

# Chocolate: A Marvelous Natural Product of Chemistry

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Chocolate, a natural product, is as much a part of our daily lives as television or cell phones. Nevertheless, most of us are completely unaware of the complex chemistry and technology involved in the production of a simple chocolate bar. Beginning chemistry students are rarely exposed to natural products and can benefit by becoming aware of the complexities of chemistry in nature. In an age when students frequently question the relevancy of their chemistry class, what could be more relevant than a study of chocolate?

## History

Chocolate in one form or another has been around for a very, very long time. While there is a lot of folklore about the history of chocolate, only the more verifiable facts will be dealt with here. It is likely that chocolate can be traced back to the early Olmec civilization (1500–400 B.C.E.), the first human civilization in what is now southern Mexico and Central America. The Maya established the first known cocoa plantations in the Yucatan Peninsula. The first European encounter with cocoa came with Columbus on his fourth and final voyage to the New World. However, Columbus apparently never tasted chocolate and sailed off to Panama in pursuit of gold. Other Spaniards, invading the Yucatan Peninsula and Mexico in the early 1500s, quickly discovered that cocoa beans were of great value. They were used to produce a highly prized drink and were also used as currency. Around 1500 C.E., 100 cocoa beans could purchase one slave or 10 beans could purchase a rabbit or the services of a prostitute (1).

While the Spanish recognized the value of cocoa beans, they were originally repulsed by the drink. Gradually, they began to accept it, but transformed it from a cold, bitter, and frothy drink to a warm, sweet, and spicy one. The natives made their cocoa frothy by pouring the beverage from a height from one vessel to a second. The Spaniards beat it with a large wooden swizzle stick to obtain the froth.

The first documented arrival of cocoa in Spain was in 1544 and the first official shipment of beans reached Seville from Veracruz in 1585. Chocolate found great popularity in the Spanish court during the first half of the 17th century, and its appeal gradually spread through the aristocracy of Europe. It was considered to have great medicinal value, which only increased its popularity. Additionally, it was known throughout Europe that the strong taste of chocolate made it an effective disguise for poison (2)!

This popular drink was very fatty by modern standards. In 1828, the Dutch chemist Conrad van Houten devised a method to press out some of the fat from the cocoa bean. This fat is called cocoa butter. In the same year, he developed the “Dutch” process, which is the addition of alkali (potassium or sodium carbonate) to chocolate. Originally, the pro-

cess was thought to increase the solubility of cocoa, but in fact only darkens it and improves its dispersability. In 1847, Fry & Sons combined the cocoa butter with other non-pressed (i.e., full fat) cocoa and added sugar to produce the first chocolate bar. Almost 30 years later, Swiss innovator Henry Nestlé, inventor of condensed milk, and Swiss chocolatier Daniel Peter collaborated and added dried milk to produce the first milk chocolate. Rudolph Lindt further improved the flavor and texture of the product in 1879 with the introduction of a kneading process called conching. These changes proved popular and soon national variations developed (3).

The name “cocoa” (or “cacao”)<sup>1</sup> is thought to be borrowed from the Mixe-Zoquean language family and was originally *kakawa*. It was so esteemed that it was named “food of the gods”; hence, in 1735 Linnaeus gave it the scientific name, *Theobroma cacao*.<sup>2</sup> The earliest Aztec name for chocolate drink was *cacahuatl*, “cacao water”. While there is a vigorous and often humorous discussion about the true root of the word chocolate, it is clear that in some way, the Spaniards transformed it into chocolatl, which then easily became chocolate (4).

## From the Cocoa Tree to the Chocolate Bar

Cocoa beans are the seeds of the *Theobroma cacao* tree. While originally native to Central and South America, the tree is now cultivated in suitable environments around the world in an area within 15 to 20 degrees of the equator. It is an unusual tree in that it forms flowers from small cushions on its trunk and large branches (see pages 1074 and 1076). The small flowers are pollinated by midges and produce pods that vary from 100 to 350 mm in length and weigh from 200 g to 1 kg when mature. The pods contain 30 to 40 almond-shaped beans surrounded by a sweet pulp. Since these beans are bitter, it is likely that the sweet pulp first attracted humans to the cocoa (5, 6).

