

Chocolate and Health

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TÁMOP-4.1.1.C-12/1/KONV-2012-0014

"Élelmiszerbiztonság és gasztronómia vonatkozású egyetemi együttműködés, DE-SZTE-EKF-NYME " projekt segítségével jött létre

Introduction

Probably there isn't another group of food products that is as popular as the confectionery products. Who doesn't like chocolate in different flavours and shapes? But candies are just as popular, and they also can be found in wide variety on the store shelves. One of the physiological reasons for the popularity of confectionery products is that people prefer the sweet taste out of all the basic tastes. Another reason is hidden in the characteristics of the products. The ingredients and the production technologies provide a wide range of variety in products that is unique among food products. Besides several foreign products we can find many national and even hungaricum products like szaloncukor, cherry liqueur chocolates, Dianás cukorka, Negro candy or Tibi chocolate.

In recent years the potential harmful effects of sweets become the center of attention due to the increased influence of media. On the other hand just like there isn't a food product with only positive health effects, there isn't a food product with only negative health effects as well. Obviously we compare good quality and - from a food safety point of view - impeccable products. The confectionery products differ in structure and in composition. Thus their effects on health is also different. There are certain products with higher and lower nutritional value as well.

It is a little known fact that the bioactive compounds that can be found in chocolate (flavone derivatives) have a unique free radical chelator ability. Another important physiological effect can be attributed to the alkaloids in cocoa beans which enhance the endorphin production of the body, thus not only a putative but a real "happy feeling" can be connected to chocolate consumption.

Furthermore it is also remarkable that there are many confectionery products that have a significant amount of dietary fiber, so they have a place in a healthy diet.

Between main meals the blood sugar level of the human body decreases, which leads to feeling tired and discomforted. This is not the same as feeling hungry. Consuming a certain amount of sweets increases the blood sugar level, and the feeling of well-being restores.

In connection with consumption we must emphasize the importance of self control, of course not only regarding sweets... The energy density of sweets is very high, in

other words that means that products with relatively small mass release a great amount of energy. Obesity – one of the endemics of our time – cannot be seen as the result of only one product or one group of products. We need to realize that our energy intake and expenditure has to be in balance with each other. If this harmony is disrupted for a longer time, obesity is inevitable. In summary the problem isn't caused by one or a few products, but by the decomposition of balance.

Cookies and chocolate always were and still are an important part of the survival kit of military pilots, and it's also known that the troops of Hannibal carried honey biscuits with them. But of course sweets are mainly meals of our peaceful days and holidays.

The popular Hungarian treat, cherry liqueur chocolates (WHAT) can be given as a gift on many occasions, and through its production technology (HOW) and the introduction of its machines (WITH) the reader will be introduced to the most common methods and ingredients (FROM) of the confectionery industry, also touching the environmental and economic effects of the production. Cherry liqueur chocolates are real hungaricums, its production started at the turn of the last century in the famous Gerbeaud factory. This chapter tries to give an answer to the 'WHY' question by presenting a product that requires a lot of different technological solutions during its production.

However the authors aspire to cover everything, it is inevitable that the detailed review of many ingredients, machines and technologies will be left out due to limited quantity reasons. A great help for the creation of the chapter were a lot of books written by Ferenc Mohos, which we recommend to anybody who wants to dive deeper into the subject.

1. Confectionery products and their characteristics

1.1 Nutritional biological aspect of confectionery products

A lot of products with different content and physical characteristics make up the group of confectionery products. What's common in these products is the sugar content and because of that the sweet taste and high energy content, the great enjoyment value and the pleasant flavor. The sweet taste is the most favored taste of mankind, almost everyone regardless of age and sex love sweet tasting foods. Unfortunately because of the high energy content excessive consumption has big risks, which isn't the fault of the confectionery industry, but the result of inappropriate consumer behavior. It is a proven fact that the body needs carbohydrates which according to our knowledge can be covered mainly from slowly degrading starch. Mainly but not only, because occasionally the body needs rapidly-digested sugars (simple sugars) too. Take for example athletes, blue collar workers or tasks that require great mental input like a difficult test or exam. If we would like to remain fair, we have to take into account all the studies that focus on the positive physiological effects of sweets. For example the article of Waterhouse and his co-workers called Lancet (1996) published in a prestigious scientific paper is about the antioxidant compounds of chocolate. People of ancient Indian cultures also experienced the fact that is proven today: chocolate contains numerous physiologically useful bioactive materials that help to retain mental health and decrease the production of free radicals in the organism. The polyphenols that can be found in cocoa powder and chocolate play an important role in the regulation of the blood cholesterol level.

As it was mentioned before simple sugars are essential for the body. The most important simple sugars are: the most common sugar in nature the grape sugar or glucose and fructose found in higher concentrations in fruit and honey also called fruit sugar. Cane and beet sugar (sucrose) is the most significant one in our everyday life, which is a disaccharide that is formed when a glucose and a fructose molecule are joined together and a molecule of water is removed from the structure. Sucrose is mainly produced from sugarcane or sugarbeets, the two names of sucrose refer to the basic ingredients as well, however chemically the same substance is derived from both of these materials. That is commonly known as sugar. We use this in our households as granulated sugar and powdered sugar, and that makes the confectionery industry sweet.

1.2 Product knowledge – Definitions

The confectionery industry can be divided into the following groups based on the ingredients and the technology of the products:

Candy making

hard candy has an amorphous structure and is made out of carbohydrate syrup soft candy is made out of a carbohydrate mixture of fluid and solid phases (fondant) caramel is made out of a carbohydrate syrup with additional substances (milk, cream, coffee, malt etc.)

products made with gelling agents (gummi candy, gels)

candy-like fruit products (candied fruit)

products made with the extract of the roots of the liqourice plant (black licorice)

sugar containing mixtures (lemonade powder)

pressed and poured pastilles

icings

dragées

products with high sugar content made from oily seeds (marzipan, persipan, nougat) fillings

Production of cocoa and chocolate

Products of cocoa beans processing without sugar:

cocoa

cocoa butter

cocoa powder

Powdered mixtures, cocoa and chocolate powders

Chocolates and desserts:

chocolate bars (dark, milk, white chocolates)

filled chocolates

covered chocolates

Production of bakers' confectionery

-cookies

-honeyed cakes

-long lasting crumpets

-wafers

Production of coffee and coffee-substitutes

-roasted coffee beans

-coffee substitutes

Regulation of confectionery products

The regulations for confectionery products can be found in the Codex Alimentarius Hungaricus which consists of three volumes and of course refers to other foods as well:

Vol. I. contains the guidelines of the European Union – these are mandatory in every member state

Vol. II. contains the regulation of those products that aren't regulated by the European Union, but have regulations in Hungary. If a manufacturer uses the same names for its product that are defined in Vol. II. then it has to be regulated by it.

Vol. III. contains the examination methods that are used for defying the parameters stated in Vol I-II.

The European Union finds the regulation of cocoa and chocolate products so important that it published a separate compulsory guideline that got its place in the first volume of the Codex Alimentarius Hungaricus (later as CAH or MÉ) numbered MÉ-1-3-2000/36. (the number 1 refers to the first volume, the number 3 stands for 3rd modification).

The MÉ 2-84: Confectionery products means that it's in Vol. II. and it is the 84th products group, this discusses the characteristics of confectionery products (except for cocoa and chocolate products).

Definitions

MÉ-1-3-2000/36: Cocoa and chocolate products (Abstract from Hungarian Codex Alimentarius)

1§

This definition states that cocoa and chocolate products are classed according to supplement one.

4§

This regulation came into effect in 2007. january 1 and simultaneously the first edition of MÉ 1-3-2000/36 ratified in 2001 was revoked.

5§

This regulation contains the 2000. june 23. 2000/36/EK parliamentary guideline for cocoa and chocolate products.

Supplement one for regulation 1-3-2000/36 The names, definitions and characteristics of products.

Names and definitions

Cocoa butter

Cocoa, cocoa powder

Fat-reduced cocoa, fat-reduced cocoa powder

Powdered chocolate, chocolate in powder

Drinking chocolate, sweetened cocoa, sweetened cocoa powder

Chocolate (dark)

It is produced from cocoa products and sugar, fulfills the terms in point b., contains at least 35% total cocoa dry matter, out of which there is at least 18% cocoa butter and at least 14% no-fat cocoa dry matter.

but if the names is supplemented with these words:

"vermicelli" or "flakes": products consisting granulated or flaked parts have to contain at least 32% total cocoa dry matter out of which there is at least 12% cocoa butter and at least 14% no-fat cocoa dry matter.

"couverture": The products has to contain at least 35% total cocoa dry matter out which there is at least 31% cocoa butter and at least 2,5% no-fat cocoa dry matter Milk chocolate

Family milk chocolate

White chocolate

Filled chocolate, chocolate with filling, chocolate with centre

Chocolate a la taza

Chocolate familiar a la taza

Pralines

Bite-sized chocolate that is

Filled chocolate or

Solid chocolate or a type of chocolate defined in points 3., 4., 5., 6., and the combination of other foods, supposedly if chocolate takes up at least 25% of the total weight of the product

Optional permitted ingredients

Calculating percentages

Sugars

The sugars in this regulation are not confined to those that are recited in the regulation MÉ 1-3-2001/111 "Sugar confections for human consumption".

VEGETABLE FATS REFERRED TO IN ARTICLE 2(1)

The vegetable fats referred to in Article 2(1) are, singly or in blends, cocoa butter equivalents and shall comply with the following criteria:

they are non-lauric vegetable fats, which are rich in symmetrical monounsaturated triglycerides of the type POP, POSt and StOSt;

they are miscible in any proportion with cocoa butter, and are compatible with its physical properties (melting point and crystallisation temperature, melting rate, need for tempering phase);

they are obtained only by the processes of refining and/or fractionation, which excludes enzymatic modification of the triglyceride structure.

In conformity with the above criteria, the following vegetable fats, obtained from the plants listed below, may be used:

Usual name of vegetable fat	Scientific name of the plants from which	
	the fats listed can be obtained	
1. Illipe, Borneo tallow or Tengkawang	Shorea spp.	
2. Palm-oil	Elaeis guineensis, elaeis olifera	
3. Sal	Shorea robusta	
4. Shea	Butyrospermum parkii	
5. Kokum gurgi	Garcinia indica	
6. Mango kernel	Mangifera indica	

Furthermore, as an exception to the above, Member States may allow the use of coconut oil for the following purpose: in chocolate used for the manufacture of ice cream and similar frozen products.

MÉ 2-84; Confectionery products (extract)

Alcoholic filling: filling of different compositions (eg. fondant) containing at least 2% alcohol or fruit preserved in alcohol or alcoholic drinks etc.

Fondant: a polydisperse system, which on average contains 10-25 micrometers long sucrose crystals (solif phase) and saturated sugar solution (liquid phase); in the liquid phase sucrose, glucose syrup and other carbohydrates (invert sugar, fructose, sorbitol) are dissolved and a small amount of air is also present in form of bubbles.

Hand-made dessert: a dessert, whose main manufacturing procedures are carriead out by hand.

1.3 The evolution of pralines, history of the product

The praline as the name indicates is a bite-sized sweet. Instead of praline it is often referred to as dessert as well, but we must emphasize that the name "praline" can only be used if chocolate constitutes not less than 25 % of the total weight of the product. The production of pralines is made up of two stages: making of the chocolate mass and the preparation of other elements (eg. filling).

Conception and spreading of fondant manufacturing

The first fondant candy was made in France, and it spreaded from here across Europe, thus in Hungary as well. Fondant is a sugar mass made by the crystallization of a supersaturated solution, to which they add some kind of acid, which inverts the sugar to some extent. In the beginning they simply cooked the sugar mass in a cauldron over fire. After cooking they placed the cauldron in water in order to cool it while stirring it to create the microcrystalline structure. In Hungary Stühmer and Gerbeaud were the two confectioner who implemented fondant manufacturing, they were the first to use the tabulating machine in the 19th century, which was a double hulled, water cooled tabulating machine. The mechanization of fondant manufacturing is also related to their work.

The spreading of chocolate manufacturing in Hungary

The first written documents about Sebestyén Baldi making chocolate in Buda are from the 1700s. Back then pharmacists were the ones to make chocolate. In the beginning of the 19th century confectioneries and consumers covered their demand by imported chocolate. In 1845-46 the first chocolate factory was founded by Mátyás Dremmel, later Ferenc Heidrich and Frigyes Stühmer made chocolate in Hungary. Unfortunately Heidrich and Dremmel's economic failure threw back the Hungarian chocolate manufacturing as well, both of them were making only chocolate products which weren't enough to stay on the market. Stühmer besides chocolate manufacturing also made candies. After that many factories were founded that produced chocolate or had mixed manufacturing profile. Such factories were: Fiume Chocolate Factory, Péter Weisz, Lajos Schmidt, Károly Wikus, Emil Gerbeaud. Preservation of fruits

Fruits at first were preserved in honey, spirits and must in households, later the method was used in the pharmaceutical industry and then in confectionery. Honey processors preserved fruits in honey, later the method of preservation in sugar spreaded too. In the 17th century preservation of fruits in alcohol and by boiling spreaded gradually from households to the industry.

The history of the evolution of cherry liqueur chocolates

In Hungary confectioners could engage themselves in chocolate manufacturing from 1859, this circumstance led to the elaboration of chocolate specialities. Henrik Kugler opened his first, soon-to-be-famous confectionery on Gizella Square in Budapest. Not having any successors he asked for the help of a Swiss confectioner (Finaz) to recommend him somebody. So Emil Gerbeaud arrived in Hungary from Switzerland in 1884, who was the descendant of a famous family of confectioners. The young man became an excellent successor to Kugler. In 1886 he built a small chocolate factory in his shop which later was relocated in Duna Street in 1904. He started to make chocolate sweets out of which his invention the cherry liqueur chocolate and the chocolate dragée, which then spreaded across the world as Gerbeaud specialities." (Gundel-Harmath, 1979. 294.)

The cherry liqueur chocolate was made with two technologies. The old method is based on the use of formed shells which was filled with a single cherry preserved in pálinka, and with fondant diluted with cherry juice then the shell was closed with chocolate. After filling and freezing the chocolates are removed from the moulds and wrapped. "Another method for making cherry liqueur chocolate, the hand dipped cherry liqueur chocolate around the 19-20th centuries was introduced by Róbert Gnosz the production leader of Gerbeaud, and the Hungarian confectioners get acquainted with the technology through Gerbeaud. The production was widely known in Hungary in the first half of the 20th century." (Borsódy, 1995. XLII.)

At the turn of the century two confectionery receipt books mention chocolate sweets, but the receipt of cherry liqueur chocolate cannot be found in any of them. So the technology of chocolate cherry liqueur obviously was a secret of the shops (eg. Gerbeaud). After the death of Emil Gerbeaud (1919) the cherry liqueur chocolate was marketed as it can be found in Lelóczky's price-list with the date of 1926. october 5. where it was advertised with the price "1kg cognac-cherry K110000" and later in the

price-list without a date (around 1930): "Lukács r.t. Price-list of chocolate and sweets – fondée 1892 – Budapest VI. Andrássy road 70.".

Later on it became the favorite product of the upcoming and populous city public, and became an elegant gift.

1.4 Types and groups of dessert products

Grouping of soft candies (Identification number: MÉ 2-84/03)

Fondant candy (Id number: MÉ 2-84/03/1): it is made out of fondant mass, natural flavorings and additives (eg. fruit particles, oilseeds, marzipans, persipans, milk-derivatives, cocoa powder, cream, etc.) perhaps with the use of artificial flavourings and colourings, by molding in different shapes.

Jelly sweets (Id number: MÉ 2-84/03/2): They are gelatinous with easily deformable structured colloid systems, which are made with sugar, glycose syrup, or invert sugar syrup, different gelling agents and additives (flavourings, colourings) formed by molding and are covered with a protecting layer (sugar, chocolate, etc.)

Gummi candy (Id number: MÉ 2-84/03/3): it is made with sugar, glycose syrup or invert sugar syrup, different gelling agents (gum arabic, gelatin etc.), it is a flavoured and coloured, rubbery, flexible soft candy formed by molding

Desserts are products made without coating or by dipping, forming and filling from corpora of different types and shapes.

Note:

For coating and forming chocolate, coverture chocolate, milk chocolate, coverture milk chocolate, white chocolate and other coating masses (cocoa, milk with cocoa etc.) are used.

The production technology of desserts

Similarly to nugats, desserts can be real or dessert-like products.

Manufacturing of traditional and handmade dessert types. Their main ingredients are sucrose, oilseeds (almonds, peanuts, walnuts), semi-finished confectionery products (french fondant, chocolate mass), processed fruit (cherry preserved in spirits, candied fruits), alcoholic drinks (egg flip, rum, liqueurs).

There are desserts in fancy boxes and unique desserts as well (cherry liqueur chocolates, chocolate-flip cakes, egg flip cakes). Today handmade desserts are rarer and quite expensive. For example you can buy items like this in the Százszorszép fany box. They typically contain real layered nougat cubes coated with chocolate,

brittles, nougat pastilles and marzipans etc. Handmade cherry liqueur chocolates also belong here. They are made with the use of cherries preserved in 70% alcohol. Then they are dipped in fondant and chocolate with chocolate seconation on top.

The ingredients of machine-made sweets are the same as handmade sweets. Mass production is cheaper, for example they can produce desserts on a Cavemil production line too. However machine-made sweets don't fall back too far behind handmade sweets in terms of selection, but they serve the demands of a different clientele.

Dessert-like products contain non-noble nougats or simply fondant corpora that are coated with chocolate.

1.5 Marketing of specialities and Hungaricums

Cherry liqueur chocolates are considered a Hungaricum, a Hungarian product that has no match in the world.

On the Hungarian chocolate market the share of pralines showed 16 percent in 2003 and 2004. The leading role was taken by non-alcoholic pralines with 50% of the shares, after them came the alcoholic desserts with 22% and the mixed products with 28%. Considering their prices this order stands still, non-alcoholic pralines are the most expensive then the alcoholic and the mixed pralines follow them. The price difference is proximately 800 forint/kg between the non-alcoholic and the mixed pralines.

The centre of the production and distribution of cherry liqueur chocolates is still the capital. Fundy Inc. and Red Cherry Inc. produce around 800 tons of handmade cherry liqueur chocolates a year, while by mechanical method Bonbonetti Inc. (formerly: Stollwerck-Budapest Confectionery Inc.) produces proximately 750-800 tons annually. Another major company on the market is Szerencsi Bonbon Inc.

Recently a couple smaller company outside this region attempts to manufacture this product. Some of these companies however use coating mass instead of chocolate. These products cannot be called 'cherry liqueur chocolates', who does this commits food adulteration.

Bonbonetti Inc. patented the name and the graphic of packaging: in 1994 in Hungary and in the EU countries the name 'cherry liqueur chocolate', in 1997 the name 'Cherry Queen' and its graphic in Hungary and many other European countries.

2. Typical ingredients of confectionery products

2.1. Materials of fondant manufacturing

Sugar (sucrose,cane or beet sugar) is the most important disaccharide. It is a white, chrystalline compound, soluble in water. In acidic solution it hydrolyzes and breaks down to two components, glucose and fructose. The result of hydrolysis is a 1:1 ratio compound of glucose and fructose is called invert sugar. Invert sugar is less prone to crystallization.

