JACK N. LOSSO

The Maillard Reaction Reconsidered

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COOKING AND EATING FOR HEALTH

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To

My children:

Mariel, Boriss, and MerryJean

My wife:

Jane

For your unconditional love and support

and

My late brothers and sisters:

Hugo, Beatrice, Boniface, Rose, and Diama

For your love and support and not being around long enough to share with us

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Preface

Food is health, personal, regional, national, and international security. To defend the ascendant French Empire, Napoleon Bonaparte turned to food science and technology and offered a monetary reward to anyone who could invent a process of preserving foods for his soldiers. Nicholas Appert, a French brewer and Paris chef, spent the next 14 years perfecting canning partridges, vegetables, and gravies. After he had perfected the process of sealing food in airtight jars, he sent samples to Napoleon's army. The soldiers rated the food excellent and fresh. Canning was born, and Napoleon personally awarded the equivalent of $5000 to Nicolas Appert in 1809. Since that time, processed and preserved foods have saved billions of lives worldwide.

Globalization has created unprecedented opportunities for the food industry from farm to the human gut. Restaurants, including fast food and sit-in restaurants or school cafeterias, are bourgeoning around the world as convenience and world travel have become the way of life. To feed the world, food has to be processed and preserved. Food scientists and engineers develop processed foods that fill the world's food supermarket shelves and are used in restaurants, hospital and school cafeterias, and at home.

Food is medicine. The food that we consume from breakfast to dinner or at movie times is metabolized, and the metabolites have an impact on our health, mood, behavior, and performance throughout our lives. Louis-Camille Maillard (1878–1936), a French chemist and physician, reported in 1912 that in the human body reactive sugars such as glucose or fructose continuously react with proteins containing lysine, arginine, or histidine amino acid to produce compounds known as advanced glycation end products (AGEs) that play a role in the pathogenesis of chronic diseases, particularly diabetes. It took until the 1970s when scientists began to understand that AGEs mediate the complications of illnesses such as diabetes and tissue modification during human aging. In the presence of excess glucose or fructose, the sugar can also auto-oxidize and form reactive dicarbonyls, such as methylglyoxal, and the latter reacts with proteins to form AGEs.

Food is a biological material obtained from land animals, birds, fish, vegetables, fruits, or seeds, after the animal or bird has been slaughtered or the fruit or vegetable has been cut. Beef sirloin is a cut from a slaughtered cow. Salmon or catfish filet is a cut from a slaughtered salmon or catfish. Cheese is a by-product of milk fractionation. As such, foods contain variable amounts of carbohydrates, lipids, minerals, proteins, vitamins, pigments, and micronutrients and are very susceptible to biochemical interactions and microbial deterioration. Food scientists and engineers develop preservation techniques to keep food safe and palatable.

The discovery of fire gave humans the ability to prepare healthy and safe food from raw animal or agricultural products. Louis Pasteur discovered and demonstrated the ability of heat treatment to kill microorganisms in food and make food safer. While Pasteur focused on the efficacy of cooking at low temperature to develop safe and healthy foods, there are several other forms of heat treatment that can be applied to raw agricultural products to prepare tasty meals.

Cooking food is not only an art, but a combination of art and science such as chemistry, and involves the interactions of carbohydrates, lipids, proteins, minerals, vitamins, salt, and micronutrients at temperatures that can range from freezing to flame temperatures. According to the French chemist Antoine Lavoisier, nothing is lost during cooking but matter is transformed. During cooking, new desirable and undesirable chemicals are generated.

In recent years, convenience in many sectors of life has become essential for business. To meet consumer demand for convenience, thermal and nonthermal techniques have been developed that deliver food that is tasty and microbiologically safe. At the same time, consumers have been accustomed to an open-ended high temperature and short-time cooking techniques that encompass baking, frying, grilling, broiling, bricking, microwaving, or searing food as the easy answer to deliver tasty and flavorful foods. Despite warnings by medical doctors and certain media, it has been reported that the American eating habit worsened in 2013 compared to years before.

According to Lavoisier and Maillard, the application of high temperatures to a biological mixture such as food cannot go without consequences. The Maillard reaction is responsible for the flavor of baked, barbecued, broiled, grilled, roasted, seared, microwaved, or flamed foods. As the cooking temperature increases, the Maillard reaction generates a mixture of flavorful, often toxic, and sometime carcinogenic compounds in foods depending on the cooking conditions. Reactive dicarbonyls are bioavailable and easily react with proteins or enzymes and disrupt protein or enzyme functionality. About 10% of ingested AGEs remain inside the body, accumulate in different tissues over time, and induce oxidative stress. Chronic oxidative stress induces chronic inflammation; and chronic inflammation is the hallmark of chronic degenerative diseases, including obesity, diabetes, eye disease, anemia, kidney diseases, hypertension, osteoporosis, sarcopenia, cardiovascular disease, multiple sclerosis, cancer, and Parkinson's and Alzheimer's diseases. Therefore, diet-related diseases, including obesity and others, and food safety issues cannot be addressed by chefs and nutritionists alone without the critical involvement of food scientists and engineers.

This book is divided into three parts. Part I describes the Maillard reaction in layman's terms to let those in culinary schools and cafeterias understand the chemistry that goes on when food ingredients are mixed in the presence of heat. Inflammation in health and disease focuses on maternal in utero inflammation as a risk factor for adulthood disease. In Chapter 3, the author presents some of the tastiest and popular foods ever designed by mankind that are yet rich in inflammatory AGEs.

Part II of the book links the Maillard reaction products to chronic inflammatory degenerative diseases, including obesity, diabetes, hypertension, kidney, atherosclerosis, osteoporosis, eye health, multiple sclerosis, erectile dysfunction, insomnia, cancer, and Parkinson's and Alzheimer's diseases. Through each chronic disease, the risk factors, including foods, are presented and protective foods are suggested.

Part III of the book covers champagne, caviar, good cuisine, and ice wine. The gut is the epicenter of healthy life, suggesting that healthy gut is healthy life. The most coveted diets, including the Western, traditional Mediterranean, and the Okinawan diets, are discussed. However, in between the West and Japan, there are regions called the "Blue Zones" where centenarians live and are active members of their communities. The adoption of Japanese and Mediterranean diets has brought significant confusion in food outlets where consumers are presented westernized variations of the Japanese or Mediterranean foods that are unfortunately AGEs rich.

Champagne, caviar, good cuisine, and ice wine help develop a healthy pantry both at home and away from home. Cooking techniques are discussed, including advantages and disadvantages associated with each technique. It is suggested that healthy gut and healthy life start with a good cuisine at or away from home that addresses healthy children's foods because children represent the future. The health benefits of champagne and caviar are presented, and ice wine is introduced as the dessert wine for laisser le bon temps rouler.

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I bear the responsibility for any errors that remain in the text.

