

## Effect of Food Processing on Flavanols

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### ABSTRACT

The strong correlation between dietary habits and some chronic diseases have been reported in numerous studies. In recent years, compounds with functional properties that provide specific health benefits to human have become popular. Flavanols, a subgroup of phenolic compounds, are generally found in green tea, cocoa, coffee, red grapes and apples. These monomeric bioactives are known as potent antioxidants. During various food processes these compounds expose to certain thermal or mechanical treatments and biochemical reactions. All of these applications lead to reversible/irreversible alterations in the structure of flavanols. Mainly the conversions affect appearance and sensorial characteristics of foods. On the other hand, bioavailability of flavanols is also influenced depending on structural changes of monomeric units. In this review, the effect of prominent processing techniques on flavanol contents of several foods is discussed.

**Key Words:** Catechin, Fermentation, Thermal treatment, Non-thermal treatment

### Gıda İşlemenin Flavanoller Üzerine Etkileri

#### ÖZET

Sağlık üzerine belirli yararlar sağlayan fonksiyonel özelliklere sahip bileşikler son yıllarda popüler hale gelmiştir. Fenolik bileşiklerin bir alt grubu olan flavanoller genellikle yeşil çay, kakao, kahve, kırmızı üzüm ve elmada bulunmaktadır. Bu monomerik biyoaktifler güçlü antioksidanlar olarak bilinmektedir. Çeşitli gıda işlemleri sırasında bu bileşikler bazı ısı veya mekaniksel uygulamalara ve biyokimyasal tepkimelere maruz kalmaktadır. Bu uygulamaların tümü flavanollerin yapısında geri dönüşümlü/geri dönüşümsüz değişimlere yol açmaktadır. Değişimler esas olarak gıdaların görünüşünü ve duyu özelliklerini etkilemektedir. Diğer yandan flavanollerin biyoyararlılığı da monomerik birimlerdeki yapısal değişimlere bağlı olarak etkilenmektedir. Bu derlemede önemli gıda işleme yöntemlerinin, çeşitli gıdaların flavanol içeriği üzerine etkileri ele alınmıştır.

**Anahtar Kelimeler:** Kateşin, Fermantasyon, Isıl işlem, Isıl olmayan işlem

#### INTRODUCTION

“Process” is defined as a series of actions applied in a specific order to obtain specific results. A manufacturing process starts with raw materials and ends with products and by products [1]. Food processes have negative impacts such as loss of vitamins and other nutrients; formation of toxic compounds like acrylamide

besides positive effects such as inactivation of pathogens, toxins and enzymes; improvement of digestibility and palatability; enhanced functional properties; prolongation of shelf-life [2]. In addition to conventional heat treatments (roasting, frying and sterilization etc.), novel methods such as high pressure processing, pulsed electric field applications (PEF) and irradiation can be used in various stages of production.

Bioactive substances are defined as “extra-nutritional components generally present in small amounts in botanical products and foods rich in lipids” [3]. Omega-3 fatty acids, dietary fiber, probiotics, phytosterols, tocopherols, carotenoids and polyphenols are a few examples of bioactive components [4, 5]. These are frequently used in the production of functional foods to which consumer’s tendency has increased in recent years. Several research studies revealed that consumption of functional foods prevents/retards formation of cardiovascular diseases, cancer, diabetes and atherosclerosis [6].

Flavanols, a sub-group of polyphenols, are abundantly found in cocoa, green tea, red grape, red wine and berries. These are well known by their strong anti-oxidative properties. The main food processes applied to foods rich in flavanols are fermentation, roasting and drying. This review deals with the influence of various food processes on flavanol compounds.

## FLAVANOLS

Polyphenols are a large group of secondary metabolites derived from phenylalanine in plants. In chemical perspective they are defined as “substances that have an aromatic ring bearing one or more hydroxyl groups” [7]. A part of phenolic compounds is effective in formation of taste of, particularly bitterness and astringency, vegetables and fruits. A part of them provides development of colour shades like yellow, yellow–brown and red–blue in vegetables and fruit [8]. Phenolic compounds have anticarcinogen, antibacterial and antiallergic effects biologically [9]. Furthermore their high antioxidative potential due to their tendency to chelate metals is well known. In particular they possess hydroxyl and carboxyl groups that may chelate iron and copper [10].

Phenolic compounds are divided into two groups: flavonoids and phenolic acids. Phenolic acids are classified into two subgroups, hydroxybenzoic acids and hydroxycinnamic acids, whereas flavonoids have six subgroups due to difference of connection between two aromatic rings called as anthocyanidins, flavanols, flavones, flavanols, flavanols and isoflavones [11-13]. Coumaric acid, caffeic acid, ferulic acid and cinnamic acid are examples to hydroxycinnamic acids; salicylic acid, p–hydroxybenzoic acid, gallic acid and vanilic acid are examples to hydroxybenzoic acids [14].

Flavanols, also known as catechins, are also called as flavan–3–ol since they have a C<sub>6</sub>–C<sub>3</sub>–C<sub>6</sub> skeleton with a hydroxyl group in position three of C – ring and they are biosynthetic precursors of proanthocyanidins [15]. Flavanols, which are found commonly in nature, are (+)–catechin, (–)–epicatechin (EC), (+)–gallocatechin (GC), (–)–epigallocatechin (EGC), gallic acid esters such as (–)–epicatechin gallate (ECG) and (–)–

epigallocatechin gallate (EGCG) [16]. Flavanols are colourless and water soluble compounds and take place as “midproduct” in flavonoid biosynthesis. They can easily condense with oxygen both chemically and enzymatically and form proanthocyanidins [17].

Flavanols can scavenge free radicals *in vitro* and *in vivo*. Physiologically foods and beverages rich in flavanols can influence platelet aggregation, vascular inflammation and endothelial nitric oxide metabolism and may confer protective effects against neurodegeneration [18].

## FOOD PROCESSING

### Fermentation

Fermentation is one of the oldest non-thermal processes in which foods are undergone chemical changes by microorganisms but in case of tea “fermentation” means enzymatic oxidation of monomeric polyphenols particularly by polyphenol oxidase. Three commercial types of tea are commonly present in world market: green tea (non-fermented), oolong tea (semifermented) and black tea (fermented). The major catechins found in fresh tea leaves and green tea are EGCG, EGC, ECG and EC [19].

The most significant change that occurs during fermentation is the conversion of colorless catechins to a complex mixture of yellow–orange to red–brown secondary phenolic substances named as theaflavins and thearubigins [20]. In Figure 1, precursors of theaflavins are illustrated. Black tea contains approximately 31% flavonoids as 9% catechins, 4% theaflavins, 3% flavanols, and 15% undefined catechin condensation products while green tea contains approximately 33% flavonoids as 3% flavanols and 30% catechins [22].