In Hungary the most important raw material for sugar production is sugar beet.

The most significant commercially used types of sugar:

crystal sugar: relatively big in size, white or yellowish

refined crystal sugar: quite small particle size, whiter in colour

sugar cube: granulated sugar is pressed into bars, then dried and cut into cubes powdered sugar: crystal sugar is ground into powder. Its disadventage is that it's hygroscopic thus in moist places it agglomerates.

A good quality sugar is white, odourless, its crystals have the same size, its sucrose content meets the required value. (MÉ 2-83 principle)

Glucose syrup is made from the hydrolysis of starch. Its carbohydrate content is made up of glucose, maltose and dextrins.

Two types of glucose syrup:

glucose syrup: made with acidic hydrolysis, contains more glucose than latose or dextrins.

maltose syrup: made from the amylase-enzymic hydrolysis of starch, where maltose is dominant.

Glucose syrup is essential for two reasons: it increases the solubility of sugar in water, makes it possible to create an amorphous (glass-like) sugar structure, in which sugar is not crystallized but solved. This charachteristic is important in the making of certain products.

Characteristics of glucose syrup:

water content: around 80%

DE-equivalent (dextrose-equivalent): 35, 45% (hereinafter for the sake of simplicity we count with 40%, which is usually matches the most common value)

Invert sugar syrup

It is made from the acidic or invertase enzymic hydrolysis of cane/beet/sugar – where the ratio of glucose and fructose is 1:1.

Isosugar: around half of the glucose from the complete hydrolysis of starch is converted into fructose by isomerization, the content of the resulting solution is very similar to the content of the invert sugar syrup, its water content is aound 30%, in confectionery industry its use is limited, but it is essential in soft drink industry.

2.2. Ingredients of products containing cocoa

After decreasing the cocoa butter content of the cocoa mass (by pressing) we get the cocoa cake, after powdering it we get cocoa powder. The quality of cocoa powder can be improved by alkaline, enzymatic or watery digestion. The basis of alkaline digestion is that we add alkali-carbonate, hydrogen-carbonate, ammonium carbonate etc. solved in water to the heated (70-75°C) cocoa mass. Due to the effects of these materials the polyphenol compounds of the cocoa mass become claret in colour in an alkaline medium, and a part of them forms a condensational product which gives water-insoluble, dark coloured pigments. After that the digested cocoa powder is pressed, that way the cocoa butter content decreases from 55% to 10-24%, after cooling it is ground and packed. The cocoa powder is usually around 10-12%.

Vegetable fats used in confectionery

The confectionery industry mainly uses three types, their grouping happens according to their use:

Cocoa butter

Cocoa butter alternatives

Cream fats

The difference between the 2nd and the 3rd types is in their consistency. We will discuss this question in the following.

Cocoa butter

Cocoa butter is a vegetable fat extracted by different methods (pressing, extraction) from cocoa beans. In solid form it has pale-yellowish colour, when melted it is yellow. Its colour when melted cannot be darker than the colour of a 0.2% potassium-dichromate solution. Its flavour and odour is significantly aromatic, pleasurable. Its consistencyat room temperature is solid, fragile if we start rubbing it without warming it up we get an unspreadable powder which due to pressing coheres again.

Chemically cocoa butter is a mixture of triglycarides, it also contains a small amount of physiologically important fat-soluble vitamins and other biological active substances. The percentage compositin of cocoa butter is the following:

Table 1. The composition of cocoa butter

Components	Composition (%)
glycerides	97-99
free fatty acids*	0.5-2.0
unsaponifiables	0.2-0.5
water	0.01-0.03
ash	0.006-0.02
purines**	0.005-0.03
* - converted to oleic acid	

** - mainly caffeine

The types of triglycerides affect the physical behavior and charachteristics of cocoa butter. Its favourable melting properties are provided by having big amounts of triglycerides whose middle fatty acid group is unsaturated. The percentage composition of fatty acids found in the triglycerides of cocoa butter and the types of these triglycerides are the following:

Table 2. Triglycerides and their compositions

Fatty acid	Composition (%)	Triglyceride	Compositon (%)
Palmitic acid	23-30	PUP	14.1
Stearic acid	32-37	PUS	39.3
Oleic acid	30-37	SUS	27.4
Linolic acid	2-4	PUU	6.4
		SUU	8.9
		other	3.9

P – palmitic acid

S – stearic acid

U – unsaturated acids (oleic, linolic acid)

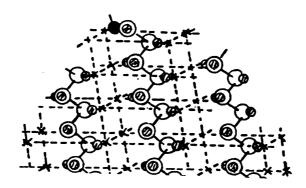


Fig. 1. Crystalline structure of fatty acids

The colour of cocoa butter produced with properly guided and carried out technological processes is pale-yellow, it is homogeneous in mass according to the stable modification (there's no crystal modification) and its melting properties are favourable (homogeneous crystals).

Physical and chemical indices give us information about the quality of cocoa butter. In case of fine quality cocoa butter these are the following:

Cloud point	32.8-35.0°C
Clearing point	31.8-35.5°C
Pour point	30.0-31.5°C
Acid value	1.6-6.0
Acid index	0.9-3.4
Saponification value	192-197
lodine value	33.5-38.0
Peroxide value	2

Table 3. Characteristics of cocoa butter

If we comply the parameters of production and storage cocoa butter can be stored for years without deterioration. It has great resistance against rancidity when stored in a place shielded from light, that is because of the fatty acid composition and the antioxidants found in the unsaponifiable part (0.008% tocopherol).

Cocoa butter makes up the coherent dispersion of the chocolate mass and during the tempering of the chocolate mass we have to create the most unstable type V β

crystal form of cocoa butter, then during molding the cocoa butter rate of chocolate mass (approx. 30-38%) has to crsytallize in this modified crystal form. Optimally the type V β crystal form converts quite slowly into truly stable type VI β crystal form.

So the technologically suitable – the least unstable – crystal form is the type V β crystal form, which is important because:

the unstable crystal forms transform slowly into VI β crystal forms, while heat releases, which melts a certain amount of cocoa butter and this melted coca butter diffuses on the surface of chocolate slabs where it sets and creates a greyish layer, this process is called fat bloom.

the rigid properties of well tempered chocolate are more favourable, conchiodal fracture

the contraction of type V β crystal form is the highest, thus well tempered chocolate can easily be removed from the metal molds unlike wrongly tempered chocolates, the rate of contraction is about 7%.

The contraction of cocoa butter during crystallization (cooling from 30°C to 10°C):

Table 4. The contraction of the crystal forms of cocoa butter

α crystal form (unstable)	7.0%
IV-β' crystal form (unstable)	8.3%
V-β crystal form	9.6%

(More about the crystal forms of cocoa butter see in reference)

Cocoa butter alternatives

To reach the desired consistency with cocoa butter alternatives we need a certain part of the oleic acid to create an ester with the central alcoholic hydroxyl of the glyceride. This can be achieved by technically fractionated crystallization and transesterification. With crystallization we secure the desired gross fatty acid composition, and with transesterification we secure the proper distribution of fatty acids inside the glycerine molecule.

There are cocoa butter equivalent (CBE) and cocoa butter improver (CBI) fats and cocoa butter substitutes (CBS) containing lauric acid and cocoa butter replacers (CBR) not containing lauric acid.

CBE and CBI fats can be added to chocolate with a maximu of 5%, while CBS (eg. palm kernel oil) and CBR (cottonseed oil, palm oil, soy oil) fats can only be used in compound chocolates. These fats don't require tempering, and their brilliance and

contraction are excellent. However their incompatibility with cocoa butter raises concerns.

Characteristics	Pressed cocoa butter	Coberine Calvetta	Illexao TYP JL		
				3092	3096
Refractive index nD40	1,4576	1,4579	1,4573	1,4611	1,4586
Flow melting point 0C	32,5	32,6	28,8	35,5	35,9
Clear melting point 0C	34,1	34,3	30,8	44,0	46,9
Difference of two melting points	1,6	1,7	2,0	8,5	11,0
Pour point 0C	33,5	33,9	31,9	38,1	36,4
Penetration at 200C					
50 g cone	0,5	0,5	0,5	0,5	0,5
100 g cone	2,0	2,2	2,1	2,7	2,2
200 g cone	5,0	7,0	7,2	8,4	7,2
400 g cone	13,8	16,8	16,3	18,1	17,3
800 g cone	26,2	28,3	27,5	29,0	29,8
thermopenetration with					
100 g cone					
20 0C	1,5	1,6	1,6	1,8	2,0
22 0C	1,7	1,8	1,7	2,0	2,3
24 0C	1,8	1,9	1,8	2,2	3,0
26 0C	2,5	2,8	2,4	3,0	4,8
28 0C	5,5	6,5	6,6	4,4	8,7
Thermopenetration with 100 g cone					
30 0C	15,7	18,0	19,2	5,7	16,8
32 0C	37,2	52,5	39,8	8,2	26,7
Composition with gaschromatography analysis					

1. caproic acid C6 %	0	0,6	traces	0	0
2. caprylic acid C8 %	0	0,1	traces	0	0
3. capric acid C10 %	0	0,3	traces	0,1	0,1
4. lauric acid C12 %	0	2,0	traces	0,1	0,1
5. myristic acid C14 %	traces	0,8	0,8	0,1	0,2
6. palmitoleic acid C16-1	0,3	0	0	0	0
%					
7. palmitic acid C16 %	29,4	34,4	60,1	4,0	27,3
8. stearic acid C18 %	33,6	27,8	8,1	52,7	36,6
9. oleic acid C18-1 %	33,3	30,8	28,3	37,0	31,5
10. linoleic acid C18-2 %	2,8	2,8	2,1	4,5	3,6
11. linolenic acid C18-3 %	0,2	traces	0,2	0,2	0
12. arachidic acidC20 %	0,4	0,4	0,3	1,1	0,7

Characteristics of confectionery cream fats

Their name indicates well their main use: they are ingredients of different creams. Their characteristics are determined by two main demands:

proper quality keeping in watery media as well (acidic media), proper resistance against oxidation, anti-oxidation and anzymic and alkaline hydrolysis, but it's worth to mention that against enzymic and alkaline hydrolysis none of the fats is resistant, not even cocoa butter!

their consistency has to be similar to butter, so that we can make a cream with traditionally pleasant consistency

The use of butter in confectionery products is limited by its unsatisfying shelf life, because it can become rancid relatively easily. On the other hand the great advantage of butter is that apart from milk fat it contains protein too, which helps the formation of a more stable emulsion. Because of this confectionery cream fats are usually added to the product with protein or other emulsifier to create an emulsion in which the coherent phase is a watery solution that contains the flavours of the cream (fruit aroma + flavouring acid). The way we create an O/W emulsion.

However most if the confectionery cream fats are used to make nougat-like creams which have a water content of 1-2%. In these the coherent dispersion is the melted

cream fat – for the proper distribution of the 1-2% water and to keep the emulsion we use emulsifiers.

We can use cream fats in many products, so these must have satisfying shelf life from many perspective, unless we want to use differents fats for every product which is also very problematic. With keeping some technological rules we can solve a lot of tasks by choosing the right fat. These rules are:

We must work with such seeds and milk derivatives that don't contain lipase enzyme (eg. mold); the lipase enzyme can break down the most stable fats and an unpleasant, soapy taste developes in the fat, which can turn a lot of products unconsumable by humans.

Confectionery cream fats cannot have fatty acid fractions that contain shorter carbon chains than C12, because these can cleave easily from the glycerine molecule

It's very useful if the cream fat contains anti-oxidants, because these can prevent rancidity; currently in Hungary the use of propylgallate is permitted with 0.2%, in some places BHA is permitted (butylated hydroxyamisole) as well, before using anti-oxidants we have to revisit the related provisions (dosage, utility etc.). According to experience common soy lechitin has some anti-oxidant effects, and it is used widely in confectionery as an emulsifier.

It is significant to the consistency characteristics of cream fats that around $20^{\circ}C$ – room temperature – certain fractions are melted but they only melt fully when heated to body temperature (approx. 35-36°C). At this temperature we get a homogeneous fluid mass. This means that in a wide range of temperature cream fats have a plastic, creamy consistency.

The comparison in Table 6. shows that what are the main differences between the dilatation characteristics of cocoa butter and a cream fat:

0C	Cocoa butter	Cream fat
20	74	25
25	68	16
30	51	11
35	0	0

Table 6. Dilatation (mm³) / gram

During the manufacturing of cream fats they start with differrent ingredients and by selective hydrogenation and fractionated chrystallization and by the repeated mixing of the proper fractions they create the cream fat with the desired consistency.

2.3. The specialities of raw material procurement, the importance of Fair Trade approach

The Fair Trade movement was started after the Second World War by charity groups like Oxfam, Hivos or Caritas with the goal to help and improve the most disadvantaged communities of the world by introducing their products on the market and incresse their profits. As an answer to the realisation that not every country and their population share fairly on trade and on its improvements.

So the essence of fair trade is that the participants agree on prices that are independent from the usual world market prices and they truly express the material input of the manufacturers. The fair trade organisation offers a fair price and a safe market to the small producers of the developing countries. In return it demands and checks that the small producers create their goods under basic humane, social and environmental norms. The idea is that the comsumers of the developing countries perhaps are willing to pay 30-50% more than usual for a pack of coffee if they know that it was made by environmentally friendly methods and under humane conditions and it helps local development.

The basic goals of fair trade are the folloring:

To increase the income of producers and the standard of living, to improve the chances of market access, to enforce the producer unions through higher prices and long-term trade relations

To support the development of disadvantaged groups, to protect children from exploitation

To inform the consumers of developing countries about the bad effects of international trade on small producers so that they can use their purchasing power for good

To campaign for the change of traditional international trading rules and habits

To protect human rights by the support of social justice, environmental friendliness and economic safety

Fair trade products are a bit more expensive than traditional products but in return the consumer gets checked, high-quality products.

At the end of the '90s researchers showed that the group of responsible consumers who purchase fair trade products is growing in the developed countries of the EU. From a survey conducted by the European Commission we know that all in all 11% of EU citizens have purchased a fair trade product. However the results of member states were very different from 3% in Portugal and Greece to 49% in the Netherlands. Currently in the EU the most common products (from the Third World) on the market are: coffee, tea, sugar, chocolate, cocoa, honey, banana, handmade products (also clothes). Four fair trade marks are in use: Max Havelaar, Transfair, Fairtrade Mark and Rättvisemärkt which appear so far only on coffee, cocoa, tea, banana, sugar and honey.

In Hungary the awareness and affectation of fair trade products are still elementary. At Ökofeszt in the spring of 2005 then in the summer at many other festivals fair trade coffee shop were quite successful. In the summer of 2006 the first fair trade café was opened in Budapest. At the Treehugger Dans' Bookstore and Café besides browsing through books you can enjoy a cup of coffee as well exclusively made from fair trade coffee.

In Hungary the price sensitivity of consumers are very high and the awareness requires some attention too, therefore the newly founded Fair World Fair Trade Association set their primary goal to inform the people and to raise awareness. The Association tries to raise people's awareness on the problems of the Third World and fair trade as a possible solution.

3. Chocolate mass production

The major processes of chocolate production are usually listed into two groups. Traditional technology proceeds from cocoa beans and cocoa mass production is also the part of the technology. In smaller plants cocoa bean processing can be rarely found. For the better understanding of material characteristics we discuss the traditional production technology since in this way all of the most important steps can be reviewed. Thus, the production technology can be seen in its whole complexity.

In Europe the cocoa mass production - the base of chocolate production- is not general. Bigger factories have the ready-made mass in from nearby cacao bean production sites. These sites are of course in the hands of the factories thus despite the regional separation the technological approach is standard.

Thus, besides the primary processing of cocoa the secondary processing steps – which include mass production - also occur near to the production site.

3.1. Cocoa bean processing on production site

Cocoa tree (Theobroma Cacao L.) belongs to the family Sterculiceae. Into this family many other tropic trees and scrubs are listed. The economic significance of this family are given by cocoa bean and cola nuts. Within Theobroma genus 13 species are known which are substantially different in their shape of flower and fruits, and in their size. Besides the grown species others like Theobroma sativa Lig. Et le Bey (Var. Laucospertma and Var. Melanospera) andTheobroma leiocarpa Bern has great importance.

There are two groups of Theobroma according to the morphological differences of the grown fruits, seeds (beans) based on the vital and obvious genetic differences:

Criollo meaning: native (the name of American-born offsprings of Spanish parents) The fruit is elongated (its diameter is less than half of its length), five more or less deep, fore-and-aft groove, warty, white peelings, typical top morphology. The oval shaped seeds are loosely embedded into the flesh, they have white cotyledons.

Forastero meaning: alien species. The fruit is more roundish than Criollo (the diameter is bigger than half length of the fruit). There are no typical markings on the smooth and solid peelings; the fruit has no typical top morphology. The seeds are

embedded into the flesh in triangular shape, very tight to each other. The cotyledons are violet-blue.

The hybrid of Criollo and Forastero is called Trinitario.

The 90% of grown cocoa belong to the species Theobroma leiocarpa Berh., or its varieties and hybrids. On the main plantation sites (western Africa and Brazil) forastero cocoa are grown. The remaining 10% is criollo or "aromatic" cocoa whose quality properties can be lead back to the pure criollo namely Theobroma Cacao L. The pure, white seeded criollo is grown very rarely. Countries formerly only growing criollo now use a significant amount of hybrid plants with forastero.

The native home of cocoa tree is probably the northern part of South America, here it grows in the rainforests around the Amazonas and Orinoco river.

The cocoa tree is mid-high, irregular, often fragile and not very thick in diameter (approx. 20 cm), evergreen, its leaves are dark green, when young they are reddish in colour. The tree can grow up to 10-15 meters, but on average it is about 6 meters high, however for easier cultivation they cut them back to 4 meter high trees on the plantations.

The cocoa tree – depending on the soil – either grows a 1 meter long taproot and a fine lateral root system or in case of soils based on clay the taproot develops poorly and the most junctions are located closer to the surface. The cocoa tree is always deciduous, depending on the type and place it replaces its leaves three or four times a year.

Depending on the type the cocoa tree starts to bloom after 18 months – 3 years. The fruits of a cocoa tree are bolls which has a short stem, the fruit is about 15-25 cm long, 7-10 cm thick widens on the bottom and sometimes ends in a peak. Inside fruit there are 5 rows in which there are 20-50 elongated, egg-shaped seeds. The colour of the seed is different in cocoa types just like their sizes; the length is 1.5-3 cm, the width is 1-2 cm and the diameter is 0.5-1 cm.

Cocoa on the world market today consists of cocoa grown on artificial plantations only. The climate has to be steadily warm, the air and soil moisture has to be high for the trees. The optimal temperature should be around 25°C throughout the year. The night temperature shouldn't decrease below 20°C, during the day it should rise above 30°C but not over 35°C. In South America the average annual temperature is about 21°C which is great for cocoa trees.

Besides the temperature the proper amount of precipitation is significant which mustn't be less than 1250 mm annually.

The area between 15° north latitude and 15° south latitude is optimal for cocoa planting. Height above sea level is also important, high plains (approx. until 600 meters above sea level) are the most favourable. Close to the Equator height up to 1000 meters above sea level is also affordable.