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PART I

The Maillard Reaction and Foods

The Maillard reaction (MR), referred to in honor of the French chemist and medical doctor Louis Camille Maillard (1878–1936) who first enunciated the process in 1912, is one of the most important interactions in food systems especially in the restaurant industry. The reaction occurs between a reactive aldehyde usually a reducing sugar and an amine group and is favored by heat. The MR affects the aroma, appearance, and flavor of several types of foods including bread crust, pizza, peanut butter, cheese, condensed sweetened milk, roasted coffee, roasted chicory, grilled poultry or red meat, dry soups, biscuits, protein and cereal bars, breakfast cereals, beer, and cola. The MR also affects the nutritional quality of foods that have undergone the reaction.

Chapters 1 and 2 describe the MR and elaborate on the reaction so that we all can understand why this reaction is very important to all chefs, culinologists, food services, restaurant industry, school and hospital cafeterias, parents, individuals, and students in culinary schools and culinology. Caramelization is considered as a special case of the MR and will also be discussed because it is an important nonenzymatic browning reaction of interest to all groups mentioned earlier.

The MR delivers tasty foods that are very good to the palate. Yet it is being shown that the tasty foods that billions of individuals crave for around the world are proinflammatory. Books, review papers, research papers, proceedings, and monographs have been and are being written on both the positive effects of the MR on gastronomy and the side effects of inflammation. These chapters concisely address both aspects.

CHAPTER 1

Introduction to the Maillard Reaction

1.1 INTRODUCTION

This chapter will cover the basic of the Maillard reaction (MR) that students in culinary schools and culinology, chefs, and individuals in the restaurant industry need to know because they develop MR regularly in several aspects of their occupation in the kitchen. However, before describing the MR, a brief introduction on the history of modern restaurant is presented.

The first contemporary restaurant "Le Restaurant Boulanger" opened in Paris, France, in 1765 and was developed by Mr. Boulanger also known as Champ d'Oiseau. Before 1765, Mr. Boulanger was selling a bouillon made from a meat juice concentrate that he developed to help people restore strength especially women after labor/childbirth or individuals who were tired. Because he was using food to restore strength in people, Mr. Boulanger was called a "restaurateur" or the person who restores strength and health. Unlike the inns that opened for certain hours, where there was no menu and the food selected by the chef was served to all customers sitting on several joint tables, Boulanger developed a premise that opened all day and where customers sat on a single table, ordered from a menu, and were served by a server. He named the venue "restaurant," meaning a place to restore strength.

Other businessmen embraced Mr. Boulanger's idea and started serving bouillons made of meat and vegetables to the weak and sick. In 1782, Antoine Beauvilliers opened the first high-end contemporary restaurant in Paris, named it "Grande Taverne de Londres" and served his customers foods similar to what was served at Versailles and wine in bottle similar to restaurants in London. Grande Taverne de Londres remained the best restaurant in Paris for more than 20 years. The French Revolution contributed to the rise of the restaurant business in France. The revolution left several chefs unemployed. Many regional leaders moved to Paris leaving their families behind in the country side. Several restaurants opened in Paris where chefs trained in some of the best culinary schools found employments and became "restaurateurs." By 1789, there were hundreds of restaurants in Paris, and by 1810, the number went up to about 3000.

In the United States, the first French-style restaurant opened in Boston in 1794. Customers sat on single tables, the food was brought on the table, and customers served themselves. The gold rush in California (1848–1855) saw the rise of the restaurant industry on the West Coast. Expensive French food, champagne, and oysters were served to gold prospectors when they "hit it rich."

The industrial revolution whereby individuals had to perform duties far away from home and in offices also contributed to the development of the restaurant industry and convenient foods. In order to run a cost-effective business, the restaurant industry had to rely on cost-effective ingredients. It turned out that ready-made food ingredients were more cost-effective than make-as-you-go ingredients. Globalization and the development of middle class in emerging economies in Asia, Middle East, Africa, and South America are also contributing to the proliferation of restaurants in every country around the globe.

At the farm gate, produce can be classified into different categories including (1) produce that are ready to eat as food such as berries, certain fruits, and nuts and (2) produce that require further processing including coffee, milk, cereals, eggs, meat, seafood, certain fruits and vegetables, and oilseeds. However, in some cases, ready-to-eat foods can also be used as ingredients in operations such as baking or frying.

The food industry uses appropriate technologies including drying at low or high temperature and precooking at low or high temperature to provide ready-to-use ingredients or foods depending on applications. For instance, butter can be used as spread (ready-to-eat food) or as ingredient for making waffles, rolls, potato salad, or frying foods. Similarly, cheese can be used as is on sandwiches or added to dough for lasagna or pizza preparation.

Recent studies have shown that several food ingredients or ready-to-eat foods are rich in proinflammatory compounds. The following paragraphs first explain how some processing technologies turn natural produce into proinflammatory food ingredients or ready-to-eat foods. Similarly, the paragraph shows how cooking in restaurants, school cafeteria, hospital, correction cafeteria, or at home can also turn healthy produce into proinflammatory compounds for the human body.

1.2 THE MAILLARD REACTION IN FOOD PROCESSING AND COOKING

1.2.1 Definition

The MR occurs between a reducing sugar (Table 1.1) and available amine group in the amino acid lysine, guanidino side of the amino acid arginine, or imidazole side of the amino acid histidine in a protein, an amino acid, peptide, protein hydrolyzate, phospholipid, or nucleic acid (Table 1.2). Table 1.3 lists some dietary sources of reducing compounds.

1.2.2 Steps and Benefits of the Maillard Reaction in Food Processing and Cooking

In 1912, Louis Camille de Maillard, a French chemist and physician, discovered that when a reducing sugar such as glucose or fructose is in the presence of a long-lived protein such as collagen or lens proteins at body temperature, the sugar binds to the protein and the sugar–protein complex may play a major role in the development and progression of chronic diseases, particularly diabetes [1]. The reaction between such a protein and carbohydrate has been named “the Maillard reaction.” The MR occurs as part of normal human aging process but is accelerated under pathological conditions whereby the body contains unusual and unnecessary high levels of sugar.

The MR can also rapidly occur in foods during processing or cooking when a protein and reactive sugar (including lactose, which is the sugar in milk; ribose, which is the sugar in meat; fructose, which is the sugar in most fruits, honey, or most soft drinks) with or without fats are heat-treated at temperatures such as 32°C, which is as low as the cheese making temperature. The reaction is accelerated by heat and is fast forwarded when the protein and sugar react under dry heating conditions including baking, blackening, braising, broiling, frying, grilling, roasting, sautéing, or searing.

Since several food products or ingredients contain a mixture of proteins rich in amino acid lysine, arginine, or histidine and reactive sugar and are processed at a temperature close to or higher than the body temperature, the MR occurs regularly during cooking. The reaction becomes complex when nucleic acids (found in baker’s yeast) and/or lipids (fats or oils) are involved in. Food composition, type of sugar, temperature of cooking, moisture content, acidity of food, and method of cooking are very critical to the completion of MR. When the reaction occurs in presence of lipids, yeast, and temperature, more flavorful compounds are formed.