Since tea is greatly consumed all over the world, many studies concentrated on its nutritional and functional properties are present. Kim et al. [23] investigated changes in polyphenolic profile of teas having different degrees of fermentation (0%, 20%, 40%, 60% and 80%). They reported that from green tea (0%) to black tea (80%) EGCG, EGC, EC and ECG decreased by 74%, 91%, 51% and 62% respectively while gallic acid increased. Gallo–flavanols are more reactive due to three hydroxyl groups in B ring and so during fermentation gallated catechins were transformed into non–gallated catechins by releasing their free gallic acid. When this explanation is considered, it is expected that gallo–flavanols (EGC and EGCG) decreased more than catechol–flavanols (EC and ECG) as determined in this research. Same mechanism was suggested by Zuo et al. [24].

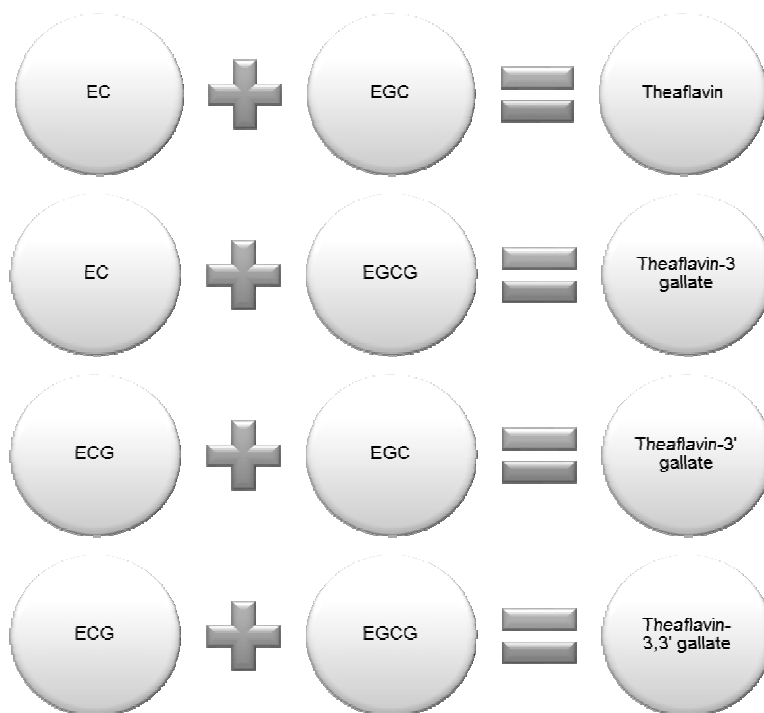


Figure 1. Components of major theaflavins [21]

Zuo et al. [24] stated that as fermentation progressed, catechin contents of teas decreased significantly. Green tea had the highest catechin content as compared others. Muthumani and Kumar [25] declared that in black tea manufacturing catechins were oxidized during 3 hours of fermentation and the rate of oxidation was in the following order: EGC > EGCG > ECG. None of these compounds were found to be exhausted completely. Due to oxidative degallation, (+)-catechin and gallic acid were liberated and their amounts remained almost constant. They also reported that oxidation was faster in initial stages of 3 hours fermentation. Because of insoluble complexes formed between oxidized polyphenols and polyphenol oxidase, activity of the enzyme declined with increased fermentation time. In a different research by Obanda et al. [26] tea leaves were fermented at 20°C and 30°C for 60, 90, 120 and 150 min. It was found that higher fermentation temperature speeded up reactions and led to faster depletion of catechins. At the end of fermentation at 30°C, EGCG and ECG were not detected in contrast to Muthumani and Kumar's study. As fermentation time increased, amounts of EGC, (+)-catechin, EGCG and ECG decreased. Dou et al. [27] reported that approximately catechins and proanthocyanidins decreased by 30% and 20% respectively during oolong tea manufacture. This might be due to oxidation and polymerization of catechins to form theaflavins.

Another food product, in which fermentation has great importance, is cocoa. As in tea, there are many researches interested in cocoa fermentation in literature. In this section result of these will be discussed. Cocoa

beans are raw material for chocolate production. Polyphenols constitute 12–18% of the dry weight of whole cocoa beans. The major cocoa polyphenols are catechins (37%), anthocyanins (4%) and proanthocyanidins (58%) [28]. EC is the most abundant catechin with up to 35% of polyphenol amounts. (+)-catechin, GC and EGC are also found in cocoa beans [29]. The main stages of production are pod opening, fermentation, drying, roasting, grinding and alkalization (Dutch processing). In particular fermentation and alkalization have significant effects on flavanol contents of cocoa beans. Lima et al. [30] defined lactic acid bacteria, acetic acid bacteria, spore forming bacteria of the genus *Bacillus* and yeasts as the dominant microflora in cocoa bean fermentation. Microbial activity leads to formation of a range of metabolic end-products such as alcohols, acetic acid and other organic acids during fermentation [31]. At the end of fermentation, generally pH increases. Catechins are susceptible (in particular EGCG and EGC) to alkaline and neutral pH conditions while they are stable (in particular EC and ECG) in acidic pH values [32]. In aerobic fermentation EC, (+)-catechin and anthocyanidin molecules are oxidized and polymerized into condensed tannins in the presence of polyphenol oxidase [33]. These insoluble tannins (Fig. 2) are responsible for desired cocoa flavour. For reduction of bitterness and astringency in cocoa beans by oxidation of bitter -taste catechins, fermentation has crucial role. (+)-catechin and (-)-EC are considered as the building blocks of proanthocyanidins [34].

Hurst et al. [36] found that when beans were fermented, large loss of EC and (+)-catechin occurred. On the

other hand (–)-catechin formed. They suggested that heat of fermentation might be responsible for the formation of this enantiomer to a certain extent. This epimerization (seen in Fig 3) – reversible conversion of catechins into their corresponding stereoisomers – leads to decrease of cocoa polyphenols' bioavailability because absorption of monomers into blood stream was found as in the following order: EC > (+)-catechin > (–)-catechin [37].

Medium fermented (4 – 5 days) Ivory Coast and heavily fermented (up to 10 days) Papua New Guinea cocoa beans were analyzed for their polyphenol profiles by

Payne et al. [38]. They determined that EC decreased by 86% and 94% and (+)-catechin decreased by 80% and 89% in medium fermented and heavily fermented cocoa beans respectively. In another study, in which cocoa beans were fermented for 1-6 days, effect of fermentation time on polyphenol contents of cocoa beans was studied. As fermentation duration increased, EC content of cocoa beans dropped off significantly (60%) but (+)-catechin concentrations did not change. This decrease in EC content was explained by diffusion out of the bean cotyledons, polyphenol oxidation and condensation [39]. Similar results were reported by [40-43].