The soil has to be rich in organic materials and has to be cultivated to a certain depth so the root of the cocoa tree can grow properly.

For the proper growth of the cocoa tree optimal light and wind conditions are needed. Cocoa producing areas: Central America (Mexico, Costa Rica, Panama), West Indies (Dominican Republic, Trinidad, Grenada), Tropic South America (Ecuador, Venezuela, Brazil) Tropic Western Africa (Ghana, Nigeria, Ivory Coast, Cameroon, Togo, Fernando Po, San Thomé, Principe, Congo), Asian and Oceanian areas.



Figure 2. The cocoa bean

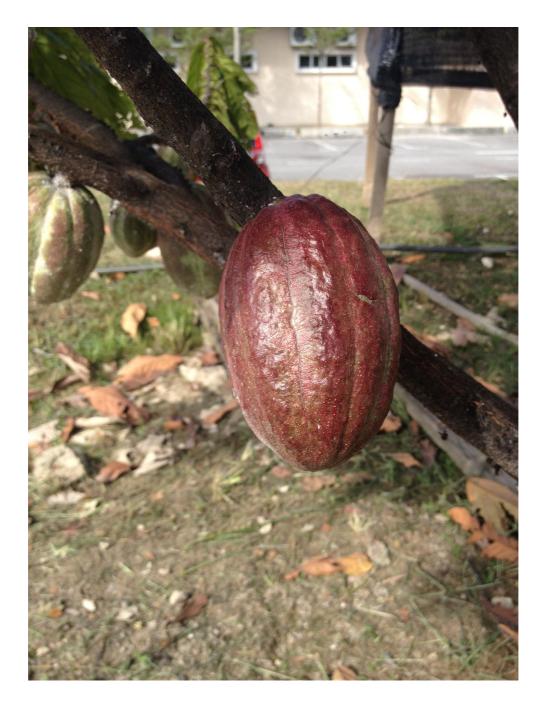


Figure 3. The fruit of a cocoa tree (Photo by author in Malaysia, 2015)

The primary production of cocoa

The primary production of cocoa means all the activities through which we get cocoa material ready for industrial processing. The primary production takes place on the production site.

Fermentation:

The unopened fruits are delivered to the fermentation site. Here the fruits are cut open by a machete. Then the seeds are removed from the fruit by hand or tools.

The goals of the fermentation of raw cocoa beans are:

removing the pulp from the beans

developing the aroma and compounds inside the cocoa beans that after drying and roasting we get the typical cocoa aroma

During fermentation carbohydrates are broken down and start to ferment due to fungi and bacteria. These outer activities start such chemical reactions inside the cocoa beans that provide ideal circumstances for the fermentation of the pulp thus the unpleasant flavor and odor that are originally inside the seeds disappear and we get the desired aroma.

On commercial cocoa beans we can often observe such faults in quality that are results of poorly carried out fermentation.

Color	Flavour	рН	structure
brown	Clear, harmonized, free from strange aromas	5.5	loose

Table 6.7. Characteristics of fermented cocoa beans

Drying:

After fermentation the water content of the cocoa beans is around 60%. In this state they cannot be transported or stored until the water content is reduced. Practically carried out drying also favors for the aroma developing activities. The endosperm gets a dark brown colour, its structure will become looser. Drying can happen naturally, by sunlight, or artificially with many methods.

After drying the fermented cocoa beans are ready to be transported to the site of secondary production where they make chocolate or cocoa powder out of them under industrial conditions.

As we mentioned before this usually takes place near the site of primary production.

6.3.2. Cocoa mass production

Cocoa mass production is a coherent technological process in cocoa powder, cocoa butter and chocolate production as well. Its procedures are shown in the following figure.

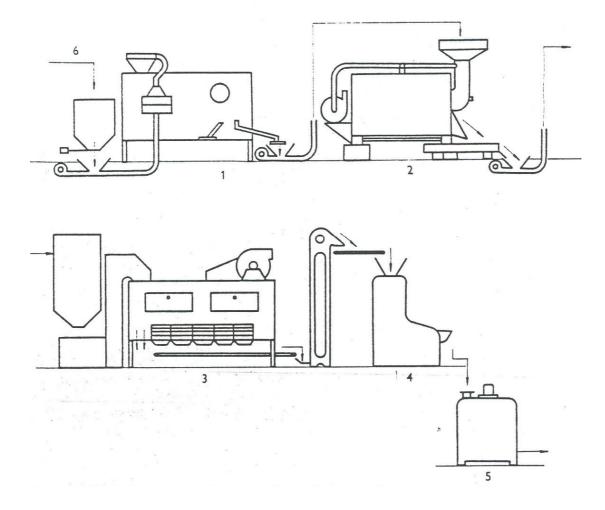


Figure 4. Schematic figure of classical cocoa mass production

1.cleaning, 2. roasting, 3. de-shelling, 4. grinding, 5. fine grinding, 6. cocoa bean raw material

Storage of cocoa beans

If cocoa beans arrive in bags, containers from the production site (primary production), the weight of these bags are usually around 60-63 kg. The bags are stored on pallets, the highest pressure that still doesn't damage the cocoa beans is 4000N/m2, this means 8-9 rows on top of each other. In case of criollo beans 10000N/m2 pressure is allowed.

If we store the beans in silos the input and output happens by machines with care, not to break the beans.

The water content of the cocoa beans can increase from 7-8% to 11-12% at 70-90% relative humidity, this condition is favorable for molds. Thus the relative humidity of the air contacting the cocoa beans has to be below 70%.

Cleaning, sorting, classification of cocoa beans

Most of the cleaning machines operate with sieves, brush machines and magnets where different separating processes are carried out in combination with each other.

Cleaning is important for the quality of the product, and it serves as protection for the grinding machines later in the process (surface of the grinding wheel). The sorting and classification provides the evenness of characteristics (size, type).

Cocoa beans cleaning and sorting machines

The cocoa beans arriving in the factory can contain a lot of contaminations (metal, stones, sand, dust etc.) which have to be removed before storing them in silos.

Besides removing contaminations we have to sort the cocoa beans. The precondition of good quality end product is that we separate the big, intact, healthy beans from the broken, light beans and the shell pieces.

Machines used for cocoa bean cleaning and sorting operate according to shape, size and specific gravity.

For the cleaning and sorting of cocoa beans they often use machines with plane sieves. It is very important to store beans around the same size in the same silos.

The frame of the machine is made up of a welded reinforced steel box. Inside this the coarse and fine sieves are suspended. The sieves are suspended above each other by a steel frame so that they can move together.

The sieves are moved by an electric motor with the help of a flywheel and a fan belt. The impulse power of an eccentrically placed counterweight on the flywheel provides the swinging movement of the sieves. In the front part of the machine there is an air duct where pneumatic cleaning can be performed.

Another great way to clean and sort cocoa beans is the use of pneumatic cleaning and sorting machines. With this method we can sort them by shape and specific gravity. With the structure of the machine we can separate three fractions. This machine is usually used in combination with other cleaning machines, and it is part of a production line. Most commonly they use the combination of these thus the cleaning and sorting can happen at the same time.

Combined cleaning and sorting machine

The combination of the elements of pneumatic and sieving machines allows us to separate more fractions than the machines mentioned before.

Roasting of cocoa beans

During roasting the temperature in the inner part of the cocoa beans reaches 100°C, but it's not above 130°C. In result of roasting the water content of cocoa beans decreases from 6-8% to 1.5-2.5%. The duration of roasting is about 30-50 minutes, but it highly depends on the type of the roasting machine, the type of the cocoa beans and the initial water content.

During roasting the typical flavor and aroma develop as well as colour materials inside the cocoa beans, later these can be found in the nibs after de-shelling.

Cocoa bean roasting machines

We can divide these machines according to:

their mode: continuous and periodic

the type of thermal transport: thermal conduction, thermal flow, and the combination of these two

heating energy: gas, steam, oil or electrical heating machines

Every roasting machine has an additional part that cools down the roasted beans quickly, thus preventing over-roasting.

Roasters

The type of thermal transport in roasters with rotating bean baskets is based on the combination of thermal conduction and thermal flow. The air heated by a burner heats up the lateral surface of the basket from the outside, and the air can be channeled through the basket horizontally and here it heats up the beans directly. Thus roasting can be performed by only outer heating and both outer and inner heating as well.

Roasters with rotating baskets are periodic machines with manual, semi-automatic or fully automatic control.

The two ends of the basket are manufactured to be shield-like, from which the first shield can be opened to empty the basket.

Inside basket the beans are moved by specially manufactured mixer elements – bended arms perpendicular to each other. Also the rotation of the basket moves the beans around.

After heating the basket the cocoa beans can be loaded into the machine by opening the loading cap. Then the roasting happens automatically according to the given parameters (temperature, time). To the sound of the alarm the cocoa beans have to be removed to the cooling part. It is a basic principle that we mustn't operate a roaster without a properly connected cooling unit.

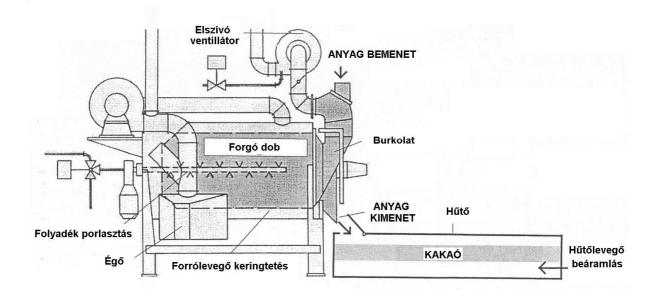


Figure 5 Cocoa bean roasting machine

Winnowing and coarse grinding of roasted cocoa beans

As a result of these processes the shell and the radical separate from the valuable endosperm a.k.a. the nibs. The nibs are ground into 2-5 mm sized pieces.

In the first phase of winnowing the roasted cocoa beans are coarse ground to loosen up the connection between the endosperm and the shell, then the nibs are sorted according to size. Finally the nibs and the shell pieces are pneumatically separated. The nibs can contain 2% shell parts maximum – this is allowable from a medical point of view, and to protect the grinding machines we shouldn't go higher than this, besides it's not even legal.

Cocoa bean cracking and winnowing machines

In the nibs a higher percent of shell and radical has a negative effect on the quality of the product, so the endosperm has to be separated from these materials. The tool of separation is called a winnower.

Winnowers break the cocoa beans loosened up by roasting in disc or cylindrical grinders. During grinding it is important to achieve a coarse fraction, because if it's too fine the separation will be difficult. The sorting of shell parts happens pneumatically on sieves according to different specific gravities. The removal of the radicals is possible because of the difference between the shapes of the endosperm and the radicals.

The roasted cocoa beans are delivered to the grinder via elevators located on the top of the machine. Magnets are placed in the inlet gullet remove the metal pieces. From the gullet the cocoa beans are released in between the discs of the grinder where they are cracked and the radicals are freed. The distance between the two discs is adjustable, and we can influence the quality and quantity of the broken fraction. The cocoa bean arrives centrically between the discs, where the segments and the centrifugal force break the beans. The broken beans then are moved onto the smallest part of a series of vibrational sieves. Here on this sieve system the mixture is separated into seven parts from 0.75 mm to 8 mm, which all contain broken endosperm and shell parts. These separated fractions fall down into vertical shafts while air is being ventilated against the cocoa bean flow. The speed of ventilated air in different shafts can be adjusted by the opening and closing of horizontal flaps, so the separation of the endosperm happens according to the difference in specific gravity.

Fine grinding of the nibs

During fine grinding the solid nibs with particle size around 2-5 mm we get a cocoa mass with particle size 50-100 micrometers /0,050-0,100 mm/, which at room temperature is in liquid plastic form. Particle size is the basic characteristic of cocoa mass. If they make cocoa powder the biggest particle cannot be bigger than 50-70 micrometers, because there won't be any further grinding process in the technology. At chocolate making 100 micrometers is still affordable, because the mill grinder will set the final particle size in the product.

Today fine grinding is executed in only two steps by connecting two machines in one line. After the first part the biggest particles are about 200-300 micrometers in size, the second part is always the bead mill.

Machines of nib grinding

The nibs contain 48-56% cocoa butter in cells. During grinding these cells are torn apart. Cocoa butter is released, due to frictional heat it melts and creates a suspension with other particles, which is in a dense liquid state and we call it cocoa mass or cocoa paste. The cells of the kernel are about 23-40 microns in size, while the thickness of the cell membrane is about 12 microns. The rate of grinding should be chosen according to the intended use of cocoa mass. For cocoa powder we need the mass to have the particle size of 20 microns. For chocolate mass we can have a cocoa mass with bigger particles because we will grind it even further later on. The type of the grinding machine has to be chosen according to the production technology. The water content, the shell and radical content influences the fineness of nib grinding. Water content above 2% makes the grinding process very difficult, because the material will become viscous, while a drier material will be more rigid and easier to grind. The shell and the radicals are harder and tougher than the kernel so they won't break as easy. In a good quality cocoa mass the amount of shells and radicals are less than 2%.

The alkaline treatment of cocoa nibs makes the grinding process easier because it loosens up the material. During grinding we have to reduce a certain amount of the heat caused by friction. This task is carried out by air and water cooling.

Bead mill

The fine grinding happens in the tank of the grinder due to the mixing of the material and the beads. Grinding actually happens because of two different mechanisms. One: the particles in the gaps between the beads are mechanically pressed. Two: because of the speed difference between the beads hydraulic shear force affects the particles.

The mixing is performed by an agitator with specially designed mixer elements. The edges of the properly elaborated rotating mixer parts of the agitator apart from the grinding effect don't serve as axial transportation.

The material of the beads has to be chosen according to the material that we want to grind. For the grinding of the cocoa mass steel beads are perfectly suitable due to their specific gravity and rigidity.

For finer, easier to grind materials smaller beads are suitable. For tougher materials bigger beads are necessary. Bigger beads doesn't only mean bigger weight or higher kinetic energy but higher speed differences between them too.

In case of continuous bead mills the fineness of the mass can be altered by changing the amount of material we add into it. To achieve this they connect a pump to the grinder tank with adjustable performance.

The shear forces arising in the grinding zones of a bead mill depends on the speed conditions, the size of the beads and the viscosity of the material that we grind.

Most part of the energy used for mixing is transformed into heat that we have to reduce via cooling.

The bead mill is made up of three main parts: the fuselage containing the motor, the grinding tank and the pump.

The grinder tank is 50 or 100 liters large, double walled can be used for cooling and heating and is made from a special abrasion-resistant steel. On the bottom part there is a valve through which the material enters the tank to be ground. Through this same valve we can remove the beads for repairing.

The finely ground mass leaves the tank on the top through small gaps about 1 mm in diameter. The size of the diameter is chosen according to the sizes of the beads.

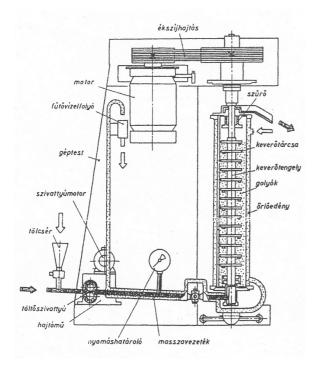


Figure 6. Cocoa bean grinding with ball mill

Storage of the liquid cocoa mass

Cocoa mass is stored in heated tanks at 60-70°C while mixing it. Inside tanks planetary mixers prevent layering according to specific gravity. Because the viscosity of the cocoa mass is relatively low and the cocoa particles can settle on the bottom quickly. Planetary mixers move the mass against gravity as well.

The most common contamination in confectionery industry is air pollution, which can happen due to evaporation waste, dust, or the waste from roasting. Evaporation waste occurs during concentration (this doesn't mean to harm the environment because we talk about water evaporation) and there are also roasting and baking wastes in confectionery (in cocoa beans roasting doesn't come with a measureable amount of dust emission, but thermal degradation takes up about 2% of the loss and the water emission here is about 4%). We come across baking waste during the making of pastry products. The energy source of roasters, ovens and boilers providing steam energy is almost exclusively natural gas, so the environmental impact of products of combustion is not significant (nitrogen-oxide, sulfur-oxide etc.). Dust loss is quite low but because the confectionery industry uses dusty materials at great amounts (flour, milk powder, powdered sugar, cocoa powder) we have to talk about them.

The production of cherry liqueur chocolates doesn't have that much pollution with it, only the washing water deserves some attention because of its sugar and fat content – to reduce these traditional solutions are suitable (fat trap etc.).

During cocoa production air pollution arises during the roasting of the cocoa beans. The emission of roasters can be reduced by using proper cleaning equipment. Usually among emission reducing techniques still the end of pipe techniques are popular, for example: settling tanks, cyclones, bag filters, absorption, condensation, wet oxidation (odors) and other chemical reactions. These techniques should be replaced for the Best Available Technologies and the goal is as the definition tells us: "prevention of environmental impact or – if that can't be carried out – reducing it".

3.3. Cocoa powder and cocoa butter production

Cocoa powder production

Cocoa powder is made from chemically treated cocoa material by separating the cocoa butter from the cocoa solids (cocoa presscake) by pressing, then the presscake is pulverized.

In the case of modern cocoa powder production the process starts by measuring the quality of the cocoa beans, for this they choose a type of cocoa beans that are rich in color and flavor. in the production of commercial cocoa powder they always use chemical treatment in order to improve the flowability of the powder and to deepen the inner/outer color. This doesn't mean the improvement of color as if we need to cover up some faults, but it is an important basic method in cocoa powder production. Chemical treatment of the cocoa mass

Depending on the chemical treatment we distinguish commercial cocoa powder and industrial cocoa powder as an end product. For the digestion of industrial cocoa powder we can only use clear water, we cannot use alkalis because the remaining cations in the product cause saponification if the industrial cocoa powder gets in contact with a media that contains fat.

During this process the pH of the cocoa mass is set to a neutral or slightly alkaline value (pH=8). Alkaline digestion is the most common method when the poly hydroxy phenol compounds of the cocoa mass become dark red and a part of them transforms into phlobaphenes which is a water-insoluble darkly colored pigment. As a result of the treatment the pressing of cocoa butter becomes easier (lower pressure can be used).

Pressing of the cocoa mass, production of cocoa butter and presscake

Pressing as we know is filtration under pressure. Before pressing the cocoa butter content of the cocoa mass is between 50-55%. The cocoa butter content of commercial cocoa powder often reaches 24%, however from a physiological point of view lower values are advised. The so called outer color of the cocoa powder justifies the relatively higher value, because the higher the amount of cocoa butter the darker the outer color will be after good tempering. (The so called inner color is the cocoa color appearing in drink form.)

Other characteristics of cocoa mass before pressing:

temperature: 60-60°C (increases during pressing)

max. 1.5% water content; if the water content is higher than this the pressers can be damaged, so the viscosity of the cocoa mass has to be kept at a lower value. This has to be measured and checked frequently during pressing.

The temperature of the coco mass has to be set before pressing in a buffer tank.

The pre-tempering of the pressed cocoa, coarse and fine grinding

The pressed cocoa has to be pulverized in two steps – fine-grinding cannot be carried out without pre-grinding.