Table 1.1 Reducing Sugars and Some of Their Dietary Sources

Glucose (dextrose)	
	Grapes
	Fruits and vegetables (apple, date, fig, pepper, tomato, onion, and others)
	Grain products
Fructose	
	High-fructose corn syrup
	Maple syrup
	Watermelon
	Most fruits
Xylose	
	Corn cob
	Pecan shell
	Cottonseed hulls
Ribose	
	Meat
Ribose 5-phosphate	
	Human and mammalian cells
Sucrose (hydrolyzes into glucose + fructose during freezing, dehydration, or storage)	
	Sugar cane
	Maple syrup
Lactose (hydrolyzes into glucose and galactose)	
	Human milk
	Cow's milk
	Goat milk
	Camel milk
Maltose (glucose + glucose)	
	Malt
	Maltose syrup
L-rhamnose	
	Buckthorn
	Okra
Arabinose	
	Plant gums
Galactose	
	Lactose
	Pectin
	Mucilages

In foods, the MR is best illustrated by the crust on bread or pizza, roasted coffee, peanut or nut butter, and the dark brown color in beer, on flamed chicken, barbecued beef roast, or many other foods (Figure 1.1). As the cooking temperature increases, the MR gives food a distinct aroma and flavor that enhance the palatability of the cooked food. Broiling or grilling meat, grilling cheese, flaming chicken, frying meat or fish, searing fish or pizza, sautéing food, or roasting nuts with or without sugar all expose foods to MR.

Once initiated, the speed of the MR increases during most standard food storage conditions even in food products that contain very little amounts of water. The MR occurs in dry milk powder, condensed and evaporated milk, and protein and cereal bars during storage. The MR is amplified when the food product is stored at very high temperature.

Table 1.2 Reactive Primary or Secondary Amine Groups and Food Sources

ε-Amine group of lysine
Guanidino group of arginine
Imidazole group of histidine
Phosphatidylcholine (found in egg yolk and soyabean oil)
Phosphatidylethanolamine (found in egg yolk and soyabean oil)
Phosphatidylserine (found in egg yolk and soyabean oil)
Deoxyribonucleic acid (found in yeast)
Ribonucleic acid (found in yeast)
Milk
Cream
Butter
Egg whites and yolks
Nuts and nut fragments
Cocoa solids
Collagen and gelatin
Cereal flour and starch
Oilseed and legumes
Whey
Red meat
Poultry
Fish
Seaweeds

Table 1.3 Dietary Sources of and Reducing Compounds

Corn starch
Maltodextrins
Aldehydes
Ketones
Orthophenols
Ethanol
Fruit juices
Ascorbic acid

Figure 1.1 Classical example of MR.

1.2.3 Desirable Attributes of the Maillard Reaction

Since the discovery by Robert Ling on the malt flavor and the relentless pursuit of the MR by food scientists and engineers, several in food research and industry have doubled down on the MR for tastier and more flavorful foods. Others have looked at economic and technological considerations and investigated other attributes such as improved organoleptic, antioxidative, and emulsifying properties and even anticarcinogenic properties of the MR. Recent studies are revealing and challenging. The next paragraphs will briefly delineate some of the desirable attributes such as aroma, flavor, taste, and color that food scientists and flavorists have been encouraging when promoting the MR in food product development. Bread, biscuit, breakfast cereals, and processed milk are universal foods and typical examples of food products that draw their worldwide acceptability because of the MR.

1.2.3.1 Improved Aroma and Flavor of Cooked Foods

The MRs impart desirable aroma to the food and enhance food palatability. Both volatile and nonvolatile flavor compounds are also formed during the MR, and food manufacturers and chefs/cooks need it to improve and enhance the sensory attributes of heat-treated food. Flavor formation during the MR is the function of the type of amino acids in the protein, sugar, temperature, pH, time, and moisture content. Sugar and amino acid composition often dictate the type of flavor compounds formed. For instance, the interaction between the amino acid cysteine and ribose derived from nucleotide in meat muscle leads to the formation of sulfur-containing compounds that characterize the flavor of cooked meat. Bread, rice, and popcorn flavor is mostly associated with the amino acid proline [2]. In roasted coffee, the MR is associated with the nutty and roasted flavor/aroma, bitter, burnt, and astringent flavor/aroma.

1.2.3.2 Improved Colors and Increased Palatability

Because we eat with our eyes, toasted cereal, roasted red meat and coffee, or brewed beer have colors that make these foods or beverages very appealing to the eye. The MR imparts desirable aroma and colors that enhance the color and palatability of the foods mentioned earlier and others including pizza, lasagna, dark beer, macaroni and cheese, protein and cereal bars, and peanut butter. The list of foods that are palatable because of the MR is very extensive and can include a wide range of food products in grocery stores.

1.2.4 Undesirable Attributes and Health Significance of the Maillard Reaction

As well, several undesirable products are also formed during and depending on the extent of the MR. The early stage of MR is associated with the formation of small but very reactive molecules including glyoxal, methylglyoxal, 3-deoxyglucosone, and reductones [3–5]. It is the high chemical reactivity of these small molecules that drives the MR to the development of several undesirable molecules including advanced glycation end products (AGEs) and melanoidins. Some of these small molecules include hydrogen peroxide, acrylamide found in some types of French fries, furans found in bread crust, dicarbonyls found in some carbonated beverages and AGEs that characterize individuals with diabetes or high blood sugar, and sugar-bound insulin that cause insulin insensitivity in individuals who develop insulin resistance.

1.2.4.1 Loss of Color and Darkening of the Final Product

Excessive MR can lead to undesirable product color change. Excessive dark color on barbecued or roasted meat is a good example of excessive MR. Dark roasted coffee is another good example.

1.2.4.2 Loss of Protein Biological Value

Lysine is an essential amino acid that is in high amount in meat, egg, and fish. During the MR, the biological value of the lysine is lost. Animal studies have shown that when the MR is formed between a reducing sugar and a protein rich in lysine, the lysine in the ensuing complexes cannot be used by animals for growth. This reduction in nutritive value has also been shown in humans.