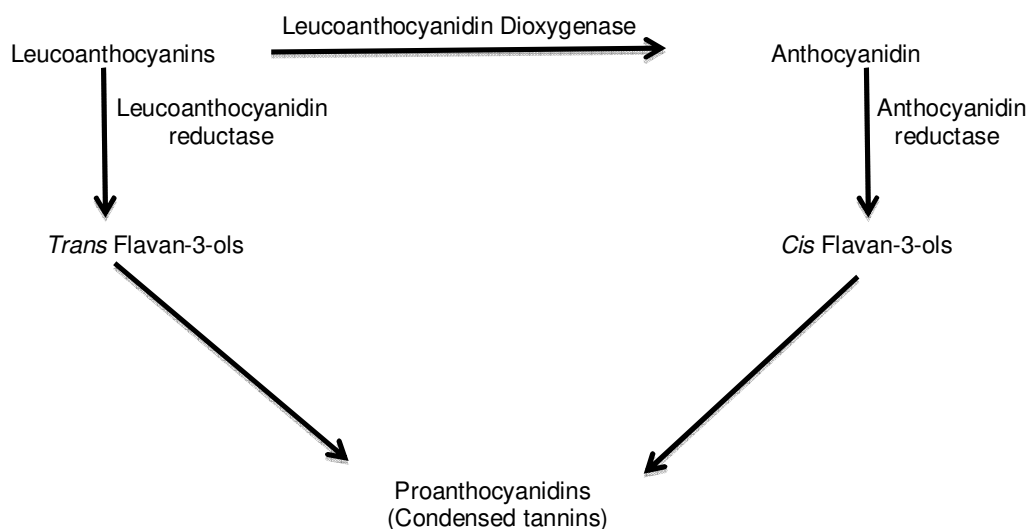


Figure 2. Proanthocyanidin General Pathway [35]

All of these point to the fact that rises in temperature and pH during fermentation increase epimerization and degradation of catechins. On the other hand enzymatic reactions of catechins cause desirable flavor and sensorial changes in foods such as cocoa, coffee and tea.

### Thermal Processing

For preservation and preparation of foods various thermal processes are used. These methods cause undesirable changes such as loss of vitamins/minerals, texture and flavor as well as desirable changes such as protein coagulation, starch swelling, textural softening and formation of aroma compounds [44]. In this context particularly drying and roasting, which are used extensively in catechin-rich foods, will be discussed.

Drying of fruits/vegetables is one of the preservation methods that makes possible to consume fruits/vegetables every period of year. Madrau et al. [45] applied two different air drying temperatures (55°C and 75°C) to apricots until 80% dry matter content. As temperature increased, catechin and EC were completely destroyed by processing but decrease in catechins was significantly more marked in the samples

dried at 55°C. It was found that EC loss was temperature dependent in general. These are in common with results of Pedroza et al. [46]. It was also observed that sun-drying had similar effects on pears' phenolic compounds [47].

*Centella asiatica*, a perennial herb, was dried using air – oven (45°C, 48 h), vacuum oven (45°C, 5 h, 15 psi) and freeze drier (-20°C/24 h; -45°C/3 days). Different drying techniques affected the individual flavonoids differently. Air oven drying resulted in the highest bioactive compounds degradation followed by vacuum oven and freeze drying. Especially flavan-3-ols were found more thermostable. Catechin decreased by 34.9%, 65.2% and 78.1% after freeze drying, vacuum oven and air oven drying treatments respectively [48]. This degradation was explained by phytochemicals' thermal breakdown that affects integrity of cell structure and hence leads to migration of components. These components are exposed to some chemical reactions by enzymes, light and O<sub>2</sub> [49]. Wojdyło et al. [50] applied four different drying methods (convection, freeze drying, vacuum drying, vacuum microwave drying) to two different strawberry cultivars. Generally in freeze drying and vacuum microwave drying levels of (+)-catechin increased due to depolymerized effect of proanthocyanidins and their conversion into elementary

units. Probably food processes accelerate release of more bound phenolic compounds. Although disruption of cell walls may also trigger the release of oxidative and hydrolytic enzymes that destroy antioxidant activity in

fruits, high temperatures of drying processes would deactivate these enzymes and prevent phenolic compounds loss [50].

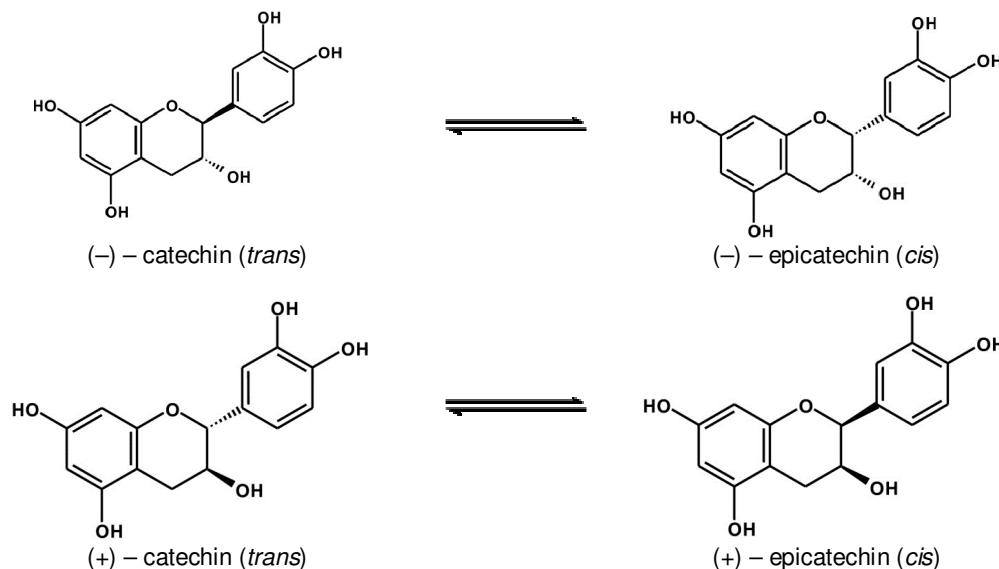


Figure 3. Epimerization of catechins

Grape seed flour (GSF), a waste product of wine making, can be used as a rich antioxidant source in foods. Ross et al. [51] investigated influence of thermal processing on GSF due to many food processes mostly have a thermal stage. GSF was heated at 120, 150, 180, 210 and 240°C for 10, 20, 30, 40, 50, 60 and 90 min in a convection oven. Catechin and epicatechin contents significantly decreased at higher temperatures than 120°C after 10 min. This degradation was explained by susceptibility of catechin and EC to non – enzymatic condensation and polymerization at elevated temperatures. GC content increased at 120 and 150°C with increasing heating time while reached a maximum at 180°C in 20 min and at 210°C in 10 min of heating. The reason of this increase could be due to liberation of phenolic compounds. Similar results were obtained by Kim et al. [56]. On the other hand Stach and Schmitz [53] reported that EGC and EGCG decreased, (+) – catechin increased, ECG and EC contents were almost constant in green tea brewed at 90°C and hold at 70°C, as time increased. Wang et al. [54] determined that degradation was faster below 44°C and epimerization of GCG into EGCG was faster than degradation above 44°C. These degradation reactions include dimerization, hydrolysis, oxidative and polymerization reactions [55]. Epimerization became prominent at the temperatures higher than 98°C in green tea infusions [54]. This conversion was in agreement with results of Kim et al. [56], Murakami et al. [57], Ito et al. [58] and Seto et al. [59]. However Chen et al. [60] detected that EGCG, ECG, EGC and EC were susceptible to epimerization and converted to their corresponding epimers, namely GCG, CG, GC and (–) – catechin at 120°C for 30 min in brewed green tea drinks. Also Li et al. [61] reported that although *cis* – configured catechins (EGCG, EGC, ECG