At figure 7. we can see the particle distribution of a properly ground cocoa powder. The average particle size is below 10 micrometers, which shows great sensory characteristics next to flavor, odor and color properties. The basic requirement for cocoa powder on the world market is that 99.5% of the particles have to be smaller than 70 micrometers and the shell content has to be below 1.75%. The acceptable values of microbiological state are also defined.

During the two step grinding the cocoa butter in the cocoa material has to be tempered, we have to bring it through a temperature profile that causes the forming of stable crystals. Because there are completely different conditions in pressed cocoa than there are in chocolate (differences in cocoa butter content and consistency) the process of tempering is also different from the tempering of chocolate. This process is a much less researched field, but some principles from cocoa butter polymorohia are valid here as well:

The temperature of the presscake has to be set at 40°C, at this temperature the cocoa butter in the presscake melts completely, here the cocoa powder flavoring mixture can be added to the coarsely ground presscake. This is a mixture of vanillin solved in alcohol or Peru-balm coriander oil etc.

It's important that after coarse grinding the temperature has to remain around 40°C and only in the fine grinder can the temperature be decreased gradually so that the temperature of cocoa powder leaving the mill is around 20-24°C then it is further cooled down in cyclones to 16-18°C.

Usually the design of the cocoa mill is that it can crystallize a significant amount of cocoa butter in the cocoa powder to a stable form in the connected cyclone system. It is also common that after the mill + cyclone system there is a fluidized bed dryer which creates the nice dark brown-dark red outer color.

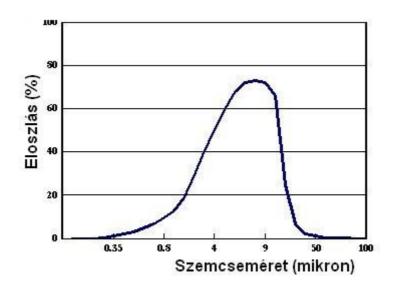


Figure 7. Particle distribution of cocoa powder

Characteristics of a good quality cocoa powder:

pleasant cocoa odor,

dark red, dark brown color,

in drinks the particles set slowly.

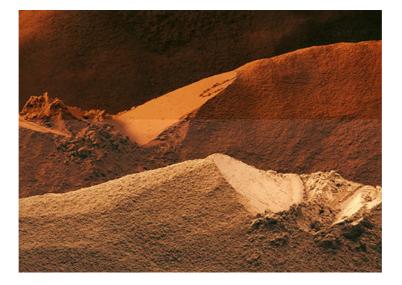


Figure 8. The cocoa powder

Cocoa butter production

The production of cocoa butter and of cocoa powder happens in the same technological process. A couple of standpoints require us to talk about cocoa butter production separately.

Because cocoa butter can appear as a separate product in a crystallized form (in bars). This doesn't necessarily mean bars like chocolate bars - higher amounts are crystallized in blocks. 'Tabling' in chocolate or cocoa production is a synonym for the process of cooling/solidification of cocoa butter by crystallization. Crystallization means the setting of the temperature of cocoa butter around 40°C, then as in chocolate production (see 5.1.) the temperature is gradually decreased to 27-28°C then with a little heating the temperature is raised around 29-30.5°C. Forming into blocks is rather time-consuming because the cooling is carried out in 6-8°C chambers and the bigger the mass that should be cooled the smaller the surface area and that means slower cooling process, while the cocoa butter shouldn't be moved around.

If the cocoa butter is really formed into bars tempering has to be carried out as we discussed, but the cooling of the formed cocoa butter has to be performed slowly and gradually. Because the cocoa butter contracts by 9% in volume and if this happens too fast the bars will crack. The cocoa butter won't be damaged by this, but because of the fault in quality the whole process has to be repeated.

The two basic use of cocoa butter:

chocolate making

medicine

The principles of cocoa butter made for medical use can be found in the Pharmacopoea Hungarica. One of these principle states that the acidity of cocoa butter must not be higher than a certain value, other states that the product cannot contain any physical contaminations.

In medicine for the production of rectal suppositories cocoa butter is an ideal material, because at 32-33°C it's completely solid but at 36.5°C it melts perfectly.

We need to mention that for both chocolate and medicine production we can only use cocoa butter that was made by pressing alone. It is known the we can produce cocoa butter by expeller technique but this product is not permitted to be used in chocolate of medicine production in the civilized countries.

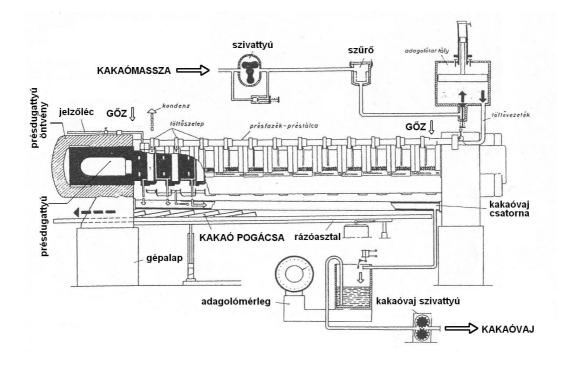


Figure 9. Modern cocoa butter pressing machine

Instant cocoa powder as a convenience product

Its goal is to improve the humidity and solubility of the cocoa powder by using proper additives to create suitable physical properties.

Powdered foods are usually coarse disperse or micro heterogeneous systems. Their common characteristic is that in liquid form an air film layer forms at the powder-liquid interface which slows down the solubility of the particles. In many cases of dissolving with the help of mixing agglomeration can occur which harms the efficiency of solubility. The process of instantization prevents this undesirable condition by creating capillaries in the agglomerates which suck up the solvent – in this case milk or water.

In cyclone agitators we can create a homogeneous sweetened cocoa powder mixture by pulverization of 20% cocoa powder (particle size: 18-20 μ m) and 80% finely ground powdered sugar. In agglomerating chambers with the pumping of low-pressure steam the misture content of the mixture is set to 3.5%. The final miosture content of the agglomerate (~ 2%) is set by a 50°C turbulant air flow. The speed of miosturizing and dissolving of the product increse from 70% to 100%.

Characteristics of istant products:

fast and good moisturizing ability

fast sinking of particle in fluids

good dispersibility

fast solubility

The point of instantization is that the physic-chemical properties of the particles are form favorably.

3.4. Production of chocolate liquor by traditional and modern methods

Chocolate production

Chocolate is a product made from cocoa mass, cocoa butter, sucrose, concentrated milk, almonds, hazelnuts or coffee if needed, maximum 1% surface active agents as additives (almost exclusively lecithin) product flavored with vanillin. Milk chocolate is a chocolate product that contains milk derivatives too. However for example in

England when using milk derivative made from whole milk the name milk chocolate is allowed to be used. The so called dark chocolates don't contain milk derivatives.

Finely ground almonds, hazelnuts and coffee can be used for chocolates, but coarsely a wide variety of materials can be added to them.

These requirements can change according to different regulations, but the following viewpoints have to be valid at all times:

Chocolate is a special group of products in confectionery - and the preservation of its position is our main goal

Because for its production we use expensive materials (cocoa mass, cocoa butter), using cheaper ingredients without informing the consumer could lead to the delusion of consumers and the delusion of the product group. Almonds, hazelnuts and coffee are just as expensive and novel ingredients as cocoa, so their use is not objectionable. Every other ingredient however can be used in chocolates only if it is marked on the package.

If we talk about chocolate production we always mean barred (solid, unfilled) firm chocolates.

The processes and methods for milk chocolate production are shown on the following figure:

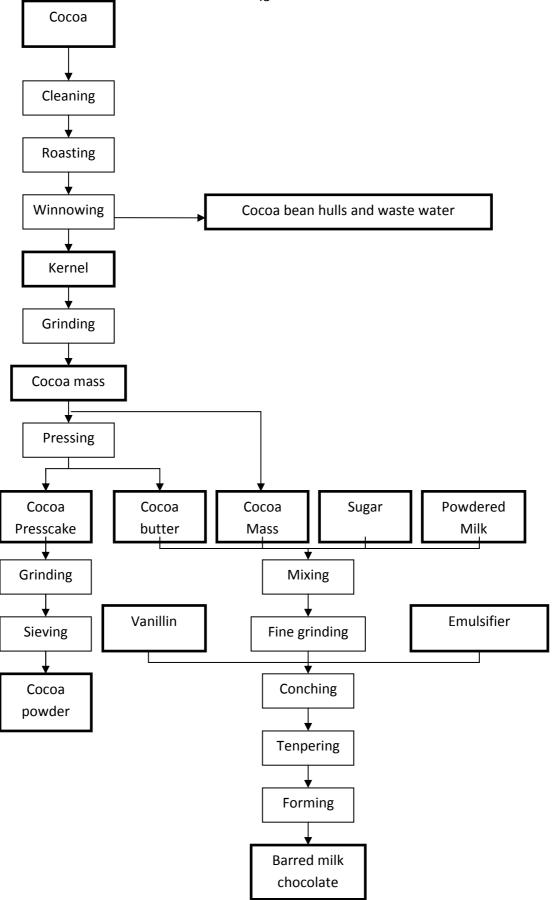


Figure 10. The technology of milk chocolate production

Preparation processes of chocolate production

This means the production of cocoa butter and cocoa powder that we discussed earlier.

Production of powdered sugar

One of the most important processes of chocolate production is the highly energy demanding process of crystal sugar grinding. This can be acquired from sugar mills. The storage of sugar happens in bags or silos. Whatever the type of storage is, it is very important that the relative humidity of their contacting with the sugar is under 75%, because over that value the sugar can easily agglomerate. It's worth mentioning the sugar agglomeration can happen due to many other reasons thus sugar grinding deserves great attention and practically automatic control.

Another circumstance of sugar grinding is that the mixture of powdered sugar and air can lead to an explosion (dust explosion).

Preparation of milk ingredients

If we work with powdered milk, storage can happen in bags or silos. If special dairy products are added to the chocolate (eg. milk crumb etc.) special processing methods are necessary. The production of these ingredients can be interpreted as a preparation process of chocolate productions.

The main process of chocolate production

In the primary process chocolate liquor is made, out of which different chocolate products are created.

Processes: blending, homogenization.

During these processes the powdered sugar, the cocoa mass and a part of the cocoa butter are measured together and homogenized. Back then this process was performed periodically in a melangeur. Today only continuous production machines are used for this process. For periodic conching they use Z-arm mixers which apply great mechanical force to homogenize the rigid mass. In continuous conches the pumps get the cocoa mass in the machine from the side perpendicular to the axis of an endless rotating pulley, which provides and intensive conching process so that the material will be fully homogenized.

The developing chocolate material with coarse particle is usually called chocolate paste.

Fine grinding of the chocolate paste

This process is performed by a typical machine of chocolate production the roll mill which consists of 5 rolls it is also called as a five roll mill (for cocoa mass production back then they used 9 roll mills instead of bead mills). On Figure 11. the schematic working principle of the five roll mill is shown.

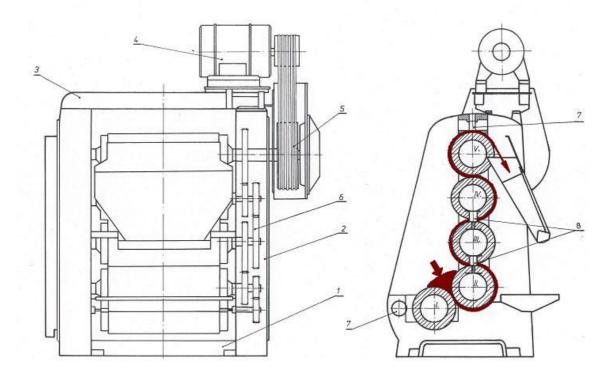


Figure 11. Operation on the five roll mill

1.base plate 2.fram 3.bridge 4.motor 5.fan belt 6. gear 7.piston 8.counter piston

The rolls (I.-V.) move in the same direction but at different speed while the gap between the roll pairs decreases. The rev of the rolls grows 10 times higher. The temperature of the hollow rolls is adjustable. Usually the temperature of the rolls from I to IV increases while the surface of the fifth roll is cooled.

Even today we don't have an explanation to why the chocolate paste sticks to the rolls and why the rolls give the paste to each other, many scientists examined this

problem (eg. Tódor Kármán's hydrodynamic principle). Both requirements are needed for the roll mill grinding to work: these requirements are mainly influenced by the water content and the fat content of the chocolate paste.

During roll mill grinding the powdered sugar particles are ground further just like the milk particles primarily the size of the lactose particles is decreased. In a good quality chocolate the size of the biggest particles is not over 30 micrometers, but it mustn't be over 50 micrometers. Due to fine grinding the surface area of the solid particles is increased the plastic (doughy) consistency of the chocolate changes to a powdery material. The coherent disperse media which is made up of fats (cocoa butter + milk fats) cannot provide plastic state if the degree of grinding is too high, this requires extra cocoa butter and the production becomes very expensive, because cocoa butter is the most costly ingredient.

But the properly fine particle size is fundamentally important for the satisfactory value, because if our tongue can sense the particle it will feel like sawdust.

Therefore fine grinding is an important process. As a regular rule we can say that too fine grinding has not caused negative effects on chocolate, it rather increased its quality, therefore even from the creation and the pricing of the product we have to aim for proper fine grinding. But we also need to keep in mind that fine grinding is a very energy demanding process so with the decrease of the particle size the required energy increases. We shouldn't start sparing the cocoa butter at fine grinding but before fine grinding at blending where the butter content of the chocolate liquor is set to 26-28% (the lower this value is the better providing that the grinding can be carried out); the mixing after blending has to be very intensive in order to melt the fats completely to gain a fatty chocolate paste. Another important rule for cocoa butter sparing is that after fine grinding we have to start conching in a dry low of cocoa butter medium (kneading-resting).

In summary: fine grinding has to be performed carefully with aiming for the highest quality because this process has a great influence on the quality of our final product. If the fine grinding wasn't satisfactory then we have to repeat it, but this is time and energy consuming.

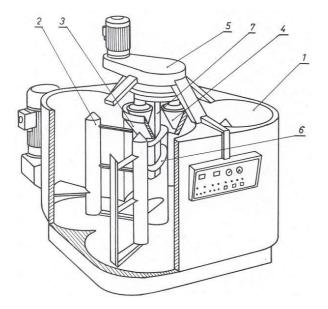
Conching of the chocolate - smoothing

This is the most typical and complex process of chocolate production. It is performed by liquefying the powdery chocolate material gained by fine grinding with some cocoa butter in conches. Liquefying happens with 28-30% cocoa butter content maximum so we can conch it "dry". This is followed by "pasty" conching where the cocoa butter content is raised by 2% thus we reach the final cocoa butter content of 31-33%. At coverture chocolates this value can be higher. At the end of conching soy lecithin is added to the chocolate liquor, and if necessary some PGPR (polyglycerol-polyricioneleate) emulsifier which is usually added to coverture masses. Lecithin reduces the viscosity, PGPR reduces the surface tension.

Conches can perform difficult material handling processes (mixing, kneading, aeration). In the beginning they had a clam-like design. This is where the name originates from 'conching' (concha: clam in Spanish) when the chocolate liquor is moved around, mixed, kneaded and aerated by cylindrical mixing elements. Nowadays we have more intensive solutions so the traditionally time consuming process now can be performed in 48-72 hours for dark chocolates and in 8-27 hours for milk chocolates.

In Figure 12. we discuss some practically used conches. These machines follow different processing methods, but they can apply the same shear force on the chocolate liquor which is one of the basic requirements of modern chocolate production.

Today even more modern conches appeared which function as reactors while providing powerful blending.



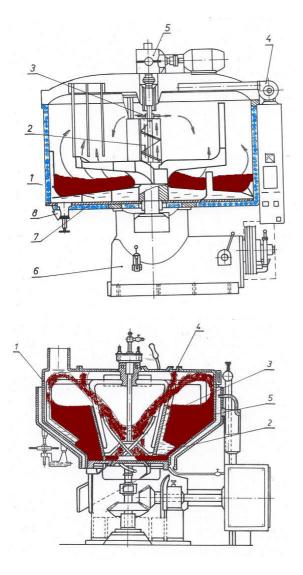


Figure 12. Methods for chocolate conching

The basic rule for the time of conching is that the longer the conching is the better the quality of the product will become, to mark the end of conching we need the sensory

opinion of the chocolate master too, because during conching the taste of the chocolate changes hourly.

The changes during conching are the following:

Decrease of water content

With water vapor most of the volatile substances (primarily organic acids, formic acid, acetic acid, propionic acid etc.) are removed as well. The change can be modeled as an ordinary differential equation. According to Mohr and Bartusch during the conching of dark chocolates the agglomeration and the disintegration of particles repeat periodically. During agglomeration aroma formation happens, during disintegration the volatile substances are released (their enrichment happens during aroma formation) and the specific surface area increases which starts surface reactions, the particle adhesion intensifies, the aroma formation starts and a new period starts. Periodicity also appears in the cyclical release of acids, and the adhesion between particles also changes cyclically as examined by viscosimetry.

According to Mohos' model the exponential decrease of water content is significant to the actual water content of chocolate liquor. To this a cyclic change is superposed – and the root of these two is the apparent water content of the chocolate which can be defined in a drying oven by gravimetry (actual water content is determined chemically by Karl Fischer's method, and it measures the chemically bound water not the full water content).

Because at conching the water content is removed (from the starting actual water content of 0.8-1.5% it exponentially decreases to the minimum limit of 0.3%) the apparent water content can be shown in an exponentially decreasing function and a cyclically changing v/t/ function that superposes to this one.

Reactions of aroma formation

These are mainly oxidative reactions that occur in the cocoa material with close connection with the water content of the media. Conching also influences the aromas in milk, a part of this is also the result of the reactions in the water medium. However researches on this field go way back, a lot of questions still need to be answered to fully understand these changes.

Physical-chemical changes

These are mainly colloidal changes being expressed in the change of consistency, this includes the rounding of particles, which is one of the measureable effect of conching (this isn't actual grinding).

It's important to know that chocolate is actually a dielectric material in which cocoa butter as the coherent disperse medium results the development of electric properties. Thus for example the conching of chocolate was explained along with electrostatic phenomena. Even if this isn't completely acceptable it is still a fact that electrostatic charges can occur at the tabling of chocolate between the forming machine and the chocolate molds.

Conching – for the intensification of physical-chemical changes – practically is performed in highly viscous medium ("dry" conching), so the total fat content of the liquor should be around 30% at the start. At the last 2-3 hours of conching the rest of the cocoa butter is added and in the last 30 minutes the necessary lecithin and PGPR is added. This provides the intensive kneading and the proper homogenizing. At the end of conching the chocolate liquor is flavored with vanillin extract or vanillin dissolved in alcohol, then it is stored in a buffer tank with heatable walls and a mixer.

New trends in chocolate production

Chocolate production is the main part of the confectionery industry where a very expensive technology processes the materials, it is energy demanding, mechanization and automatization is almost complete. The main steps of this development are the following.

Development in nib grinding

It was a basic realization by Niediek that the cocoa nibs and the sugar should be ground separately and with different optimal machines. For the nibs it is some kind of pre-grinder + bead mill, for sugar these are different sugar mills.

