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REVIEW ARTICLE

FURAN IN ROASTED, GROUND AND BREWED COFFEE

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ABSTRACT

Coffee is the most popular hot beverage in the world. The annual coffee production in 2010, 2014 and 2016 was 8.1, 9.0 and 9.3 million tons respectively. There are more than 100 coffee species, but only two of them: Arabica (*Coffea arabica*) and Robusta (*Coffea canephora*) have gained commercial importance. During roasting of green coffee beans not only desirable compounds are formed, that exert positive influence on the taste and flavour of coffee, but also small quantities of undesirable ones. Furan (C_4H_4O) is one of the latter.

Furan is a volatile compound (boiling temp. of 31.4 ^{o}C) formed during thermal processing of food. The toxicity of furan has been well documented and it is classified as "possible human carcinogen" (Group 2B) by the International Agency for Research on Cancer. Various pathways have been reported for furan formation during food processing. It can be formed from carbohydrates, amino acids by their thermal degradation or thermal re-arrangement and by oxidation of ascorbic acid and polyunsaturated acids and carotenoids. High concentrations of furan have been reported in coffee, baked and roasted food and in food subjected to preserving in cans and jars. Furan levels in brewed coffee are typically near or below 120 μg/L, but it can approach thousands μg/kg in roasted whole beans or ground coffee. The highest concentration of furan in roasted coffee reaches the level of 7000 μg/kg. Taking into account that coffee is the most popular hot drink, it becomes the main contributor to furan exposure from dietary sources for adults.

In this article the published scientific papers concerned with the presence of furan in roasted non-brewed and brewed coffee have been reviewed. The formation mechanisms and occurrence of furan in coffee and the harmful influence of furan on the consumer health have been discussed.

Key words: *furan, roasted coffee, brewed coffee, green coffee beans, roasted coffee beans*

STRESZCZENIE

Kawa jest jednym z najpopularniejszych napojów w świecie. Roczna produkcja kawy w 2010, 2014 i 2016 roku wynosiła odpowiednio 8,1, 9,0 i 9,3 mln ton. Liczba wypijanych na świecie w ciągu dnia filiżanek kawy sięga 1,4 mld, a w ciągu roku – ponad 500 mld.

Istnieje ponad 100 gatunków kawy ale tylko 2 z nich: Arabika (*Coffea arabica*) i Robusta (*Coffea canephora*) – zyskały znaczenie handlowe. W procesach palenia ziaren kawowych powstaje wiele związków chemicznych wywierających korzystny wpływ na smak i aromat, ale także niewielkie ilości związków niepożądanych. Jednym z takich związków jest furan.

Furan (C_4H_4O) jest bezbarwną, lotną cieczą (temp. wrzenia 31,4 ^{o}C), powstającą z węglowodanów, aminokwasów, kwasu askorbinowego, kwasów wielonienasyconych i karotenoidów podczas termicznej obróbki żywności. Toksyczność furanu została dobrze udokumentowana a furan został sklasyfikowany jako „potencjalny czynnik rakotwórczy dla ludzi" (Grupa 2B) przez Międzynarodową Agencję Badań nad Rakiem. Wysokie stężenia furanu stwierdzono w żywności smażonej, pieczonej, prażonej, a także pakowanej w puszkach i słoikach. Najwyższe stężenia furanu występują w ziarnach palonej kawy – do 7000 μg/kg. W napojach kawowych zawartość furanu wynosi 20 – 120 μg/L.

Kawa jest najpopularniejszym napojem. Stanowiąc źródło znacznych ilości furanu jest ona głównym składnikiem diety dorosłych wprowadzającym furan do organizmu. W prezentowanej pracy dokonano przeglądu naukowych publikacji dotyczących obecności furanu w kawie palonej i w napojach kawowych. Przedstawiono mechanizmy powstawania furanu oraz poziomy jego zawartości w kawie oraz dyskutowano szkodliwy wpływ furanu na zdrowie konsumentów.