and EC) degraded over time, the *trans*–configured catechins (GCG and CG) initially increased in concentrated green tea samples. Increase in *trans*–configured catechins continued until 90 min at 120°C and then reached a plateau. They suggested that *cis*–configured catechins followed first order degradation whereas *trans*–configured catechins were produced under thermal process conditions as isomerization products and were also consumed as reactants in degradation process during the “plateau” stage.

Some vegetables and fruits need to be cooked to be consumed. Cooking introduces changes in appearance and texture as well as flavour and nutritive value [62]. Xu and Chang [63] investigated effects of boiling and steaming process at atmospheric condition and high pressures on pinto beans and black beans, which have attracted attention in recent years because of their functional pigments and health – promoting effects. Atmospheric and pressure boiling caused a decrease in (+) – catechin, (+) – EC and ECG contents while pressure steaming resulted an increase in (+) – catechin and (+) – EC and a decrease in (+) – ECG contents significantly. Atmospheric steaming only reduced epicatechin–gallate. The increase of (+) – catechin in pressure steaming may be attributed to release of basal structural compound (catechin) from condensed tannins through a depolarization process upon thermal and pressure conditions. Wang et al. [64] reported that steaming and roasting decreased ECs of tea whereas catechins were increased. This increase was explained by isomerization of ECs, which involves a change in configuration at C–2 position without changing optical rotation at high temperatures. This isomerization between “*cis*” and “*trans*” forms is reversible. At the end of study they

revealed that catechins in 2,3-*trans* structure were thermodynamically more stable than epicatechins in 2,3-*cis* structure so catechins isomerized at lower rate than epicatechins. Different food matrices affect stability of catechins. Sharma and Zhou [65] ordered green tea catechins according to their stability in biscuit baking as (-) - CG > (-) - GCG > (-) - ECG > (-) - EGCG. Due to epimerization the amount of (-) -CG was found to be higher than that added initially in the dough. The considerable loss of catechins could be due to the combined effect of alkaline pH of the system, the interactions of catechins with certain components in the dough, the epimerization and oxidation of catechins during baking and the degradation of catechins during the various biscuit making stages including mixing and baking [65].

Baking and roasting are principally same unit operation. Terminology differs in widely usage; baking is usually applied to flour based foods or fruits; roasting to meats, nuts and vegetables [66]. Coffee and cocoa are the most common roasted products. Payne et al. [38] declared that there was a dramatic loss in total EC content at roasting temperatures higher than 70°C. For instance, when unfermented cocoa beans were roasted at 120°C, the increase in total catechin level was about 696% in comparison to catechin levels of unroasted beans. They suggested that roasting above 70°C generates significant amounts of (-) -catechin probably due to epimerization of (-) -EC. Also Hurst et al. [36] reported that when cocoa beans were roasted progressively under low, medium and high roast conditions, there was a progressive loss of (-) -EC and (+) -catechin and an increase in (-) -catechin with higher roast levels. The reason of this could be the epimerization of (-) -EC to (-) -catechin due to high temperatures of roasting process. These results are in agreement with the results of Jolić et al. [67] and Kofink et al. [68]. On the other hand Caligiani et al. [69] determined that the amount of (-) -EC in cocoa beans decreased and (+) -catechin increased during roasting as a consequence of thermal isomerization of (-) -EC. Oliviero et al. [70] stated that antioxidant activity decreased in parallel with decrease in catechin content during roasting in cocoa bean model systems. Kendari et al. [71] studied effects of vacuum roasting on catechin content of cocoa powder. They applied roasting under vacuum (45.6 and 60.8 cmHg) and non-vacuum at three roasting temperatures (100, 110, 120°C) for 25, 35 and 45 minutes. During non - vacuum roasting catechin was degraded but in case of vacuum roasting catechin concentration increased until 25<sup>th</sup> minutes. The highest catechin content was obtained by vacuum roasting at 60.8 cmHg for 25 minutes. Temperature did not have significant effect on catechin content in vacuum roasting treatment. Both lower O<sub>2</sub> concentration in roasting space and possible degradation of procyanidin or proanthocyanidin could be the reason of the increase in catechin contents of vacuum-roasted cocoa powders. Accordingly Hečimović et al. [72] reported that flavan-3-ol content of coffee generally increased with prolonged roasting degree. They claimed that coffee roasting contributes to development of beneficial flavan-3-ol compounds as a consequence of Maillard reactions.

Roasting is also commonly used in the post - harvest processing of nuts. Schmitzer *et al.* [73] roasted hazelnuts in an electrical oven at 140°C for 15 minutes. They determined that thermal treatment had negative effect on catechin and EC contents on hazelnuts. Flavan-3-ols (catechin+epicatechin) content decreased with roasting. In another research carried out by Chandrasekara and Shahidi [74], whole cashew (*Anacardium occidentale* L.) nuts were roasted at 70°C for 6 h or at 130°C for 33 minutes. In general high temperature roasted nuts had higher (+)-catechin, (-)-EC and EGC amounts. The HPLC results of the study suggest that liberation of these compounds due to degradation of proanthocyanidins and isomerization of flavan-3-ols during heat treatment. These results are in accordance with Belviso et al. [75], who declared that flavanols [(+)-catechin and (-)-EC] content significantly increased in licuri (*Syagrus coronata*) fruits during roasting at 170-190°C for 1 h.

In addition to studies mentioned above, a few researches studied effects of various thermal processing methods on phenolic profiles of non-alcoholic and alcoholic beverages by Czyżowska and Pogorzelski [76], Fuleki and Ricardo-Da-Silva [77], Hernandez et al. [78], Spanos et al. [79], Spanos and Wrolstad [80], Spanos and Wrolstad [81].

