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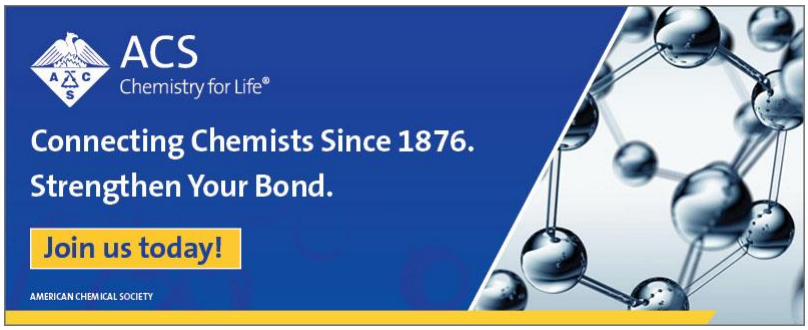

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Carolyn Virca
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www.acs.org/heroes

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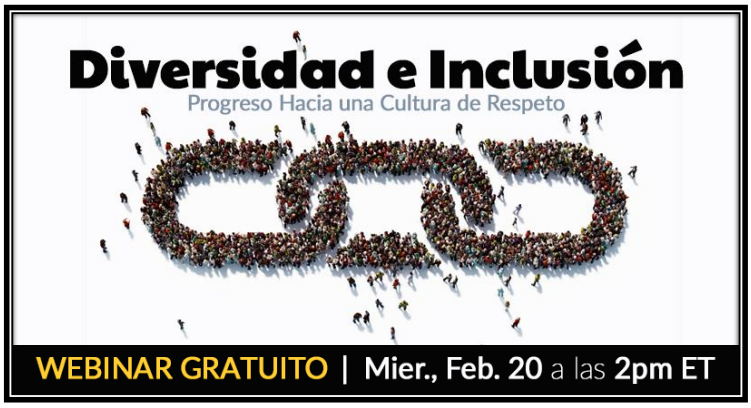

Experts

Ingrid Montes
Universidad de Puerto Rico, Recinto de Río

Bibiana Campos Seijo
Chemical and Engineering News

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ACS Division of Agricultural & Food Chemistry

ACS Technical Division
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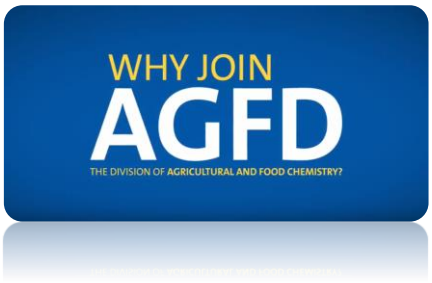

AGFD brings together persons particularly interested in the chemistry of agricultural and food products, both raw and finished; to foster programs of general papers and symposia on special topics dealing with this field of chemistry; to promote such other activities as will stimulate activity in and emphasize the importance of research in agricultural and food chemistry.

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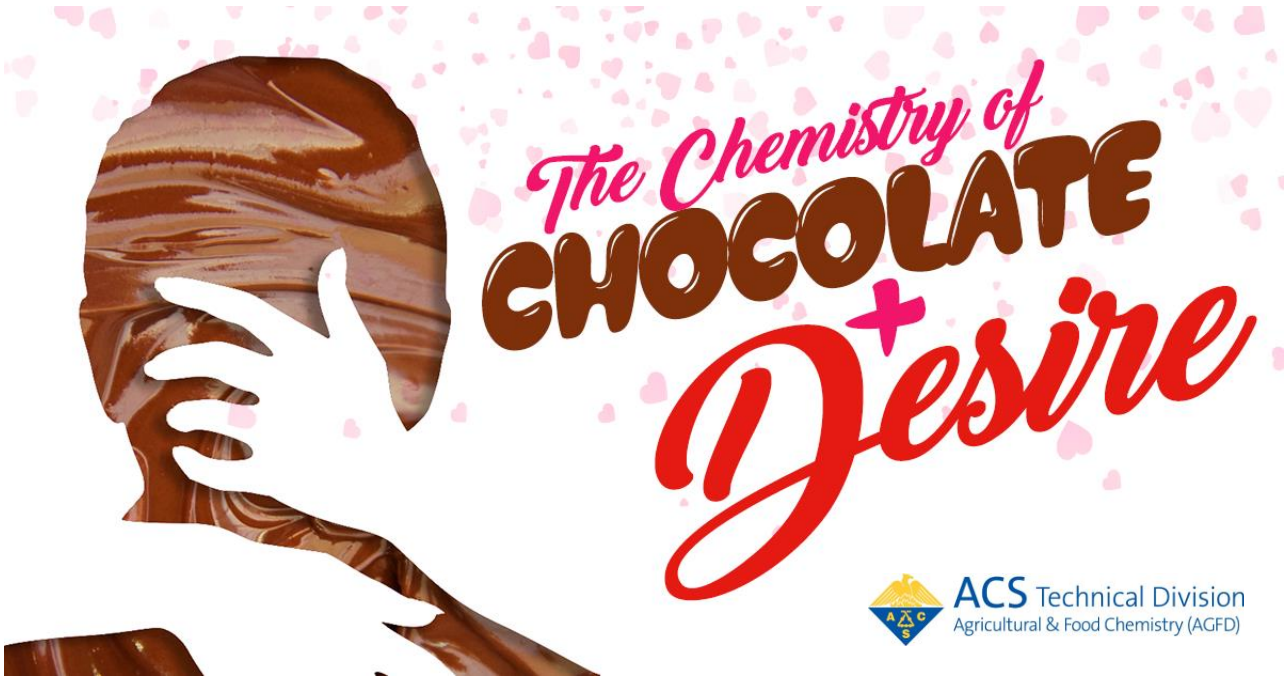