Development in chocolate liquor conching

However the design of conches went through great changes thus making the process more intense – the explanation of conching means something else in this case. It means that the many different reactions happening during conching should be applied separately for every ingredient, namely:

the cocoa mass, before using it in chocolate production, is lead through a film evaporator, which decreases the acidity and the water content

the milk ingredient is added in milk crumb form, so they try to achieve an optimal state from a milk flavor standpoint. The choco crumb method by Cadbury-Baker-Perkins is the simultaneous preparation of the milk material and the cocoa mass.

the Wiener method means the kneading, grinding and aeration of chocolate liquor in 24 hour cycles in so-called Attritor machines. This method is seemingly controversial to Niediek's realization, but really they are in harmony with each other, because with traditional conching the collective grinding of cocoa material, sugar and powdered milk would be unimaginable.

The grinding conche developed by MacIntyre (UK) and Lloveras which performs grinding with intensive aeration and conching in the same place at the same time. The Spanish Lloveras company combines these methods with a bead mill too.

The most effective form of chocolate production with the highest quality has not yet been developed, so new innovations can be expected.

3.5. Environmental effects of cocoa and chocolate mass production, methods for the reduction of pollution

Package

For packaging the large amount of products the confectionary industry uses a wide variety of tremendous amount of packaging material. Currently the large amount of packaging waste loads communal waste in small scale production whereas in large-scales selective utilization is typical. In respect of collection site development, recycling and eradication confectionary industry keeps up with the requirements.

The cherry chocolate liqueurs are wrapped apiece, usually in golden foil. In lot of cases there a placed in gift boxes. They can be found in plastic cylindrical, or in other (i.e.: heart-shaped) stripping too. Accordingly aluminium, paper and plastic packaging material is needed during the package of the finished product. For the reduction of the waste of these packaging materials the internationally accepted three R (Recovery, Reusing, Recycling) methods are applicable.

In case of paper packaging material there are two ways of recycling: waste recycling and burning. These products are well combustible and their emission is very low. The base of waste recycling is the resumption of paper. In case of plastic packaging material the plastic waste is re-granulated before use while antioxidants and stabilizers are added to the melt, although the recycling can be solved by multicomponent injection moulding too. A small rate of plastic packaging material is degradable by biodegrading, photodegrading, and dissolving.

Biodegradable packaging materials are paper, cardboard, textile, wood, and to a certain extend metals (corrosion). Since they are natural, they have their place in the natural recycling process. Plastic packaging materials cause the biggest problems. Plastic packaging material derived environment pollution is a multilevel process. During the polymer synthesis, processing harmful substances are emitted by the use of additives (emollients, stabilizers). From packaging materials interacting with product harmful substance can migrate to the food, during their burning harmful substances can get into the air (dioxin, hydrochloric acid, etc). Modern incineration sites can deal with this problem but their creation need tremendous amount of financial investment.

For the redemption of synthetic polymers the below enlisted renewable raw materials could be used:

polysaccharides (i.e.: starch, cellulose, pectin)

proteins (i.e.: gelatine, prolamine, gluten)

lipids (i.e.: fats, wax)

polyesters (i.e.: microbial polyhydroxibutirate/valerate)

Starch is the most commonly used biopolymer especially used during the first method since it is cheap, produced in large amounts and easy to handle. From cellulose viscous foil and cellulose acetate can be produced. With biotechnological processes (bacterial fermentation of carbohydrates) thermoplastic biopolymers can be produced. In case of vegetable oils the starting elements are the composition of fats and oils or what you might call fatty acids. Gelatine (waste of meat industry) is dissolves well in warm water, biodegradable. It can be used as foil and injection moulding material. In package material production it can be used as foil for gift boxes.

4. Further materials needed for cherry liqueur chocolate production

4.1. Production of fondant mass

Fondant is a microcrystal structural cream-like product made up of sucrose, starch syrup, and concentrated sugar solution. Moisture content is between 8-14%. Fondant is used for production of various products in the confectionary industry as raw material thus it is a very important ingredient of hand -and and machine shaped cherry liqueur chocolates.

In older instruments the final condensation of the diluendum - which is the result of the pre-condensation- is done periodically or continuously (coil-pipe) on atmospheric pressure. The temperature of the final condensation is between 116-120 °C. In modern instruments this process can be fastened by using vacuum, which of course needs lower temperature. Below the major steps of fondant production are discussed. Please note that these steps are also used in the confectionary industry for the production of sugar content products.

Dissolving sugar. Sucrose and starch syrup is added in respect of the different candy making processes in different ratios. In starch candy production respectively to sucrose content 50%, in soft candy 25% starch syrup is added. In modern plantations continuously working meters allocate the proper amount of raw materials into the dissolution and pre-condensation devices provided by mixers (SOLVAMAT, CONTIMELT). The result of dissolution and pre-condensation is a 70-75% diluendum.

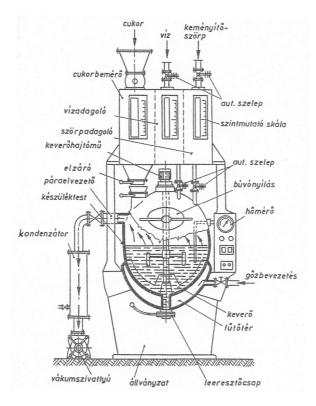


Fig 13. Sugar dissolver-boiler

Condensation. The diluendum needs to be condensed to a certain point of dry matter content depending on the finished product (starch candy or soft candy). For soft candy 86-88% production, for starch candy 98-99% production dry matter content is needed. In respect of these terms there a various types of condensers and the further production technologies needs different setups. In respect of this fondant production is discussed below.

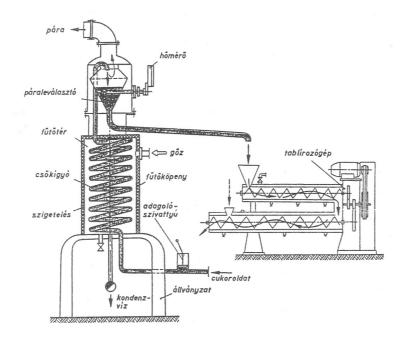


Fig. 14 The working principles of fondant producing facility

Fondant crystallization

Fondant crystallizer is usually built-in with the condenser. (Fig. 6.14). The essence of crystallization is that with intensive mixing, cooling and by transmission this mass becomes microcrystal in its structure. The sizes of the crystals in the fresh fondant are 10-40 μ m if older technology is used. This type of fondant needs to rest till the equalization of the crystal sizes. During rest re-solution and the growth of the crystals take place. Thus, the result is a homogeny of 18-20 μ m crystals. In modern fondant production facilities by the respective increase of the rev in the mixer (app. 350 rev/min) the homogeny of <20 μ m crystals are ensured (BAKER-PERKINS plant).

Fondant flavoring, coloring

Fondant mass is flavored and colored on the right temperature (80-85 °C) before production. For flavoring ground oilseeds (cacao, nuts), ground coffee or milk product is used. The flavored and colored fondant mass is stored at 80-85°C, the product is shaped at this temperature.

Fondant product shaping by molding

Fondant products ("parlor candy"- or szaloncukor, drageé and other corpora) are made by pouring in powder-molds (fine grain-starch like rice-starch). On automatized production lines (Mogul system) where the production takes place. Here the forming of molds and the fondant loading happens continuously (Fig. 6.15.). The depowdering of solidified corpora (the molded and solidified shape) are done by machines. Then the fondant corpora are finished by surface supplementation (candying, when the surface of the product is covered by crystalized sucrose), dipping in chocolate, pelleting.

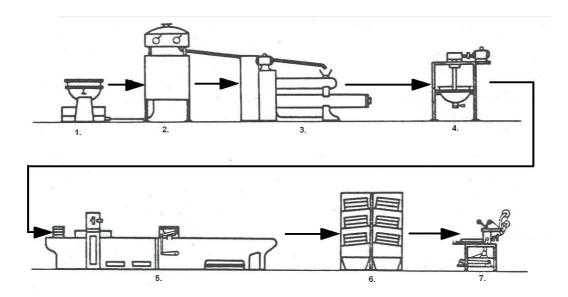


Fig. 15. The schematic view of fondant production (by molding)

1. Dissolving sugar, 2. Sugar mass condensation, 3. Crystallization, 4. Flavoring, 5. Pelleting 7. Packaging

4.2. Making of alcoholic cherries

The basic ingredient which develops the desired product characteristics is black cherry. The flesh of the fruit remains relatively fresh during alcoholic preservation. The fruit after 3-4 weeks absorbs the cognac. This type of alcohol is important because it can dissolve the fondant which is essential for the development of pleasant taste and texture.

The selected cherries are blanched until they rip or some of them start to rip. Then the water is drenched, the fruits are dripped off on a sieve then they are immediately put into cognac or rum alcohol (or pure alcohol). We can add some coloring too.

5. Production of cherry liqueur chocolates

5.1. The warming and tempering of chocolate liquor

The polymorphism of cocoa butter

It is a phenomenon when a chemical material in solid phase forms more structurally and physically different modifications and this is called polymorphism.

It's typical for this phenomenon that some modifications are only constant in a certain temperature interval. If the transition from one modification to another is reversible we talk about entropy if it is irreversible we call it monotropy. The polymorphism of cocoa butter is monotropic: there are five distinguishable crystal modifications.

the γ -modification happens at the fats cooling of the cocoa butter, melting point: 18°C the α -modification develops from γ -modification, if the overcooled cocoa butter then is suddenly heated, highly unstable, melting point: 23°C

 β 'IV – modification can be created directly, if the melted cocoa butter is crystallized around 24°C. melting point: 28°C, at 28°C it is stable for 30 days

 β V-modification can develop from unstable β '-modification by a very slow tansition, but it can also develop directly (eg. tempering); the β -modification starts to soften at 20°C and is completely melted at 25°C

the β VI-modification under optimal storage conditions transforms to a stable form over months, melting point: 34-36°C

The following figure shows the distribution zones of the crystal forms of cocoa butter. We can see that usually two crystal forms are present in cocoa butter, but at 15-17°C there are three present at the same time. The δ -, α - and β '-modifications, furthermore at 20-23°C the α -, β '- and β modifications are present, while over 28°C there is only the stable β -modification.

Different nomenclature is known for the crystal modification. The use of Greek letters was introduced by Larssen. The modern names were introduced by Wille and Lutton, simultaneously with Larssen. Today's nomenclature was developed from these different formations. According to this we distinguish five types of crystal forms, out of which the β VI is the most stable which is created from the β V-form by shearing. (Fig. 16.)

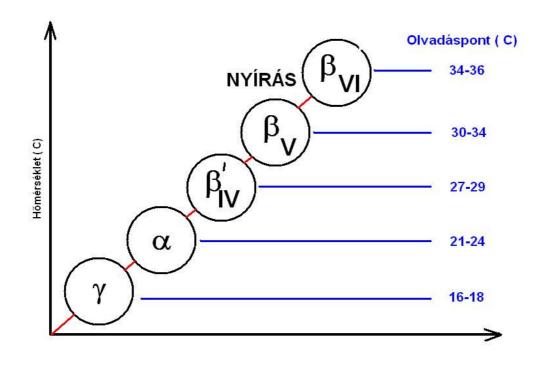


Fig. 16. Development of cocoa butter crystal forms

According to thermodynamics two modifications can only be in balance with each other if the sum of their energy state is equal to each other. This circumstance is equal to the equilibrium of free enthalpies and free energies. (With crystals at common pressure these two are basically the same.)

The modifications transform into each other by the restructuring of unit cells, and this restructuring supposes proper mobility for unit cells. Mobility is fairly limited, but it largely increases due to the rise of temperature. Thus the transformation of crystal modifications is a rather slow process, and it is even slower when the temperature is lower as well. This is the explanation on why unstable modifications can exist for long period of time at certain temperatures without transforming into a more stable modification.

As a regular rule we can say that if there is a possibility for more crystal formations to be present, then the smallest free enthalpy form never develops, because the voluntary free enthalpy decrease always occurs gradually in steps. This is called the Gay-Lussac-Ostwald step rule. But this isn't a strict rule.

We need to look for the reason of the delayed development of higher melting-point stable crystal modification in the higher activation energy for the development of a more stable modification.

Cocoa butter has very unique consistency properties, which make it capable for barred chocolate production. Up until 30°C the solid phase dominates in the solid-liquid rate of cocoa butter, then around 30-36°C the solid phase melts and at body temperature we can't find any solid part. The solidity below 30°C is a very important characteristic both from a technological and a storage viewpoint, but for digestion complete melting at 36°C is preferable.

The cocoa butter alternatives used for barred chocolate-like nougats try to mock these properties:

below approx. 30°C the consistency is solid

at 36°C the alternative has to melt as well

conchoidal fracture, which is a very unique characteristic of cocoa butter and chocolate products

chemical resistance against rancidity and saponification, but we have to mention that the chemical resistance of cocoa butter not only comes from its tocopherol content but it is also the result of the lack of fatty acid chains shorter than C12.

The procedures of chocolate product manufacturing

These procedures are the following:

storage of chocolate liquor

tempering of chocolate liquor (beginning of controlled crystallization)

adding of tempered chocolate liquor (grinding)

solidification of the designed form (performing crystallization)

separation of solid chocolate product and the metal mold

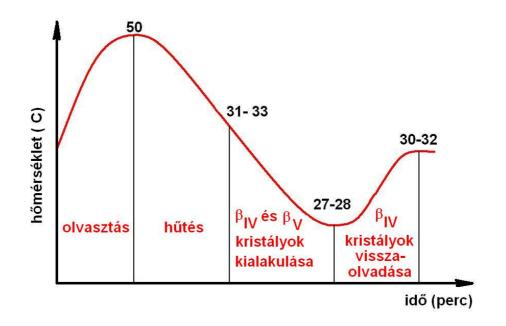
This process is called chocolate formation.

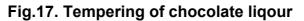
Tempering of chocolate liquor

The tempering of chocolate liquor is the injection of (β V) cocoa butter crystal modification to the melted chocolate to star the crystallization of the cocoa butter content of chocolate liquor.

So the tempering of chocolate is pre-crystallization, by which the injected crystal modifications are developed in the liqour.

Tempering has to be performed under such circumstances that in the first part of the process a lot of stable β V-modified crystal clusters should develop. The tempering of chocolate liqour can be considered succesful if the fat phase contains 3-5% stable crystal forms.





Tempering in practice:

First phase

The chocolate liquor is cooled down from 40-45°C to 32°C. Here a great amount of stable β crystal modification develops and the viscosity of the cocoa butter increases. Second phase

The chocolate liqour is cooled down from 32° C to 28° C. Stable β crystal modifications continue to develop, the viscosity of cocoa butter increases further. Third phase the present unstable β -modifications melt

the viscosity of cocoa butter decreases, the processes following tempereing can be carried out more easily

We have to mention that there are other methods for tempering too. The temperatures above cannot be applied for every type of chocolate. These are modified for milk chocolates, because milk fat has a lower melting point than cocoa butter. Actually these fats don't have an exact melting point, but a softening temperature interval. There aren't exact tempering temperatures, but the most common tempering method for milk chocolate is the following:

First phase: cooling from 40-45°C to 32°C

Second phase: cooling from 32°C to 26-27°C

Third phase: heating from 26-27°C to 28-29°C

We must start tempering with perfectly melted chocolate liquor.

If the production isn't continuous, or the making of chocolate liquor and of the products happens separately, then before tempering we have to heat the chocolate up to at least 40°C because then it is provided that we start tempering with crystal cluster-free liquor.

Machines of chocolate liquor tempering

The figure below shows the periodic machine. The walls and the bottom of the machine can be cooled and heated by water. The mixer stirs the chocolate liquor on the 25°C surface that starts the crystallization. After cooling the chocolate liquor is heated again to decrease viscosity. The disadvantage of the machine is its low performance and the lack of instrumentation.

Continuous tempers

The Lauenstein temper is show on Fig. 18. The chocolate liquor is heated in a bigger double-walled tank, and kept on a 40°C temperature then it is moved the tempering machine. Inside the temper there are three separatable cooling and heating zones, these provide the temperature for tempering.

The properly tempered chocolate liquor is transported through pipes that are heatable by water directly to the forming machines. At this machine any excess chocolate can be circulated back to a tank that serves as a buffer tank.

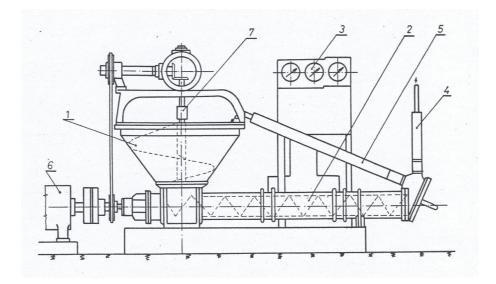


Fig. 18. Continuous tempering machine

1. tank, 2. tempering cylinder, 3. thermometer, 4. heatable pipe, 5. motor, 7. mixer Carle-Monanari continuous temperer

The temperature of the chocolate liquor in the tank is set to 40°C. To the main tank two cooling cylinder with the same capacity are connected by pipes and pumps, one of the cylinders tempers for 33°C, the other tempers at 27°C. The two different temperature chocolate liquors are homogenized in the mixing tank, thus reaching the temperature of 30-31°C (Fig. 19.). We can see that this tempering process is different from the one we discussed earlier.

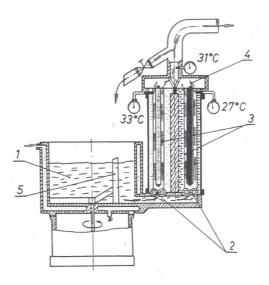


Fig. 19. Carle-Montanari continuous temper

1. tank, 2. pump, 3. cooling cylinders, 4. mixing tank, 5. mixer

The tempered chocolate liquor is transported to the forming machine. The forming machine moves the chocolate from the tempering tank to molds on a moving belt according to volume. After molding the chocolate material is de-aerated by vibration, then it reaches the three cooling tunnels. At first they go through at 12-15°C, in the middle at 4°C, finally at 12°C. From well tempered chocolate a product with smaller specific surface area is created so it can be removed from the mold easily. Today the whole process is automated.

The formed chocolate then is stored in refrigerated rooms and packaged. For the packaging of barred chocolates they use an automatic wrapping machine. First the chocolate is wrapped in aluminum foil then in colorful plastic or paper.

Enriched chocolate (with hazelnuts, almonds) is also produced on fully automated production lines. The materials and the chocolate are mixed after tempering, then a forming machine with a special mixer and feeder moves them into molds. The other processes are the same as they were in the case of other products.

5.2. Handmade cherry liqueur chocolate production

Cherry liqueur chocolate is about 10-13 g in weight, round; 2-3 cm in its diameter, its height is the same as its diameter, dome-shaped, shiny, brown chocolate dessert. The top of each has a chocolate loop (so-called snurni). The dessert is made of semi-sweet chocolate, carefully selected, preserved (in ethanol) cherry with 70% alcohol content, and fondant.

The chocolate cod contains alcoholic deseeded cherry, surrounded by the liquefied fondant cod. Altogether these ingredients results a pleasant, harmonized product. The chocolate pieces are packed in golden (sometimes red) foil.

Handmade cherry liqueur chocolates are different in their sizes because of the different cherry sizes; mechanically made chocolates are the same in their sizes.