### Non - Thermal Processes and Other Food Processes

Thermal treatments, the most common preservation technique, ensure safety of foods but only they cause undesirable physical, chemical and sensorial changes. Therefore, alternative or novel food processing technologies are being explored and implemented to provide safe, fresher-tasting, nutritive foods without using of heat or chemical preservatives [82]. These are irradiation, high pressure, pulsed electric fields, pulsed white light, ultrasound and UV radiation [83].

Park et al. [84] irradiated green tea leaves with a far-infrared (FIR) heater during roasting and drying steps. FIR irradiation significantly affected catechin composition of green tea. Especially in a treatment (roasting by fryer & FIR + FIR after drying by fryer) EGCG and ECG levels increased compared with non-irradiated control. The possible cause of this increase was explained by Gulati et al. [85], who suggested that microwave energy have prevented the binding of polyphenol and catechin to leaf matrix and so extractability of catechins increased. Normally C, CG, GC and GCG is not found in green tea leaves but under high temperatures catechins are epimerized at C2-position and converted into these compounds. By reason of this mechanism FIR application resulted in catechin formation. Except one FIR treatment (drying by fryer & FIR after rolling) EC, ECG, EGC, EGCG and GC levels were increased by FIR [84]. Kim et al. [86] reported that a combined treatment (roasting by FIR and after drying by heating pan FIR irradiation) increased EGC, EC, ECG and EGCG contents of green tea. Similar results were presented by Lee et al. [87], who

irradiated green tea leaves with FIR for 10 min at eight different temperatures (80, 90, 100, 110, 120, 130, 140 and 150°C). They obtained the highest catechin contents at 110°C but offered irradiation at 90 and 100°C by taking into consideration sensorial acceptability. Another factor that increases flavanol contents could be ability of FIR to cleave covalent bonds and releasing antioxidants such as polyphenols, flavonoids, and tannins [88]. Microwave is one of the alternative methods and used commonly in numerous foods. Hayat et al. [89] applied microwave treatment to citrus mandarin pomace powder with different time and power combinations. Although irradiation for 10 min caused an increase in total catechin content, there was a sudden decrease during prolonged time at 250 W. Similar findings were also obtained in irradiation of citrus mandarin peels [90]. Similarly Breittellner et al. [91] declared that gamma irradiation led to significant reduction in (+)-catechin levels of strawberries.

Another minimal processing technique, pulsed electric field (PEF), becomes popular recently. In a study by Schilling *et al.* [92] apple mash was treated with three different electric field strengths (1, 3 and 5 kV/cm). This application caused no statistically significant difference on catechin and epicatechin contents. On the other hand PEF treatment resulted in higher (+)-catechin and (-)-EC contents in red grapes [93].

High – pressure treatment, another common non – thermal process, increased total catechins in apple juice [94]. As far as our literature survey could ascertain many researchers [36][38][95] reported that especially alkalization step in cacao processing caused a decrease in (-)-EC, (-)-catechin and (+)-catechin contents, with the exception of Jolić et al. [67], who stated an increase in (+)-catechin content after alkalization.

## CONCLUSION

Taking into account all of these studies given above, it can be clearly understood that epimerization is the first and oxidation is the second crucial reason of catechin degradation in phenolic rich foods during processing. In particular polyphenol oxidase induced oxidation reactions cause colour changes. These changes are desirable in some cases such as black tea or cocoa, but sometimes they need to be prevented as in fruit juices or wine making. Generally high temperatures promote epimerization reactions. All of these reactions result in sensorial differences in foods.

In general the degree of epimerization, polymerization or oxidation depends on many factors including concentration and chemical structure of phenolic compounds, interactions with other food components and properties of food matrices. For instance, as mentioned before catechins are less stable at alkaline or neutral pH. Certain pretreatments may be effective in some foods in order to prevent chemical transformation of flavanols during food processing. Additionally activities of some enzymes –in particular polyphenol oxidase– should be controlled.

Novel non-thermal processing techniques are promising treatments to minimize heat induced alterations in foods. However it should be noted that number of studies related to these technologies are insufficient. As in thermal preservation and processing methods, emerging techniques should be examined extensively by scientific researches and their effects on flavanols should be revealed. Furthermore *in vitro* studies dealing with bioaccessibility/bioavailability of flavan-3-ols should be carried out to determine the indirect influences of various processing methods on human health.

## REFERENCES

- [1] Berk, Z. 2009. Food Process Engineering and Technology. Academic Press, USA.
- [2] Van Boekel M., Fogliano, V., Pellegrini, N., Stanton, C., Scholz, G., Lalljie, S., Somoza, V., Knorr, D., Jasti, P.R., Eisenbrand, G. 2010. A review on the beneficial aspects of food processing. *Mol. Nutr. Food Res.* 54(9): 1215-1247.
- [3] Kitts, D.D.1994. Bioactive substances in food: identification and potential uses. *Can. J. Physiol. Pharmacol.* 72: 423-424.
- [4] Pennington, J.A.T., 2002. Food composition databases for bioactive food components. *J. Food Comp. Anal.* 15: 419-434.
- [5] Erbaş, M. 2006. Yeni Bir Gıda Grubu Olarak Fonksiyonel Gıdalar. *Türkiye 9. Gıda Kongresi*, 24-26 Mayıs 2006, Bolu, Türkiye, Bildiriler Kitabı, 791-794p.
- [6] Shahidi, F. 2004. Functional foods: their role in health promotion and disease prevention. *J. Food Sci.* 69(5): R146-R149.
- [7] Shahidi, F., Naczk, M. 2004. Phenolics in Food and Nutraceuticals. CRC Press LLC, USA.
- [8] Cemeroglu, B., 2004. Meyve ve Sebze İşleme Teknolojisi 1. Cilt. Gıda Teknolojisi Derneği Yayınları No:35, Ankara.
- [9] Eruçar, S. 2006. Bazı Bitkisel Çayların Fenolik Madde Profili ve Antioksidan Aktivitelerinin İncelenmesi. Yüksek lisans tezi. İstanbul Teknik Üniversitesi Fen Bilimleri Enstitüsü, İstanbul.
- [10] Michalak, A. 2006. Phenolic compounds and their antioxidant activity in plants growing under heavy metal stress. *Polish J. of Environ. Stud.* 15(4): 523-530.
- [11] Acar, J., Gökmen, V. 2007. Fenolik Bileşikler ve Doğal Renk Maddeleri. In *Gıda Kimyası*, Edited by İ.Saldamlı, Hacettepe Üniversitesi Yayınları, Ankara, 587p.
- [12] Turhan, S., Üstün, N.Ş. 2006. Doğal Antioksidanlar ve Gıdalarda Kullanımları. *Türkiye 9.Gıda Kongresi*. 24-26 Mayıs, Bolu, Türkiye,Bildiriler Kitabı, 273-276p.
- [13] Seyoum, A. Asres, K., El-Fiky, F.K. 2006. Structure-radical scavenging activity relationships of flavonoids. *Phytochemistry* 67: 2058-2070.
- [14] Karadeniz, F., Ekşi, A. 2002. Gıdalardaki başlıca fenolik bileşikler. *Dünya Gıda* 1: 80-85.
- [15] De Pascual-Teresa, S.; Moreno, D. A.; García-Viguera, C. 2010. Flavanols and anthocyanins in cardiovascular health: a review of current evidence. *Int. J. Mol. Sci.* 11(4): 1679-1703.

