1 mg·kg⁻¹ to 6.55 mg·kg⁻¹ and from 1.10 mg·kg⁻¹ to 41.35 mg·kg⁻¹, respectively. The significantly highest MGO content was determined in sulfured dried apricots (19.96–41.35 mg·kg⁻¹), which contained considerably more MGO than sun-dried apricots.

Keywords

dried fruit; nut; glyoxal; methylglyoxal; advanced glycation end product; Maillard reaction

Advanced glycation end products (AGE) are stable toxic end products, mainly formed by the Maillard reaction, which is non-enzymatic glycation. AGE are compounds formed endogenously in the body and exogenously in foodstuffs, in particular during heat treatment. Unlike endogenous AGE, exogenous AGE (dietary AGE) are formed at a much higher rate [1, 2]. In addition to the Maillard reaction, AGE can also be formed through oxidation of glucose, proteins and lipids, and via the polyol pathway. Various parameters, such as temperature, pH, humidity, amine and free carbonyl groups, affect these reactions [3].

Glyoxal (GO) and methylglyoxal (MGO) are reactive α -dicarbonyl compounds, which are precursors of AGE. These compounds are formed

during food processing, such as frying, roasting and baking, or during storage. GO and MGO are often formed by lipid peroxidation, saccharide autoxidation or microbial fermentation [3]. These intermediate compounds react with amino groups of proteins to form final AGE. Reaction with a lysine residue of a protein leads to the formation of N- ϵ -carboxymethyllysine from GO and N- ϵ -carboxyethyllysine from MGO. This process takes place within weeks or months and is irreversible. The content of N- ϵ -carboxymethyllysine in food increases with increasing the contents of lipids and proteins. High-fat food products such as butter, olive oil, cookies or biscuits, contain high levels of N- ϵ -carboxymethyllysine [1].

The formation of AGE occurs in three stages

Jale Catak, Mustafa Yaman, Ömer Faruk Mizrak, Department of Nutrition and Dietetics, Faculty of Health Sciences, Istanbul Sabahattin Zaim University, Halkali Central Campus, Halkali, Küçükçekmece, 34303 Istanbul, Turkey.

Halime Ugur, Department of Nutrition and Dietetics, Faculty of Health Sciences, Kütahya Health Sciences University, Evliya Çelebi Campus, 43100 Kutahya, Turkey.

Esra Yıldırım Servi, Istanbul Sabahattin Zaim University, Food and Agricultural Research Center, Halkali Central Campus, Halkali, Küçükçekmece, 34303 Istanbul, Turkey.

Correspondence author:

Jale Catak, e-mail: jalecatak@gmail.com

as a result of the Maillard reaction. First, the aldehyde group of reducing sugars reacts with the N-terminal end of the free amino groups of proteins, lipids or nucleic acids (mostly lysine, arginine or sulfur-containing amino acids), and the Schiff base is formed. This first step occurs within hours [4]. In the second stage, the Schiff base is chemically re-arranged within days and forms Amadori products, also known as early glycation products. The reactions forming a Schiff base at the initial stage and Amadori products at the intermediate stage are reversible. Amadori products are subjected to further chemical reactions such as oxidation, reduction or hydration in the advanced stage. In this way, they form reactive carbonyl intermediates consisting of GO, MGO, and 3-deoxyglucosone [3].

AGE are considered harmful because they stimulate oxidative stress and inflammation, leading to various diseases such as atherosclerosis, hypertension, diabetes, kidney failure, Alzheimer's disease, Parkinson's disease, multiple sclerosis and cancer [2, 5]. Increased concentrations of GO, MGO and 3-deoxyglucosone are found in the plasma of Type 2 diabetes mellitus patients. The glucose concentration is high in diabetic patients due to the low levels of insulin secretion from the pancreas. So, increased glucose reacts with body proteins two or three times more than in healthy humans to, produce highly reactive GO and MGO. There is strong evidence that uptake of dietary AGE is associated with serum AGE levels. An AGE-restricted diet has been reported to decrease serum AGE levels in individuals with Type 2 diabetes mellitus [6].