The pods ripen in five to six months and are harvested by hand. They are opened with a knife or a wooden club and the beans are scooped out. The beans are heaped together in a pile or placed in a box and covered with banana leaves so that outdoor fermentation can begin. Fermentation lasts from five to seven days, depending on bean type and growing area. The beans are then dried for one to two weeks to remove moisture and produce a hard bean, suitable for shipping to the manufacturer. Roasting of the bean follows.<sup>3</sup> Roasting may last from 70 minutes to almost two hours and is absolutely essential for the full development of chocolate flavor and aroma. The shell is next removed from the “nib” (kernel) in a process known as winnowing. The nib is then ground in a process that generates enough heat to melt the cocoa butter in the bean and form a liquid called “chocolate liquor”. The chocolate liquor is non-alcoholic and is composed of about 55% fat, 17% carbohydrate, 11% protein, and most of the remainder is tannins and ash. Depending

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on its source, it may also contain theobromine, an alkaloid related to caffeine, in quantities ranging from 0.8% to 1.7%. Caffeine is found in lesser quantities. Theobromine and caffeine are both methylxanthines. Theobromine is a smooth muscle stimulant, while caffeine is predominately a central nervous system stimulant. When solidified, the liquor forms bitter (unsweetened) cooking or baking chocolate (7).

Next, the liquor may be pressed in a process that subjects it to pressures of 40 to 50 MPa. This yields the rich and highly saturated cocoa butter, as well as a dry cake that can be ground and sifted to produce drinking or baking cocoa powder. Basically, all manufactured chocolate confectioneries are chocolate liquor with optional additions of sugar, cocoa butter, cocoa solids, and condensed or dried milk.

Products differ by the quantity of the various ingredients present. First, these ingredients must be blended to produce a homogeneous mixture. This so-called chocolate crumb mixture is then combined with the proper quantity of cocoa butter to adjust the fat content to the desired level. The chocolate crumb must now be refined by precision steel roll refiners, which pulverize the crumb into smaller, more uniform particles. Typical particle size is now about 20  $\mu\text{m}$  (0.02 mm). This refining produces chocolate with a smoother "mouth feel".<sup>4</sup> Next, this paste is subjected to the conching process, which causes both flavor and textural changes in the chocolate paste. It is so-named because the original conches resembled seashells. This stage can last anywhere from 72 to 96 hours.

Near the end of conching, the fat content is standardized and an emulsifier, usually lecithin, is added. The critical operation of tempering follows. Chocolate is polymorphic and can be made to crystallize in five to six different crystalline forms. However, only the stable, higher melting forms will give chocolate its characteristic snap, gloss, and texture. Tempering involves cooling the chocolate so that most of its crystalline forms are present. It is then reheated to liquefy the lower melting forms and leave the most stable crystals as seed crystals when the chocolate is eventually cooled. The quality of the raw materials and the end products are tested by a variety of analytical methods as well as sensory evaluation (8, 9).

**Table 1. Compounds Identified in Chocolate**

Compounds	Aliphatic Type	Aromatic Type	Heterocyclics	
Hydrocarbons	15	32	Pyrrroles	10
Alcohols	23	5	Pyridines	8
Aldehydes	18	6	Quinoline	1
Ketones	25	5	Pyrazines	74
Esters	44	12	Quinoxalines	3
Ethers	8	3	Oxazoles	4
Nitrogen Compounds	9	4	Furans	19
Sulfur Compounds	12	2	Pyrones	4
Acids	22	15	$\gamma$ -Lactones	6
Phenols		7	Thiazones	3
Total	176	91		132

During the year 2001, Americans consumed 3.3 billion pounds of chocolate, yielding an estimated \$13.1 billion in retail sales. If countries are ranked by per capita consumption, the Swiss consume the greatest quantity at 22.36 pounds per person. Americans rank 11th with a consumption of 11.64 pounds per person. Chocolate manufacturing is a serious business (10).

## Chemical and Physical Changes during Processing

Chocolate is a natural food and is a mixture of many chemical compounds. In fact, approximately 400 compounds (Table 1) have been identified in chocolate following fermentation and processing (11).

