

## Food and Beverage Methylxanthines, Glycoalkaloids, Pyrolizidines and Phenolic Alkaloids: Processing Effects

Ozlem TOKUSOGLU<sup>1,2</sup>,

### Abstract

Food and beverage alkaloids can be take part in food chemistry, food industrial applications, food supplement and medical drug fortifier. Alkaloids are aminoacid derivatives that have a bitter taste and are found as secondary metabolites in potato plants as potatoes glycoalkaloids and in tomato plants as tomatine glycoalkaloids. Piperidine alkaloids from black peppers with pyridine structured alkaloids.

Caffeine, theobromine and theophylline in most consumed non-alcoholic beverages such as coffee, tea, cocoa majorly and chocolate and herbal teas as less are classified as methylxanthine alkaloids. Caffeine is found in varying quantities in the beans, leaves, and fruit of some other plants including kola nuts, yerba mate, guarana berries etc where it acts as a natural pesticide that paralyzes and kills certain insects feeding on the plants. Caffeine content depends on strength of the brew, growing conditions, processing techniques and other variables.

A specific alkaloids in foods and beverages can alter after food processing containing cooking, boiling, steaming, frying, brewing etc. as conventional food processing,. Also food and beverage alkoids can be altered by novel food processing like gamma irradiation and microwave processing. In this point; toxicity, carcinogenic, toxigenic structure and anticancer /cancer formation should be dealed.

**Key words:** Alkaloids, Methylxanthines, Glycoalkaloids, Pyrolizidines, Food, Beverage

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<sup>1</sup>Celal Bayar University, Engineering Faculty, Department of Food Engineering, Manisa, Turkey

<sup>2</sup>Dokuz Eylül University Technology Development Zone, DEPART Technopark, SPİL INNOVA Ltd.Şti, İzmir, Turkey

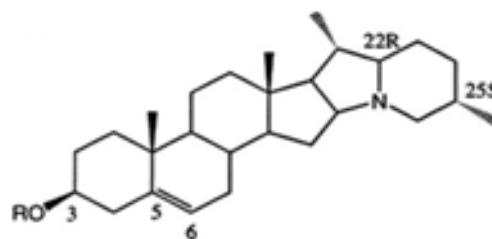
## Introduction

Alkaloids are a class of naturally occurring chemical substances which mostly include biologically important amine structures and contain some related constituents in plants based food and beverages and animal based foods. Alkaloid compounds demonstrate greatly diverse matrix and origins as well as pharmacological and/or nutraceutical action which often show a marked physiological action. Food and beverage alkaloids can be taken part in food chemistry, food industrial applications, food supplement and medical drug fortifier.

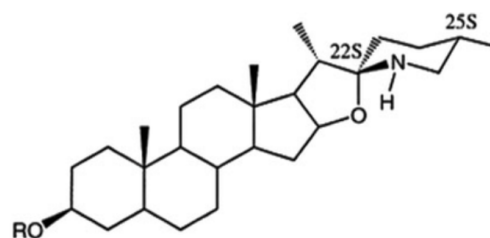
Apart from nutritional compounds, potatoes also contain glycoalkaloids, viz. naturally accumulated toxins during potato growth and storage. Glycoalkaloid accumulation is triggered by environmental (natural and human stimulated) stress. Major glycoalkaloids in potatoes are  $\alpha$ -solanine,  $\alpha$ -chaconine and solanidine (Figure 1a). As stated by the World Health Organization, the safe level of glycoalkaloids in fresh potato tubers is considered to be from 20 to 100 mg kg<sup>-1</sup> (Zarins and Kuruma, 2017; FAO, 1992). It is known that glycoalkaloid intoxication might cause digestive troubles, diarrhoea and vomiting, but higher doses can cause nerve system damage, coma and even death (Friedman, 2006). The potato bitter taste is one of the indicators of increased glycoalkaloid concentration and is common in potatoes (fresh weight) that have more than 140 mg per kg of glycoalkaloids. Some in vitro studies show certain beneficial effects of glycoalkaloids, for instance, anticancer influences (Friedman et al., 2005). It has been evaluated that this possibly positive value of glycoalkaloids still needs to be well studied and admission of glycoalkaloids for medical aims can not be performed directly from fresh or processed potatoes. The glycoalkaloid concentration in potato tubers depends upon genetics, environmental and physical stresses and it is indicated that damage during harvesting, transportation or storage raises glycoalkaloids. It is reported that prolonged storage of potatoes should be done at a temperature of 7°C, since higher temperature can stimulate accumulation of glycoalkaloids (Zarins and Kruma, 2017).