In today's modern diet, consumption of processed, heat-treated, fat- and sugar-rich foods is gradually increasing. It is assumed that a high consumption of this diet can increase the accumulation of AGE in the body. A daily AGE intake exceeding 16 000 kU per day is considered high [3]. The daily intake of N- ϵ -carboxymethyllysine and N- ϵ -carboxyethyllysine, estimated based on a food frequency questionnaire for people suffering from diabetes mellitus and cardiovascular diseases, was 3.1 mg·d⁻¹ and 2.32 mg·d⁻¹, respectively [2].

High performance liquid chromatography (HPLC) is an accurate analytical method for the determination of α -dicarbonyl compounds. Pre-column derivatization is required because there is no chromophoric group in the analysed chemical structures. The derivatization reagents 4-(2,3-dimethyl-6-quinoxaliny)-1,2-benzenediamine, o-phenylenediamine and 4-nitro-1,2-phenylenediamine can generate quinoxaline structures by reaction with α -dicarbonyl compounds [7].

Nuts and dried fruits are convenient to consumers as a snack product, which also have beneficial health effects. In the 2018–2019 report, the International Nut and Dried Fruit Council reported that the consumption of selected oilseeds and dried fruits was approximately 4.5 and 3.3 million tons, respectively [8].

Nuts investigated in this study were heat-treated, roasted and contained high amounts of lipids, while dried fruits contained saccharides. In general, GO and MGO can be formed in lipid- and sugar-rich foods. These α -dicarbonyl compounds react with proteins to form final harmful AGE during extended storage times. Since AGE are formed in a longer time, it is essential to identify these precursors in nuts and dried fruits to predict the final levels of AGE. In the literature, there is limited data on precursors of AGE in nuts and dried fruits [1, 9, 10]. This study aimed to determine the contents of GO and MGO in nuts and dried fruits, which have an essential place in our diet, for contributing to the dietary AGE database, and to assist dieticians in creating AGE-restricted diets, which have a potential to play an important role in human health.

MATERIALS AND METHODS

Chemicals

Glyoxal, methylglyoxal, methanol, sodium acetate, 4-nitro-1,2-phenylenediamine, acetonitrile, fructose, glucose and saccharose were obtained from Sigma-Aldrich (St. Louis, Missouri, USA).

Samples

A total of 55 samples were studied, 38 of them being various raw and roasted nuts and 17 various dried fruits. They were purchased from various markets in Istanbul, Turkey.

Extraction and derivatization of glyoxal and methylglyoxal

The extraction method for GO and MGO in foods described by MAHAR et al. [7] was used with some modifications. First, all samples were homogenized with a kitchen blender. Then, 5 g of each sample was weighed into a 50 ml plastic tube and 20 ml methanol was added. The sample was extracted using an Ultra-Turrax homogenizer (IKA, Staufen, Germany) for 2 min and centrifuged for 5 min at 8000 \times g. Next, 0.5 ml of the liquid sample was taken into a 10 ml glass tube and 1 ml sodium acetate buffer (0.1 mol·l⁻¹, pH 3) was added. Afterwards, 0.5 ml of derivatization

solution (4-nitro-1,2-phenylenediamine in 1% methanol) was added. The mixture was incubated at 70 °C for 20 min and then filtered through a cellulose acetate filter (pore size 0.45 μm).

High performance liquid chromatography

GO and MGO were determined by HPLC according to the analytical method described by MAHAR et al. [7] with some modifications. The Shimadzu LC 20AT pump with a Shimadzu SPD-20A UV/Vis detector (Shimadzu, Kyoto, Japan) was used in the analysis. The mobile phase consisted of methanol-water-acetonitrile (42 : 56 : 2, v/v/v). The wavelength was set at 255 nm. GO and MGO were separated in an Inertsil ODS-3 column (250 mm in length, 4.6 mm in diameter, 5 μm particle size; GL Sciences, Tokyo, Japan) at a flow rate of 1 $\text{ml}\cdot\text{min}^{-1}$. The oven temperature of the column was set at 30 °C.