### Curing

As stated earlier, the mature cocoa bean must be fermented if any chocolate flavor is to develop. This is known as curing. Fermentation can be carried out several different ways but all depend on heaping a pile of fresh beans, along with enough pulp for microorganisms to produce heat, while limiting access to air. What actually happens during fermentation is still the subject of much research and is not entirely clear. The rotting is initiated by the wide range of microorganisms present when the pod is opened. Apparently, the beans briefly germinate but are soon killed by the high temperature and acidity present. This is important, as non-germinated beans do not produce a chocolate flavor in the finished product (12).

Biochemical transformations within the bean lead to the formation of numerous flavor precursors. Flavor precursors are chemicals that react to form other substances, which ultimately produce the chocolate flavor. Amino acids and peptides are the major nitrogen-containing flavor precursors formed during an anaerobic phase. During an aerobic phase, many oxygen-controlled reactions occur. Acetic acid, the major acid formed during fermentation ( $\text{CH}_3\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$ ), and the heat generated during fermentation are responsible for the bean death mentioned above. Proteins and polypeptides react with polyphenols to give a brown color (13).

### Drying

During the drying phase, moisture and volatile or low-boiling acids, such as acetic acid, are lost. The characteristic brown color of chocolate develops. The resulting beans are less astringent but still bitter.

### Roasting

Roasting or controlled heating of the cocoa beans is probably the most important step in processing. The chemical reactions in this process are often appropriately called the "browning reactions" but are also referred to as carbonyl-amine reactions, non-enzymatic browning, or Maillard reactions. These are a complex set of reactions that occur between amines, usually from proteins or amino acids, and reducing sugars such as glucose, fructose, maltose, or lactose in the presence of water. While it is tempting to try to characterize these reactions with a few specific examples, it is important to recognize that in the realm of natural products, many reactions occur concurrently with a variety of starting materi-

als and yield different intermediates and products. The intermediates may or may not have a flavor of their own. Some act as catalysts or inhibit further reaction. These are the reactions that are responsible for the complex products that impart the characteristic flavor, texture, and color to cooked foods. They may be separated arbitrarily into three stages, and each stage may have numerous interacting steps that are difficult to further separate.

The simplest and best-understood step is the initial step as shown in Figure 1. As an example, a primary amino acid and a carbonyl group from a reducing sugar (D-glucose) or aldehyde condense to form a compound that then isomerizes or changes its orientation in space. This is important because later reactions cannot occur without these rearranged end products. Characteristic chocolate aromas can be produced by thoroughly mixing equal volumes (a spatula full each) of amino acids such as threonine, leucine, or glutamine with glucose in 10 mL of water and heating to 100 °C in a water bath.

It is the intermediate stage that allows for the generation and interaction of many compounds that yield the numerous flavor components or flavor notes. Figure 2 shows how these reactions begin with the isomerized products from the initial stage (Figure 1) and suggests how the intermediate products may react to form final products. While some

of these reactions have been characterized, the chemistry involved, such as the Amadori rearrangement and Strecker degradation, is far too complex for beginning chemistry students. The term "browning reaction" comes from the final stage. It is at this point that the dark brown pigments, the insoluble melanoidins, are formed.

The structures of the melanoidins are poorly defined. They are reported to possess molecular mass of up to 100,000 Da. However, no single melanoidin has been isolated or characterized. They come in a large range of flavors and are chiefly responsible for much of the color that develops when foods are baked, roasted, or toasted (14–17).

## Composition

In addition to the previously mentioned components, chocolate liquor contains about 55% of a fat called cocoa butter. A sample of cocoa butter can easily be obtained by placing three or four squares of baking chocolate (solidified chocolate liquor) in a 25-mm × 150-mm test tube and warming undisturbed for four to five days in a 38–40 °C oven. The cocoa butter separates out and rises to the surface of the liquid. It is pale yellow in color and has the distinctive aroma of chocolate. This is a dramatic way to demonstrate that chocolate is indeed a mixture of various ingredients.