- [16] Hollman, P.C., Arts, I.C. 2000. Flavonols, flavones and flavanols – nature, occurrence and dietary burden. *J. Sci. Food Agric.* 80: 1081-1093.
- [17] Saldamlı, İ., 2007. Gıda Kimyası. Hacettepe Üniversitesi Yayınları. Ankara.
- [18] Hackman, R. M., Polagruto, J. A., Zhu, Q. Y., Sun, B., Fujii, H.; Keen, C.L. 2008. Flavanols: digestion, absorption and bioactivity. *Phytochem. Rev.* 7: 195-208.
- [19] Wang, H., Provan, G.J., Halliwell, K., 2000. Tea Flavonoids: Their functions, utilisation and analysis. *Trends in Food Science & Technology* 11, 152-160.
- [20] Graham, H.N., 1999. Tea. In Wiley Encyclopedia of Food Science and Technology. Edited by F.J. Francis, Wiley Interscience, New York, 2724p.
- [21] Hilal, Y., Engelhardt, U., 2007. Characterization of white tea – comparison to green and black tea. *J. Verbr. Lebensm.* 2: 414-421.
- [22] Wiseman, S.A., Balentine, D.A., Frei, B., 1997. Antioxidants in tea. *Crit. Rev. Food Sci.* 37(8): 705-718.
- [23] Kim, Y., Goodner, K.L., Park, J., Choi, J., Talcott, S.T., 2011. Changes in antioxidant phytochemicals and volatile composition of *Camellia sinensis* by oxidation during tea fermentation. *Food Chem.* 129: 1331-1342.
- [24] Zuo, Y., Chen, H., Deng, Y., 2002. Simultaneous determination of catechins, caffeine and gallic acids in green, Oolong, black and puerh teas using HPLC with a photodiode array detector. *Talanta* 57: 307-316.
- [25] Muthumani, T., Kumar, R.S.S., 2007. Influence of fermentation time on the development of compounds responsible for quality in black tea. *Food Chem.* 101: 98-102.
- [26] Obanda, M., Owuor, P.O., Mang'oka, R., 2001. Changes in the chemical and sensory quality parameters of black tea due to variations of fermentation time and temperature. *Food Chem.* 75: 395-404.
- [27] Dou, J., Lee, V.S.Y., Tzen, J.T.C., Lee, M., 2007. Identification and comparison of phenolic compounds in the preparation of oolong tea manufactured by semifermentation and drying processes. *J. Agr. Food Chem.* 55: 7462-7468.
- [28] Hii, C.L., Law, C.L., Suzannah, S., Misnawi, Cloke, M., 2009. Polyphenols in cocoa (*Theobroma cacao* L.). *As. J. Food Ag-Ind.* 2(4): 702-722.
- [29] Wollgast, J., Anklam, E., 2000. Review on polyphenols in *Theobroma cacao*: changes in composition during the manufacture of chocolate and methodology for identification and quantification. *Food Res. Int.* 33: 423-447.
- [30] Lima, L.J.R., Almeida, M.H., Nout, M.J.R., Zwietering, M.H. 2011. *Theobroma cacao* L., "The Food of the Gods": quality determinants of commercial cocoa beans, with particular reference to the impact of fermentation. *Crit. Rev. Food Sci.* 51: 731-761.
- [31] Jespersen, L., Nielsen, D.S., Hønholt, S., Jakobsen, M., 2005. Occurrence and diversity of yeasts involved in fermentation of West African cocoa beans. *FEMS Yeast Res.* 5: 441-453.
- [32] Zhu, Q.Y., Zhang, A., Tsang, D., Huang, Y., Chen, Z., 1997. Stability of green tea catechins. *J. Agr. Food Chem.* 45: 4624-4628.
- [33] Schinella, G., Mosca, S., Cienfuegos-Jovellanos, E., Pasamar, M.Á., Muguerza, B., Ramón, D., Ríos, J.L., 2010. Antioxidant properties of polyphenols – rich cocoa products industrially processed. *Food Res. Int.* 43: 1614-1623.
- [34] Dixon, R.A., Xie, D., Sharma, S.B. 2005. Proanthocyanidins – a final frontier in flavonoid research? *New Phytol.* 165: 9-28.
- [35] Martens, S., Preuß, A., Matern, U. 2010. Multifunctional flavonoid dioxygenases: Flavonol and anthocyanin biosynthesis in *Arabidopsis thaliana* L. *Phytochemistry* 71: 1040-1049.
- [36] Hurst, W.J., Krake, S.H., Bergmeier, S.C., Payne, M.J., Miller, K.B., Stuart, D.A., 2011. Impact of fermentation, drying, roasting and Dutch processing on flavan-3-ol stereochemistry in cacao beans and cocoa ingredients. *Chem. Cent. J.* 5: 53.
- [37] Donovan, J.L., Crespy, V., Oliveira, M., Cooper, K.A., Gibson, B.B., Williamson, G., 2006. (+) – catechin is more bioavailable than (-) – catechin: Relevance to the bioavailability of catechin from cocoa. *Free Rad. Res.* 40: 1029-1034.
- [38] Payne, M.J., Hurst, W.J., Miller, K.B., Rank, C., Stuart, D.A., 2010. Impact of fermentation, drying, roasting and Dutch processing on epicatechin and catechin content of cacao beans and cocoa ingredients. *J. Agr. Food Chem.* 58: 10518-10527.
- [39] Aikpokpodion, P.E., Dongo, L.N., 2010. Effects of fermentation intensity on polyphenols and antioxidant capacity of cocoa beans. *Int. J. Sustain. Crop. Prod.* 5(4): 66-70.
- [40] Gil, A., Rojas, L.F., Atehortua, L., Londoño, J., 2011. Effect of Fermentation and Sun Drying on Phytochemical Composition of Native Colombian Cocoa. 2011 CIGR Section VI International Symposium on Towards a Sustainable Food Chain Food Process, Bioprocessing and Food Quality Management, April 18-20 2011, Nantes, France, 1-6p.
- [41] Camu, N., De Winter, T., Addo, S.K., Takrama, J.S., Bernaert, H., De Vuyst, L., 2008. Fermentation of cocoa beans: Influence of microbial activities and polyphenol concentrations on the flavour of chocolate. *J. Sci. Food Agric.* 88: 2288-2297.
- [42] Nazaruddin, R., Seng, L.K., Hassan, O., Said, M., 2006. Effect of pulp preconditioning on the content of polyphenols in cocoa beans (*Theobroma cacao*) during fermentation. *Ind. Crop Prod.* 24: 87-94.
- [43] Kim, H., Keeney, P.G., 1984. (-) – Epicatechin content in fermented and unfermented cocoa beans. *J. Food Sci.* 49: 1090-1092.
- [44] Ohlsson, T., 2002. Minimal processing of foods with thermal methods. In Minimal Processing Technologies in the Food Industry. Edited by Ohlsson T. & Bengtsson, N. Woodhead Publishing Limited, Abington Hall, Abington, Cambridge CB1 6AH, England, 288p.
- [45] Madrau, M.A., Piscopo, A., Sanguinetti, A.M., Del Caro, A., Poiana, M., Romeo, F.V., Piga, A., 2009. Effect of drying temperature on polyphenolic