Słowa kluczowe: *furan, kawa palona, kawa parzona, zielone ziarna kawy, palone ziarna kawy*

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INTRODUCTION

Coffee is the most popular (after water) beverage in the world and it is consumed for its unique taste, flavour and stimulating or relaxing effects. Coffee is also used for social reasons, which is evident from 400-year history of coffee houses [19]. The annual coffee production in 2010, 2014 and 2016 was 8.1, 9.0 and 9.3 million tons respectively [4, 5]. Every day over 1.4 billion (1.4×10^3 million) cups of coffee are consumed worldwide, it means more than 500 billion cups per year. In Poland the statistical annual consumption of coffee beans reaches 2.3 kg per person, while the European leaders are Finnish, who consume 12.2 kg [24]. The coffee business is the second largest after petroleum business and provides an employment for over 20 million people. Coffee is commercially cultivated on plantations in countries located between the tropics in more than 70 countries, but Brazil, Colombia, Ethiopia, Vietnam, Indonesia and India are the leading producers [19]. With an export of almost 1.57 million tons in 2013 and 2.18 million tons in 2015 of green coffee beans Brazil is the world`s largest exporter [4, 46].

There are more than 100 coffee species, but only two of them: *Coffea arabica* (Arabica coffee) and *Coffea canephora* (Robusta coffee) have gained commercial importance with about 64% and 34% of total worldwide production respectively [47]. The details on the coffee origin and plants, species and varieties, producing countries and processing of crops to obtain green bean coffee by dry or wet technologies can be found elsewhere [41]. For this work the following aspects are important:

- chemical composition of green bean coffee, influence of roasting of green beans and then grinding on transformations of some chemical compounds during these processes;
- influence of reasonable and excessive drinking of coffee on consumer health;
- formation of furan during coffee roasting and its presence in brewed coffee.

This paper is a concise review of the papers that have been published mainly for the last ten years and concerned with the presence of furan in food. The special attention has been paid to the presence of furan in roasted and brewed coffee.

FURAN IN FOOD – ITS SOURCES AND TOXICITY

Furan is colourless, heterocyclic, aromatic compound with boiling temperature of 31.4 °C. Its presence in food has been known since the 1930s [21]. In the past the best source of information on the presence of furan and its derivatives in food was the review article by *Maga* [27]. Furan is formed in food as a result of heating or exposure to ionizing or ultraviolet radiation [12, 13]. Such processing of food as cooking, roasting, frying, baking, pasteurization and sterilization are the main causes of furan formation [40].

There are various pathways of furan formation, such as:

(i) thermal degradation of carbohydrates alone or in presence of amino acids,
(ii) thermal degradation of some amino acids,
(iii) oxidation of ascorbic acid at elevated temperatures,
(iv) oxidation of polyunsaturated fatty acids (PUFA) and carotenoids.

All these potential pathways of furan formation have been illustrated in Figure 1.

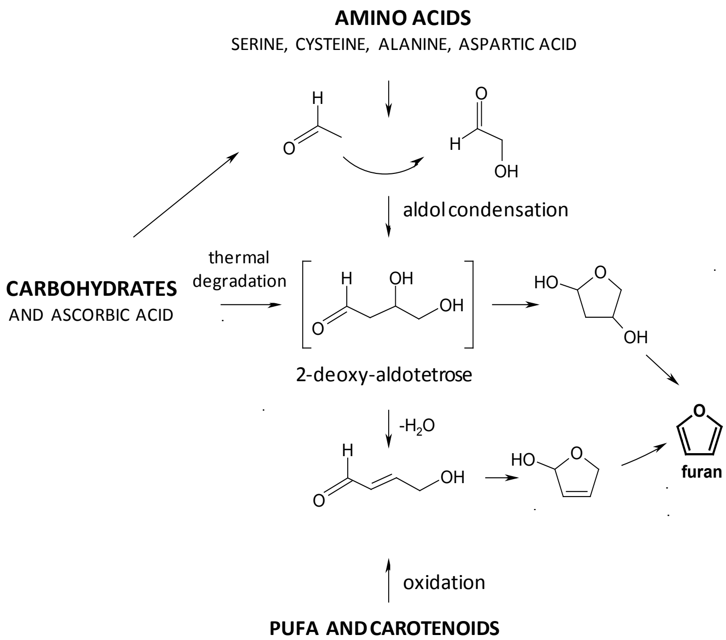

Figure 1. Pathways of furan formation in food [35]