The traditional, handmade method of "cognac cherry" production was described first by Károly Hagn in his cook-book published in 1943 (Confectioner in war and peace, and the master of honey-bread): "The carefully selected, uniform morello -cherries are destemmed, washed, placed in clean jars. Then rum or cognac are poured onto the cherries and closed hermetically. Let the cherries ripen for a few weeks. Then the cherries are poured onto a sieve thus the rum or cognac is dripped off. We deseed the cherries. Fondant is warmed and liquefied with rum or cognac to the proper density. With this liquefied fondant the cherries are filled.

Next, fondant is warmed and liquefied with cognac to the proper density. Warm up to a very high temperature. The filled cherries are coated with this liquefied fondant by using dipping-wire, placed onto papers for dripping. Advisable to dip the base previously, for extra strength. Do not dip too thinly because it can run off. The desserts are packed in silver or golden staniol-foil." (Hagn, 1943. pg59.)

Today black cherry is used for cherry liqueur chocolate production. The cherries are dipped in hot fondant, they let them cool down (the step of fill are missed, the fondant cop is as delicious without it, it creates a liqueur-like liquid in the product). The congealed, fondant covered cherries are placed to a chocolate base, then, the semi manufactured products are dipped in tempered chocolate mass by using dipping-fork. After this the chocolate loop on the top is made (snurni).

5.2. Machine formed cherry liqueur chocolate production

Since the traditional, slow, work-demanding, handmade cherry liqueur chocolate production could not satisfy the need for the dessert in the 1960s the machine

formed cherry liqueur chocolate production method had to be elaborated. A very important step before the preservation is in the production is the selection of cherries according to their sizes. If the sizes of the cherries fluctuate the waste rate increases, since the machines cannot keep up with the fluctuation of the cherry size.

The machine made cherry liqueur chocolate production consist of four things: chocolate shell, deseeded cherry, fondant, chocolate base. - for production other substances cannot be used!

-The shells are made in plastic molds, which get on the production line in rounds. The first step is the shell production during which tempered chocolates is poured into the forms then they are cooled down, and solidified in a tunnel freezer. (Described beforehand)

-This step is followed by the adding of the alcoholic cherry, after which the filling of fondant happens. The molds get back to the tunnel freezer, where the filling solidifies.

-Next the chocolate base is added followed by a cooling step.

-The product is removed from the molds.

The last step is the packaging of the dessert apiece by using shiny, golden foil. The type of the finished packaged product can be various. Usually, they are packed in gift boxes containing 10, 12, 15, 30 piece of chocolate but there are 3 pieces containing foil package, and there is a 1.3 kg cylindrical, or heart shaped, transparent plastic package too.

5.3. Storage and logistics

Food safety

Nowadays food safety has become one of the most important things in the industry. Because of consumers consciousness, the purchasing regulations of commercial chains, and legal regulations besides quality food safety gets special attention. In an optimal case these regulations were used by the producers, but food safety is more than food hygiene.

Although confectionary products do not belong to the category of "dangerous" products, there are some critical points. These points do not necessarily correlate

with the critical points of HACCP system; rather they indicate those steps of production processes which need more attention than usual.

Pralines or dessert, bonbons are very popular products of confectionary industry. Because the nature of these products they are usually bought as gifts or surprises. Thus we make sure about the good quality, and the pleasing package of the products. The consumers think of the safety of the product as self-evidently good. In Hungary, cherry liqueur chocolate belongs to the above described popular category, so below, the food safety aspects of confectionary industry will be discussed through this product.

Avoiding the detailed discussion of production technology, the production can be divided to for parts: chocolate mass production, alcoholic cherry preparation, fondant production, and at last bonbon production.

During chocolate production the quality of ingredients, physical and microbial pureness has an important role. Today cocoa mass are bought ready-to-use by chocolate factories, the quality needs to be monitored during purchasing. Sugar is available in crystal form, which has to be very pure (99.9%). In the production of milk chocolate mass the milk dry matter can be ensured by adding skimmed, whole milk powder, or whey powder. In case of these substances the microbial state can cause problems. Special challenge is the purchase of emulsifying agents. Lecithin is made from soy beans at large scales and the insurance traditional (not GMO) soy ingredients cause an increased problem. Because of the expectation of the consumers largest producers take pains over this question. During the production the physical and chemical contamination can cause problems. Chocolate mass can be well stored, and handled. The alcoholic preservation is less problematic from a microbial point of view unlike the chemical contamination (herbicides) or the unfinished deseeding procedure. Cherry liqueur chocolate gets its silky, pleasantly sweet flavor from the fondant mass. Fondant is condensation and crystallization of sugar and starch syrup. During fondant production the proper temperature should be applied because the high sugar content can be the seed-bed of microbes, although this amount of sugar content is toxic for most microbes.

Cherry liqueur chocolate production can be conducted in two ways: handmade and mechanically controlled way. During handmade production amount of hand work, and incubation time between each process can increase the contamination from the air. That is why plant hygiene (personnel and equipment) should be respected.

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Although cherry liqueur chocolate does not mean to be a risky product from a food safety point of view, by the reason of chemical and physical requirements. During production the keeping of regulations is the guarantee or the safety of the product. During ingredient purchase one must aim to be able trace the origin of the ingredients which have to be guaranteed by the producer.

Cherry liqueur chocolate is a special threat for the consumer: If the cherry in not fully deseeded the consumer's tooth can break by biting on the remaining seed. This can have serious effects on the producer! Hungarian cherry liqueur chocolate is almost the only product among this type of cherry-products in the word that is guaranteed to be deseeded.

Logistics – distribution

Under distribution chain those decisions and activities are meant those needs to be organized to get the product to the final consumer. After the production of confectionary products transport activities has to be organized during which the viewpoint of environmental production must be considered, since the product distribution can reach to huge distance. By organizing the commercial channels, and logistic systems the aspects of environmental protection also has to be organized.

For environmentally friendly distribution is characteristic that it tries to minimize the transportation package, and to choose the shortest route. The modern attitude prefers material- and energy saving transportation systems, and it aims to choose the purest commercial channel and to build the so-called re-distribution channels. Despite the former, common, one-directional organizing method in the above described distributional method the producer has to ensure the collection of the package waste, and preparation of recycling too. In an environmental-oriented corporation subsystem takes care of the product distribution to be on time in the right amount. Besides the generally required economic efficiency factors (i.e.: cost-reduction) in this functional area spare resource and environmental protection viewpoints can be realized.

During the large-scale production and distribution of cherry liqueur chocolate the above described viewpoints have to be predominated. In case of handmade products the transportation and distribution to the neighboring areas is easy to conduct and the distribution causes less pollution.

6. Special praline products and their production

6.1. Other ingredients for praline production

Oil seeds. The raw material of chocolate and cocoa production is cocoa beans. For desserts, novel nougats almonds, hazelnuts and walnuts are needed. Apart from these peanuts, soy, peach kernels are also used.

White rolled fondant. The preheated fondant is diluted and then heated further. Protein is added. It is heated up to 50-55°C. It is flavored with lemon of almond essence.

Colored rolled fondant. Pink: Properly diluted fondant is colored red, then with some protein it is heated up to 50-55°C.

Green rolled fondant. The process is similar to white rolled fondant. The effect of the green coloring can be eased with some yellow coloring. It is flavored with pineapple ester.

Cake rolled fondant. The fondant is made just like the ones before, but here it is heated up to 40°C. The icing is thicker and less rigid.

Brittle production

While marzipan products are made from unroasted oil seeds and sugar and the nougat products are made from roasted oil seeds and sugar then brittle products use both these two materials roasted or dried. Another difference is that in the former products the oil seeds should be as homogeneous as possible, here oil seeds are added more coarsely.

The first step of brittle production is that in a cauldron over fire sugar is being melted. Part of the heated sugar caramelizes, thus gaining a yellow-brownish color. After that the roasted seeds can be added to the sugar. For the making of soft brittle starch syrup can be used. The brittle mass then is poured on a marble table and sheets are formed. Brittle shouldn't be the coating of other products without any other coating because the caramelized sugar is very hygroscopic and it can be very sticky, except for Dobos cake whose coating is the so-called Dobos-sugar. Dobos-sugar is strawyellow caramelized sugar.

It's best for brittle if it is formed at 70°C, because at this temperature brittle is formable but not sticky. The making of the sheets can happen by a rolling pin manually, the stickiness of the brittle can be balanced with the dusting of talc or in bigger factories for the same reason they use paraffin oil or talc. The lower cylinder

has to be knurled otherwise it won't move the material further. For the formation of brittle the table has to be oiled as well or else the material will stick.

The sheets are formed by cutting. For this process disc knives are usually used. The gap between the knives is adjustable.

We go through the brittle twice with the disc knives, once alongside once across. Thus we get square or rectangle shapes sheets. Decorating brittles can be pressed easily with little work just like hard candy.

We can make good quality filling brittles if we replace a part of the sugar or all the sugar with honey. Of course brittle created with honey is softer. Brittles are usually not flavored but we can with some orange peels or candied orange peels.

6.2. Mechanical formation of praline products

The processes of formation are shown on figure 20.

Steps:

Tempering of the molds, adding the chocolate liquor to the molds, then spreading by shaking, forming of the chocolate shells by rotating the mold in 180°, solidifying the shells in a refrigerating tunnel, tempering the fillings then adding them in the chocolate shells, solidifying the filling in a refrigerating tunnel, sealing the filled shells with chocolate, solidifying the bottom of the shells in a refrigerating tunnel, finally removing the desserts from the molds.



Fig. 6.20. Process of dessert production

We can observe that the three formation processes follow each other:

shell formation (not removing from the molds)

cream formation (not removing from the molds)

sealing the shells, then removing them from the molds

The three formation processes are the consequence of the three separatable structural elements of the dessert:

shells

fillings (cream)

sealing

In Hungarian confectionery there are high performance, multipurpose forming machines with which we can produce desserts, filled barred chocolates, such a machine is the CAVEMIL-275 which is shown on Fig. 6.21.

The machine can be divided into these three main sectors:

shell forming (I.),

cream filler (II.),

sealing unit (III.)

Their common characteristic is that besides chocolate they contain other materials, fillings with different composition and consistency. The appearance of the products vary: barred, slabs, but the most common ones are filled desserts which are about 10g in weight.

The filled chocolate forming machines have high performance, are highly mechanized, fully automated.

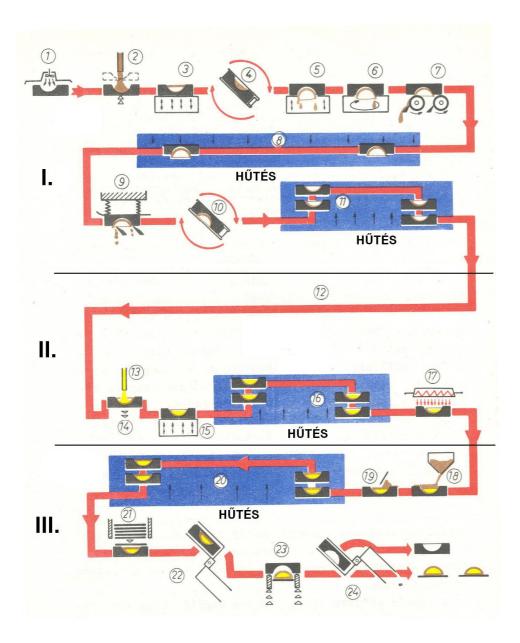


Fig. 21. CAVEMIL machine

1. warming of the molds. 2. chocolate adding, 3. vertical vibration, 4. rotator, 5. vibrational dripping, 6. circular shaker, 7. wiping cylinders, 8. refrigerator, 9. knife remover, 10. rotator, 11. vertical refrigerator, 12. conveyor belt, 13. filling feeder, 14.

mold lifter, 15. vibrational phase, 16. vertical refrigerator, 17. mold warmer, 18. chocolate feeder, 19. excess chocolate remover, 20. vertical refrigerator, 21. tray feeder, 22. mold rotator, 23. product remover, 24. separation of the product and the molds

One-shot instruments

For the production of filled products (like desserts, barred or any other product) the time required for production, the length of production line, and the size of plantation has to be determined not to skip the classic three steps. The technological time requirement can be shortened to a certain extend by intensification. The one-shot formation principle broke with the traditional principles and with a new solution it produces the filled product in one step. On the figures the steps of praline production is shown.

It needs to be mentioned that other products (i.e. barred, filled, or seasonal products) can be produced with this method.

According to the most modern technologies the adding of shell and filling can be realized in a "pipe-in-pipe" feeder: the outer pipe adds the chocolate for the shells, 0,1 s after the end of shell formation the inner pipe adds the filling into the shells, then the two parts are cooled down.

In this case of production technology in one step the shell, filling, and base is formed.

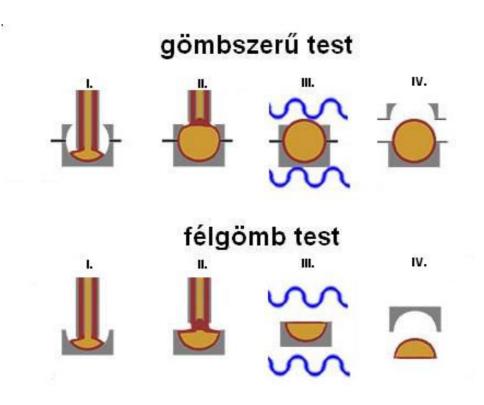


Fig. 22. The principles of one-shot formation

The opening process of production is the warming of the molds, the closing one is the removing the finished product from the molds. In between the opening and closing steps there are three steps of formation units. Figure 6.22. shows that the formation principle of the two types of geometric products are identical. The first process is the simultaneous adding of the chocolate of shells and the filling, then in the second step the outer shell formation takes place (there is no filling dosage). The cooling is the last step after which the finished product is removed from the molds. Formation by freezing

For the fastening of small, filled products there is a new way of production, which shorten the shell formation. Besides it makes a more economical way of production since it ensures a thinner (thus cheaper) shell production.

In this process the chocolate mass poured into the negative molds is pressed with the cooled molds thus the tempered mass between the form and punches can solidify quickly. The advantage of this method is that a very thin shell can be made in various forms. In the first step the tempered chocolate mass is poured into the negative molds then the molds are shook. The formation is realized in the third step when the cooled positive punches are pressed into the chocolate-filed negative ones forming the end-product. After this the shell is solidified, and filled.

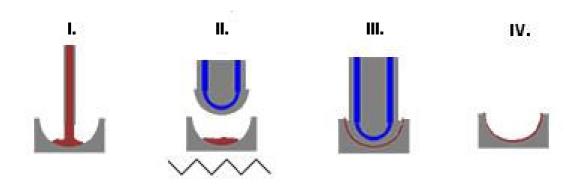


Fig. 23 Formation by freezing

The wide variety of form can be observed in the pralines therefore the formation processes considered as very important processes. From the things above it can be seen that with the improvement of instrumentation and technology there are newer and better solutions. The main objective is to sustain food safety, economic production, the expansion of product varieties, and insurance of flexible production programs.

In the confectionary industry there is an intense competition in all around the world, which has to be taken up by the Hungarian enterprises. If the skill, intention and venture do not meet the Hungarian confectionary production will wither which will be everybody's loss.

Chocolate as the Medical Food

As Lippi (2013) said "Cocoa and chocolate represent also today an important occasion of confrontation in terms of medicine and dietetics. In the past, when no effective therapeutic means existed, the only possibility to recover from disease was to use lifestyle and diet as strategies to ensure physical and mental well-being. The concept of a "life regime" in the classical world was expressed by the term díaita/diaeta (which had nothing to do with adjusting rations according to an individual's physical and biometric conditions, as it does today). Its meaning was far broader, encompassing all the areas that were not determined automatically by nature and that humans thus could plan of their own accord such as one's relationship with air and water, food and drink, motion and rest, sleep and wakefulness, dejections and sexuality, love and passion. These rules were collected in the *Regimina Sanitatis*, which were codi fi ed during the Middle Age: the doctor could, indeed, intervene to cure the sick man, but also the sound, making the required changes to the way of living, using food and drink.

Castelli et al (2012) mentioned Chocolate was considered medicinal in ancient times [1]. Following on the Olmecs, Mayans, andAztecs, the Spanish and other Europeans identi fi ed many medicinal uses [2]. Chocolate consumptionhas also long been associated with pleasure. Popular claims confer on chocolate the properties ofbeing a stimulant, relaxant, euphoriant, aphrodisiac, tonic, and antidepressant [3]. In recent years, the consumption of cocoa has been associated with healthy effects preventing oxidativestress. Throughout this chapter, and indeed the whole book, the bene fi cial actions of cocoaproducts on the cardiovascular system and central nervous system are presented; moreover, experimentalstudies suggest that cocoa has positive effects on the modulation of cancer development andimmune function, including in fl ammatory process. Here we focus on the recent literature showing theclinical effects of cocoa and, where clinical evidence has not already been reported, on experimental

models in vivo.

Visioli (Interest in the biological activities of cocoa polyphenols is steadily increasing. In fact,the high polyphenol content of cocoa, coupled with its widespread presence in many food items, render this food of particular interest from the nutritional and "pharmacological" viewpoints. Indeed, the number of publications concerning cocoa and chocolate is increasing steadily. Of such publications, an increasing proportion concerns the effects of polyphenols and, in particular, flavonoids on human biology and health. As outlined in detail in other chapters of this book, research is unraveling new and diversified healthful actions of "minor constituents" of cocoa. This is also reflected by the increasing number of patents covering industrial processes that aim at maintaining the highest possible amounts of polyphenols in cocoa. In fact, the current

manufacturing process destroys roughly 95% of the polyphenols originally present in the cocoa bean.

The Potential Role of Cocoa Polyphenols in Human Health

Of the several compounds found in the cocoa bean that might be beneficial for the humanbody, e.g., proteins, fiber, minerals, etc., the main focus of research revolves aroundpolyphenols. Of note, bioavailability of cocoa polyphenols is quite low, but depends on the matrix in which the cocoa polyphenols are delivered. Further, current efforts to increasebioavailability might lead to the formulation of cocoa-based products that, in theory, should confer increased healthy benefits. For the time being, based on the growing body of scientific evidence pointing to the benefits of a diet rich in polyphenols, includingthose from cocoa, many commercial chocolate brands are starting to promote their products on the strength of the high phenolic content of cocoa. As an example, special processeshave been developed which preserve up to 80% of the natural polyphenol content ofraw cocoa without the use of extracts, additives or other chemical substances. One of the downsides of this technology is that the resulting product is often very bitter

and disliked by the consumer. To compensate for this, several approaches are being studied,

including the addition of calorie-free sweeteners and/or soluble fiber. In brief, theindustrial result of the growing number of studies that point to healthful effects of cocoaflavonoids is the formulation of novel chocolates with modulatory effects on human physiology.