Method validation and quantification

Method validation of GO and MGO analysis was carried out using AOAC guidelines [11]. The validation parameters of the method are shown in Tab. 1. Linearity was determined between 0.2 $\mu\text{g}\cdot\text{ml}^{-1}$ and 2 $\mu\text{g}\cdot\text{ml}^{-1}$ for GO and MGO using five calibration levels in triplicate. The limit of detection (LOD) and limit of quantitation (LOQ) were determined based on the signal-to-noise (S/N) ratio of 3 and 10, respectively. Quantification was done using external standard calibration based on peak area. Precision was assessed regarding repeatability and reproducibility by analysing roasted hazelnut sample ten times on the same day and three times on different 3 days, respectively. Besides, 0.2 $\mu\text{g}\cdot\text{ml}^{-1}$ of GO and MGO were spiked to a roasted hazelnut sample to check the recovery of the method. All analyses were performed in triplicate ($n = 3$) and represented with standard deviation.

RESULTS AND DISCUSSION

Chromatographic separation

An HPLC chromatogram of GO and MGO in raw cashew is shown in Fig. 1. As seen in the chromatogram, GO and MGO were well separated using the HPLC method. Instead of the Zorbax 300 SB-C-18 column (Agilent Technologies, Santa Clara, California, USA) used in the reference method, we used an Inertsil ODS-3 HPLC column, which allowed better separation in our study.

Tab. 1. Validation parameters of the method for determination of glyoxal and methylglyoxal.

Analytical parameters	Glyoxal	Methylglyoxal
Linear range [$\mu\text{g}\cdot\text{ml}^{-1}$]	0.2–2	0.2–2
Correlation coefficient	0.998	0.996
LOD [$\text{mg}\cdot\text{kg}^{-1}$]	0.005	0.004
LOQ [$\text{mg}\cdot\text{kg}^{-1}$]	0.015	0.012
Repeatability limit r	0.06	0.05
Reproducibility limit R	0.11	0.08
Recovery [%]	95.3–98.2	96.0–100.0

LOD – Limit of detection, LOQ – Limit of quantification.

Method validation and quantification

The method validation results are shown in Tab. 1. As seen from the table, the calculated LOQ was found to be 0.015 $\text{mg}\cdot\text{kg}^{-1}$ for GO and 0.012 $\text{mg}\cdot\text{kg}^{-1}$ for MGO. The Repeatability limit (r) and reproducibility limit (R) of GO and MGO were 0.06 and 0.05, and 0.11 and 0.08, respectively. These values showed good reproducibility for both analytes. Recovery values for GO and MGO ranged from 95.3 % to 98.2 % and from 96.0 % to 100.0 %, respectively.

Glyoxal and methylglyoxal in nuts

The types of nut samples and the measured amounts of GO and MGO in nuts are given in Tab. 2, together with fat contents declared on the label and the fat values derived from the literature. The determined contents of GO and MGO ranged from 0.02 $\text{mg}\cdot\text{kg}^{-1}$ to 8.77 $\text{mg}\cdot\text{kg}^{-1}$ and from 0.04 $\text{mg}\cdot\text{kg}^{-1}$ to 6.20 $\text{mg}\cdot\text{kg}^{-1}$ in the nuts, respectively. GO was not detected in 7 out of 38 nut samples, while MGO was not detected in 4 samples. Comparing the contents of GO

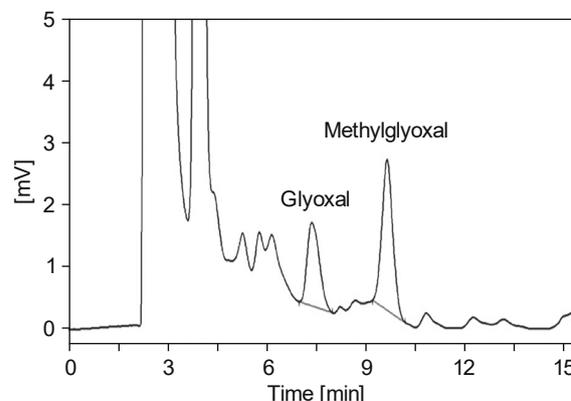


Fig. 1. HPLC chromatogram of glyoxal and methylglyoxal in raw cashew.

Tab. 2. Contents of glyoxal and methylglyoxal in nuts.