There is a lot of papers on furan formation and its presence in food. In this paper only some examples of book chapters [17, 51], doctoral thesis [28], and some review papers [3, 9, 11, 12, 15, 23, 29, 32, 33, 35, 39, 40, 49] are cited. The paper [9] with 66 references is a concise review of the papers published till 2010. The cited research papers dealing with occurrence, formation and mitigation of furan in food are briefly summarized.

Presence of furan in food has gained extremely strong interest among food chemists. It has been known for years that furan is toxic and carcinogenic as it was proven with studies on laboratory animals (rats and mice). In 1995 IARC (International Agency for Research on Cancer) classified furan as "possibly carcinogenic to humans" (Group 2B) [20]. In the opinion of European Food Safety Authority (EFSA) evidence indicates that furan-induced carcinogenicity is probably attributable to a genotoxic mechanism [10]. Furan may cause gene mutations, chromosome aberrations and sister chromatid exchanges in cultured mammalian cells and chromosomal aberrations in mice bone marrow cells [6]. Its genotoxic mechanism was confirmed in numerous tests which allowed to detect different types of mutations caused by cytotoxic reactive metabolite of furan (cis-2-butene-1,4-dial – BDA) formed in the liver.

The BDA is able to react with deoxyribonucleotides *in vitro* and form unstable DNA adducts [6, 31]. Furan is rapidly absorbed and extensively metabolised after ingestion by rats and mice. Due to its low polarity, it penetrates biological membranes. Chronic exposure to furan may result in hepatocytes proliferation which promotes the liver carcinomas response. Furthermore, for rats of both sexes, a dose-dependent increase in the frequency of hepatocellular adenomas and mononuclear leukemia occurrence was observed. The high frequency of cholangiocarcinoma occurrence was also proven [6]. Regarding human organism, furan can penetrate through both the digestive and respiratory systems – whilst preparing food. The presence of furan has been proven in more than 300 products as a result of heat treatment. The second highest furan content (after coffee) amounting up to 200 μg/kg was found in baked products, such as cookies, chips and crispy breads [31]. It is worth mentioning that statistical Polish consumes about 2 kg such products per year [22] and with them about 400 mg of furan. Considerable amounts of furan were also determined in caramel, bread, roasting sauces and soy sauce [23]. Besides, the opinion that furan volatilizes from food packaged in non-hermetic containers is questioned by the results. Moreover, the high furan content was confirmed in food packed in sealed containers. A large surface of some products packed this way indicates furan binding by adsorption. Furan may occur in products subjected to spray drying or microencapsulation, especially where the gas is trapped mechanically inside microgranules [23]. Furan was also found in ready-to-eat bottled meals for children in the amounts reaching 112 μg/kg [31].

In 2010 report of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) provides the benchmark dose lower limit BMDL10 of 0.96 mg/kg body mass per day, which made possible to set a margin of exposure (MOE) [6, 31]. The risk assessment may have resulted in a health based guidance value such as Tolerable Daily Intake (TDI) or, in the case of substances that are both genotoxic and carcinogenic, the MOE with, if needed, a recommendation to reduce exposure to as low as reasonably achievable. This is so called ALARA approach [48]. By now no epidemiological study connected to furan in humans has been made available. JECFA calculated the following dietary exposures for furan: 1 μg/kg body mass per day for the general population, and 2 μg/kg body mass per day for consumers with high exposure to furan. These estimates cover potential dietary exposure for children as well as adults [9]. The mean dietary exposure (μg/kg body mass per day) to furan are in Europe – 0.29-1.17 for adults, 0.27-1.01 for infants of 3-12 months, in North America (USA) – 0.25-0.26 for adults, 0.23 for children of 2-5 years, 0.41 for infants up to 12 months, in South America (Brazil) – 0.46 for infants of 6-11 months [9].