Vascular Function of Cocoa

The effects of cocoa on blood pressure were first observed in the Kuna tribe, who consumehigh amounts of cocoa polyphenols (approximately 900 mg/day) and reside in theLas Bals islands of Panama. The inhabitants of this archipelago have lower blood pressure than their genetically-identical compatriots who inhabit the mainland. Therefore, arole for cocoa in lowering blood pressure has been proposed and controlled experimentshave been carried out, as reviewed hereafter. Nitric oxide (NO) bioavailability represents a main contributor to endothelial dysfunction, which, in turn, has been suggested to be the earliest triggering event in atherogenesis[6, 7]. Accordingly, impaired endothelium-dependent vasorelaxation has beendescribed in human conditions characterized by an increased risk for developing atherosclerosisand its clinical sequelae, essential hypertension, i.e., hypercholesterolemia type 2 diabetes, obesity and aging [8]. Thus, the hypothesis was formulated thatpolyphenols and flavonoids, particularly the subclass of flavanols, might improve NOdependentperipheral glucose uptake, i.e., insulin sensitivity, in both normal and insulinresistant conditions. This hypothesis has been tested with several polyphenol-rich foodsand beverages, such as tea. As far as cocoa is concerned, it was shown that flavanolrichdark chocolate decreases blood pressure and improves insulin sensitivity and NOdependentflow-mediated dilation in healthy subjects [9], essential hypertensives withnormal glucose tolerance [10], and glucose intolerant hypertensives (Chapter 9). In addition, data from in vivo experiments report an impaired NO-mediated endothelial functionduring acute hyperglycemia [11]. Some experiments in healthy volunteers explored the acute effects of an oral glucose tolerance test alone and after three days of eitherflavanol-rich or flavanol-poor chocolate administration on vascular health. The resultsshow an amelioration of vascular function that follows cocoa intake, suggesting that regularconsumption of cocoa-based products (within a balanced and equicaloric diet) mightconvey beneficial effects in endothelial dysfunction patients.

In addition to vascular function, Grassi et al. [9, 10] investigated the effects of flavanolrichdark chocolate on insulin resistance. The authors, as fully described in Chapter 9,demonstrated a significant amelioration of the index of insulin resistance using the homeostasismodel assessment of insulin resistance (HOMA). In contrast, flavanol-rich dark chocolate administration did not influence the two indexes of insulin sensitivity, namely quantitative insulin sensitivity check (QUICKI) and insulin sensitivity (ISI). This is probably due to the difference in study periods, i.e., three days vs fifteen days [9, 10], and the small number of healthy subjects that have been evaluated. Taken together, these findings suggest that cocoa flavanols may contribute to protection of the vasculature by decreasing stress-induced hyperglycemia and improving the global cardiovascular risk profile. Mechanistically, a study conducted in C57BL/KsJ-db/db obese diabetic mice indicated that cocoa dose-dependently prevented hyperglycemia [12], thereby supporting the evidence

that cocoa flavanols might not only counteract blood pressure elevation (as suggested by the epidemiological studies performed on the Kuna Indians) but also positively influence glucose homeostasis.

In humans, by using noninvasive ultrasound measurements of flow mediated vasodilation, Hermann et al. [22] showed that dark chocolate, but not white chocolate improves endothelial function and platelet function in young healthy smokers, a group chosen because they have impaired endothelial function and platelet hyper-reactivity. In summary, cocoa and its polyphenols are able to positively modulate vascular function, possibly via concomitantly increasing NO production and limiting its inactivation by free radicals. Although

we should keep in mind that vasculo-impaired patients are often overweight and/or insulin-resistant, and therefore, need to follow hypocaloric and sugar-restricted diets, the inclusion of cocoa products, namely those rich in flavanols, might be a valuable tool to accompany and support pharmacological therapy.

Others, eg Castell et al (2013) reported that over the last few years, clinical trials have indicated that cocoa-derived products are able to reducesome factors involved

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in the risk of cardiovascular disease: high blood pressure (BP), excessive plateletactivation, and high LDL concentration and oxidation, among others.

Dark chocolate consumption has been associated with lower BP [25-28], although some trialshave also reported con fl icting results [29, 30]. Recent meta-analyses including 10-13 trials conducted in hypertensive and normotensive individuals in the last 15 years have concluded that dark chocolateis superior to a placebo in reducing systolic hypertension or diastolic prehypertension, and as a result, the authors felt that cocoa products could be recommended as a treatment option for hypertension[31, 32]. However, most of these studies included a relatively small number of subjects, and theirresults are questionable due to their lack of rigor or parallel bioavailability studies [33, 34] . Davinsonet al. [35] , using four different doses of cocoa fl avanols, report the reduction of the mean arterial BPin 52 postmenopausal women with untreated mild hypertension, although no evidence of doseresponse was observed. The lowering BP activity of cocoa has also been found in patients with coronaryartery disease (CAD) [36]. Blood pressure reduction after the consumption of a high dose of darkchocolate for 3 months in a study performed in 102 patients with prehypertension/stage 1 hypertensionand established cardiovascular end-organ damage or diabetes mellitus has been reported [32] .

On the other hand, it has been suggested the role of theobromine in decreasing BP. However, Van DenBogaard et al. [37], in a double-blind placebo trial using fl avanol-rich cocoa beverages with natural oradded theobromine, concluded that although after 2 h of consumption the central systolic BP wassigni fi cantly lowered by the theobromine-added beverage, the 24-h ambulatory or central BP was notaffected.

The BP-lowering properties of cocoa may be associated in part to modulation of endothelial function[38, 39]. In this regard, a recent study associates the action of fl avanols with the optimal nitricoxide (NO) concentrations that produce vasodilatation and therefore a decrease in BP [40]. Cocoaflavanols attenuated an exercise-induced increase in BP in a study of 21 volunteers after a single servingby improving endothelium-dependent fl ow-mediated dilatation (FMD) [41]. However, other studies

have shown an effect on FMD without modulation of BP [42]. Moreover, in recent years, some mechanisms for this effect have been suggested. Heiss et al. [36]

]recently demonstrated that in patientswith CAD, the improvement in endothelial function associated with cocoa fl avanols is mediated, aftera dietary high- fl avanol intervention lasting for 30 days, by an enhancement in the number and function of circulating angiogenic cells. Positive effects on the reduction of platelet aggregation by darkchocolate have been reported as well, but neutral effects have also been found [43].

The saturated fat present in dark chocolate does not adversely affect the blood lipid pro fi le. On the contrary, and due to its richness in polyphenols, both the short- and long-term interventions, performeduntil now with cocoa, evaluating this aspect seem to signi fi cantly reduce serum LDL and totalcholesterol (TC) and increase HDL concentrations [44, 45]. In most studies, consumption of cocoasources induced a reduction in LDL and TC in hypercholesterolemic individuals [43] or in healthy

subjects [46] .

Moreover, the effects of chronic cocoa consumption on in fl ammatory cellular and serum biomarkersrelated to atherosclerosis, an important factor in the development of heart disease, have also beenreported [47]. A recent trial involving volunteers with a high risk of cardiovascular diseases takingcocoa with skimmed milk for 4 weeks showed the effect of cocoa on increasing plasma HDL anddecreasing plasma oxidized LDL concentrations [48]. Therefore, this action adds new evidence to thebene fi cial role of cocoa fl avonoids in preventing cardiovascular diseases.Overall, epidemiological studies suggest that cocoa has a clear cardiovascular-protective effect byimproving endothelial function and decreasing platelet aggregation and blood pressure. However,more studies focused on establishing optimal doses are required.

Cocoa as a source of antioxidant molecules

Many of the bene fi cial effects of chocolate are associated with the antioxidant effects of the polyphenolscontained in cocoa. These polyphenols, mainly fl avanols such as catechin, epicatechin, and procyanidins, give chocolate antioxidant activity. In addition, condensed tannins (proanthocyanidins)may also become bioactive

antioxidants after colonic fermentation [4, 5]. One serving of dark chocolateis thought to impart a greater antioxidant capacity than the average amount of antioxidants consumeddaily in the United States [6]. However, there is some dispute about its antioxidant action whencocoa is consumed with milk: some studies reported a decrease of this activity when added to milk [4], while other studies suggest that milk only lowered the excretion of some urinary metabolites [7].

The antioxidant activity of cocoa fl avanols is attributed to their capacity to neutralize free radicals, inhibit the enzymes responsible for reactive oxygen species (ROS) production, chelate metals, and upregulate antioxidant defenses [8]. Quercetin, a minor fl avonoid in cocoa, and other non flavonoidcompounds present in cocoa, particularly methylxanthines, also contribute to cocoa's antioxidantactivity by neutralizing radicals and chelating metal ions [9]. On the other hand, it has been proposedthat ingested fl avonoids produce no direct antioxidant effect in vivo but modify proteinkinases mediatingsignal transmission, thus inducing antioxidant gene expression or inhibiting oxidant gene expression [10]. However, despite these antioxidant characteristics, fl avonoids in excess or in the presence of redox-active metals can become prooxidants [11] .A large number of in vitro studies have demonstrated the antioxidant properties of cocoa [8, 12]. Going beyond in vitro assays, a smaller number of studies have investigated the effects of cocoain vivo. Cocoa intake increases total antioxidant capacity (TAC) and decreases lipid oxidation productsin plasma [13] and tissues [14], an effect that can be attributed to fl avonoid accumulation [15]. Cocoa intake is able to induce antioxidant enzymes such as superoxide dismutase and glutathioneperoxidase [16]. Cocoa also improves antioxidant defenses in oxidative stress situations. Thus, a longtermdiet supplemented with cocoa fi ber reduces lipid peroxidation in hypercholesterolemic rats [17], and cocoa supplementation reduces plasma 8-isoprostane in obese diabetic rats [18].

In addition to the in vivo assays in animals, the antioxidant power of cocoa and chocolate has been assessed in dietary intervention trials in humans [19]. In the plasma of healthy volunteers consumingdark chocolate, increased TAC and decreased presence of lipid oxidation products have been reported[20]. Similar results were found in volunteers who consumed procyanidin-rich chocolate [21]. In these studies, enhancement of TAC was greatest 2 h after chocolate ingestion and

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returned to basalvalues 6 h after cocoa intake, probably because of the short plasma half-life of fl avonoids and theiruptake in cells. A crossover trial on 12 healthy volunteers consuming dark chocolate, dark chocolatewith full-fat milk, or milk chocolate showed that 1 h after the ingestion of dark chocolate, plasma TACvalues increased by 20%, whereas no changes were reported after ingestion of dark chocolate withmilk or milk chocolate [22].

An interesting report shows the action of cocoa on prooxidant situations. The consumption of100 g of chocolate (0.2% polyphenols) for 2 weeks counteracted oxidative stress in soccer players, aswas shown by reductions in plasma malondialdehyde and a -tocopherol increases [23] (Castell et al, 2013).

Cocoa Polyphenols as Antioxidants

Visioli et al (2012) give an overview of polyphenols and its effect in cocoa in their book. It should be underscored that randomized trials of antioxidant supplements, namely vitamins such as vitamin E and beta-carotene, have mostly yielded negative results [23]. Conversely, a wide body of epidemiological studies demonstrate that whole foods, and their polyphenols, are beneficial to health [24]. Most attention has been paid to the antioxidant activities of polyphenols, mainly because of biochemical studies that show

how oxidative stress increases the risk of degenerative diseases. Also, most polyphenols and, in particular, ortho-diphenols are strong antioxidants in vitro. Accordingly, several studies have measured the in vitro antioxidant activity of foods and beverages as components of the diet. Indeed, the total polyphenols in fruits, vegetables, beverages, nuts, spices, oils, and chocolate have been determined using a sample preparation technique which hydrolyzes sugar-bound polyphenols. Chocolate provides 4% of the total daily antioxidants in the USA, and recently published data compared both chocolate bars and chocolate drinks. Data for commercial chocolate bars from the US and Europe, especially those with the percentage of cacao listed in the label, are also available. However, we are just now beginning to understand that the mechanism of action of polyphenols is not always

an antioxidant one and most likely involves the metabolites rather than the original polyphenols [25, 26]. For example, polyphenols produce benefits in endothelial function, platelet activation, blood pressure and flow, and gene expression [25, 26].

While most of the suggestive evidence comes from in vitro studies, in vivo (animals, humans) trials are needed to clearly establish causation and to prove the biological activities of cocoa beyond any doubt. Accordingly, Vinson and co-workers were the first to investigate the effect of cocoa powder in an atherosclerotic hamster model [27]. Cocoa, added to the diet at a human dose equivalent to two normal dark chocolate bars per day inhibited the development of atherosclerosis by 38% . In addition, cocoa decreased LDL, increased HDL, and decreased lipoprotein oxidizability, hence positively modulating the plasma lipid profile and one surrogate marker of cardiovascular disease. Two human studies were also carried out by the Vinson group and the Penn State University [27, 28]. This was a single dose study, in which dark chocolate and cocoa powder were given to fasting humans to investigate the post-prandial protection of LDL+VLDL from oxidation. The authors reported inhibitory effects of cocoa, while the fat and sugar placebo produced an increased oxidation of LDL+VLDL, i.e., increased postprandial oxidativestress. Based on the Vinson and other studies, including long-term supplementations, cocoa is able to significantly increase HDL, increase plasma antioxidant capacity, and decrease the oxidizability of LDL [29, 30]. The mechanisms by which cocoa exerts these potentially anti-atherosclerotic activities are yet to be fully elucidated and are shared by other polyphenol-rich foods. Indeed, there is growing evidence that polyphenols are able to increase HDL concentrations, but the precise nature of this effect remains obscure. It is noteworthy, as mentioned, that cocoa has one of the highest content of flavonoids amongall foods. Therefore, its contribution to the overall lipid-modulating effect of the diet islikely to be relevant.

The antioxidant effects of cocoa flavonoids in humans have been extensively investigated in the past few years, mostly by the Serafini group. As an example, the group showed that the acute ingestion of 100 g of dark chocolate by healthy subjects was able to improve plasma total antioxidant capacity (TAC) and (-)-epicatechin plasma levels [31]. However, these effects were markedly reduced when dark chocolate was consumed with milk or when milk instead of dark chocolate was eaten [31]. An explanation is that proteins of the food matrix in which cocoa is eaten, in this

case milk, might bind flavonoids and reduce theirbioavailability and therefore, their potential antioxidant properties in vivo. It must be underlined that the effects of milk on polyphenol bioavailability and thus, biological activities are still controversial. As an example, evidence showed that the improvement of flowmediateddilation (FMD, a marker of vascular function), induced by the ingestion of 500mL of black tea infusion was completely abolished by addition of milk to tea [32]. Conversely, Schroeter et al. [33] showed that consumption of a single dose of liquid chocolatemixed with milk did not abolish its antioxidant effect. The very low amount of milk addedto chocolate (3%) might explain these findings. In summary, the addition of milk to cocoafoods and beverages might decrease absorption of polyphenols and limit the health effects of cocoa. However, this hypothesis requires further, solid confirmation. To establish causality, one needs to correlate the increase in plasma TAC that followsingestion with the absorption of cocoa polyphenols. To this end, 80 g of procyanidinrichchocolate was given to humans and the rapid absorption of (-)-epicatechin was demonstrated, peaking in plasma after two hours [34]. In association with the increase in plasma(-)-epicatechin levels, a parallel increase in plasma TAC and a decrease in the concentration of plasma oxidation products was shown. However, when three different doses(27, 53, and 80 g) of the same chocolate were given to the subjects, no significant increase of TAC or decrease of lipid peroxidation levels were observed, despite the doseresponse increase in plasma (-)-epicatechin levels [35].

In terms of circulating markers of lipid peroxidation, Wiswedel et al. [36] showed that acute ingestion of a cocoa drink by healthy volunteers was able to lower plasma levels ofF2-isoprostanes, a validated biomarker of lipid peroxidation. Conversely, Mursu et al. [30]showed a lack of effect on plasma isoprostane levels following daily ingestion of 75 g/dayof dark chocolate for three weeks.

To summarize, cocoa is rich in polyphenolic molecules that exhibit powerful antioxidant

activities in vitro. Whether these activities can be reproduced in vivo, i.e., after ingestion, remains to be fully established, mostly because of the low bioavailability of these compounds and the lack of appropriate biomarkers of oxidative stress and antioxidantactions.

The stringent phenolic compounds contained in the pigment cells of cocoa cotyledons are defensiveprotections that the plant uses to repel animals and microbes. However, these compounds are responsiblefor the bitter and astringent taste of cocoa developed during the processing steps, such as fermentation. In the unfermented cocoa beans the amount of polyphenols is around 2 wt.% [23], whereasfermented cocoa beans contain 6% of phenolic compounds. Among the polyphenols, the main compounds are catechins (e.g., (-)-epicatechin, (+)catechin,(+)-gallocatechin, and (-)-epigallocatechin), anthocyanins (e.g., cyanidin-3cyanidin-3-(alpha) а -L-arabinosideand (beta) b -D-galactoside), and proanthocyanidins (e.g., fl avan-3,4-diols). In particular, the latter can form oligomers via condensation with the carbons C-4 and C-8 or C-4 and C-6 (Fig. 8.3).

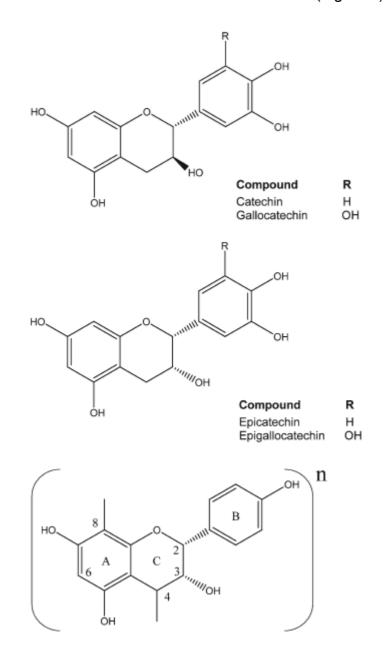


Fig 1. Chemical structure of poliphenols in cocoa

Moreover, some hydroxybenzoic and hydroxycinnamic acids are present in cocoa beans, and theirconcentration depends on the temperature reached during the roasting step. In the fi nal product, chocolate, the amount of polyphenols depends on the percentage of nonfat cocoa solids [24]. Indeed, polyphenols are present in high concentrations in dark chocolates, in which the content of cocoa solid

is higher than in milk chocolate.

The amount of polyphenolic compounds also depends on the provenience of the cocoa beans and

can vary dramatically from region to region. However, during fermentation, the content of polyphenols

is greatly modi fi ed. In fact, polyphenols diffuse in the cells, and they are degraded by polyphenol oxidase,

with a consequent decrease of the amount of fl avonoids. Moreover, the degradation of anthocyanins

during the fermentation modi fi es the color of the beans, which is initially purple and then becomes

brown. The amount of phenols also decreases with roasting steps at high temperature and long times.

Organic Acids in cocoa

The kind and amount of organic acids contained in cocoa beans depend on the maturation and fermentation stages. Also, geographical origin is another important factor to determine a total and/or single acid composition of the beans. The most common organic acids are citric, oxalic, malic, acetic, and formic. The most important is acetic acid because of its in fl uence on the taste of cocoa (Fig. 2.).

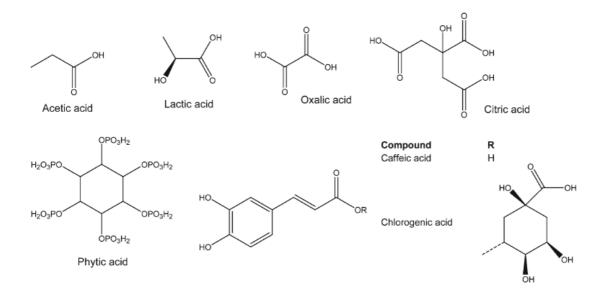


Fig 2. Structure of molecules in some organic acid in cocoa bean

Indeed, fermentation and drying duration affect the amount of acetic acid, which is produced by the fermentation of lactic acid and ethanol. During this step, acetic acid destroys the cells of the cotyledons and diffuses into the beans, making possible the reactions between phenolic compounds, proteins, and oxygen, which lead to less bitter complexes and develop the fl avor of cocoa [25].