Sample No.	Sample type	Fat content (declared or derived from literature) [g·kg ⁻¹]	Glyoxal [mg·kg ⁻¹]	Methylglyoxal [mg·kg ⁻¹]
1	Sunflower seed, roasted	3.120	0.070 ± 0.004	3.121 ± 0.187
2	Sunflower seed, roasted	5.202 ^a	0.111 ± 0.007	3.735 ± 0.224
3	Sunflower seed, black, roasted	3.906 ^b	nd	1.470 ± 0.088
4	Sunflower seed kernel, roasted	4.980	0.181 ± 0.011	2.245 ± 0.134
5	Pumpkin seed, roasted	5.000	0.060 ± 0.004	1.228 ± 0.074
6	Pumpkin seed, roasted	4.030	0.070 ± 0.004	0.664 ± 0.004
7	Pumpkin seed, roasted	4.996 ^a	0.030 ± 0.002	0.322 ± 0.019
8	Pumpkin seed, roasted	4.996 ^a	0.040 ± 0.002	0.423 ± 0.025
9	Pumpkin seed, raw	4.996 ^a	0.020 ± 0.001	0.091 ± 0.005
10	Almond, shelled, roasted	5.022 ^a	0.030 ± 0.002	3.322 ± 0.199
11	Almond, shelled, roasted	5.022 ^a	0.030 ± 0.002	4.721 ± 0.283
12	Almond, shelled, roasted	5.300	0.221 ± 0.013	1.631 ± 0.098
13	Almond, shelled, raw	4.930	nd	nd
14	Almond, shelled, raw	4.900	nd	nd
15	Almond, shelled, raw	4.993 ^b	nd	nd
16	Hazelnut, roasted	6.240	0.352 ± 0.021	0.705 ± 0.042
17	Hazelnut, roasted	6.150	0.262 ± 0.160	0.453 ± 0.027
18	Hazelnut, roasted	6.128 ^a	0.302 ± 0.180	0.423 ± 0.025
19	Hazelnut, raw	6.070	0.910 ± 0.005	0.121 ± 0.007
20	Hazelnut, raw	6.150	0.810 ± 0.005	0.111 ± 0.007
21	Hazelnut, raw	6.075 ^b	0.121 ± 0.007	0.171 ± 0.010
22	Cashew, oil-fried	4.635 ^b	1.399 ± 0.840	3.382 ± 0.203
23	Cashew, oil-fried	4.635 ^b	0.745 ± 0.450	1.872 ± 0.112
24	Cashew, oil-fried	4.635 ^b	1.369 ± 0.820	2.114 ± 0.127
25	Cashew, raw	4.385 ^b	0.453 ± 0.270	1.228 ± 0.074
26	Cashew, raw	4.385 ^b	0.624 ± 0.370	1.148 ± 0.069
27	Peanut, roasted, salty	5.220	nd	0.352 ± 0.021
28	Peanut, roasted, salty	4.542 ^a	nd	0.423 ± 0.025
29	Peanut, roasted, salty	4.580	nd	0.211 ± 0.013
30	Unshelled peanut, roasted	4.924 ^b	1.661 ± 0.990	6.201 ± 0.371
31	Unshelled peanut, roasted	4.924 ^b	1.158 ± 0.690	3.654 ± 0.219
32	Unshelled peanut, roasted	4.924 ^b	0.896 ± 0.540	1.822 ± 0.109
33	Pistachio nut, roasted	5.370	0.242 ± 0.140	0.886 ± 0.053
34	Pistachio nut, roasted	4.220	0.141 ± 0.008	2.285 ± 0.137
35	Pistachio nut, roasted	4.996 ^a	0.221 ± 0.013	0.725 ± 0.043
36	Walnut, shelled, dried	6.010	3.473 ± 0.208	0.040 ± 0.002
37	Walnut, shelled, dried	5.580	8.768 ± 0.525	nd
38	Walnut, shelled, dried	6.482 ^a	0.403 ± 0.024	2.416 ± 0.145

Values are mean ± standard deviation ($n = 3$). nd – not detected.

References: a – TürKomp Turkish Food Composition Database [18], b – USDA FoodData Central [19].

and MGO in the samples, MGO was higher in 36 out of 38 samples. All the analysed nuts contained higher levels of MGO than GO except for two samples of walnut. Raw nuts contained lower levels of GO and MGO than processed and heat-treated nuts.

The highest GO contents were determined

in roasted unshelled peanuts (0.9–1.66 mg·kg⁻¹) and in oil-fried cashews (0.75–1.40 mg·kg⁻¹). In raw almonds, GO was not detected. Among the heat-treated nuts, GO was not detected in all 3 samples of roasted salted peanuts, and pumpkin seeds contained the lowest amounts of GO (0.03–0.07 mg·kg⁻¹). It can be seen from the results

that dried walnuts had a remarkably high content of GO (3.47–8.77 mg·kg⁻¹) in 2 out of 3 samples.