- content and antioxidant activity of apricots. *Eur. Food Res. Technol.* 228: 441-448.
- [46] Pedroza, M.A., Carmona, M., Pardo, F., Salinas, M.R., Zalacain, A., 2012. Waste grape skins thermal dehydration: potential release of colour, phenolic and aroma compounds into wine. *TCYT* 10(3): 225-234.
- [47] Ferreira, D., Guyot, S., Marnet, N., Delgado, I., Renard, C.M.G.C., Coimbra, M.A., 2002. Composition of phenolic compounds in a Portuguese pear (*Pyrus communis* L. Var. S. Bartolomeu) and changes after sun-drying. *J. Agr. Food Chem.* 50: 4537-4544.
- [48] Mohd Zainol, M.K., Abdul-Hamid, A., Abu Bakar, F., Pak Dek, S., 2009. Effect of different drying methods on the degradation of selected flavonoids in *Centella asiatica*. *Int. Food Res. J.* 16: 531-537.
- [49] Davey, M.W., Van-Montagu, M., Inze, D., Sanmartin, M., Kanellis, A., Smirnoff, N., Benzie, I.J.J., Strain, J.J., Favell, D., Fletcher, J., 2000. Plant l-ascorbic acid: Chemistry, function, metabolism, bioavailability, and effects of processing. *J. Sci. Food Agr.* 80: 825-860.
- [50] Wojdyło, A., Figiel, A., Oszmiański, J., 2009. Effect of drying methods with the application of vacuum microwaves on the bioactive compounds, color, and antioxidant activity of strawberry fruits. *J. Agr. Food Chem.* 57: 1337-1343.
- [51] Ross, C.F., Hoyer, C., Fernandez-Plotka, V.C., 2011. Influence of heating on the polyphenolic content and antioxidant activity of grape seed flour. *J. Food Sci.* 76(6): C884-C890.
- [52] Kim, S.-Y., Jeong, S.-M., Park, W.-P., Nam, K.-C., Ahn, D.-U., Lee, S.-C., 2006. Effect of heating conditions of grape seeds on the antioxidant activity of grape seed extracts. *Food Chem.* 97: 472-479.
- [53] Stach, D., Schmitz, O.J., 2001. Decrease in concentration of free catechins in tea over time determined by micellar electrokinetic chromatography. *J. Chromatogr. A* 924: 519-522.
- [54] Wang, R., Zhou, W., Jiang, X., 2008. Reaction kinetics of degradation and epimerization of epigallocatechin gallate (EGCG) in aqueous system over a wide temperature range. *J. Agr. Food Chem.* 56: 2694-2701.
- [55] Okumura, H., Ichitani, M., Takihara, T., Kunimoto, K.-K., 2008. Effect of cyclodextrins on the thermal epimerization of tea catechins. *Food Sci. Technol. Res.* 14(1): 83-88.
- [56] Kim, E.S., Liang, Y.R., Jin, J., Sun, Q.F., Lu, J.L., Du, Y.Y., Lin, C., 2007. Impact of heating on chemical compositions of green tea liquor. *Food Chem.* 103: 1263-1267.
- [57] Murakami, I., Nakamura, T., Ishibashi, Y., Shibuya, R., Ayano, E., Morita-Murase, Y., Nagata, Y., Kanazawa, H., 2006. Simultaneous determination of catechins and procyanidins in bottled tea drinks by LC/MS. *Chromatography* 27(1): 27-33.
- [58] Ito, R., Yamamoto, A., Kodama, S., Kato, K., Yoshimura, Y., Matsunaga, A., Nakazawa, H., 2003. A study on the change of enantiomeric purity of catechins in green tea infusion. *Food Chem.* 83: 563-568.
- [59] Seto, R., Nakamura, H., Nanjo, F., Hara, Y., 1997. Preparation of epimers of tea catechins by heat treatment. *Biosci. Biotech. Biochem.* 61(9): 1434-1439.
- [60] Chen, Z.-Y., Zhu, Q.-Y., Tsang, D., Huang, Y., 2001. Degradation of green tea catechins in tea drinks. *J. Agr. Food Chem.* 49: 477-482.
- [61] Li, N., Taylor, L.S., Ferruzzi, M.G., Mauer, L.J., 2012. Kinetic study of catechin stability: Effects of pH, concentration, and temperature. *J. Agr. Food Chem.* 60: 12531-12539.
- [62] Vacklavik, V.A., Christian, E.W., 2008. *Essentials of Food Science – 3<sup>rd</sup> Edition*. Springer Science + Business Media LLC, USA.
- [63] Xu, B., Chang, S.K.C., 2009. Total phenolic, phenolic acid, anthocyanin, flavan-3-ol, and flavonol profiles and antioxidant properties of pinto and black beans (*Phaseolus vulgaris* L.) as affected by thermal processing. *J. Agr. Food Chem.* 57: 4757-4764.
- [64] Wang, L.-F., Kim, D.-M., Lee, C.-Y., 2000. Effects of heat processing and storage on flavanols and sensory qualities of green tea beverage. *J. Agr. Food Chem.* 48: 4227-4232.
- [65] Sharma, A., Zhou, W., 2011. A stability study of green tea catechins during the biscuit making process. *Food Chem.* 126: 568-573.
- [66] Fellows, P., 2000. *Food Processing Technology Principles and Practice – 2<sup>nd</sup> Edition*. Woodhead Publishing Limited, England.
- [67] Jolić, S.M., Redovniković, I.R., Marković, K., Šipušić, D.I., Delonga, K., 2011. Changes of phenolic compounds and antioxidant capacity in cocoa beans processing. *Int. J. Food Sci. Tech.* 46: 1793-1800.
- [68] Kofink, M., Papagiannopoulos, M., Galensa, R., 2007. (-)-Catechin in cocoa and chocolate: occurrence and analysis of an atypical flavan-3-ol enantiomer. *Molecules* 12: 1274-1288.
- [69] Calgiani, A., Cirilini, M., Palla, G., Ravaglia, R., Arlorio, M., 2007. GC-MS detection of chiral markers in cocoa beans of different quality and geographic origin. *Chirality* 19: 329-334.
- [70] Oliviero, T., Capuano, E., Cämmerer, B., Fogliano, V., 2009. Influence of roasting on the antioxidant activity and HMF formation of a cocoa bean model systems. *J. Agr. Food Chem.* 57: 147-152.
- [71] Kendari, T., Harijono, Yuwono, S.S., Estiasih, T., Santoso, U., 2012. The change of catechin antioxidant during vacuum roasting of cocoa powder. *J. Nutr. Food Sci.* 2: 174. doi:10.4172/2155-9600.1000174
- [72] Hečimović, I., Belščak-Cvitanović, A., Horžić, D., Komes, D., 2011. Comparative study of polyphenols and caffeine in different coffee varieties affected by the degree of roasting. *Food Chem.* 129: 991-1000.
- [73] Schmitzer, V., Slatnar, A., Veberiz, R., Stampar, F., Solar, A., 2011. Roasting affects phenolic composition and antioxidative activity of hazelnuts (*Corylus avellana* L.). *J. Food Sci.* 76(1): S14-S19.
- [74] Chandrasekara, N., Shahidi, F., 2011. Effect of roasting on phenolic content and antioxidant