However, organic acids represent the antinutritional compounds contained in cocoa, and, accordingto their quantity, they may have adverse health effects. The amount of phytic acid is reduced during the processing of cocoa, and its concentration depends on the type of cocoa and the strength of the roasting step. Phytic acid may have effects at the intestinal level, where it forms insoluble complexes with Ca $^{2+}$, preventing its absorption. On the other hand, oxalic acid (0.3–0.5% in cocoa powder) produces insoluble oxalates that bind to calcium and, as a consequence, inhibits its absorption.

Cocoa and its effect for the Nervous System in Humans and Animals

Following Castelli et al (2013) the scientific proof of the bene ficial effects of chocolate and cocoa on the nervous system has emergedover the last decade [49]. Cocoa can have beneficial effects on cognitive function and mood and canalso protect nerves from injury and inflammation [50].Eating chocolate could help to sharpen the mind and give a short-term boost to cognitive skills. Ithas been reported that the consumption of a cocoa drink boosts blood fl ow to key areas of the brainfor 2–3 h [51]. Increased blood fl ow to these areas of the brain may help to increase performance inspeci fi c tasks and boost general alertness over a short period. These fi ndings raise the prospect ofingredients in chocolate being used to treat vascular impairment, including ischemic cerebrovascularsyndromes, dementia, and strokes. The study also suggests that cocoa fl avanols could be useful inenhancing brain function in situations where individuals are cognitively impaired such as fatigue, sleep deprivation, or possibly aging. It is suggested that these various independent observations of the effect on blood vessels of drinking fl avanol-rich foods could be because of the increase in circulatingNO, as mentioned above.

Preliminary or pilot evidence has shown that fl avanol-rich cocoa can increase cerebral blood flowboth in healthy elderly subjects [52] and in healthy young participants, as measured by functionalmagnetic resonance imaging (fMRI) in response to a cognitive task (the task-switching paradigm)[53] . It should be noted, however, that in the fMRI study, no signi fi cant effects were observed in participants'behavioral reaction times, the effect of switching between two sets of rules, or heart ratesafter the ingestion of the fl avanol-rich cocoa. The authors hypothesized that the fMRI changes mayhave been related to cognitive changes that were not evident in the behavioral measures used in theirproject, especially in the young, healthy participants who were probably functioning at a high level ofcognitive ability. However, a clinical study [54] failed to support the predicted beneficial effects ofshort-term consumption of dark chocolate and cocoa on any of the neuropsychological or cardiovascularhealth-related variables measured. This double-blind, placebo-controlled, fixed-dose, parallelgroupclinical trial was performed on 101 healthy volunteer subjects who consumed a 37-g darkchocolate bar and about 240

mL of an arti fi cially sweetened cocoa beverage or similar placebo productseveryday for 6 weeks. No signi fi cant group-by-trial interactions were found for the neuropsychological(self-report history questionnaire assessing medical and psychiatric histories), hematological(coronary risk panel and C-reactive protein test), or BP variables examined.

It has been reported that, in the elderly, a diet high in some fl avonoid-rich foods is associated withbetter performance in several cognitive abilities in a dose-dependent manner [55]. Other studies indicatedthat in young adults, in terms of cognitive performance, an acute dose of cocoa flavanolsimproved spatial memory and performance in some aspects of the choice reaction time task [56, 57].

These effects might be explained by the increased cerebral blood flow caused by cocoa but may alsobe due to induced retinal blood flow changes.

The effect of chocolate on fatigue appears to have been first described by the Aztec EmperorMontezuma II, (more precisly Moctezuma) who noted, "...the divine drink, which builds up resistance and fights fatigue. A cup of this precious drink [cocoa] permits man to walk for a whole day without food."



Fig Moctezuma the emperor of Aztec Empire

The Badianus Codexpublished in 1552 noted the use of cocoa flowers to treat fatigue [2]. According to a recent study [58],consumption of a fl avonoid-rich chocolate product eases the symptoms of chronic fatigue. Results of asmall, double-blind, randomized, pilot crossover study on ten subjects with chronic fatigue syndrome(CFS) indicated that daily consumption of a high-cocoa liquor/polyphenol-rich chocolate signi fi cantlyimproved symptoms of chronic fatigue after 8 weeks, compared with a cocoa liquor polyphenol-free/low chocolate. Anandamide, previously called arachidonylethanolamide, has a structural similaritywith tetrahydrocannibol, and other strongly related compounds that are found in cocoa. There are alsocompounds like N-acylethanolamines that block the breakdown of anandamide in cocoa. It may be the

synergy of these compounds in chocolate that accounts for the results seen in this study. A number ofbiological systems have been implicated in CFS, and there is mounting evidence that oxidative stresscontributes to the disease process and to some of the symptoms of the illness. The benefits of chocolatemay be due to the flavonoids protecting cells like neuronal cells from oxidative stress. The brain is

more vulnerable to oxidative stress than other organs due to its low-antioxidant protection system andthe increased exposure of target molecules to ROS, one of the major damaging agents involved in ageassociateddecline [59] . Some parameters related to neurotransmission also decline during normalaging [60] . Cellular studies examining the potential mechanisms of neuroprotection by flavonoids havebeen published, demonstrating that epicatechin prevents neuronal cell death caused by oxidized LDLinducedoxidative stress. Furthermore, it has been shown that these neuroprotective mechanismsinvolve the modulation of the mitogen-activated protein kinase (MAPK) signaling cascade [61] .

Chocolate contains many chemicals that can affect our mood: caffeine, tyramine, fl avonoids, phenylethylamine, and others. A theory is that these natural chemicals raise serotonin and endorphinconcentrations that make us feel good and have a calming effect on brain function, but this does nothappen to everyone [3]. Numerous studies have explored the link between chocolate and mood includingdepression. Macht et al. [62] gave pieces of chocolate to subjects after viewing film clips that werechosen to induce anger, fear, sadness, and joy. Results indicated that the quality of emotions can affect that themood-elevating properties of chocolate can be enhanced with intention [63]. According to anotherstudy [64], eating chocolate reduces negative mood compared to drinking water, whereas no or onlymarginal effects on neutral and positive moods were found.

A study based on a survey using a web-based questionnaire of 2,692 persons who were sufferingfrom clinical depression [65] included 61% individuals classi fi ed as "cravers" with the majority beingwomen. This group rated chocolate's capacity to improve their depressed mood as moderate to veryimportant. The study says that, after eating chocolate, the volunteers were more likely to feelsignificantly less anxious and irritated. It also stated that the craving might predict atypical depressionstatus. It overviewed chocolate's effects on mood state, noting its many

psychoactive ingredients, including several biogenic stimulant amines, two analogues of anandamine (producing effects akin tocannabinoid-inducing euphoria), and interactions with several neurotransmitter systems (dopamine, serotonin, and endorphins). Some studies have suggested that carbohydrate craving is more closely linked to the opioid rather than to the serotoninergic system, with endorphins alleviating dysphoria.

Thus, chocolate cravings may advance biological mechanisms potentially settling limbic cortexmediatedactivation [3].

Phenylethylamine is chemically and pharmacologically related to catecholamines and amphetamine, and its deficit may contribute to a state of depression. The most important methylxanthinesfound in cocoa are caffeine and theobromine. Like carbohydrates, caffeine could be a self-medication for people who suffer from depressive symptoms. For example, sedation is an important symptom indepression, and methylxanthines can induce a bene fit arousal through an interaction with adenosinereceptors [66] . Cocoa contains several unsaturated Nacylethanolamines, which are structurally related to an and a mide, and high levels of these substances could interact with other active compoundsof chocolate and provoke a sensation of well-being [67]. Finally, magnesium, one of the most quantitatively significant minerals in cocoa, is known to be potentially effective for treating depression inrelation to the intraneuronal magnesium de fi cits in depressive patients [68].

Another clinical study showed that depressed moods were signi fi cantly related to higher chocolateconsumption, with fi ndings being similar in both men and women [69] . Higher Center for EpidemiologicStudies Depression Scale (CES-D) scores within the provisionally depressed range (above the depressionscreen threshold) were associated with still greater chocolate consumption.

Clinical observations in Parkinson's disease (PD) patients also suggested an increased chocolateconsumption [70]. 498 PD patients and their partners were evaluated through a structured self-questionnaireasking for consumption of chocolate and nonchocolate sweets, changes in chocolate consumptionduring the course of the disease, and depressive symptoms. Consumption of chocolate wassigni fi cantly

higher in PD patients compared to controls. Although reasons for increased chocolate

consumption in PD remain elusive, it may hypothetically be a consequence of the high content of variousbiogenic amines potentially in fl uencing brain monoamine metabolism and/or caffeine analogues with potential antiparkinsonian effects.

Another area of interest of the effects of chocolate on the nervous system is anxiety. A clinical trialperformed on 30 human subjects classi fi ed into low and high anxiety traits using validated psychologicalquestionnaires showed that daily consumption of 40 g of dark chocolate for up to 14 daysreduced the urinary excretion of the stress hormones cortisol and catecholamines [71].

Polyphenols and fl avanols, in particular, appear today to offer new and interesting opportunities toregulate mood and brain disorders. Thus, cocoa fl avanols could enable us to enjoy the benefits ofchocolate as a therapy, without the excessive and potentially adverse effects linked to carbohydratesand lipids. However, further studies are necessary in order to identify the active constituents in thenervous system among the various cocoa polyphenols and to understand their mechanism of action in the brain.

Positive effect of cocoa for Inflammatory Response and ImmuneFunctions

In general, fl avonoids are associated with an anti-in fl ammatory action. In this regard, the flavanolscontained in cocoa have also been the object of studies, but more of these have been performedin vitro. The anti-in fl ammatory role of single cocoa fl avonoids (epicatechin, catechin, procyanidins)has been ascertained and is focused on the secretion of in fl ammatory mediators such as cytokines,NO, and ROS by macrophages and other leukocytes [12] . However, there have been few in vivo and human studies until now.

In an ex vivo approach, it has been demonstrated that a cocoa diet in rats decreases the secretion oftumor necrosis factor alpha (TNF- a), interleukin 6 (IL-6), NO, and ROS from macrophages [72, 73].

More interestingly, there are studies suggesting the anti-in fl ammatory effect of cocoa on experimentalmodels. The oral administration of a cocoa polyphenolic fraction to mice can inhibit ear edema in adose-dependent manner [74]. Moreover, rats that received cocoa for a week developed a lower pawedema induced by carrageenan and by bradykinin [73, 75]. On the other hand, the effect of a longcocoa diet on experimental models with chronic in fl ammation such as adjuvant arthritis and collageninducedarthritis has been reported. The clinical in fl ammation in these animals is only mildly modulated by a cocoa diet, although it does decrease the oxidative stress produced by the chronicinflammatory response [76, 77].

With regard to studies on humans, it has been reported that supplementation with cocoa productsin healthy humans does not affect inflammation markers [78]; however, a recent cross-sectional analysisshowed that the regular intake of dark chocolate by a healthy population in southern Italy isinversely related to serum C-reactive protein concentration [79]. More recently, Monagas et al. [47]reported the effect of cocoa consumption for 4 weeks on some serum inflammatory biomarkers, andthey observed the decrease of some adhesion molecules involved in the recruitment of inflammatorycells, thereby suggesting new evidence about the anti-inflammatory potential of cocoa.

With regard to the immune system, the modulatory effect of cocoa fl avonoids on lymphocyte cellactivation and cytokine secretion has been described in vitro [80]. Regarding in vivo effects, it hasbeen reported that a cocoa-enriched diet is capable of modifying the composition and functionality of several lymphoid tissues, including the gut-associated lymphoid tissue (GALT). In particular, cocoaintake reduced the proportion of Th lymphocytes in the spleen, Peyer's patches, and mesenteric lymph

nodes [72, 81]. Moreover, a cocoa diet does not modify the proliferative response or IL-2 secretion inthese tissues but does reduce the IL-4 production by splenocytes [72, 82]. Rats fed a cocoa dietshowed lower serum IgG, IgM, and IgA concentrations [72], and the diet attenuated antibody responsein immunized rats, which mainly affects the Th2-related isotypes [82]. Similarly, a cocoa diet wasable to attenuate the speci fi c antibody response in a model of chronic in fl ammation [76]. Moreover,

in the GALT, a cocoa-enriched diet decreased IgA secretion into the gut, and this was accompaniedby a reduction in the gene expression of several molecules

involved in IgA-secreting cell activation,gut homing, and IgA synthesis [83, 84]. Likewise, cocoa-fed animals showed a modified TLR expressionpattern in gut tissues, which may re fl ect a change in the crosstalk between microbiota and bodycells induced by a cocoa diet [83, 84].

In summary, the results obtained from experimental animals suggest the immune modulation capability of cocoa, especially on pathologies where antibodies are harmful mediators such as in autoimmuneand allergic diseases. However, no human studies in this area have been performed until now.

Dangerous and potential dangerous materials in cocoa

Metals

Manton (2013) reported some aspects of non-nutritive constituent of cocoa in his book chapter.

Lead

Lead occurs in house dust and soil and in the diet. It is absorbed through the gut, and upon enteringplasma, about 50% is sequestered in bone and more than 99% of the remainder becomes bound to thered cells. Clinical Pb poisoning in adults typically manifests itself as peripheral neuropathy resultingin wrist drop and, in children, as encephalopathy. Such cases seldom occur today thanks to vigorouslyenforced regulations and overall awareness of the danger through aggressive advertising. Of interesthere is subclinical poisoning, the sequelae to sustained exposure to low levels of Pb. In children, de fi cits in IQ are well documented [25, 26], and a blood Pb concentration of 10 m g/dL is taken as thethreshold of harmful neurodevelopmental effects [27], though some would have that figurereduced [28]. Blood Pb concentration has been shown to correlate with blood pressure in adult

men[29], in black as opposed to white men and women [30], and in perimenopausal and postmenopausalwomen [31]. Lead is excreted through the kidney and follows first-order kinetics with a half-life of about 20 days so that blood Pb concentration can be calculated for a given intake and body mass.

Difficulties arise because the absorption of Pb varies in the presence of Ca and because Pb may bealmost completely absorbed if it is ingested on an empty stomach, as happens when children mouthsoiled fi ngers and hands. To account for variations in day-to-day exposure, the concept of a provisionaltolerable weekly intake (PTWI) was introduced by the United Nations' Joint Expert Committeeon Food Additives (JECFA) and set at 0.025 mg/kg body weight. This figure, however, has beenrevoked on the grounds that it is associated with a de fi cit in IQ of three points in children and anincrease of 3 mmHg in systolic blood pressure in adults and so cannot be considered as healthprotective [32] .

Cadmium

Plants readily take up Cd that is naturally present in soil [33, 34] , rendering exposure universalwhether through the diet or through smoking. Absorbed through the gut, it is detoxi fi ed by binding tothe cysteine-rich protein metallothionein, which is synthesized de novo in the liver, and is ultimatelystored in the cortex of the kidney where it has a half-life of about 15 years. Occupational exposuremay produce renal tubular damage usually monitored by the excretion of the low-molecular-weightprotein b 2 microglobulin. There is evidence, however, that low-level environmental exposures damagethe kidney [35– 37] and cause bone loss in women [38, 39] and possibly also breast cancer [40] .In view of the long half-life of at least a month and implemented a provisional tolerable monthly intake (PTMI) of0.025 mg/kg body weight [32] , superceding the PTWI of 0.007 mg/kg body weight. In an independentreview, the European Food Safety Authority concurred with this figure [41] .

Nickel

The diet contains large amounts of Ni which plants take up to different degrees from the soil.Gastrointestinal absorption is low at about 1%. The principal health effect of nickel is allergy whichaffects 10–20% of the population. Sensitized individuals will develop a skin rash after contact withnickel or nickel-plated objects such as buttons or jewelry. Occasionally ingestion of food items suchas chocolate with a high nickel content results in eczema [42, 43]. There is no PTWI for nickel, onlya tolerable daily intake (TDI) of 0.012 mg/kg body weight [44].

Pesticides

Urban dwellers encounter agricultural pesticides as residues in food, and most have detectable quantities of the environmentally more persistent varieties in their adipose tissue. The organochlorines areof particular concern in that they are potential endocrine disruptors and carcinogens [45]. That they might cause breast cancer has been examined by several groups over the period 1995–2005 withoutany clear-cut positive correlation being found [46–52]. On the other hand, an association has been

found with non-Hodgkin's lymphoma and the organochlorine heptachlor epoxide and, at the highestconcentrations in adipose tissue, with dieldrin and chlordane [53]. Blood serum levels of b hexachlorocyclohexane(beta-HCH), which constituted 5–14% of technical grade lindane, have been foundassociated with Parkinson's disease [54, 55]. Up to this point, the residues of a few pesticides in cocoabeans have been regulated. The Codex Alimentarius set maximum residue limits (MRLs) of 0.2 mg/

kg for endosulphan (an organochlorine insecticide) and metalaxyl (a systemic fungicide) and 0.01 mg/kg for the fumigant phosphine (hydrogen phosphide) [56]. The US FDA placed an action level of 1 mg/kg for DDT, TDE, and DDE and 0.5 mg/kg for benzene hexachlorideand lindane [57]. Most recently, the European Union has published MRLs for a large number of pesticidesin fermented cocoa beans

[58] , a decision that has caused some concern in the cocoa industry[22] . The US EPA lists tolerances for some substances in cocoa beans and cocoa products [59] . Theseinclude pyriproxyfen (0.02mg/kg), a pesticide that acts on larvae, pyrethrins (1 mg/kg), and the newlyintroduced insecticide chlorantraniliprole (0.08 mg/kg) [60] . It lists tolerances for several herbicidesincluding glyphosate (0.2 mg/kg) and paraquat (0.05 mg/kg), for the fungicide chlorothalonil (0.05 mg/kg), and for residues of the fumigants phosphine (0.1 mg/kg) and sulfuryl fl uoride (0.2 mg/kg). Itshould be mentioned that Bateman [22] does not record pyriproxyfen, chlorantraniliprole, or chlorothalonilas being used on African plantations but notes that the herbicide 2,4-D, which for cocoa isomitted from the EPA list, is widely used.

Mycotoxins

Aflatoxins

Having caused widespread poultry poisoning in the 1960s through consumption of contaminated feed[61], the a fl atoxins have been scrutinized for their potential of causing human disease, chiefly through the consumption of maize and peanuts. Although in large doses they cause liver cancer in rats, theyhave not been conclusively shown to be carcinogenic in humans [62]. During the fermentation, drying, and storage of cocoa, the mycotoxin-producing *Aspergillus* species flourish, but for reasons notclearly understood, little aflatoxin is produced [63].

Ochratoxin A

Ochratoxin A, which is also produced by *Aspergillus* species, is of widespread occurrence ingrains and nuts and, if contaminating animal feed, in meat and milk and thus also in breast milk.

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