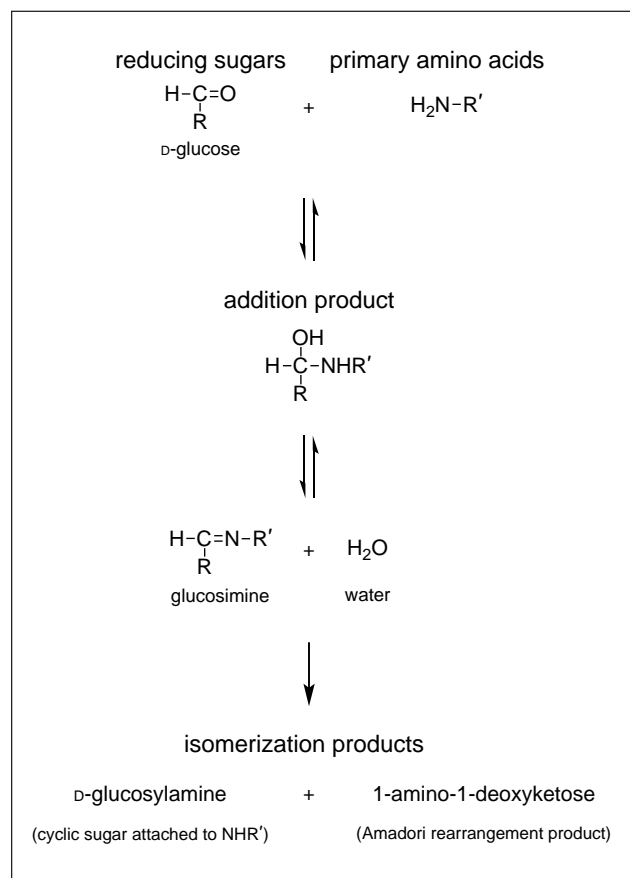


Figure 1. The initial stage of the browning or carbonyl–amine reactions is shown as a reaction of a reducing sugar with a primary amino acid to form addition products, which ultimately yield isomerized end products.

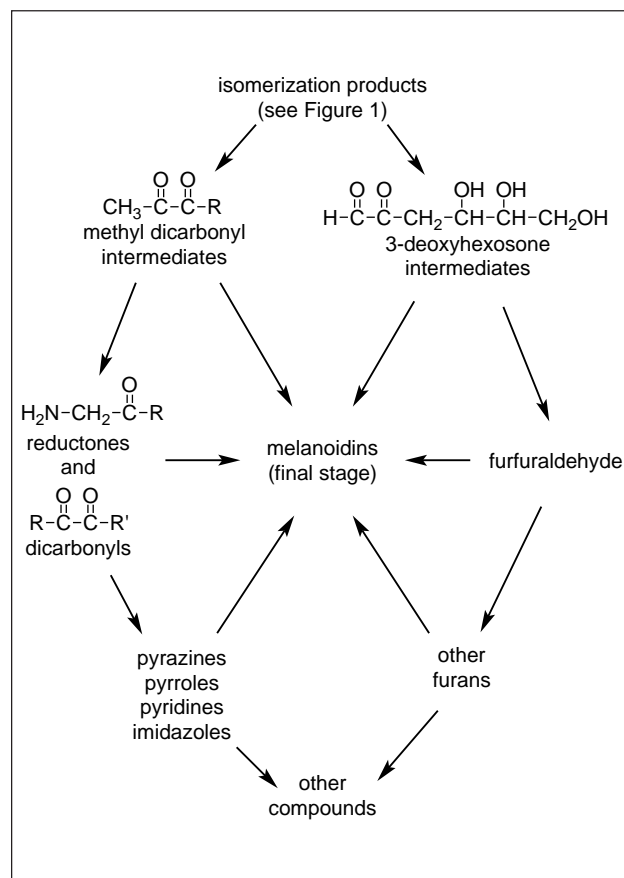


Figure 2. The intermediate stage of browning or carbonyl–amine reactions shows how complex these reactions are and suggests how the intermediates may react to form the final melanoidins.

All fats are mixtures of triglycerides; that is, three fatty acids<sup>5</sup> are attached to a glycerin backbone, which might be described as appearing like a capital E. It is interesting to note that the melting properties of a particular cocoa butter depend on the region of its production. Generally, the nearer to the equator that the tree is grown, the softer (lower melting) the fat. These differences can be accounted for by the different triglycerides present in cocoa butter.