1.2.4.3 Effect on Allergenicity

Nuts contain allergens that affect more than 1% of the U.S. population, which represents more than 3 million people [6]. There are specific proteins in nuts that once ingested the consumer develops an allergic reaction. For instance, Ber e 1 protein is the major allergen in Brazil nut. Ara h 1, Ara h 2, and Ara h 3 are the major allergens in peanut. Amandin is the major allergen in almond. During MR, proteins react with sugars, and it has been shown that higher temperature unfolds the protein and exposes it more than when the nut is not heat-treated. The unfolding exposes more interaction sites and it has been shown that roasted nuts lead sensitive individuals to develop more allergic reactions. Therefore, in most cases, the MR does not reduce the allergenicity of nuts. For instance, Beyer et al. [7] investigated the allergenicity of two US varieties of peanut that were boiled, fried, or roasted. The allergenicity of Ara h 1, Ara h 2, and Ara h 3 were compared by a clinical chemistry technique known as immunolabeling using sera from eight patients allergic to peanut. Boiling and frying peanut reduced the amount of the marker of allergenicity also known as immunoglobulin E (IgE) bound to Ara h 1, Ara h 2, or Ara h 3. Roasting increased the amount of IgE bound to Ara h 1, Ara h 2, and Ara h 3 suggesting an increase in protein allergenicity. The allergenicity of peanut flour has also been reported in certain individuals [8]. Amandin is not affected by blanching, roasting, or autoclaving [9,10].

1.2.4.4 Hydrogen Peroxide

Roasted coffee is one the best known MR products. Hydrogen peroxide has been identified as a major product in MR mixture and coffee such as espresso [11]. In freshly brewed coffee, high levels of hydrogen peroxide that can stimulate inflammation have been measured [12]. The toxicity of hydrogen peroxide has been established as this oxidant enters the cell and increases the levels of oxygen radicals causing inflammation and cell death.

Coffee is such a popular beverage that research has often been controversial on the health benefits of this dark liquid. While Muscat et al. [12] reported on the high levels and toxicity of peroxide in coffee, Boettler et al. [13] analyzed several coffee extracts to identify antioxidant activities from brewed coffee. Chlorogenic acid is high in coffee. Inside the human body, chlorogenic acid is metabolized into caffeic acid. However, high levels of caffeic acid in the order of micromolar concentration are needed to demonstrate the antioxidative activity of coffee. Paur et al. [14] ascribed the health benefits of coffee to roasting, the dark roasted coffee being excellent against inflammation.

1.2.4.5 Acrylamide

Acrylamide is a well-known bioavailable neurotoxin [15,16]. Several investigators have documented in experimental animals and discussed the mutagenic and carcinogenic effects of heterocyclic compounds and acrylamide generated during the MR [17–19]. High levels of acrylamide can be detected on bread crust, in biscuits, coffee, cookies, corn chips, roasted almonds, potato products including French fries and potato crisps. While the daily intake may be low between 0.3 μg/kg body weight and 0.6 μg/kg body weight, regular consumption of food containing acrylamide can lead to organ accumulation of this carcinogen [20].

Since acrylamide was identified in foods by scientists in Europe and the United States, several studies have been performed in Sweden to determine whether there was an association between dietary acrylamide and certain types of cancer. The association between acrylamide intake and colorectal cancer was examined in a population-based prospective cohort of 45,306 Swedish men [21]. The men were followed for an average of 9.3 years during which 676 men developed colorectal cancer. It was concluded that there was no evidence that dietary acrylamide in amounts consumed by Swedish men is a risk factor for colorectal cancer. Mucci et al. [22] also found no evidence of association between dietary acrylamide consumed in Sweden and cancer of the bladder ($N = 263$), large bowel ($N = 591$), or kidney ($N = 133$). There was no association between dietary acrylamide and colorectal cancer in Swedish women [23]. Pelucchi et al. [24] who also carried a meta-analysis of epidemiological studies and found no association between acrylamide and human cancer suggested that although epidemiological studies have found no association between dietary acrylamide and cancer in Sweden further epidemiological studies that enroll large populations with broad exposure contrasts are warranted. While the epidemiological observations and analyses in Sweden have shown no association between dicarbonyls and colon cancer, these data cannot be literally translated to other countries. Rather, studies should be performed in every country where consumption of acrylamide-rich products such as French fries and roasted almonds are high.

The toxicity of acrylamide on male reproductive system has been demonstrated in animal studies and involves side effects in sperm nucleus and tail, depletion of antioxidant proteins, and testis DNA damage [25,26].

1.2.4.6 Furans

The flavor of breakfast cereals, pasta, coffee, commercial baby foods, and some infant formula is associated with the presence of compounds known as furans. Hydroxymethylfurfural and methylfurfural, which are prototypes of furans, have been identified in foods mentioned earlier [27]. The genotoxicity of the MR products has also been documented [28–31]. Whereas most coverage on hydroxymethylfurfural and furfural has been on their flavor-enhancing ability, the effects of chronic ingestion of these molecules have never been investigated. It may be useful to know the metabolism of these compounds.

1.2.4.7 Reactive Dicarbonyl Compounds

Flavor generation is one of the hallmarks of the MR. Certain carbonated beverages containing high-fructose corn syrup contain very reactive molecules known as α-dicarbonyl compounds including glyoxal, methylglyoxal, and deoxyglucosone. Some of these carbonated beverages also contain furans such as 5-hydroxymethylfurfural (5-HMF) [32,33]. Methylglyoxal is abundant in beverages containing high-fructose corn syrup as demonstrated by Tan et al. [33] who measured a range of 83.19–493.83 μg per serving size (354 mL). Tan et al. also measured methylglyoxal in diet beverages free of fructose corn syrup and found methylglyoxal at a range of 25.13–111.51 μg per serving size (354 mL). The highest levels of methylglyoxal per serving size were found in root beer (269 μg/354 mL or can), decaffeinated coffee (140.7 μg/cup), cola drinks (81.4 μg/354 mL or can), brewed coffee (75.6 μg/cup) [34], and honey (from as low as 100 mg/kg to as high as 1200 mg/kg) [35]. Argpyrimidine is a methylglyoxal-derived AGE that is formed by the interaction of methylglyoxal and arginine amino acid of a protein. Argpyrimidine has been detected at levels as high as 162 ± 9.05 pmol/mg protein in familial amyloidotic polyneuropathy patients and not in healthy control individuals [36]. Methylglyoxal binds to arginine residue in proteins to form an imidazole derivative. Methylglyoxal can bind to any short- or long-lived arginine-containing protein such as protamine P1 that packages sperm DNA in all mammals [37,38]. Binding to arginine may have a detrimental effect on the vasodilator nitric oxide productivity and efficacy. Nitric oxide is associated with erectile function. The potential side effects of too much exogenous or dietary dicarbonyls in diets on erectile function are not known. Reduced nitric oxide levels and activity impairs the cardiovascular system. Recently, Price and Knight [39] suggested that high levels of methylglyoxal in diabetes exacerbate the levels of protein-reducing sugar complex also known as AGEs, inflammation and may account for diabetes complication including immune suppression in diabetes.

1.2.4.8 Pyridines and Heterocyclic and Mutagenic Compounds

Pyridine is a volatile flavor compound in cooked meat as a result of the interaction between lipids and MR products [40,41]. Pyridines are well-known mutagens.

