Cacao – the acid test!

Gregory Aharonian*, President of KukaXoco and a speaker at this year's London Chocolate Forum, explains chemistry problems facing chocolate – legal liabilities due to sugar, the acid-base chemistry of debittering, and degradation of phytonutrients – and offers a new solution based on decocainized coca leaf extracts

The chocolate industry faces complex taste chemistry problems that threaten industry profits and growth. The problems arise from the intolerable bitterness of cacao, due to interactions between theobromine, diketopiperazines and flavanols. The traditional solution, relying on an addictive and toxic chemical – sugar – increasingly opens up the chocolate industry to liability lawsuits plaguing many other industries.

One partial solution for debittering, the Dutch process, relies on noxious alkaline chemicals that destroy the good nutrients in cacao. The use of safe milk protein chemicals in milk chocolates has the downside that milk proteins bind to phytonutrients. Artificial sweetening chemicals have multiple problems – some bitterness, inorganic structures, weak consumer demand, and their own health concerns.

One aspect of this chemistry is the acid-base levels of cacao compositions, including a new composition, cacao and coca leaf extract, that has a favorable acidity balance. Given the lack of readily accessible data on the acid-base chemistry of cacao and chocolate, herein is presented such data that hopefully will become the basis for an industry collaboration.

Sugar Troubles

In a troubling portent for the chocolate industry, in 2016, Johnson & Johnson was ordered by U.S. juries to pay about $200 million to three women whose lawyers convinced juries that there was enough of a connection between regular use of talcum powder, and these women's ovarian cancer. I use "enough", because the connection is not solid. In 2013, a medical study reported that between 20 and 30 percent of women who used talc powder had an increased risk of ovarian cancer [1]. This risk/reward should greatly scare the chocolate industry. Why?

In November 2016, another medical study reported that people who drink one can of soda per day had a 46 percent increased risk of developing pre-diabetes [2], and this is just the tip of the iceberg of studies documenting the devastating effect of added sugar to human health.

The relevance to the chocolate industry? The study could have easily stated: "People who eat two chocolate candy bars a day had a 46 percent increased risk of developing pre-diabetes", because the average can of soda has twice the sugar of the average chocolate bar. And these medically-documented increased risks are powerful weapons for tort lawyers in U.S. courtrooms.

Which brings us to our first chemistry problem with chocolate – having to rely on lots of sugar to make cacao palatable. The average chocolate product around the world is at least 50% sugar. On every box of Hershey's Cocoa is the standard recipe for hot chocolates, comprising two tablespoons of cocoa and two tablespoons of sugar – 50%. The classic industry manufacturing book, Sugar Confectionary and Chocolate Manufacture, by R. Lees and E.B. Jackson (Blackie Academic, 1973) is about one-third a discussion on sugar use. Sugar is as incredibly useful to the chocolate industry, as it is becoming as incredibly risky.

Dutch Process

In 1828, Coenraad Van Houten invented the first effective chemical process for partial debittering of cacao – the Dutch process, which uses highly alkaline chemicals (as nasty as ammonia) to reduce the acidity of cacao. Some background: the typically acidity of cacao ranges between a pH of 5.0 and 6.0 (ICCO placing the acidity at 5.7, which can be easily measured by putting two tablespoons of cacao powder in water and measuring with a pH meter). Water is a neutral acid-base, with a pH of 7.0, and chocolate products have pH levels close to neutral, between 6.3 and 6.7 (whole milk has a pH of 6.7, which no one thinks of as acidic). Hershey's Dutch-processed unsweetened cacao in water has a pH about 6.8 to 6.9.

What Van Houten discovered is that highly alkaline chemicals reduce the acidity of cacao. Today, a popular alkaline chemical is potassium carbonate, which has a pH level around 11. As an idea of its nastiness, the pH of ammonia is also around 11. Does anyone want to sell "ammonia-processed chocolate"? The Dutch process can be applied at multiple stages of cacao processing – to cacao nibs, liquor and cake. Arlen Moser of Blommer Chocolate has an excellent review of the Dutch process [3]. One problem with the Dutch process is that the phytonutrients in cacao mostly breakdown in high temperature environments with acidity levels above 7.0 (e.g., the Dutch process with its use of the highly alkaline potassium carbonate at a pH of 11).

Despite its debittering potential, few chocolates seem to be Dutch-processed, as few are labelled to indicate use of Dutch processed cacao. For example, Hershey's 'Special Dark' unsweetened cacao powder is a mixture of Dutch and non-Dutch processed cacao. Hillards' Pure Rich Dark chocolate bar, which uses Dutch-processed cacao ("alkali" appears

on the label) also uses lots of sugar (28 grams of sugar in a 64 gram bar, slightly less than the industry average of 50% sugar use).