- activities of whole cashew nuts, kernels and testa. *J. Agr. Food Chem.* 59: 5006-5014.
- [75] Belviso, S., Ghirardello, D., Giordano, M., Ribeiro, G.S., Alves, J.S., Parodi, S., Risso, S., Zeppa, G., 2013. Phenolic composition, antioxidant capacity and volatile compounds of licuri (*Syagrus coronate* (Martius) Beccari) fruits as affected by the traditional roasting process. *Food Res. Int.* 51(1): 39-45.
- [76] Czyżowska, A., Pogorzelski, E., 2004. Changes to polyphenols in the process of production of must and wines from blackcurrants and cherries. Part II. Anthocyanins and flavanols. *Eur. Food Res. Technol.* 218: 355-359.
- [77] Fuleki, T., Ricardo-Da-Silva, J.M., 2003. Effects of cultivar and processing method on the contents of catechins and procyanidins in grape juice. *J. Agr. Food Chem.* 51: 640-646.
- [78] Hernandez, T., Ausín, N., Bartolomé, B., Bengoechea, L., Estrella, I., Gómez-Cordovés, C., 1997. Variations in the phenolic composition of fruit juices with different treatments. *Z. Lebensm. Unters. F. A* 204: 151-155.
- [79] Spanos, G.A., Wrolstad, R.E., Heatherbell, D.A., 1990a. Influence of processing and storage on the phenolic composition of apple juice. *J. Agr. Food Chem.* 38: 1572-1579.
- [80] Spanos, G.A., Wrolstad, R.E., 1990b. Influence of processing and storage on the phenolic composition of Thompson seedless grape juice. *J. Agr. Food Chem.* 38: 1565-1571.
- [81] Spanos, G.A., Wrolstad, R.E., 1990. Influence of variety, maturity, processing, and storage on the phenolic composition of pear juice. *J. Agr. Food Chem.* 38: 817-824.
- [82] Hogan, E., Kelly, A.L., Sun, D-W., 2005. High Pressure processing of foods: an overview. In *Emerging Technologies for Food Processing*. Edited by D-W. Sun, Elsevier Academic Press, California, US, 768p.
- [83] Ohlsson, T., Bengtsson, N. 2002. Minimal Processing of Foods with Non – Thermal Methods. In *Minimal Processing Technologies in The Food Industry*. Edited by T. Ohlsson & N. Bengtsson, Woodhead Publishing Limited, England, 288p.
- [84] Park, J-H., Lee, J-M., Cho, Y-J., Kim, C-T., Kim, C-J., Nam, K-C., Lee, S-C., 2009. Effect of far – infrared heater on the physicochemical characteristics of green tea during processing. *J. Food Biochem.* 33: 149-162.
- [85] Gulati, A., Rawat, R., Singh, B., Ravindranath, S.D., 2003. Application of microwave energy in the manufacture of enhanced – quality green tea. *J. Agr. Food Chem.* 51: 4764-4768.
- [86] Kim, S-Y., Jeong, S-M., Jo, S-C., Lee, S-C., 2006. Application of far – infrared irradiation in the manufacturing process of green tea. *J. Agr. Food Chem.* 54: 9943-9947.
- [87] Lee, S-C., Kim, S-Y., Jeong, S-M., Park, H-J., 2006. Effect of far – infrared irradiation on catechins and nitrite scavenging activity of green tea. *J. Agr. Food Chem.* 54: 399-403.
- [88] Lee, J-M., Lee, S-C., 2010. The effects of far – infrared irradiation on the antioxidant activity of licorice (*Glycyrrhiza uralensis* fisch) root. *J. Food Biochem.* 34: 172-181.
- [89] Hayat, K., Zhang, X., Farooq, Um., Abbas, S., Xia, S., Jia, C., Zhong, F., Zhang, J., 2010. Effects of microwave treatment on phenolic content and antioxidant activity of citrus mandarin pomace. *Food Chem.* 123: 423-429.
- [90] Hayat, K., Zhang, X., Chen, H., Xia, S., Jia, C., Zhong, F., 2010. Liberation and separation of phenolic compounds from citrus mandarin peels by microwave heating and its effect on antioxidant activity. *Sep. Purif. Technol.* 73: 371-376.
- [91] Breitfellner, F., Solar, S., Sontag, G., 2002. Effect of gamma irradiation on flavonoids in strawberries. *Eur Food Res. Technol.* 215: 28-31.
- [92] Schilling, S., Alber, T., Toepfl, S., Neidhart, S., Knorr, D., Schieber, A., Carle, R., 2007. Effects of pulsed electric field treatment of apple mash on juice yield and quality attributes of apple juices. *Innov. Food Sci. Emerg.* 8: 127-134.
- [93] Puértolas, E., Saldaña, G., Álvarez, I., Raso, J., 2010. Effect of pulsed electric field processing of red grapes on wine chromatic and phenolic characteristics during aging in oak barrels. *J. Agr. Food Chem.* 58: 2351-2357.
- [94] Baron, A., Dénes, J-M., Durier, C., 2006. High-pressure treatment of cloudy apple juice. *LWT Food Sci. Technol.* 39: 1005-1013.
- [95] Andres-Lacueva, C., Monagas, M., Khan, N., Izquierdo-Pulido, M., Urpi-Sarda, M., Permanyer, J., Lamuela-Raventós, R.M., 2008. Flavanol and flavonol contents of cocoa powder products: Influence of the manufacturing process. *J. Agr. Food Chem.* 56: 3111-3117.