The presence of reducing sugars, amino acids, and large amount of creatine in meat or fish muscle creates favorable conditions for the formation of mutagenic heterocyclic amine compounds during frying-induced MR. The higher the cooking temperature, the faster and higher the levels of mutagens and carcinogens generated during the MR. Heterocyclic amines are commonly known mutagens. The level of mutagens formed is always a function of heating temperature suggesting that heating foods at temperatures below 100°C often leads to nondetectable levels of creatinine or other carcinogens/mutagens. High levels of pyridine, 3.3 μg/100 g duck meat, were detected when the duck meat was pan-fried. In charcoal-grilled duck meat up to 17.8 μg of pyridine per 100 g of meat was detected. Pan-frying and charcoal-grilling of duck meat also showed significant amounts, said 0.42 μg of heterocyclic amine formed per 100 g of meat. Heterocyclic amines from cooked meat are mutagens and carcinogens [42].

1.2.4.9 Advanced Glycation End Products

The MR generates AGEs such as carboxymethyllysine (CML), pyrraline, pentosidine, and furosine. Chronic exposure to or ingestion of AGE-rich diets (Figure 1.2) can, over time, impair the functions of cells that regulate the passage of macromolecules and circulating cells from blood to tissues also known as endothelial cells. Impairment of endothelial cells leads to or accelerates vascular dysfunction. About 10% of ingested AGEs is bioavailable. Bioavailable AGEs or AGE metabolites may interact with their receptor also known as RAGE and trigger a cascade of reactions that involve enhanced oxidative stress, inflammation, and the development of a wide range of

Figure 1.2 Fried foods combo.

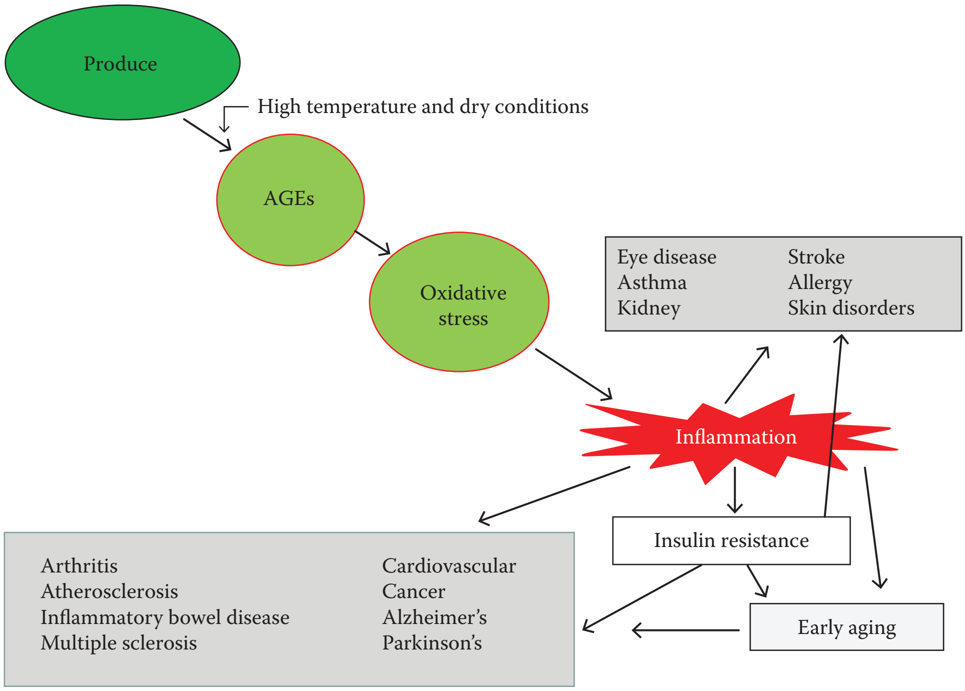

Figure 1.3 Potential effects of AGEs on the development of chronic degenerative diseases.

chronic degenerative diseases as shown in Figure 1.3. Because of AGEs association with several degenerative diseases, its inhibition or reduction in foods has been proposed and pushed by several investigators including Paul Thornalley [43–45], Helen Vlassara research group [46–49], and Thomas Henle [50–54], or discounted by others [55,56].

Recent studies have focused on the fate of dietary AGEs inside the human body. Evaporated milk, bread crust [57], breakfast cereals [58], infant formulas [59], roasted nuts and seeds [60], barbecue sauces [61], fried meat and sausages [57,62], and ice cream [63] are rich sources of CML and possibly other AGEs. Some have suggested that daily ingestion by humans of foods or beverages rich in AGEs including CML, or their precursors such as methylglyoxal and fructoselysine, increases the pool of endogenous AGEs, whereas reduced intake of dietary AGEs reduces endogenous levels of AGEs [64–66]. In one human study, 21 volunteers on high-AGE diet for 1 week gained weight and had impaired insulin sensitivity [66]. A clinical study in Taiwan investigated the association of diets with high or low levels of AGEs (pentosine, CML, and furosine) and serum AGEs (pentosine, CML, and furosine) and inflammatory markers including interleukin-1 alpha (IL-1α), monochemoattractant protein-1 (MCP-1), and glycated low-density lipoprotein (LDL) in type 2 diabetic patients [67]. Diabetic patients in two groups, one group ($N = 50$) on low daily intake of AGEs (≤ 300 μg) and the other group ($N = 68$) on high daily intake of AGEs (≥ 300 μg) were compared to control healthy subjects ($N = 74$). The study lasted 7 days during which all subjects completed a dietary record. The results showed that diabetic patients who consumed high-AGE diet had significantly higher plasma levels of AGEs, HbA1c, glycated LDL, LDL, and LDL cholesterol compared to diabetic patients on low-AGE diet and control subjects. Similarly, diabetic patients on high-AGE diet had significantly higher plasma levels of inflammatory biomarkers IL-1α, tumor nuclear factor-alpha (TNF-α), and MCP-1 compared to diabetic patients on low-AGE diet and control subjects. The activity of the antioxidant enzyme superoxide dismutase was lower in diabetic patients on high-AGE diet than diabetic patients on low-AGE diet than control subjects.

The rationale of investigating the correlation of dietary intake of AGEs and plasma levels of AGEs in diabetes patients is threefold: (1) Circulating AGEs is the hallmark that threatens the lives of diabetic patients, (2) more people are prediabetic or developing diabetes, and (3) the high medical costs and reduced productivity and life expectancy associated diabetes are causes of concern.

In the human or vertebrate body, these AGEs accumulate over the years and bind to long-lived proteins such as the plasma proteins, artery proteins, cholesterol-bound proteins also known as LDLs, lens proteins, heart proteins, muscle proteins, breast tissue proteins, and penis proteins and completely alter the functions of these proteins. In the presence of lipids, the latter react with proteins to form advanced lipid oxidation products (ALEs). A reactive sugar can also oxidize to form very small reactive compounds known as glyoxal or methylglyoxal that can combine with proteins to form AGEs. Lipids under heat can oxidize and generate glyoxal or methylglyoxal that are prone to bind to proteins and generate AGEs.