Process	Reduction of total glycoalkaloids
Frying	approx. up to 94%
Blanching	Insignificant effect
Dehydration	78–90%
Boiling	22%
Potato chips	approx. up to 82%
Peeling	approx. up to 58%
Granulation	approx. up to 90%
Cutting, slicing, rinsing with water	No effect
Baking, cooking	Insignificant effect
Pulsed electric field	Insignificant effect

**Table 1.** Process Effects on Glycoalkaloids in Potatoes (Zarins and Kruma, 2017)



Solanidine, R = H  
 $\alpha$ -Solanine, R = solatriose  
 $\alpha$ -Chaconine, R = chacotriose



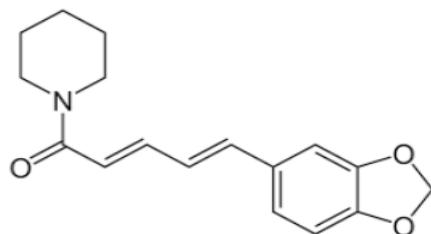
Tomatidine, R = H  
 $\alpha$ -Tomatidine, R = lycotetraose

**Figure 1a.** Glycoalkaloid solanin derivatives in potato, **b.** tomato tomatine derivative compounds

Alfa-tomatine ( $\alpha$ -tomatine) is a naturally occurring toxicant in the tomato (Figure 1b). It consists of an aglycone, the steroidal alkaloid tomatidine and of the sugar moiety P-lycotetraose (Dxylose, 2D-glucose, D-galactose). Tomato breeders using alien germplasm in their breeding programmes, should be alert not to introduce high levels of this toxicant into cultivated tomatoes. It is stated that artificially ripened fruits may contain relatively higher amounts of  $\alpha$ -tomatine than those matured on the plants. According to previous data, the contents of  $\alpha$ -tomatine in the red-ripe fruits of tomato and in those of the lines were low (< 5 mg/kg fresh weight) and the green-mature fruits of the wild species had a high content (3390 mg/kg fresh weight) of  $\alpha$ -tomatine (Van Gelder and DePonti, 1987).

Piperine is an alkaloid found naturally in plants belonging to the pyridine group of Piperaceae family, such as *P. nigrum* and *P. longum*. Piperine is the trans stereoisomer of 1-piperoylpiperidine (Figure 2). It is stated that, the maximum amount of piperine was found as 21.12 mg g<sup>-1</sup> in black pepper, while the other spices contained only traces and was detected as 11.42 mg g<sup>-1</sup> in the white pepper. It is also known as (E, E)-1- piperoylpiperidine and (E, E)-1- [5-(1, 3- benzodioxol-5-yl)-1-oxo-2, 4-pentadienyl] piperidine. Piperine is the alkaloid responsible for the pungency of black pepper and long pepper, along with chavicine (an isomer of piperine). It has also been used in some forms of traditional medicine and as an insecticide. From the extract of *P. nigrum* we have isolated an alkaloidal constituent piperidine. In vitro antitumour activity of isolated compound, piperidine was performed

by MTT assay. The compound piperidine exhibited 51.38% inhibition of HEp2 cells (Human epithiloma cells of laryax) at concentration of 5 µg/ml of the six different concentration of piperidine the highest concentration displayed a highest inhibition displayed a dose dependent antiproliferative activity on HEp2 cells (Reshmi et.al,2010)