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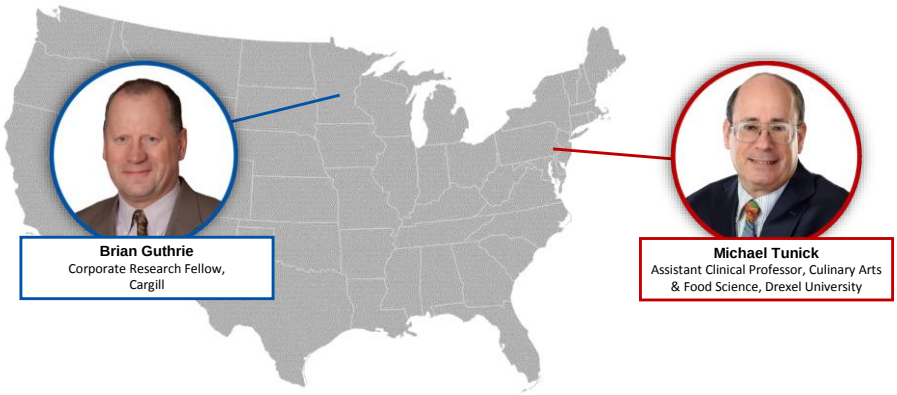
ACS Chemistry for Life®

The Chemistry of Chocolate and Desire



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Drexel UNIVERSITY

Michael H. Tunick
Center for Food & Hospitality Management
Drexel University, Philadelphia, PA

What Is Chocolate?

A semi-solid suspension of fine solid particles from sugar and cocoa (~70% total) in a continuous fat phase

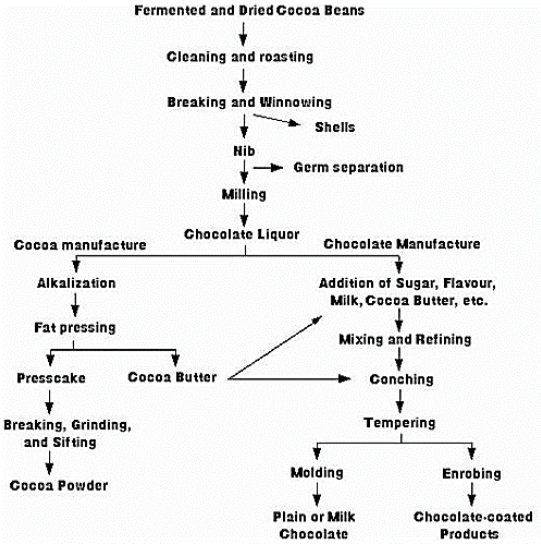
Cocoa solids are derived from beans obtained from the fruit of ***Theobroma cacao***

Origin

- Cacao previously thought to have been first domesticated in Mesoamerica
- Greatest diversity found to be in upper Amazon region
- Archaeological evidence: cacao starch grains, absorbed theobromine residues, and DNA recovered from site in southeast Ecuador
  - Dated to ~ 5,300 years ago
- Earliest evidence of *T. cacao* use in the Americas and the first unequivocal archaeological example of its pre-Columbian use in South America
- Upper Amazon region is oldest center of cacao domestication yet identified

Zarrillo et al., Nature Ecology & Evolution, Oct. 29, 2018

Manufacture



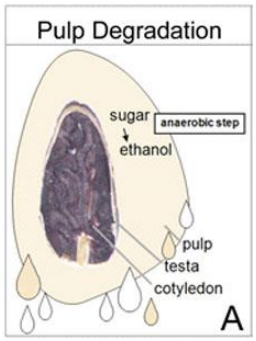
http://chocolateproducing.blogspot.com/2009/05/process-of-chocolate-manufacturing.html

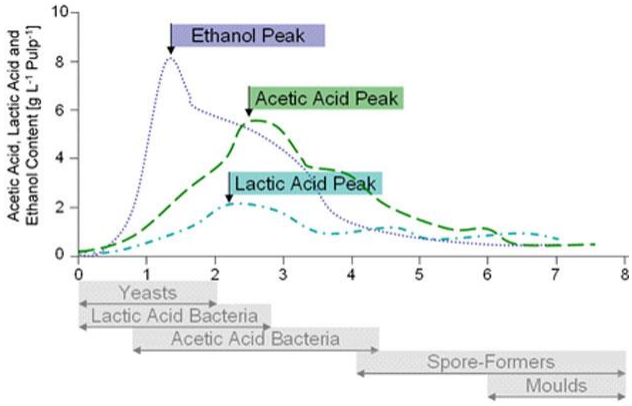
Fermentation

- Takes place in baskets, wooden boxes, or heaps stored away from light, depending on local custom
- Beans turned to ensure even fermentation
- Process lasts 5-7 days, depending on cultivar and variety

Fermentation: First Day

Anaerobic, exothermic reactions, temperature to 40°C

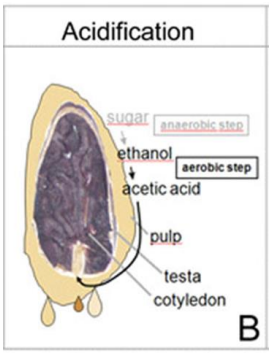


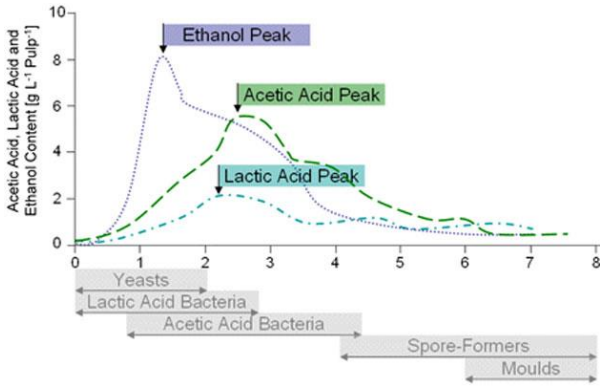


Yeast ferments sucrose, glucose, fructose

Fermentation: Next Day

Aeration from turning beans, temperature to 50°C

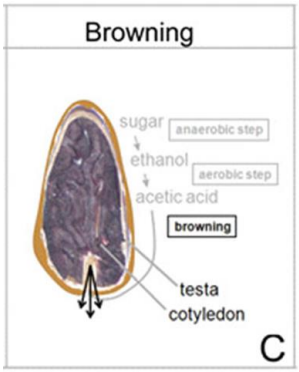




Germ within bean dies from heat, alcohol, and acetic acid
Enzymes within bean released, important for flavor

Fermentation: Last Days

Yield: 80-85% well fermented beans



Browning reactions of polyphenol with proteins and peptides produce colors characteristic of cocoa

Fermentation and Drying

Help remove natural tannins and acids present

- Tannins: 5-15% of bean by weight
- Bring astringent and bitter flavor to final chocolate

Drying limits mold growth, moisture content goes from 60 to 7.5%

- Sun-drying preferred
- Artificial drying may lead to off-flavors

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Why is it called Baker's Chocolate?