Similarly, the highest MGO values were found again in roasted unshelled peanuts (1.82–6.20 mg·kg⁻¹). In raw almonds and in one sample of dried walnuts, MGO was not detected. Processed unshelled peanuts, almonds, sunflower seeds and cashews had high levels of MGO. Among the analysed heat-treated nuts, roasted salted peanuts contained the lowest amounts of MGO (0.21–0.42 mg·kg⁻¹).

The contents of N-ε-carboxymethyllysine and N-ε-carboxyethyllysine in almonds were previously reported as 1.5 mg·kg⁻¹ and 1.3 mg·kg⁻¹ in unroasted almonds, while 3.7–4.9 mg·kg⁻¹ and 5.1–10.1 mg·kg⁻¹ in roasted almonds, respectively [10]. Comparing the GO and MGO contents in raw and heat-processed samples, the average GO content was 2–4, 3–22, 3–4, and 2–3 fold higher in roasted pumpkin seeds, almonds, hazelnuts and oil-fried cashews than in their raw counterparts. The average MGO content was 3.5–4, 163–472, 4–6 and 2–3 fold higher in roasted pumpkin seeds, almonds, hazelnuts and oil-fried cashews than in their raw counterparts.

Heat-treated nuts contained higher amounts of GO and MGO than raw nuts. This result could be affected by the cooking temperature, processing conditions, added fat and other ingredients. JIANG et al. [12] compared the content of α-dicarbonyl compounds in butter, margarine, safflower oil, beef fat and cheese after heating at 100 °C and 200 °C. Total levels of α-dicarbonyl compounds at 100 °C were higher than at 200 °C (55 fold in butter and 15 fold in margarine).

Generally, higher cooking temperatures and fat content in foods increase the production of AGE precursors [3, 13]. As seen from the tables, the declared fat content ranged from 3.12 g·kg⁻¹ to 6.48 g·kg⁻¹ in nuts. When we evaluated our results, nuts contained high levels of fat [14, 15]. High fat increases the formation AGE precursors [1]. Also, the cooking temperature is high for nuts [16]. Thus, we found high amounts of GO and MGO in nuts. Besides, unlike other roasted nuts, cashews are oil-fried. Therefore, the addition of butter and high cooking temperature could also contribute to the GO and MGO formation during heat-processing or prolonged storage.

Our results showed that processed nuts contained higher amounts of MGO than GO except for salted peanuts. These results were consistent with data reported in the literature [1, 17]. The N-ε-carboxymethyllysine content was reported as 5–77 mg·kg⁻¹ protein in roasted peanut [9]. When we compare the salted roasted peanuts and

unshelled roasted peanuts, it is seen that unshelled roasted peanuts contained remarkably higher amounts of GO and MGO. Roasted unshelled peanuts contained 9 and 29 times more GO and MGO than roasted salty peanuts, respectively. This difference may be caused by a longer storage time of unshelled peanuts.

Glyoxal and methylglyoxal in dried fruits

The types of the samples and the determined contents of GO and MGO in dried fruits are given in Tab. 3, together with contents of sugar declared on the label and sugar values derived from the literature. The determined contents of GO and MGO in dried fruits ranged from 0.1 mg·kg⁻¹ to 6.55 mg·kg⁻¹ and from 1.10 mg·kg⁻¹ to 41.35 mg·kg⁻¹, respectively. High contents of GO and MGO were determined in 15 out of 17 dried fruit samples. Both GO and MGO were not detected in dried plums. Comparing the contents of GO and MGO in the samples, MGO was higher in 16 out of 17 samples. All the analysed dried fruits contained higher levels of MGO than GO except for one sample of dried dates. The highest GO contents were seen in dried figs (2.67 mg·kg⁻¹ and 6.55 mg·kg⁻¹), while the lowest value was found in sun-dried apricots (0.1 mg·kg⁻¹). However, the significantly highest MGO contents were determined in sulfured dried apricots (19.96–41.35 mg·kg⁻¹). The lowest MGO content was determined in one sample of dried dates (1.10 mg·kg⁻¹).