Coca Leafs Extracts

But maybe acid-base manipulations are not the way forward for de-bittering cacao enough to remove much of the sugar now being used. At KukaXoco, we are using (decocainized) extracts of the coca leaf to reduce the bitterness of cacao. One interesting fact is that the extracts we use to reduce bitterness are slightly acidic (as opposed to very alkaline debittering chemicals), with pH levels between 5.9 to 6.4, just slightly below the pH levels of cacao butter and chocolate products. And better to de-bitter, ours is a room temperature process. Thus, during the manufacture of coca-chocolate products, the acidity levels never approach the hot alkaline ranges above 7.0 that degrade the phytonutrients in cacao.

Acidity and Bitterness

That the acidity level of cacao, between 5.0 and 6.0, may not be the main problem to solve for debittering cacao, can be seen with KukaXoco's simple demonstration of the debittering effect [4]. Brew one cup of coca tea in a cup of hot water for three minutes (or use about one teaspoon of decocainized coca leaf extract), and stir in two tablespoons of unsweetened cacao powder. Enough bitterness is removed that you can drink this "hot chocolate" (and it is probably the truest hot chocolate, being pure hot cacao) as enjoyably as you drink a cup of black coffee. And the bitterness is removed while not much changing the acidity of cacao powder in hot water (pH around 5.7 to 5.9).

This suggests the solution to the cacao debittering problem is not toxic alkaline chemicals such as potassium carbonate, nor consumer/financially unhealthy sweeteners – especially sugar, but rather new chemicals that interact with the many chemicals in cacao to create a new debittering process.

At KukaXoco, we are going forward with (decocainized) coca leaf extracts as this new debittering agent, for a variety of reasons. First, as a food additive, use of coca leaf extracts is already sanctioned by the U.S. FDA (U.S. 21 C.F.R. 182.20) [5], which is how CocaCola uses decocainized coca leaves to make its cola sodas. Second, coca leaf extracts, as discussed above, are very favorable to preserving the healthy phytonutrients in cacao, while making our coca-chocolates very organic. Third, supplies of coca leaf extract can be easily scaled up to meet all industrial needs. Indeed, the Andean countries – Peru, Colombia and Bolivia – would love a legal, profitable, market for the large quantities of coca leaf grown in their countries. Fourth, by keeping all ingredients on the acid-side, below 7.0, there are benefits to improving aroma [7].

INGREDIENTS	PH	PREPARATION / SOURCE
Potassium carbonate (K2CO3) (used in Dutch process, e.g., 3 parts by weight with nibs)	11	Internet - 10.5 - 11.5 (depending on concentration)
Ammonia (NH3) solution (listed here only for comparison)	11	10.5 - 11.5
Sodium Propionate (C3H5NaO2) (mold inhibitor - chocolate products)	7.5 -9.5	Typically added as 1 part in a 1000
Coconut oil (Skinny & Co.)	7.3	doesn't use heat extraction
Cacao-free chocolate flavor	7.0 - 8.5	Gen. Foods: U.S. Patent 2,835,593 (1957) (whole milk and sodium hydroxide [pH = 11.0 - 12.0], digested by pancreatin at 47 °C)
Cacao powder (Dutch processed)	7.0	Internet - 8.0 for "black" cacaos
Water (agua)	7.0	7.0 is neutral
Chocolate syrup (calcium fortified)	5.0 - 8.0	Hershey: U.S. Patent 7,829,127 (2005)
Hershey "Special Dark" Unsweetened Cacao (mix of natural and Dutch processed cacao)	6.90	2 tablespoons in 1 cup of room temperature water (pH measured at temperature of 22 °C)
Chocolate milk (Nestle Nesquik) (with salt and calcium carbonate [pH = 9.9])	6.85	Measured at 22 °C (22 grams sugar per 240 mL)
Whole milk	6.7	FDA puts range at 6.4 - 6.8 (12 grams sugar per 240 mL)
Chocolate-substitute, yeast-based	6.5 - 6.7	Coors Food: U.S. Patent 4,312,890 (1980)
Cacao butter	6.6	Lees & Jackson [1973]
Milk chocolate	6.3 - 6.7	Nestle: U.S. Patent 4,081,568 (1976) (uses trisodium phosphate [pH = 11.5 - 12.5])
Milk chocolate	6.5	Internet consensus
"Modica" chocolate (Sicily)	5.7 - 6.9	Int J Food Sci - 2011 - with vanilla and cinnamon
Mold growth which can affect chocolate products	4.5 - 6.8	
Andes Spirit "Machu" coca tea; (1 bag)	6.35	brewed 3 minutes in 1 cup of hot water (pH measured at temperature of 75 °C)
Embajada de Coca tea (1 bag)	6.30	brewed 3 minutes in 1 cup of hot water (pH measured at temperature of 73 °C)
Andes Spirit "Machu" coca tea (2 bags)	6.29	brewed 3 minutes in 1 cup of hot water, air cooled (pH measured at temperature of 24 °C)
Andes Spirit "Machu" coca tea (2 bags)	6.05	brewed 3 minutes in 1 cup of hot water (pH measured at temperature of 72 °C)
Wawasana "Madre Coca" tea (1 bag)	5.95	brewed 3 minutes in 1 cup of hot water, air cooled (pH measured at temperature of 25 °C)