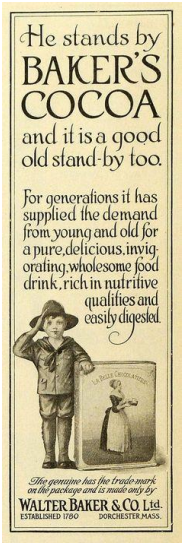
- It is used in baking
- It originated in the Baiker region of West Africa
- It was named after a guy named Baker
- Nobody knows

Chocolate Types

Baker's chocolate/bitter chocolate/unsweetened chocolate: *made from pure chocolate liquor* (100% cacao with no sugar added)

Bittersweet chocolate: *sweetened dark chocolate with sugar and cocoa butter and ≥ 35% chocolate liquor* (70-100% cacao)

Semisweet chocolate: *dark, sweetened chocolate made with ≥ 15% chocolate liquor*



1918 Ad Walter Baker Co Beverage La Belle Chocolatiere Boy Scout Kid Cocoa

Chocolate Types

Milk chocolate: *In US, must contain ≥ 10% chocolate liquor and 12% whole milk* (usually in dried form)

- Bars of fine milk chocolate generally contain 30-45% cacao
- Cheapest can have as little as 5% cacao

Dark chocolate: *15-35% chocolate liquor with cocoa butter, vanilla, sugar, or other sweetener, and usually lecithin as an emulsifier*

White chocolate: *cocoa butter* (≥ 20% in US), *sugar, milk powder, spices such as vanilla*

Milk Chocolate

Milk solids added

Milk fat: *15-20% solid at ambient temperature*

- Softens chocolate texture, used at ≤ 30% of total fat content
- Inhibits fat bloom

Milk proteins add to perceived creaminess

Sensory Attributes

Appearance: smooth, shiny, mahogany-black

Sound: clear and crisp snap when broken

Touch: should quickly start to melt in hand with no graininess in mouth

Smell: fruits, nuts, spices, flowers, sugar, etc.

Taste: bitterness with hint of acidity, sweetness with suggestion of sourness, touch of saltiness, plus characteristic flavors

Snap

Good, clean snap indicates high cacao content and well-tempered chocolate

Too dry if it splinters, too waxy if it resists breaking

Milk chocolate (lower levels of cocoa solids) and white chocolate (no cocoa solids) do not have the same snap

Opposite: crumbly

Texture

Mouthfeel and textural properties determined by unique properties of cocoa butter

Careful processing and selection of ingredients necessary to produce desirable properties

Viscosity controlled by addition of cocoa butter and surface-active ingredients (lecithin)

Particle Size

Optimization requires consideration of palate sensitivity

Product is perceived as gritty or coarse in the mouth if maximum particle size > 30 µm

Chocolate milled to maximum particle size of 20 µm will have creamier taste and texture than that with 30 µm

Cocoa Butter

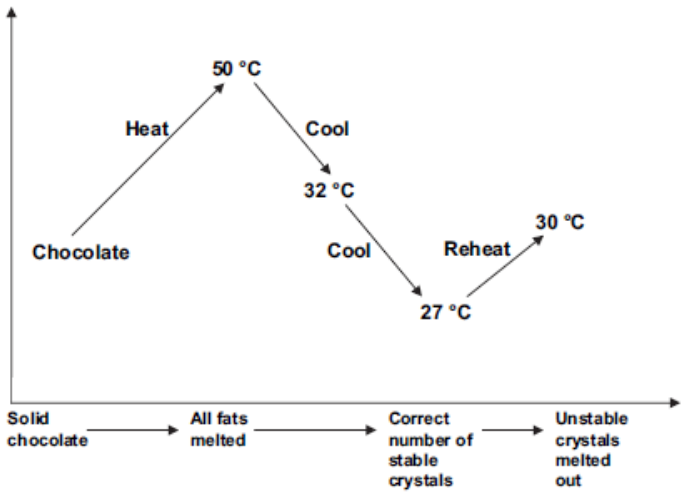
Most critical raw material for chocolate

Tree, flower, pod, seed, and postharvest handling all different from those of any other food ingredient

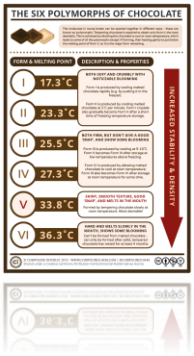
Triglycerides primarily palmitic acid (27%), stearic acid (34%), and oleic acid (34%)

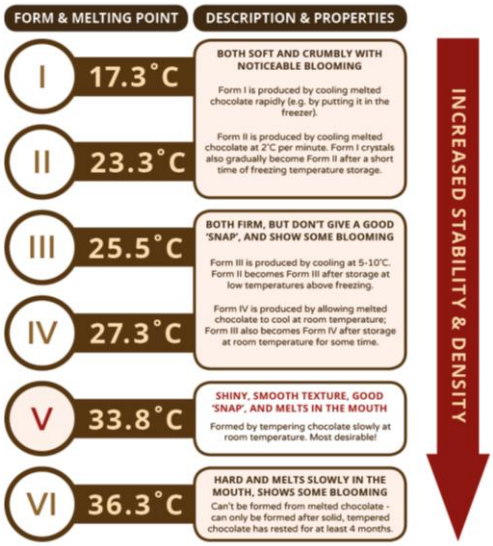
- Structure leads to unique solidification and liquefying properties
- Manufacturer can work with chocolate in ways that no other foods permit