On average, sun-dried apricots contained the least GO (0.36 mg·kg⁻¹), while dried figs had the highest GO content (3.18 mg·kg⁻¹). On the other hand, on average, dried raisins (1.60 mg·kg⁻¹) contained the least amounts of MGO, while sulfured dried apricots (31.06 mg·kg⁻¹) had the highest MGO content.

Dried fruits contain high levels of sugar [14, 15]. In the dried fruits we studied, total sugars ranged from 2.53 g·kg⁻¹ to 7.91 g·kg⁻¹. As seen from Tab. 3, sulfured dried apricots, dried figs and one sample of dried date (8.10 mg·kg⁻¹) contained remarkably higher amounts of MGO. Besides, these samples also contained high amounts of sugar (3.57–4.15 g·kg⁻¹, 5.28 g·kg⁻¹ and 7.91 g·kg⁻¹, respectively). Therefore, it is thought that the content of sugar affects MGO formation.

Importantly, sulfured dried apricots had the highest MGO contents. When comparing sun-dried and sulfured apricots, the latter contained 2–5 fold more GO and 5–10 fold more MGO than the former.

Dried figs contained high amounts of GO and MGO. GO values of in fig samples (2.67–6.55 mg·kg⁻¹) were considerably higher

Tab. 3. Contents of glyoxal and methylglyoxal in dried fruits.

Sample No.	Sample type	Sugar content (declared or derived from literature) [g·kg ⁻¹]	Glyoxal [mg·kg ⁻¹]	Methylglyoxal [mg·kg ⁻¹]
1	Apricot, sun-dried	2.609	0.101 ± 0.006	2.929 ± 0.175
2	Apricot, sun-dried	2.609 ^a	0.211 ± 0.013	4.782 ± 0.286
3	Apricot, sun-dried	2.609 ^a	0.775 ± 0.046	4.580 ± 0.274
4	Apricot, dried, sulfured	4.150	0.745 ± 0.045	31.871 ± 1.908
5	Apricot, dried, sulfured	3.580	1.721 ± 0.103	41.354 ± 2.476
6	Apricot, dried, sulfured	3.570 ^a	1.480 ± 0.089	19.962 ± 1.195
7	Raisin, dried	6.880	0.956 ± 0.057	1.429 ± 0.086
8	Raisin, dried	3.257 ^a	1.007 ± 0.060	1.319 ± 0.079
9	Raisin, seedless, dried	4.496 ^a	0.795 ± 0.048	2.054 ± 0.123
10	Fig, dried	5.288 ^a	2.668 ± 0.160	9.130 ± 0.547
11	Fig, dried	5.288 ^a	6.553 ± 0.392	8.537 ± 0.511
12	Fig, dried	5.288 ^a	0.322 ± 0.019	3.795 ± 0.227
13	Plum, dried	2.530	nd	nd
14	Plum, dried	3.540	nd	nd
15	Date, dried	6.335 ^b	1.742 ± 0.104	1.278 ± 0.077
16	Date, dried	6.500	0.292 ± 0.017	1.097 ± 0.066
17	Date, dried	7.914	1.963 ± 0.118	8.104 ± 0.485

Values are mean ± standard deviation ($n = 3$). nd – not detected.

References: a – Türkomp Turkish Food Composition Database [18], b – USDA FoodData Central [19].

than those of other samples except for one sample. MGO values ranged from 3.80 mg·kg⁻¹ to 9.13 mg·kg⁻¹ in figs. We think that the high sugar content in dried figs (5.28 g·kg⁻¹) may cause an increase in content of GO and MGO during food processing and long-term storage.

In one dried date sample (sample 17), both the contents of GO (1.96 mg·kg⁻¹) and MGO (8.10 mg·kg⁻¹) were high compared to the other two date samples. The sugar content of this sample was also extensively high, 7.91 g·kg⁻¹, which suggests that there may be a connection between sugar and formation of GO and MGO. Previous studies indicated that increased fructose was related to MGO or AGE in processed foods with Maillard reaction taking place. High levels of MGO and Amadori products from Maillard reaction are known to occur in soft drinks that contain high-fructose maize syrup. Lo et al. [18] reported high levels of GO and MGO in commercial carbonated beverages containing high-fructose maize syrup, 0.158–1.046 mg·ml⁻¹ and 0.235–1.395 mg·ml⁻¹, respectively. High-fructose maize syrup is used as a sweetener in snacks and beverages production and in and bakeries. Based on our findings, we think that product might be processed with high-fructose maize syrup because GO and MGO were very high compared to other samples. The content of fructose in high-fructose maize

syrup ranges from 42 % to 55 % of total sugar [4].