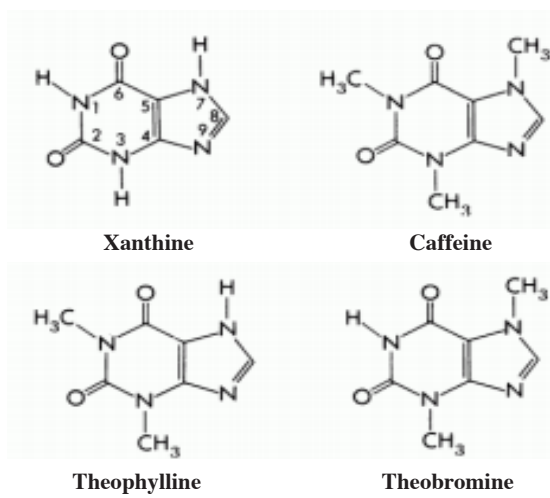


Piperine

**Figure 2.**Piperine alkaloid in black pepper

Xanthines are mostly produced by plants and animals. It is stated that xanthines are mainly involved in catabolic reactions of nucleotides and nucleic acids.; xanthine is a final product of purines through cata-bolism (Mouryaa et.al.,2019). Caffeine (1,3,7-trimethylxanthine), theobromine (3,7-dimethylxanthine), and theophylline (1,3-dimethylxanthine) are naturally occurring alkaloids that are present in tea leaves, coffee, and cacao seeds and, therefore, in the food and beverages made from them (Figure 3).These alkaloids are contained in a variety of pharmaceutical products and drugs because they possess the following properties: to stimulate the central nervous system, to induce gastric secretions, and to act as a diuretic. The recommended daily dose is 200 mg/day (5). A dose of 10 g is lethal, which is equivalent to about 100 cups of coffee. As it is part of a normal daily diet, a concentration level of 12 µg/L in urine is permitted (Lo Cocol et.al.,2007).

The detection limits of caffeine, theobromine and theophylline in food, drinks, and herbal products were found as in the range of 0.07–0.2 mg/L



**Figure 3.** Xanthine Alkaloids in Foods and Drinks

It is known that mainly 13 orders of the plant kingdom in which 100 species of methylxanthines have been detected. Content of caffeine in coffee is to be about 0.4- 2.4% dry weight. The concentration of caffeine in young leaves of *Camellia sinensis*, *Camellia assamica* and *Camellia taliensis* is 2%-3% dry weight while the content of caffeine in tea (infusion) is in between 1.0% and 3.5% of the composition.

Of these, caffeine is the greatest stimulant, and it has different health effects concerning stimulation of the nervous system, heart and glands, bronchodilation, enhanced diuresis, and suppression of appetite and tiredness Theobromine, which has a stronger diuretic effect although it is considerably weak to have much more than a slight beneficial effect on mental agility and muscular performance, and theophylline are two dimethyl-xanthines and include two methyl groups. Theobromine levels reported only 0.15-0.46% in different types of chocolates. Tea and coffee beans naturally contain theophylline.

It was detected 0.46–0.94 mg/g caffeine in chocolate samples (Tokusoglu and Unal,2002). The US Food and Drug Administration and National Soft Drink Association reported that milk chocolate includes 0.21 mg/g of caffeine. It was reported that the bitter flavor of caffeine has decreased with the sugar effect. Theobromine is most important methylxanthine in cocoa and chocolate based products (Tokusoglu and Unal,2002). Besides, mentioned data showed the theobromine (3,7-dimethylxanthine) concentrations in chocolate samples are in the range 1.17–1.96 mg/g. Theobromine levels have been varied in commercial chocolates. Tokusoglu and Unal (2002) detected that dark sweet chocolate has a lower level of theobromine (1.38 mg/g) than dark chocolate (1.93 mg/g). It was also reported that total theobromine level is high in various commercial black teas consumed in Turkey (0.19– 2.61 mg/100 mg), theobromine is a major source of methylxanthines in chocolate products. The mentioned research showed that theophylline (1,3-dimethylxanthine) at trace levels in some chocolates. (0.04–0.09 mg/g) (Tokusoglu and Unal,2002).

Tokusoglu, Unal and Balaban (2008) stated that methylxanthine derivatives of 23 black tea infusions. The data showed that caffeine levels were high (4.002-8.657 mg 100 mg<sup>-1</sup>) followed by theobromine and theophylline.

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