### Different Crystalline Forms

As mentioned previously, chocolate is polymorphic. Some fats have only one stable form while others have three, which are designated alpha ( $\alpha$ ), beta ( $\beta$ ), and beta prime ( $\beta'$ ) as identified by X-ray diffraction criteria. When two or more crystal forms give the same X-ray diffraction pattern, they receive the same name but are distinguished by subscripts ( $\beta_1$  and  $\beta_2$ ) in order of decreasing melting points.<sup>6</sup> Cocoa butter can crystallize in six forms, in the following order: gamma  $\rightarrow$  alpha  $\rightarrow$  beta<sub>2</sub>'  $\rightarrow$  beta<sub>1</sub>'  $\rightarrow$  beta<sub>2</sub>  $\rightarrow$  beta<sub>1</sub> (Figure 3). These are arranged from least to most stable. As the structure becomes denser and lower in energy, it becomes more stable and more difficult to melt (18).

When liquid cocoa butter is cooled, a range of crystal types may be present. It is thought that the unstable crystals are those in which the internal pattern creates stresses, which eventually cause a realignment of triglycerides into the stable beta forms. When the unstable crystal is formed, it releases only a small part of the heat of crystallization. Subsequently, when the unstable crystal undergoes polymorphic transformation to a more stable form, latent heat of crystallization is released, causing a rise in temperature.

The appearance of white crystals on the surface of chocolate, which is often incorrectly thought to be mold, is known as "chocolate bloom". The combination of residual liquid cocoa butter and the latent heat of crystallization push the fat between the solid particles and onto the surface of the chocolate, resulting in bloom. To keep chocolate from "blooming", it is necessary, therefore, for the chocolate maker to ensure that the cocoa butter is in the beta<sub>2</sub> form when used to make a confectionery. Bloom can also occur if the chocolate is left in the sun, allowed to melt and recrystallize without tempering.

### Tempering

Tempering turns out to be more complicated than it may appear. Any seed crystal will cause crystallization. However, the seed needs to be of correct size and well distributed throughout the chocolate. The chocolate is cooled to temperatures where the alpha and beta<sub>2</sub>' forms are produced. It is then sheared thoroughly to form many smaller crystals before it is reheated to convert the unstable crystals to stable ones. This is done by a tempering machine, and the actual temperature used depends upon the fats present in the chocolate (19).

Recall that when chocolate solidifies, latent heat of crystallization is given off. This information is used by the manufacturer to determine whether the chocolate is correctly tempered. The manufacturer simply produces a cooling curve. A plot is made of the temperature versus time. If the distribution of seed crystals is uniform, the chocolate will set

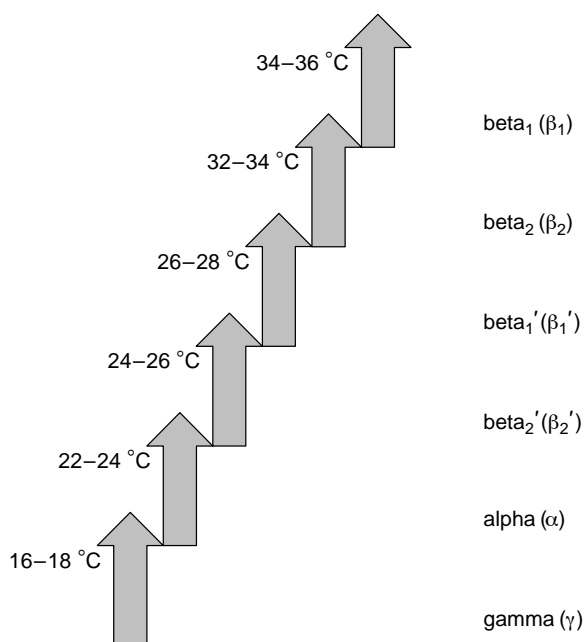


Figure 3. Various polymorphs of cocoa butter crystallize at different temperatures. Forms beta<sub>2</sub> and beta<sub>1</sub> are the most stable and therefore the highest melting.

quickly. As it does, the latent heat is released, offsetting the cooling effect of the ice, causing a rise in temperature and producing a plateau in the cooling curve.