Acid-Base Chemistry

Whatever proves to be the ultimate debittering solution, it is clear that renewed industry attention needs to be given to the acid-base and

INGREDIENTS	PH	PREPARATION / SOURCE
Andes Spirit "Machu" coca tea (1 bag)	5.85	brewed 3 minutes in 1 cup of hot water, air cooled (pH measured at temperature of 17 °C)
Wawasana "Madre Coca" tea (1 bag)	5.72	brewed 3 minutes in 1 cup of hot water (pH measured at temperature of 72 °C)
Andes Spirit "Machu" coca tea (1 bag)	5.53	brewed 5 hours in room temperature water (pH measured at temperature of 22 °C)
Inka Verde coca tea (1 bag)	5.44	brewed 3 minutes in 1 cup of hot water, air cooled (pH measured at temperature of 21 °C)
Inka Verde coca tea (1 bag)	5.40	brewed 3 minutes in 1 cup of hot water (pH measured at temperature of 72 °C)
Novo Andino Oruro coca tea (1 bag)	5.20	brewed 3 minutes in 1 cup of hot water (pH measured at temperature of 68 °C)
Cacao beans, unfermented	6.1 - 6.3	Univ. Ghana 2013 study
Hershey Unsweetened Cacao	5.85	2 tablespoons in 1 cup of room temperature water (pH measured at temperature of 23 °C)
Hershey Unsweetened Cacao	5.70	2 tablespoons in 1 cup of hot water (pH measured at temperature of 72 °C)
Cacao powder	5.7	Int. Cocoa Org. (ICCO) data
Cacao powder	5.0 - 5.8	CCBOL Group, others 5.3 - 5.7
Cacao nibs (red/purple)	2.0 - 5.0	Barry Callebaut: U.S. Patent 8,460,739 (2008)
ENACO coca powder (2 teaspoons)	5.5 - 5.6	1 cup of boiling water
(pH measured at temperature of 75 °C)		
ENACO coca powder (2 teaspoons)	5.35	1 cup of room temperature water
(pH measured at temperature of 22 °C)		
Coca leaf (powder)	5.1	ENACO (Peru) - July 2016 study
Cinnamon (Sundown Naturals capsule)	5.4	1 gram powder in 240 mL water at 23 °C
Black coffee	5.1	Internet consensus puts range at 5.0 - 5.5
Black tea	4.9	Internet consensus
Chocolate-flavored yogurt	4.7 - 5.3	General Mills: U.S. Patent Application 2006/0068075 (2004)
Chocolate beverages (iron fortified)	3.5 - 6.5	Procter & Gamble: U.S. Patent 5,670,344 (1966)
Cacao butter - fruit flavored	3.5 - 5.5	U.S. Patent App. 2012/071567 (2011)
Chocolate-flavored frozen milk	3.0 - 4.5	U.S. Patent 6,423,359 (2000)
Juice of limon	2.2 - 2.8	Internet consensus (tolerably drinkable v. bitter cacao in water @ pH=5.8)
original table at: www.kukaxoco.org/debittering-process.html#ACID-BASE		

other chemical aspects of the bitter and debittering aspects of cacao use. KukaXoco is assembling, and making freely available, a database of measurements of acid-base levels of various ingredients involving cacao and chocolate. The first table of such data is available at: www.kukaxoco.org/debittering-process.html#ACID-BASE. We hope, with industry and ICCO support (more accurate measurement equipment is needed), to greatly increase the scope of this data, and to start including more data on chemical interactions [6] that lead to chocolate taste and cacao bitterness. Initial data appears in the accompanying table.

This is a dangerous, but exciting and promising time for the chocolate industry. Dangerous in that public health forces are preparing for huge battles over added sugar in all foods – including chocolate, as the world spends a trillion dollars a year on health problems such as diabetes and obesity. But exciting in that the efforts of KukaXoco and others are innovating ways forward to kick the industry's 'addiction' to sugar. And promising because chocolates with little-to-no sweeteners of any sort become health foods that can command premium markets in the marketplace. A $2 Mondelez Milka chocolate bar with sugar can become a $4 Mondelez Milk choco-health bar. Profitably and healthily delicious.