Comparing the GO and MGO levels between nuts and dried fruits, the dried fruits contained higher amounts of GO and MGO than nuts. This difference may be due to the sugar content, drying conditions and reactions with chemicals, especially sulfur dioxide. The fat and protein contents of dried fruits were very low compared to nuts. For this reason, we think that Maillard reaction cause the higher contents of GO and MGO in dried fruits.

As seen from our results, both dried fruits and heat-treated nuts contained precursors of harmful AGE. Monitoring and reducing AGE formation in foods during food processing and restricting intake of dietary AGE is essential in preventing the harmful effects of AGE on health [19]. The production of nuts and dried fruits is a growing industry with a high potential as consumers require convenience and snack foods. If the processing and storage of food are not implemented correctly, it can have adverse effects on nuts and fruit quality characteristics. Chemical and thermal pre-treatment practices are widely used in preserving dried fruit quality. Chemical applications such as dipping fruits into sulphite solutions are useful but not sustainable. Processing should be performed using a system that minimizes exposure of nuts and fruits to oxidation, heat and harmful

chemicals. Therefore, appropriate processing or pre-treatment should be selected for nut and fruit preservation. Methods with a maximum positive effect on the quality properties of these processed products should be used.

CONCLUSIONS

In this study, two major AGE precursors, GO and MGO, were determined in nuts and dried fruits. Heat-processed nuts contained significantly more GO and MGO than raw nuts. High sugar-containing dried fruits had higher contents of GO and MGO than nuts. Importantly, the sulfured dried apricots contained significantly higher levels of MGO than sun-dried apricots. Finally, this study revealed that the fat content in processed nuts and sugar in dried fruits might promote formation of α -dicarbonyl compounds. People who frequently consume foods rich in AGE will be at an increased health risk. The health problems associated with AGE can be reduced with an AGE-restricted diet. Thus, it is recommended to reduce the consumption of foods rich in AGE to reduce high AGE intake in the diet. More research is needed on AGEs in foods and their reduction in the diet.