Tempering



The Six Polymorphs of Chocolate





https://www.compoundchem.com/2014/04/19/the-polymorphs-of-chocolate

Flavor and Color

Determined by processing variables and inherent characteristics of the cocoa bean

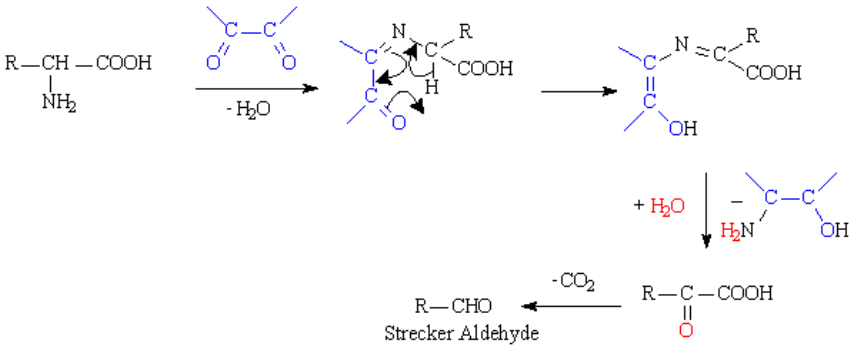
Flavor precursors develop during fermentation and primarily interact at roasting temperatures

Complex browning reactions occur during roasting

Numerous heterocyclic flavor compounds produced then contribute to the characteristic chocolate flavor

Maillard Reaction

Non-enzymatic reaction between amino acid and reducing sugar

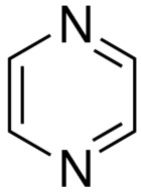


Pyrazines

Primary odor components

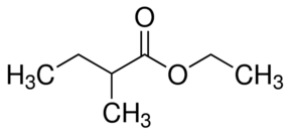
~ 80 contribute to overall flavor

Most originate from α-aminoketones by Strecker degradation and Maillard reactions during roasting



Compound	Odor quality	Sensory perception
2-Methylpyrazine	Nutty, chocolate, cocoa, roasted-nuts	Sweet chocolate, nutty
2-Ethylpyrazine	Peanut butter, musty nutty	Nutty
2,5-Dimethylpyrazine	Cocoa, rusted nuts	Sweet chocolate, nutty
2,6-Dimethylpyrazine	Nutty, coffee, green	Nutty, herbal
2-Ethyl-5-methylpyrazine	Nutty, raw potato	Nutty, hernal
2,3-Diethylpyrazine	Nutty, hazelnut, cereal	Nutty
2,3-Dimethylpyrazine	Caramel, cocoa	Sweet chocolate
2,3,5-Trimethylpyrazine	Cocoa, rusted nuts, peanut	Sweet chocolate, nutty
2,3,5,6-Tetramethylpyrazine	Chocolate, cocoa, coffee	Sweet chocolate
2,3,5-Trimethyl-6-ethylpyrazine	Candy, sweet	Sweet chocolate

Esters



Ethyl-2-methylbutanoate

Second most important odor components

Arise from amino acids and fermentation

Long chain esters produce undesirable fatty and waxy flavors

Compound	Odor quality	Sensory perception
Ethyl acetate	Pineapple	Fruity
Isobutyl acetate	Fruity	Fruity
Isoamyl acetate	Fruity, banana	Fruity
Benzyl acetate	Floral, jasmine	Floral
Methylphenyl acetate	Sweet, honey, jasmine	Floral
Ethylphenyl acetate	Fruity, sweet	Floral
2-Phenylethyl acetate	Honey, floral	Floral
Ethyl butyrate	Pineapple	Fruity
Ethyl lactate	Fruity	Fruity
Diethyl succinate	Pleasant aroma	Floral
Ethyl 2-methylbutanoate	Fruity	Fruity
Ethyl 3-methylbutanoate	Fruity	Fruity
Ethyl valerate	Fruity, apple	Fruity
Ethyl hexanoate	Fruity	Fruity
Ethyl octanoate	Fruity, floral	Fruity
Ethyl decanoate	Pear, grape	Fruity
Ethyl laurate	Fruity, floral	Fruity, floral
Isoamyl benzoate	Balsam, sweet	Floral
Methyl salicylate	Bitter-almond	Nutty
Methyl cinnamate	Balsamic, strawberry	Fruity
Ethyl cinnamate	Sweet, cinnamon-like	Sweet chocolate

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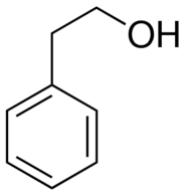
Alcohols



Arise during fermentation from microbial activity

May also result from heat degradation of amino acids

2-phenylethanol: most odor-active compound in dried and fermented cocoas

Compound	Odor quality	Sensory perception
1-Propanol	Sweet, candy	Sweet chocolate
2-Methyl-1-butanol	Fruity, grape	Fruity
2,3-Butanediol	Natural odor of cocoa butter	Sweet chocolate
2-Pentanol	Green, mild green	Vegetal
1-Hexanol	Fruity, green	Fruity, herbal
2-Hexanol	Fruity, green	Fruity, herbal
Trans-3-hexen-1-ol	Grassy, green	Vegetal
2-Heptanol	Citrusy	Fruity
1-Phenylethanol	Honey, floral	Floral
2-Phenylethanol	Honey, floral	Floral
Benzyl alcohol	Sweet, floral	Floral

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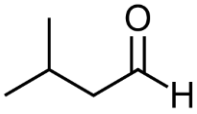
Aldehydes and Ketones