Very similar data has been reported by *Van der Fels-Klerx* et al. [48].

Among all the food products for human beings, the richest source of furan is coffee.

ROASTED AND BREWED COFFEE

The chemical composition of coffee was extensively discussed by *Farah* [14], *Oestreich-Janzen* [34] and *Stalmach* et al. [44]. The roasting process starts at about 130 °C (sugars caramelisation after water evaporation). When the temperature reaches about 170-210 °C, the chemical reactions of the *Maillard* type occur in coffee beans. During them the key intermediate compounds (according to the *Heyns* and *Amadori* rearrangements) and eventually melanoidins are formed which play important role in coffee flavour and colour. The coffee beans change colour from green to clear-brown or dark brown depending on the temperature and time of roasting. The chemical composition (Table 1) and sensorial attributes of roasted coffee differ from these ones for green bean coffee [5, 47]. The roasted and ground coffee can be brewed in various ways giving beverages very popular among consumers.

Table 1. Chemical composition of green and roasted coffee [14]

Component	Concentration [g/100 g]			
	Arabica		Robusta	
	green	roasted	green	roasted
Carbohydrates				
Sacharose	6.0-9.0	4.2	0.9-4.0	1.6
Polysaccharides	34-44	31-33	0.4	37-38
Lignins	3.0	3.0	3.0	3.0
Pectins	2.0	2.0	2.0	2.0
Reducing Sugars	0.1	0.3	0.4	0.3
Nitrogen compounds				
Proteins	10.0-11.0	7.5-10.0	11.0-15.0	7.5-10.0
Cafeine	0.9-1.3	1.1-1.3	1.5-2.5	2.4-2.5
Trigonelline	0.6-2.0	0.2-1.2	0.6-0.7	0.3-0.7
Free amino acids	0.5	-	0.8-1.0	-
Lipids				
Caffeic oil, sterols, tocopherols	15.0-17.0	17.0	7.0-10.0	11.0
Diterpenes, free and esterified	0.5-1.2	0.9	0.2-0.8	0.2
Minerals	3.0-4.2	4.5	4.4-4.5	4.7
Acids and Esters				
Chlorogenic acids	4.1-7.9	1.9-2.5	6.1-11.3	3.3-3.8
Aliphatic acids	1.0	1.6	1.0	1.6
Chinoic acid	0.4	0.8	0.4	1.0
Melanoidins	-	25	-	25

The health aspects of coffee drinking have been the subject of many controversial debates. In the past a negative picture of the influence of coffee drinking on the consumer health was created. Even recently a substantial number of papers about coffee has been negative. In the United Kingdom, for example, 51% of media publications on coffee, caffeine and health have been negative, 22% – neutral, and 27% – positive [19].

Nowadays most papers present real or possible beneficial health implications of coffee drinking even in large amounts. The beneficial influence of coffee drinking on such diseases as: type 2 diabetes, cardiovascular disease, cancer of various organs, *Alzheimer`s* and *Parkinson`s* diseases and others has been studied, reported and discussed. As these problems are very extensive and obviously beyond the scope of this paper, only few examples of papers are given here [8, 26, 37]. The simplified composition of brewed regular coffee is shown in Figure 2. Apart from desirable compounds that exert positive influence on the taste and flavour of coffee, the undesirable ones are also formed. Among them there are: ochratoxine A [36], β-carbolines (harman and norharman) [14], policyclic aromatic hydrocarbons [46], acrylamide [42, 43], 3-monochloropropane-1,2-diol (3-MCPD) [38] and furan [17, 18].

Figure 2. Cup of coffee (chemical composition, mg/100 mL) [14]

FURAN IN COFFEE

Analysing the information on chemicals gathered in Table 1 and in Figure 1 it becomes obvious that during roasting of coffee furan is formed. The presence of substrates, high temperature and low water activity create excellent conditions for furan formation. The porous structure of roasted coffee beans traps it. Roasted coffee beans contain furan in the largest quantities comparing with other food. It is generally accepted that furan concentrations in coffee change in the following order: roasted beans > roasted powder >> instant powder > brewed [48]. Some published data of the presence of furan in roasted solids (beans, ground beans, powders) and brewed coffee is listed in Tables 2 and 3.