Several research groups have analyzed a variety of foods and reported that very high levels of AGEs can easily be found in a wide range of ready-to-eat foods or ingredients for humans or pets. Bacon, cheese, peanut butter, and red and poultry meat contain high levels of AGEs. Butter contains very high levels of ALEs. For instance, raw milk has undetectable levels of AGEs, but the processing of milk generates a wide range of food ingredients or products that are enriched in AGEs. As shown in Figure 1.4, from milk we obtain fresh milk, butter, condensed milk, cheese, and powder milk. Butter is made by churning milk and is highly enriched in saturated fat. Butter is also high in ALEs. Sweetened condensed milk is made with high levels of sugars allowing the MR to take place in the presence of milk proteins and the heat treatment used for sterilization. During storage, the MR proceeds and more AGEs are formed during storage until consumption.

Cheese is produced at a temperature that is warm and AGE formation increases during cheese ripening and early storage. It has been shown that during prolonged storage, AGE levels decrease, but it is not known what the by-products of AGEs are. Powder milk is produced by spray drying liquid milk on a very hot surface to generate dried particles. The high temperature facilitates or

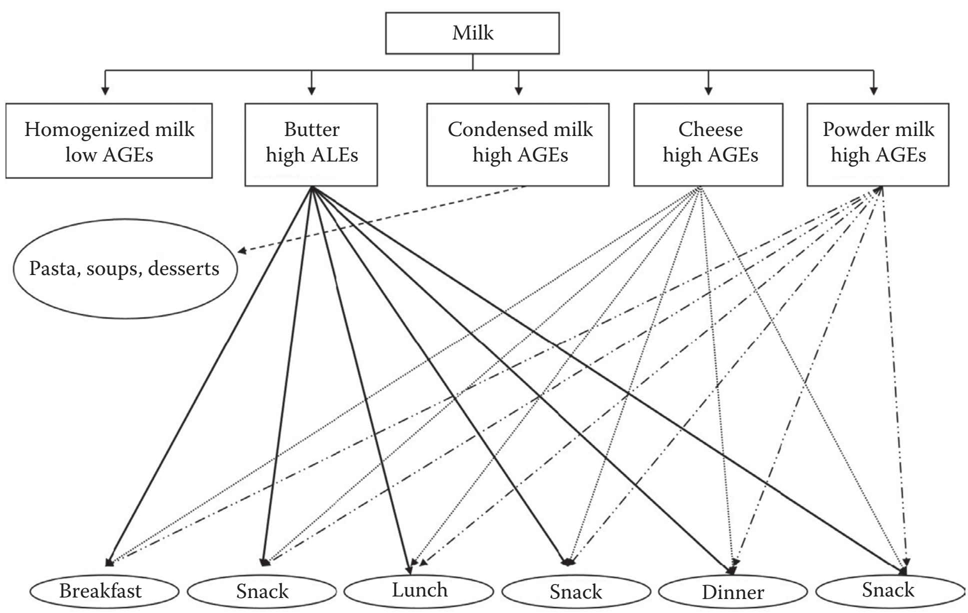

Figure 1.4 The MR during milk processing and the domino effect of a food or food ingredient containing high levels of AGEs.

exacerbates the MR giving a resulting milk powder that is very rich in AGEs. Storage of milk powder, whether nonfat or high fat, exacerbates the MR and the formation of more AGEs. Given the prevalence of butter, cheese, or milk powder in cooking at home or restaurant, a silent killer (AGEs) gets into food unnoticed and is consumed daily as often as people can consume foods containing milk products. Even if minute amounts are consumed at every meal, at the end of the day because these AGEs are present in every piece of food from breakfast to movie theater popcorn, the cumulative effect is that substantial amounts of AGEs are ingested every day. When most individuals rely on the very same dietary pattern where AGEs are found everywhere, AGEs become part of daily ingested unhealthy compounds (Figure 1.4).

Peanut butter is full of AGEs and not really health enhancing. Since peanut butter is AGE- and ALE-rich and can be consumed all day long in different types of foods including bread sandwich, cracker sandwich, cookies, and cereal bars and other different types of snacks, peanut butter is an excellent, although perhaps unwelcome, carrier of AGEs and ALEs into the human body (Figure 1.5).

The domino effect of red meat can also be presented. Nowadays, red meat can be consumed at breakfast, lunch, dinner, and in snacks (Figure 1.6). Due to the omnipresence of AGEs in red meat, spreading red meat consumption through all the daily meals may not be a good idea for healthy living.

Fructose is the sweetener in many food products from breakfast foods and beverages to evening-time beverages and foods. Because fructose is very reactive, fructose is a good precursor of AGEs. And because fructose is found in almost every food and beverages offered in commerce, fructose-containing foods are excellent warehouses of AGEs. Consumption of these foods and beverages leads to body accumulation of AGEs or AGE precursors such as methylglyoxal (Figure 1.7).

Some investigators have argued that there was no evidence that ingested AGEs accumulate inside the human body [55,68]. Others have reported that AGEs such as CML-modified human

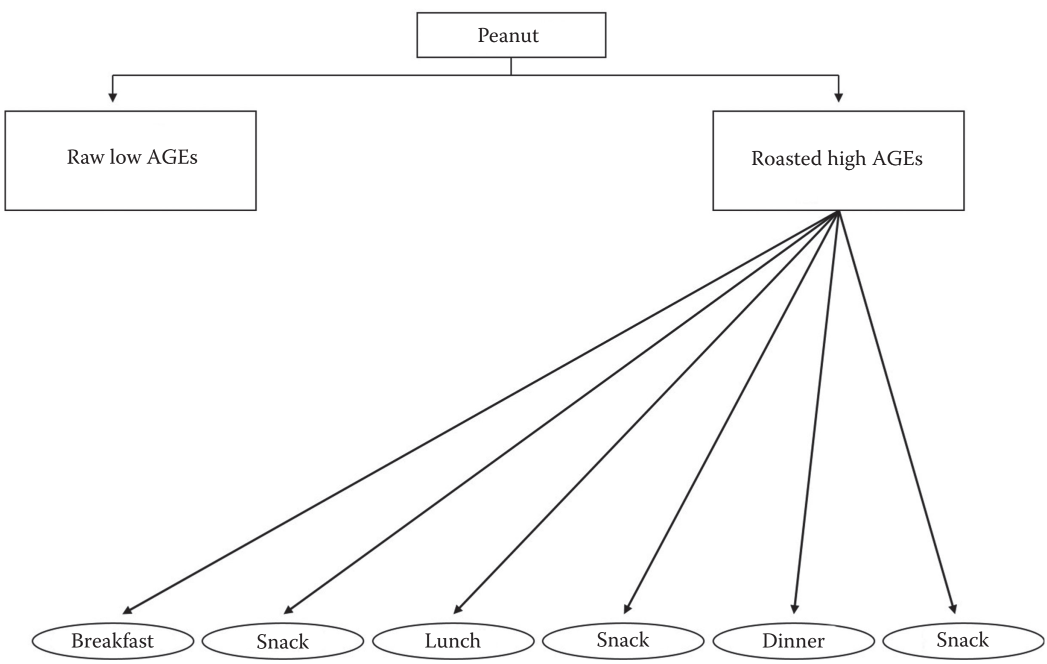

Figure 1.5 Peanut butter as an excellent source of AGEs and the domino effect of peanut butter as a source of high levels of AGEs.