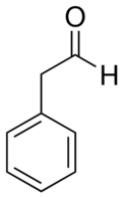


3-Methylbutanal

Formed during fermentation

Aldehydes also arise from Strecker degradation of amino acids during roasting

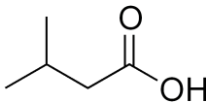
- Needed for pyrazine formation



2-phenylacetaldehyde

Compound	Odor quality	Sensory perception
2-Phenyl acetaldehyde	Honey, floral	Floral
2-Methylpropanal	Chocolate	Sweet chocolate
2-Phenylpropanal	Floral	Floral
2-Methylbutanal	Chocolate	Sweet chocolate
3-Methylbutanal	Chocolate	Sweet chocolate
2-Phenyl-2-butenal	Sweet	Sweet chocolate
4-Methyl-2-phenyl-2-pentenal	Cocoa	Sweet chocolate
n-Hexanal	Green	Herbal
5-Methyl-2-phenyl-2-hexenal	Cocoa	Sweet chocolate
2-Nonenal	Green	Herbal
Vanillin	Chocolate, sweet, vanilla	Sweet chocolate
2-Pentanone	Fruity	Fruity
2-Heptanone	Fruity, floral	Fruity, floral
Acetophenone	Floral	Floral
2-Hydroxy acetophenone	Heavy floral, herbaceous	Floral, herbal
4-Methyl acetophenone	Fruity, floral	Fruity, floral

Acids



3-Methylbutyric acid

Acetic acid most odor-active

Short chain acids mostly removed during processing

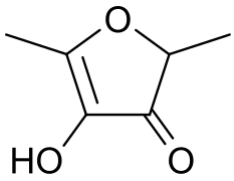
Lead to undesirable odors

Compound	Odor quality	Sensory perception
Acetic acid	Sour, vinegar	Repulsive
Propionic acid	Pungent	Bitter pungent
Butyric acid	Rancid, cheese	Repulsive
2-Methylbutyric acid	Sweaty	Repulsive
3-Methylbutyric acid	Sweaty	Repulsive
Isobutyric acid	Rancid butter	Repulsive
Isovaleric acid	Sweat, rancid	Repulsive
Hexanoic acid	Sweat, pungent	Repulsive
Heptanoic acid	Rancid, sour	Repulsive
Octanoic acid	Sweaty, fatty	Repulsive
Nonanoic acid	Fatty	Repulsive
Decanoic acid	Rancid, fatty	Repulsive
Dodecanoic acid	Metal	Undesirable
Benzoic acid	Urine-like	Repulsive
Phenylacetic acid	Sweat	Repulsive

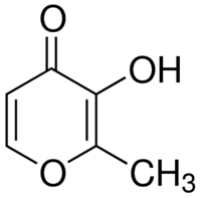
Furanones and Pyrones

Produced by degradation of monosaccharides during drying and roasting

- Confer pleasant caramel notes and enhance flavor impression
- Destroyed during alkalization



Furaneol

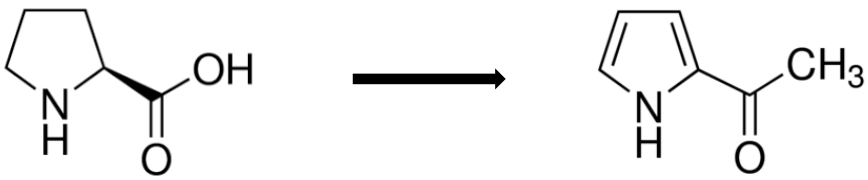


Maltol

Pyrrole

2-Acetyl-1-pyrrole produced during drying and roasting via Maillard reactions and Strecker degradation, starting from proline

- Confers caramel, chocolate, and roasted desirable notes



Other Compounds

Alkaloids, including theobromine (3,7-dimethylxanthine) and caffeine (1,3,7-trimethylxanthine)

- Bitter taste

Polyphenols in 3 main groups: catechins (flavan-3-ols), anthocyanins, and proanthocyanidins

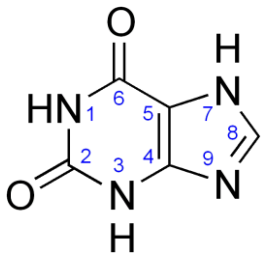
- Astringent and bitter tastes

Cravings

Most craved substance in US (Michener and Rozin, 1994; Osman et al., 2006)

Effects attributed to texture, sweetness, fat, aroma, and specific compounds

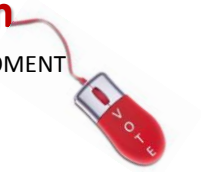
Xanthines implicated in cravings



Physiol Behav 1994, 56:419; Appetite 2006, 47:290

Audience Survey Question

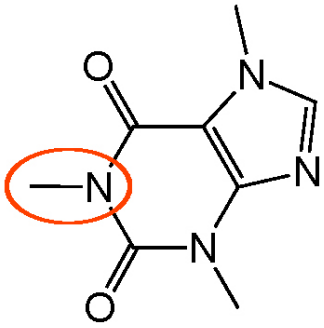
ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



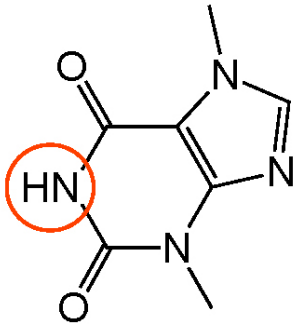
What happens in Japan on Valentine's Day?

- Men give chocolate to women
- Women give chocolate to men
- Adults give chocolate to children
- Children give chocolate to their parents
- Nothing – The Japanese don't celebrate the day

Methylxanthines in Cocoa



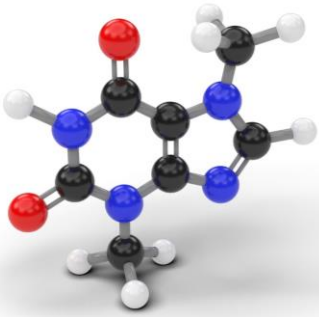
Caffeine



Theobromine

Caffeine metabolite

Theobromine



From Greek θεός (god) + βρῶμα (food)

100 g milk chocolate contains ~150 mg

100 g very dark chocolate contains ≤ 440 mg (Nehlig, 2013)

Significant effects (mood and behavior changes) not seen below 560 mg theobromine in most people (Smit et al., 2004)

Nehlig Br J Clin Pharmacol 2013, 75:716; Psychopharmacology 2004, 176:412

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Caffeine

From French café (coffee)