Table 2. Furan in coffee − data selected from [51]

Coffee Type	Country	Furan content [µg/kg] or [µg/L]		
		Average	Minimum	Maximum
Cappuccino	Australia	32.3	23.0	50.0
Ground Coffee Brewed	Australia	23.0	22.0	24.0
Flat White	Australia	33.2	25.0	53.0
Latte	Australia	22.9	7.0	49.0
Long Black	Australia	42.0	16.0	77.0
Mocha	Australia	23.5	12.0	35.0
Short Black	Australia	112.5	15.0	210.0
Ground Roasted Powder	Brazil	2998.1	1946.4	5021.4
Instant Powder	Brazil	413.0	279.0	547.0
Coffee (non specified)	EU	1691.0	2.0	6500.0
Instant	EU	589.0	8.0	2200.0
Roasted Bean	EU	2272.0	5.0	4895.0
Roasted Ground	EU	1114.0	5.0	5749.0
Brewed Coffee	Japan		5.8	150.0
Canned Coffee	Japan		4.1	150.0
Coffee (Can)	Japan	34.0 65.0	35.0	120.0
Coffee (Carton)	Japan		39.0	83.0
Coffee (PET Bottle)	Japan		43.0	120.0
Coffee Mix (Liquid)	South Korea	3.6	1.1	5.5
Coffee Mix (Powder)	South Korea	54.2	26.4	99.0
Ground Roasted Brewed	South Korea	48.5	30.7	67.1
Ground Roasted Powder	South Korea	814.1	267.1	2252.7
Instant Liquid	South Korea	3.5	0.7	4.5
Instant Powder	South Korea	90.1	22.6	224.5
Coffee Extract	Switzerland	98.0	73.0	125.0
Coffee Beans	Switzerland	4400.0	2650.0	5050.0
Instant Brewed	Switzerland	17.0	1.0	51.3
Instant Powder	Switzerland	783.3	44.0	2150.0
Roasted Brewed	Switzerland	82.9	13.0	199.0
Roasted Powder	Switzerland	1979.0	22.0	5938.0
Instant Brewed	USA	6.0	4.8	7.2
Roasted Brewed	USA	46.7	39.6	84.2

As furan is highly volatile, its presence in brewed coffee depends on the brewing procedure, and also on temperature and time after brewing. *Mesias* and *Morales* [30] reported that the furan levels in coffee beverages prepared in popular vending machines ranged from 11 to 262 ng/mL (mean 171 ± 59.8 ng/mL) and decrease rapidly after simulating the behaviour of coffee consumption (~74% after 5 minutes standing at room temperature). Assuming furan content in coffee as 6 mg/kg (Table 3), average annual intake of furan from coffee only reaches 14 mg for statistical Poles, but as many as 73 mg for statistical Finns. Furan intake from coffee ranges from 0.02 to 0.43 µg/kg body mass per day resulting in a mean exposure of 0.31 µg/kg body mass per day. This is consistent with data reported in other sources [9, 48] and reaches about 50% of the total daily furan exposure for adults.

The GC-MS (gas chromatography–mass spectrometry) is the most suitable technique for determinations of furan in food. The GC-MS is usually preceded by headspace (HS) extraction or headspace solid-phase microextraction (HS-SPMS). Owing to the high volatility of furan, the samples and standards have to be carefully prepared and they need to be cooled and handled quickly [51]. The quantification of furan in samples has been based on internal standard additions (usually deuterated furan, d_4-furan) or external calibration. Limits of furan detection (LOD) and quantification (LOQ) in food are in the range from 0.1 ng/g to 5 ng/g and from 0.4 to 13 ng/g respectively. The 32 European countries and Turkey have adopted official European Standard EN 16620:2015 for furan determination in coffee [45]. In Poland determination of furan in coffee and coffee products should be performed in accordance with the European Standard PN-EN 16620:2015 [45].