There is an interesting laboratory experiment suitable for advanced high school students where it can be demonstrated that the cooling curve for a sample of cocoa butter (obtainable at a local pharmacy) depends on two things—the temperature to which the sample is heated and the temperature of the cooling water bath.<sup>7</sup> If the sample is heated to 33 °C, only beta crystals remain and act as seed crystals causing crystallization to occur above 25 °C. When the SAME sample is warmed to 50–60 °C, all the crystals are melted resulting in crystallization of the lower melting crystal forms. If the temperature of the cooling water bath is held at 17°, the latent heat of crystallization will be observed in both cases. This is an exciting contrast to the typical cooling curve generally done in first year chemistry. It is important for students to recognize that natural products such as chocolate are mixtures and are not the pure compounds they are accustomed to encountering. For the details and the complete laboratory experiment, email the author or see ref 7.

### Chocolate and Viscosity

No survey of chocolate would be complete without mention of its viscosity. A Newtonian fluid is one whose viscosity depends solely on the temperature and pressure of the system. Non-Newtonian fluids contain solid particles that result in the viscosity being related not only to temperature and pressure, but to shear (tangential force per area) applied as well. There are three general types of non-Newtonian fluids: shear thinning (thixotropic), shear thickening (dilatant), and those in which the viscosity depends not only on the rate of shear but its duration. Chocolate is thixotropic, as are mayonnaise, margarine, and catsup.



The thixotropic nature of chocolate can be demonstrated by warming a Hershey's Kiss at 40 °C for 30 minutes on a Petri dish. Generally heating reduces viscosity and increases flow properties. However, the chocolate retains its shape and can be tipped almost vertically without starting to flow. (Careful, it may fall off the dish!) If force is then applied with a spatula, the chocolate will spread or flow easily because it is shear thinning. That explains why it is so easy to burn chocolate in a microwave—it does not appear to be melting.

Since cocoa butter and chocolate liquor are essentially Newtonian fluids, the addition of sugar and milk solids must cause the deviant behavior. In order to ensure an acceptable mouth feel, these solids are very finely divided. As the number of particles increases, the intermolecular attractions increase, producing clumps or aggregates. Additionally, the finer the particle size, the greater surface area to be coated by cocoa butter therefore reducing the liquid cocoa butter that is available for free flow; hence, the reason for chocolate's non-Newtonian behavior.

Consider what might happen as a force is applied to the liquid. First of all, the clumps or aggregates due to intermolecular attractions will be physically broken up and the chocolate will flow. The viscosity will decrease. The effect of this becomes more pronounced as the shear rate is increased; hence, the shear thinning behavior of chocolate (20–22).

### Acknowledgments

I have been using the properties of chocolate to teach chemistry for about ten years. In 1990, I received a Science Technology and Society grant from the American Chemical Society for the development of a high school curriculum using chocolate as the focal point. I am grateful for the wealth of information and encouragement received from Phil Pflaumer (Procter & Gamble, Miami Valley Laboratories, Cincinnati, OH) and Paul S. Dimick (Penn State University) both of whom are now retired. Thanks to Edward Seguine of Guittard Chocolate in Burlingame, CA. He has supported me with information and a lot of chocolate to be used in my presentations or workshops over the years!

### Notes

1. There is often confusion about the use of cacao or cocoa in describing the production of chocolate. The term "cacao" tends to be used as the botanical name when referring to the tree, pods, and unfermented beans from the pods. I have chosen to use "cocoa" throughout to simplify matters.

2. *Theobroma* means "food of the gods" in Latin; there is no bromine in chocolate.

3. There are three different methods of roasting cocoa. For a complete description see ref 6, pp 35–36.

4. Mouth feel refers to the degree of grittiness. If the particle size is larger than 30 μm (0.03 mm), the chocolate feels gritty or

sandy on the tongue.

5. Fatty acids are organic acids, saturated and unsaturated, that occur naturally in fats.

6. There are two nomenclatures used to describe chocolate polymorphs. The chocolate industry tends to number them I–VI, while the fats and oils industry prefers the Greek letters.

7. There are a number of laboratory experiments suitable for high school students described by Beckett in *The Science of Chocolate* (6) and Tannenbaum in *Lessons in Chocolate* (7).

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The structures of caffeine and theobromine discussed in this article are available in fully manipulable Chime format as JCE Featured Molecules in JCE Online (see page 1232).

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