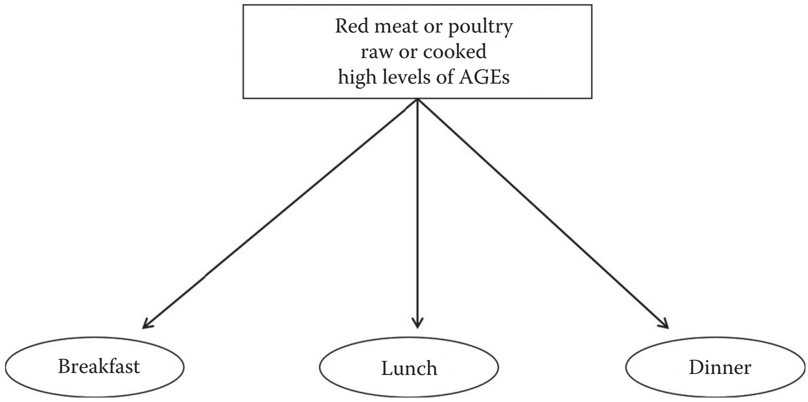

Figure 1.6 The domino effect of raw or cooked red meat as a source of high levels of AGEs.

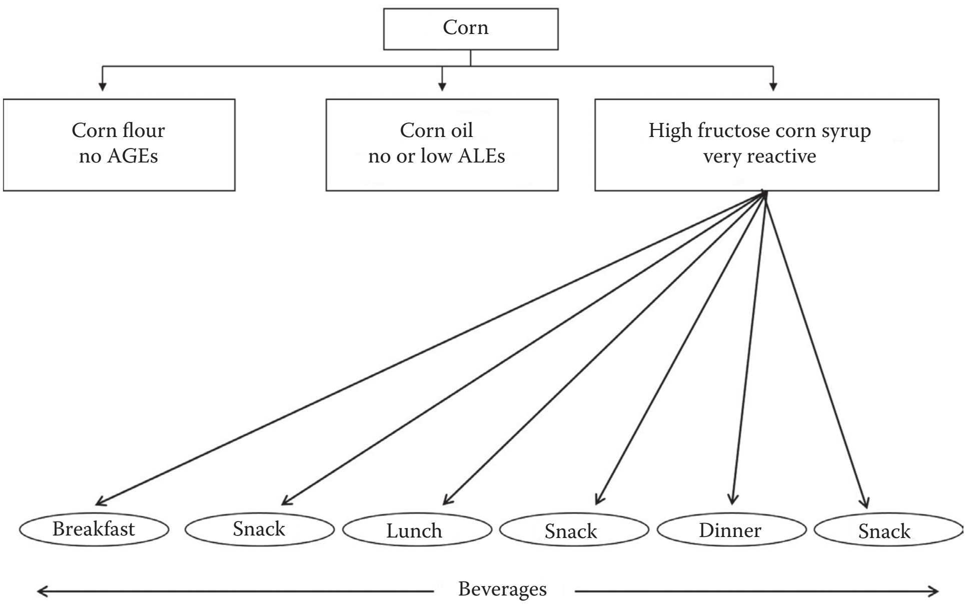

Figure 1.7 The domino effect of high-fructose corn syrup in food products.

serum albumin or glycolaldehyde-modified β-lactoglobulin are unable to bind to their receptor RAGE [69,70]. However, there are more investigators who have pointed out the negative effects of dietary AGEs on human health [56,71] than those who promote AGEs as health enhancing.

1.2.4.10 Insulin Glycation

Sugar–insulin complex also known as glycated insulin leads to decreased efficacy of insulin overtime (Figure 1.8). Abdel-Wahab et al. [72] were first to report the presence of glycated insulin in the pancreatic islets of normal animals and elevated levels of glycated insulin and proinsulin within the pancreas islets in both insulin-dependent and independent diabetic animal models. The same group injected glycated and nonglycated insulin to mice and observed that the extent of insulin glycation was inversely related to insulin biological activity and could

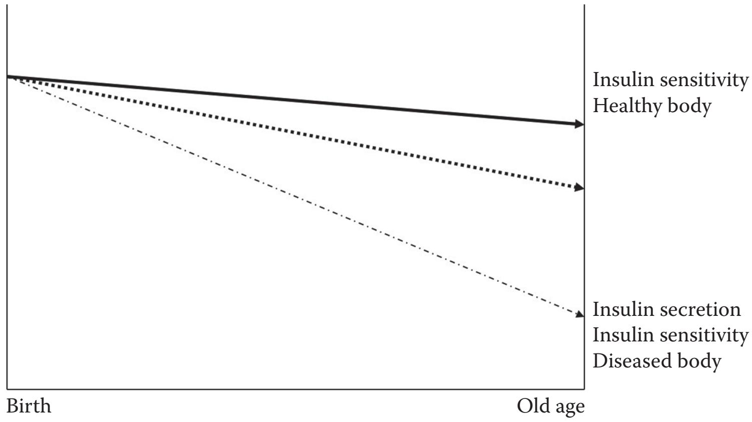

Figure 1.8 Reduced insulin sensitivity due to insulin glycation.

be related to glucose intolerance in diabetes [73]. They also questioned if glycated insulin could also be identified in humans with diabetes. McKillop et al. [74] demonstrated the presence of glycated insulin in the plasma and islets of diabetic animals supporting the hypothesis that glycated insulin plays a role in the pathogenesis of diabetes. McKillop et al. [75] also identified glycated insulin as a significant proportion of total circulating insulin in both humans and animals with type 2 diabetes. They suggested that glycated insulin may exhibit impaired biological activity including glucose clearance compared to native insulin. Finally in 2003, Lindsay et al. [76] demonstrated the presence of elevated levels of circulating glycated insulin in type 2 diabetic subjects. Recently, Oliveira et al. [77] showed that methylglyoxal, a precursor of AGEs found in baked foods, honey [78] including manuka honey that has high levels of methylglyoxal [79], and several soft drinks [33] can modify insulin and impair insulin biological activity including glucose regulation. While the antibacterial activity of honey is ascribed to methylglyoxal, the in vivo health benefits of this molecule are food for thought when honey is added to foods.