Table 3. Furan in coffee – data selected from the A to G papers published from 2009 to 2016

Coffee type BR – brewed / NBR – non-brewed	Furan content [µg/kg] or [µg/L]		Country	Reference
	Minimum	Maximum		
From Coffee Chains (BR)	44.5	234.4	Germany	[50]
Instant (BR)	0.6	11.1		
Ready to Drink (BR)	2.4	108.8		
Cameroon Arabica (BR/NBR)	34.5/54.4	40.5/60.2	Cameroon	[25]
Cameroon Robusta (BR/NBR)	123.0/211.0	138.9/241.5		
Ethiopia (BR/NBR)	56.3/199.2	63.3/231.8	Ethiopia	
India Robusta Cherry (BR/NBR)	54.1/124.0	66.5/143.8	India	
India Robusta Monsooned (BR/NBR)	92.0/445.1	111.0/528.3		
Salvador (BR/NBR)	96.7/163.2	109.7/187.8	Salvador	
Santos (BR/NBR)	63.8/466.7	67.7/587.3	Brazil	
Vietnam (BR/NBR)#	36.0/127.0	171.0/353.0	Vietnam	
Arabica Light (BR/NBR)	10.0/985.0	30.0/1373.0	Brazil	[1]
Arabica Medium (BR/NBR)	16.0/322.6	129.0/3631.0		
Arabica Dark (BR/NBR)	30.0/3262.0	170.0/4345.0		
Robusta Light (BR/NBR)	10.0/1722.0	125.0/2573.0		
Robusta Medium (BR/NBR)	12.0/3505.0	172.0/5468.0		
Robusta Dark (BR/NBR)	21.0/4859.0	279.0/5697.0		
Ground Beans (BR/NBR)	31/1222	76/1966	Denmark	[16]
Instant Powder (NBR)	39	1330		
Dark/Medium Espresso Instant Powder NBR	20	2593	Iran	[7]
Ground Coffee (NBR)	1375	6233		
Mixed Coffee Powder (NBR)	10	226		
Brewed Coffee (50 g/l)	10	35	Western Europe	[18]
Roasted Whole Beans (NBR)	2000	7000		
Roasted Whole Beans Ground (NBR)	1200	4200		
Coffee from automatic vending machine	11	262	Spain	[30]‡
Cartridge Ground Coffee	59.1	251	Canada	[2]‡
Cartridge Ground, French Press/Drip Method (Mean)		77.6/46.7		
Decaffeinated Coffee (BR)	6.63	121		
Decaffeinated Ground/Decaff.Instant (NBR)	1640/32	3450/896		
Espresso (BR)	34.9	352		
Medium Roasted (BR)	25.1	69.5		

Brewed in Turkey mode. ‡ data in ng/g.

SUMMARY AND CONCLUSIONS

Furan is a potential human carcinogen that can be formed in variety of foods such as coffee, baby food, bread, snacks etc. It is formed in food as a result of heating or exposure to ionizing or ultraviolet radiation. Such processing of food as cooking, roasting, frying, baking, pasteurization and sterilization are the main causes of furan formation. There is an evidence that furan-induced carcinogenicity is probably due to a genotoxic mechanisms, although there have been no studies conducted on humans.

Coffee is the most popular hot beverage in the world. On the other hand during roasting of coffee beans large quantities of furan are formed. As a consequence brewed coffee also contains furan. The available published information on the presence of furan in coffee (supported by detailed data) has been exhaustively analyzed. Furan dietary exposure and health aspects related to coffee drinking have also been discussed.

Average annual furan intake from coffee only ranges from 14 to 73 mg per person and 0.02 to 0.43 µg/kg body mass per day respectively, that means about 50% of the total daily furan exposure limit for adults.

It might seem interesting to try to sum up the total intake of furan from all the sources in the diet, however it needs to be stressed that the annual consumption of furan with crisps and chips (that is the second highest source of furan in food) is only about 0.4 mg per person, that means between 35 and 180 times less than furan from coffee.

Conflict of interest

The authors declare no conflict of interest.

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