REFERENCES

1. Uribarri, J. – Woodruff, S. – Goodman, S. – Cai, W. – Chen, X. – Pyzik, R. – Yong, A. – Striker, G. E. – Vlassara, H.: Advanced glycation end products in foods and a practical guide to their reduction in the diet. *Journal of the Academy of Nutrition and Dietetics*, 110, 2010, pp. 911–916. DOI: 10.1016/j.jada.2010.03.018.
2. Nowotny, K. – Schröter, D. – Schreiner, M. – Grune T.: Dietary advanced glycation end products and their relevance for human health. *Ageing Research Reviews*, 47, 2018, pp. 55–66. DOI: 10.1016/j.arr.2018.06.005.
3. Sharma, C. – Kaur, A. – Thind, S. S. – Singh, B. – Raina, S.: Advanced glycation end-products (AGEs): an emerging concern for processed food industries. *Journal of Food Science and Technology*, 52, 2015, pp. 7561–7576. DOI: 10.1007/s13197-015-1851-y.
4. Aragno, M. – Mastrocola, R.: Dietary sugars and endogenous formation of advanced glycation end-products: emerging mechanisms of disease. *Nutrients*, 9, 2017, article 385. DOI: 10.3390/nu9040385.
5. Luevano-Contreras, C. – Chapman-Novakofski, K.: Dietary advanced glycation end products and aging. *Nutrients*, 12, 2010, pp. 1247–1265. DOI: 10.3390/nu2121247.
6. Nowotny, K. – Jung, T. – Höhn, A. – Weber, D. – Grune, T.: Advanced glycation end products and oxidative stress in type 2 diabetes mellitus. *Biomolecules*, 5, 2015, pp. 194–222. DOI: 10.3390/biom5010194.
7. Mahar, K. P. – Khuhawar, M. Y. – Kazi, T. G. – Abbasi, K. – Channer, A. H.: Quantitative analysis of glyoxal, methyl glyoxal and dimethyl glyoxal from foods, beverages and wines using HPLC and 4-nitro-1, 2-phenylenediamine as derivatizing reagent. *Asian Journal of Chemistry*, 22, 2010, pp. 6983–6990. ISSN: 0970-7077.
8. Nuts and dried fruits, statistical yearbook 2018/2019. Reus : International Nut and Dried Fruit Council, 2019. <<https://www.nutfruit.org/industry/news/detail/statistical-yearbook>>
9. Wellner, A. – Nußpickel, L. – Henle, T.: Glycation compounds in peanuts. *European Food Research and Technology*, 234, 2011, pp. 423–429. DOI: 10.1007/s00217-011-1649-8.
10. Zhang, G. – Huang, G. – Xiao, L. – Mitchell, A. E.: Determination of advanced glycation end products by LC-MS/MS in raw and roasted almonds (*Prunus dulcis*). *Journal of Agricultural and Food Chemistry*, 59, 2011, pp. 12037–12046. DOI: 10.1021/jf202515k.
11. AOAC guidelines for single laboratory validation of chemical methods for dietary supplements and botanicals. Arlington : Association of Official Analytical Chemists, 2002.
12. Jiang, Y. – Hengel, M. – Pan, C. – Seiber, J. N. – Shibamoto, T.: Determination of toxic α -dicarbonyl compounds, glyoxal, methylglyoxal, and diacetyl, released to the headspace of lipid commodities upon heat treatment. *Journal of Agricultural and Food Chemistry*, 61, 2013, pp. 1067–1071. DOI: 10.1021/jf3047303.
13. Çatak, J.: Quantitative analyses of glyoxal and methylglyoxal compounds in frenchfry samples by HPLC using 4-nitro-1,2-phenylenediamine as a derivatizing reagent. *International Journal of Innovative Research and Reviews*, 4, 2020, pp. 20–24. ISSN: 2636-8919. <<http://www.injirr.com/article/view/52/40>>
14. TürKomp Ulusal Gıda Kompozisyon Veri Tabanı. (TürKomp Turkish Food Composition Database [online]. Ankara : The Scientific and Technological Research Council of Turkey (TUBITAK), 2013 [accessed 5 August 2021]. <<http://www.turkomp.gov.tr>> In Turkish.
15. USDA FoodData Central. In: U.S. Department of Agriculture [online]. Washington, D.C. : Agricultural Research Service (ARS), 2018 [accessed 5 August 2021]. <<https://fdc.nal.usda.gov>>
16. Schlörmann, W. – Birringer, M. – Böhm, V. – Löber, K. – Jahreis, G. – Lorkowski, S. – Müller, A. K. – Schöne, F. – Gleis, M.: Influence of roasting conditions on health-related compounds in different nuts. *Food Chemistry*, 180, 2015, pp. 77–85. DOI: 10.1016/j.foodchem.2015.02.017.
17. Goldberg, T. – Cai, W. – Peppas, M. – Dardaine, V. – Baliga, B. S. – Uribarri, J. – Vlassara, H.: Advanced glycoxidation end products in commonly consumed foods. *Journal of the Academy of Nutrition and Dietetics*, 104, 2004, pp. 1287–1291. DOI: 10.1016/j.jada.2004.05.214.

18. Lo, C. Y. – Li, S. – Wang, Y. – Tan, D. – Pan, M. H. – Sang, S. – Ho, C. T.: Reactive dicarbonyl compounds and 5-(hydroxymethyl)-2-furfural in carbonated beverages containing high fructose corn syrup. *Food Chemistry*, *107*, 2008, pp. 1099–1105. DOI: 10.1016/j.foodchem.2007.09.028.
19. Cengiz, S. – Kişimiroglu, C. – Cebi, N. – Çatak J. – Yaman, M.: Determination of the most potent precursors of advanced glycation end products (AGEs) in chips, crackers, and breakfast cereals by high performance liquid chromatography (HPLC) using precolumn derivatization with 4-nitro-1, 2-phenylene-diamine. *Microchemical Journal*, *158*, 2020, article 105170. DOI: 10.1016/j.microc.2020.105170.

Received 17 September 2021; 1st revised 16 January 2022; accepted 20 January 2022; published online 26 February 2022.