References:

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[3] "Alkalizing cocoa and chocolate", The Manufacturing Confectioner, June 2015, https://www.sciencedaily.com/releases/2016/11/161109140706.htm http://www.blommer.com/_documents/Blommer_Alkalizing_Cocoa_and_Chocolate.pdf

[4] www.kukaxoco.org/debittering-process.html

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[6] "Molecular definition of the taste of roasted cocoa nibs by means of quantitative studies and sensory experiments", Univ. Munster, 2006, available at: http://www.worldcocoafoundation.org/wp-content/uploads/files_mf/stark2006.pdf

[7] "Effect of pH and distillate volume on monitoring aroma quality of bittersweet chocolate", Food Quality and Prefence, 2003, https://www.researchgate.net/profile/Edy_Brito/publication/222699513_Effect_of_pH_and_distillate_volume_on_monitoring_aroma_quality_of_bittersweet_chocolate_Food_Qual/links/0c960521e44d6016a9000000.pdf

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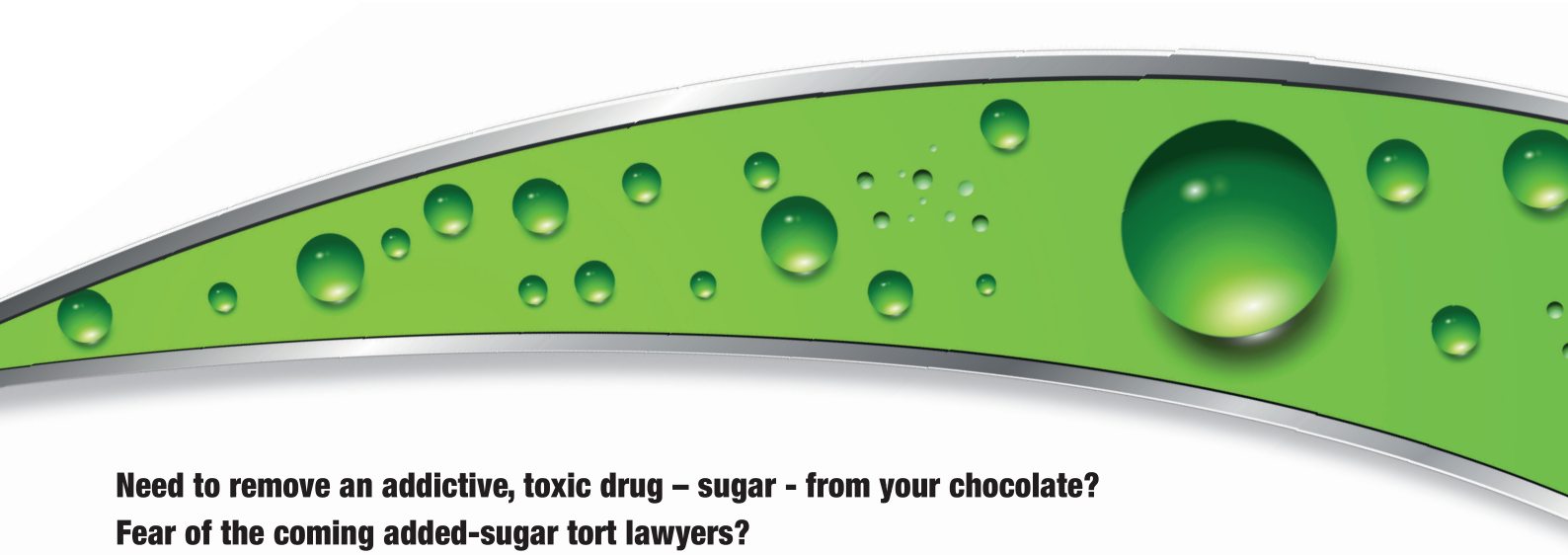
Removing Sugar from Chocolate with Coca Leaf Extracts



Need to remove an addictive, toxic drug – sugar - from your chocolate?
Fear of the coming added-sugar tort lawyers?

KukaXoco announces an consumer safe, exotic discovery - decocainized coca leaf extracts (see 21 CFR 182.20) as a de-bittering, sugar-reducing agent for unsweetened cacao.

Impact on chocolate taste and texture? None! True chocolate taste unleashed!

Powerful? Two ounces of extract eliminate 500 to 1000 pounds of sugar (and some fat) from a ton of chocolate - micrograms per bar. Can be used wherever CocaCola is sold.

Safety? Extracts are safer than salt and vanilla, no aftertaste, no gastric distress, are GRAS re FDA, non-alkaline, safely consumed in South America for hundreds of years.

Production savings? Hundreds of dollars per ton.

Profit boost? Unhealthy $2 candy bar, minus toxic sugar, now sold as a $4 health food bar with concentrated phytonutrients.

Immediate market? 300 million diabetics wanting sugar-free deliciousness.

For samples, manufacturing guidance (the "Yungas process"), and licensing opportunities, contact **Greg Aharonian** at greg.aharonian@kukaxoco.org, or at 415-981-0441.