100 g milk chocolate contains ~20 mg

100 g dark chocolate contains ~43 mg

White chocolate has none

Increases alertness, mental energy, and cognitive and psychomotor performance

- Also small increase in feelings of well-being

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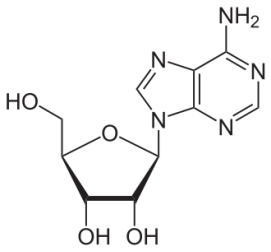
Caffeine's Mechanism of Action



Adenosine: central nervous system neuromodulator with specific receptors

Upon binding to receptors, neural activity slows, creating sleepiness

- Dilates blood vessels to ensure good oxygenation during sleep

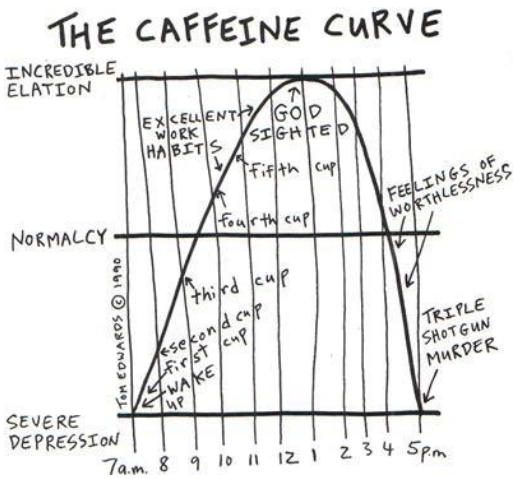
Caffeine acts as adenosine-receptor antagonist

- Binds to same receptors but without reducing neural activity
- Fewer receptors available to natural braking action of adenosine, and neural activity increases

Caffeine's Mechanism of Action

Causes pituitary gland to secrete hormones that cause adrenal glands to produce more adrenalin

- Increases energy level and alertness
- Increases production of dopamine in brain's pleasure circuits



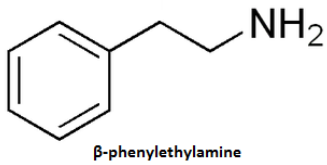
Phenylethylamine

Related to amphetamines, releases dopamine

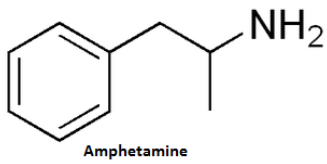
Derived from phenylalanine in body or by microbes

Typically 50-100 mg in 100 g chocolate bar

Quickly metabolized by monoamine oxidase B



β-phenylethylamine



Amphetamine

Anandamide

From Sanskrit ananda (bliss) + amide

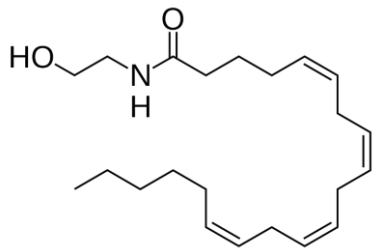
First described in 1992

50 µg/100 g cocoa bean (Nehlig, 2013)

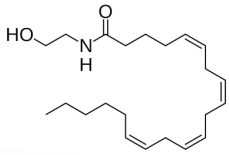
Metabolite of arachidonic acid (20:4)

Fatty acid neurotransmitter

Endocannabanoid



Anandamide Experiments



Neural receptors same ones to which THC binds

Hypothesis: endogenous cannabinoid system plays role in regulation of appetite and food intake, involved in reward processes that mediate incentive or hedonic value of food

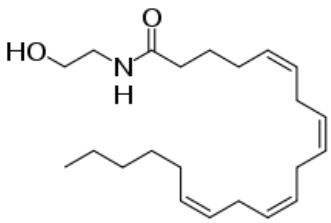
Experiments conducted on rats injected with anandamide and fed sugar and quinine solutions

Anandamide Results

Anandamide specifically amplifies hedonic impact of sweetness (prototypical sensory pleasure)

Rewarding and euphoric effects of exogenous cannabinoid drugs (such as THC) mediated by same endocannabinoid hedonic hotspot that amplifies taste 'liking'

Mahler et al., 2007



Neuropsychopharmacology 2007, 32:2267

Anandamide

Might contribute to feeling of well-being

- But rapidly broken down by fatty acid amide hydrolase
- > 30 kg chocolate to experience effects comparable to 1 dose of cannabis

Magnesium

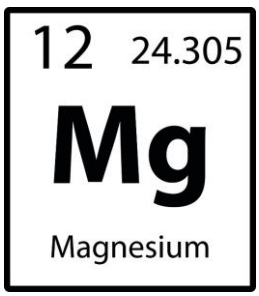
Deficiency implicated in major depression (Eby and Eby, 2006)

Craving proposed as response to Mg deficit

100 g milk chocolate contains ~63 mg Mg

100 g dark chocolate contains ~146 mg Mg

Foods high in Mg not craved, do not satisfy craving for chocolate (Parker et al., 2006)



Med Hypoth 2006, 67:362; J Affect Disord 2006, 92:149

Possibilities

Simultaneous activation of dopamine and opioid systems seen with ingestion of high fat/sugar foods

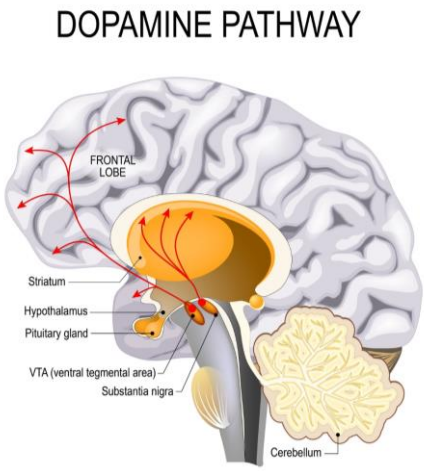
Similar to effects by dopamine agonists (amphetamine, cocaine) and opioid agonists (heroin, morphine)

Dopamines

Chocolate may interact with some neurotransmitter systems such as **dopamine** (chocolate contains dopamine precursor tyrosine), **serotonin**, and **endorphins** (contained in cocoa and chocolate)