Can the MR products formation be prevented? Yes! Go to Chapter 7, please.

1.3 CARAMELIZATION

Caramel is one of the most extensively used colorants by the flavor, drug, carbonated soft drink, and beverage industries. It is obtained by the process known as caramelization whereby sugar is heated at temperature higher than 149°C or above its melting point under alkaline (pH 9) or acidic conditions (pH 3) in absence of a nitrogen-containing compound such as amino acid, peptide, or protein. Crème brulée and Madeira wine are a delight for many food connoisseurs around the world. These two products are typical examples of caramelization products. Caramelization can occur in the presence or absence of water. In the same food, caramelization and MR may occur simultaneously. For instance during bread baking, starch is degraded into small reducing sugar molecules and the reducing sugar can be part of both browning reactions. As the pH of the reaction increases to alkaline region or the acidity decreases, thermal degradation of fructose generates high levels of reactive carbonyl compounds that polymerize into brown compounds. The chemical and physical properties of caramel products depend on temperature, pH, and heating time. Caramel products are a mixture of volatiles and nonvolatiles with a wide range of molecular size [80].

There are four types of caramels, Type I–IV, obtained when food-grade sugars are heated with

1. Sodium hydroxide (class I)
2. Sodium hydroxide and sulfur dioxide mixture or in the form of sodium sulfite or metabisulfite (class II)
3. Ammonia (class III)
4. Sugar heated with sulfur dioxide and ammonia as is or sugar heated with ammonium sulfite, ammonium hydrogen sulfite, sodium sulfite, sodium hydrogen sulfite, or sodium metabisulfite (class IV)

The only color allowed in vinegar, alcoholic beverages including whisky, beer and liqueur, soft drink beverages, desserts, ice cream, and malt bread is caramel. Information on the specifications for caramel colors can be obtained in Licht et al. [81]. Caramel I has no net charge, Caramel Color II and IV carry negative charge, and Caramel III carries a positive charge. Most soft drinks contain negatively charged tannins derived from plant barks or roots and as a result most soft drinks are negatively charged. To avoid flocculation/precipitation of the tannins, soft drink manufacturers select caramels with isoelectric point below the beverage pH. Because most soft drinks have pH around or below pH 3, class IV caramel, which has a pI between 0.5 and 2.0, is often selected and is stable in citric or phosphoric acid. Non-cola beverages with pH >3.5 can accommodate and remain stable with class I caramels including DDW #525, 528, or 570, which are slightly negatively charged. Class III caramel including DDW #301 and 304 has a pI between pH 5.0 and pH 7.0. This class caramel is used for a soft drink commonly used in Latin America under the name of Malta because this beverage is positively charged and has a pH around 4.0.

Caramel also protects food or beverage flavor from light deterioration. Caramel can substitute for gums and be used as emulsifiers in beverage formulations containing essential oils. In soft drinks caramel dosage varies from lowest in ginger ale (0.002%) and increases in products such as apple drinks, cream soda, Malta, energy drink, guarana, root beer, and cola (0.45%). Additional information on the use of caramel single-strength versus caramel double-strength can be found at www.caramel.com.

1.4 CURRENT AND FUTURE DIRECTIONS IN MAILLARD REACTION

The MR is as old as human civilization, although it was formally discovered in 1912 and was right away associated with diabetes. For decades, the food and beverage industries used it to develop flavorful and tasty food products. Since the 1970s, the association of the MR with chronic diseases has been investigated in research laboratory and clinics around the world. Despite the plethora of information on the potential health side effects associated with chronic consumption of MR product–rich foods, research findings have not completely translated into public warnings sufficient enough to move the majority away from reducing the consumption of MR product–rich foods. While several reasons can be put forward to explain the slow progress toward reducing the consumption of MR product–rich foods, it is important to suggest that the majority of people cannot think out of the box to develop tasty and flavorful foods without using reducing sugars, amino compounds, and high temperatures. However, the next chapters will show that it is possible to eat tasty and flavorful foods without the MR.

As more and more consumers become aware of the risks over benefits associated with the MR, there will be less abuse of the reaction as it has been in recent years with increased consumption of broiled, fried, and roasted foods. At the same time, the culinologists, chefs, and food scientists are being challenged to develop tasty and flavorful foods and beverages that are either MR product–less or MR product–free. Knowledge of the factors that affect the reaction is important to guide food developers into moving away from chronic use of the MR.

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Figure 2.2 Potential health risks associated with chronic consumption of Maillard reaction-rich food products.

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90. Anese M, Nicoli MC, Verardo G et al. Effect of vacuum roasting on acrylamide formation and reduction in coffee beans. Food Chemistry 2014;145:168–172. PART II The Maillard Reaction and Health Disorders The Maillard reaction products also known as advanced glycation end products (AGEs) bind to

their receptors and induce oxidative stress that in turn induces low-grade inflammation. Chronic

low-grade inflammation upgrades to inflammation. As a result of chronic inflammation, insulin

resistance develops. Insulin resistance is the common denominator for several chronic inflamma

tory degenerative diseases including obesity, diabetes, hypertension, kidney, atherosclerosis, osteo

porosis, eye health, multiple sclerosis, erectile dysfunction, insomnia, Parkinson's disease, cancer,

and Alzheimer's disease. Therefore, unhealthy diets link the Maillard reaction products to several

chronic degenerative disease development. Through each chronic disease, the risk factors and the

association or lack of AGEs have been established. Dietary approaches to prevent the development

of the disease are presented and protective foods are suggested.

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Chapter^>5: Diabetes Mellitus

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Figure 9.13 Edamame.

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PART III Champagne, Caviar, Good Cuisine, and Ice Wine

Part III entitled “Champagne, Caviar, Good Cuisine, and Ice Wine” invites the reader to enjoy

life and embrace food as a lifelong weapon against some disease development. You are what you eat.

The gut is the epicenter of healthy life, suggesting that healthy gut is healthy life. The most coveted

diets including the Western, traditional Mediterranean, and Okinawan diets are discussed. The diets

of the centenarians who live in the “Blue Zones” and remain active members of their communities

at very advanced ages are also described. The differences between the Western and Mediterranean

diets are revealed.

A healthy pantry at home or away from home is the starting point for healthy eating. The reader

is invited to think out of the traditional box and develop a healthy pantry. Food preparation tech

niques including their advantages and disadvantages are presented. Responsible entities and adults

should know how to address healthy eating to the children and youth because they represent the future and can develop better eating habits. Laisser le bon temps rouler with champagne, caviar,

good cuisine, and ice wine because after all life should be good.

Chapter^>17: Healthy Gut, Healthy Life

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Figure 17.7 Probiotic in liquid yogurt.

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Chapter^>20: Food Preparation Techniques and Potential Health Benefits

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Chapter^>22: Champagne, Caviar, Good Cuisine, and Ice Wine

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