- Contribute to appetite, reward and mood regulation

Contribution of dopaminergic system to chocolate craving and eating likely to be general, not chocolate specific



Opioids

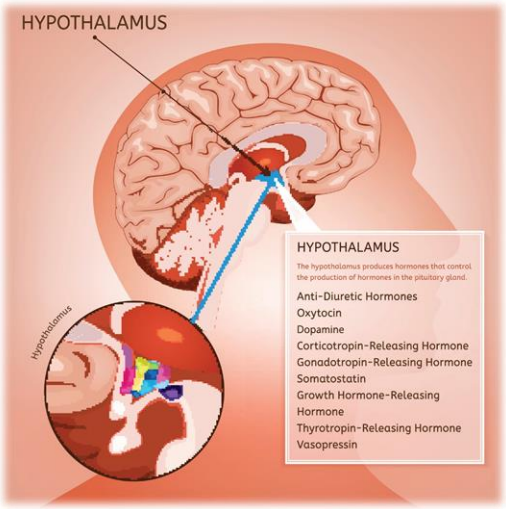
Intake of sweet food increased by opiate agonists and decreased by opiate antagonists

Opioid system plays role in palatability of preferred foods

- Endorphins released during eating could enhance pleasure of eating
- Chocolate stimulates endorphin release

Opioids can stimulate immediate release of beta-endorphin in **hypothalamus**

- Produces analgesic effect



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Serotonin

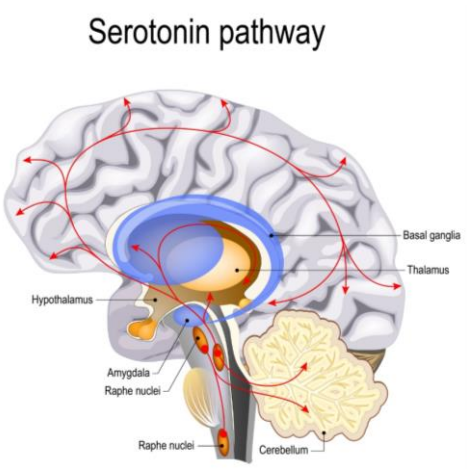
After ingestion of carbohydrates, brain serotonin concentrations rise only when protein component of meal < 2%

Chocolate contains 5% of calorie content as protein

- Negates any serotonin effect

Extreme dietary manipulations of tryptophan (serotonin precursor) result in physiological changes

- Too slow to account for mood effects described during or soon after eating chocolate



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Human Study

Tested on 280 passersby given 12.5 g chocolate

Characteristics of chocolate samples.

Chocolate type	% Cocoa	Sugar (g)	Fat (g)
Lindt® white	0	7.0	4.5
Lindt® milk	38	7.0	3.9
Russell Stover®	60	7.0[a]	3.7
Lindt® dark	70	3.5	5.5
Lindt® dark	85	1.6	5.9

Content is per 12.5 g piece of chocolate.
[a] As sorbitol.

Nasser et al., 2011

Physiol Behav 2011, 104:117

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Human Study

Tasting had measurable psychoactive effects, associated with desire to consume more

Desire proportional to sugar and fat contents and percent of cocoa

Sample with sorbitol instead of sucrose produced same results as 0 and 38% sucrose samples (all had 56% sugar)

Binding to sweet receptor (rather than taste of sugar) plays role in triggering psychoactive effects

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Men vs. Women

Men had significantly lower chocolate craving and liking scores

When asked how much more chocolate they would like to consume, men asked for 4 pieces and women 3 pieces

Women concerned with weight?

Explanation of Craving

Composite sensory properties more likely to play prominent role in chocolate liking or craving

If caloric deficit motivates chocolate craving, both milk chocolate and white chocolate should appeal equally, but don't

If psychoactive substances or Mg deficit motivate chocolate craving, both milk chocolate and unsweetened cocoa powder should appeal equally, but don't

Probably learned emotion

Aphrodisiac

Definition: substance that increases libido

Derived from Aphrodite, Greek goddess of love

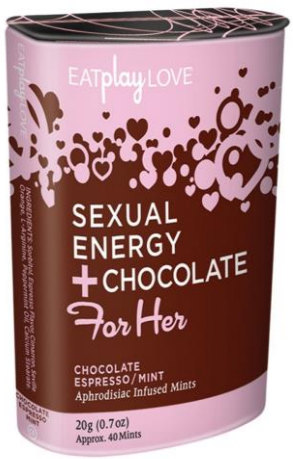
Aztecs first to attribute cocoa bean and sexual desire

Idea brought to Europe by Spanish

Eight Deer Jaguar Claw receiving chocolate from bride, 13 Serpent

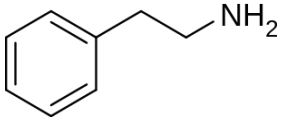
Codex Nuttall, Oaxaca, 1051 AD

Desirable Compounds

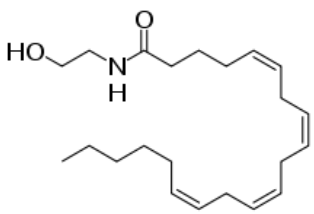


Amounts of **phenylethylamine**, **anandamide**, etc., in chocolate too small to have any measurable effect on desire

Compounds broken down too fast



Phenethylamine



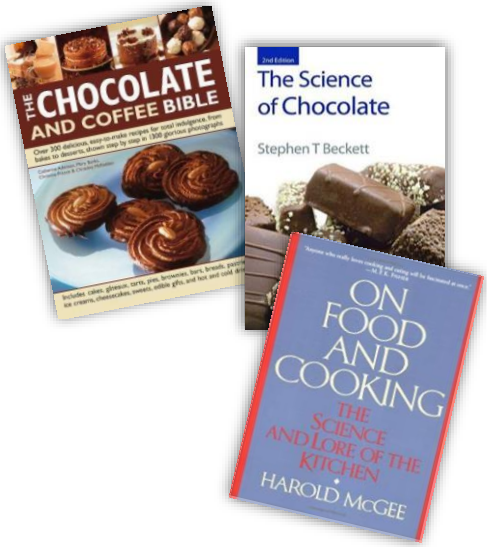
Anandamide

Aphrodisiac Qualities

Studies find **no direct link** between chocolate consumption and heightened sexual arousal

Aphrodisiac qualities **probably psychological** and not physiological

Books For Further Reading



Catherine Atkinson et al., **The Chocolate and Coffee Bible**, Hermes House, 2009. Mostly recipes, but also history and baking techniques.

Stephen T. Beckett, ***The Science of Chocolate***, 2nd edition, RSC Publishing, 2008. Details processing procedures, analyses, and nutrition.

Harold McGee, ***On Food and Cooking***, Scribner, 2004. The science and lore of chocolate and any other food you can think of.

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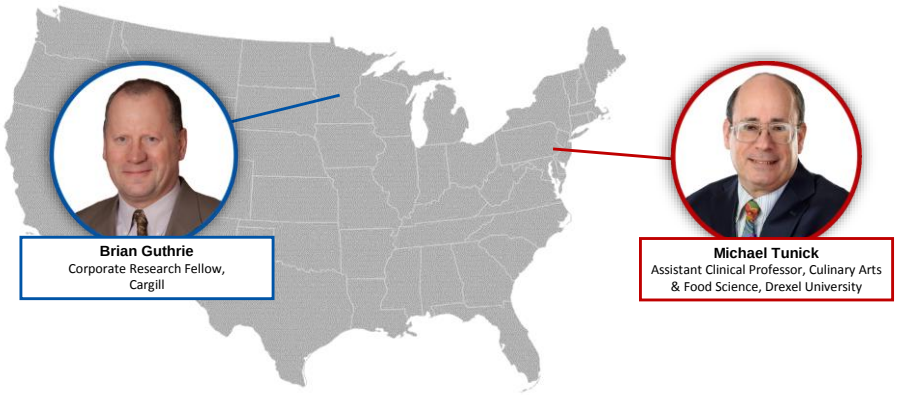

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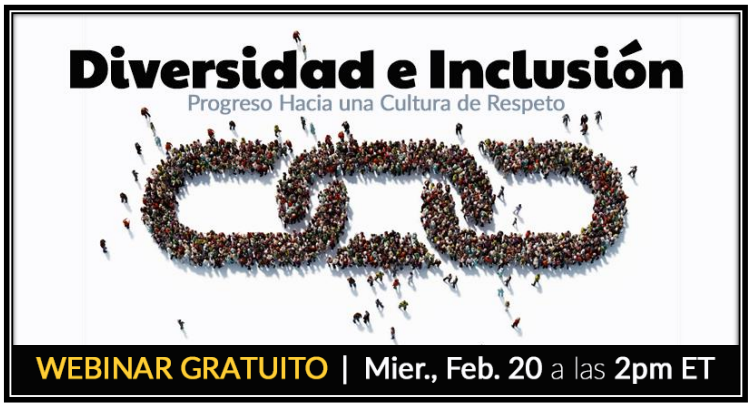

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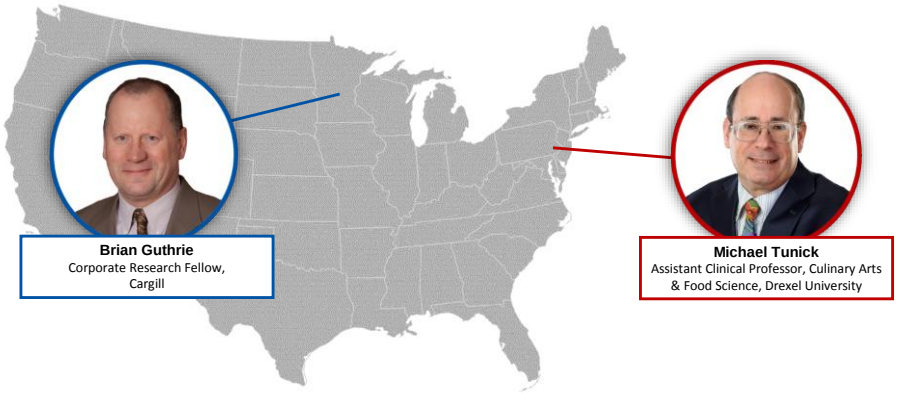

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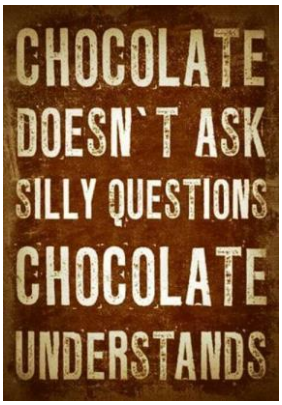
Conclusions and Final Thoughts

Compounds in chocolate not present in high enough concentrations (theobromine), do not contribute to craving (caffeine, Mg), broken down too quickly (phenylethylamine, anandamide), or too slowly (carbohydrates/serotonin) to produce aphrodisiac effect

Chocolate cravings probably stem from flavor, texture, aroma, and psychology more than specific compounds



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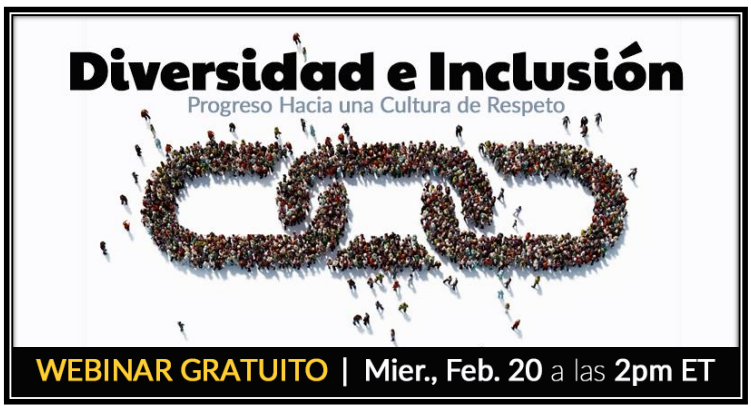

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