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Impact of Alkalization on the Antioxidant and Flavanol Content of Commercial Cocoa Powders

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Cocoa is a food ingredient that is important for the contribution of flavor to foods but is also associated with potential health benefits. The chemistry thought to be responsible for its cardiovascular health benefits is the flavanol (flavan-3-ol) antioxidants. Evidence from the literature indicates that natural cocoas are high in flavanols, but when the cocoa is processed with alkali, also known as Dutch processing or Dutching, the flavanols are substantially reduced. This paper provides a survey of the physical and chemical composition of representative natural cocoas and lightly, medium, and heavily alkalized cocoas. As part of the survey, both brown/black and red/brown alkali-processed cocoas were measured. Natural cocoa powders have an extractable pH of 5.3−5.8. Alkalized cocoa powders were grouped into lightly treated (pH 6.50−7.20), medium-treated (pH 7.21−7.60), and heavily treated (pH 7.61 and higher). The natural, nonalkalized powders had the highest ORAC and total polyphenols and flavanols (including procyanidins). These chemical measurements showed a linear decrease as the extractable pH of the cocoa powder increased. Likewise, the flavanol monomers, oligomers, and polymers all showed a linear decrease with increasing pH of the final cocoa powder. When brown/black cocoa powders were compared to red cocoa powders, similar decreases in flavanols were observed with increased alkalization. The average total flavanol contents were 34.6 ± 6.8 mg/g for the natural cocoas, 13.8 ± 7.3 mg/g for the lightly processed cocoas, 7.8 ± 4.0 mg/g for the medium processed cocoas, and 3.9 ± 1.8 mg/g for the heavily processed cocoa powders. The observed linear and predictable impact of alkalization on flavanol content is discussed with respect to other reports in the literature as well as what implications it may have on diet and food manufacturing.

KEYWORDS: Alkalization; Dutching; flavanols; flavan-3-ols; procyanidins; antioxidants; cocoa powder; cacao

INTRODUCTION

Cocoa powder is an important ingredient in the manufacture of numerous foods and beverages. Significant quantities of cocoa powder are used in the manufacture of chocolate syrups and coatings as well as other nonconfectionery food applications such as baking, flavorings in ice cream, icings, and beverages. Cocoa powder represents about 37% of the total U.S. imports of cocoa bean-related ingredients that include chocolate liquor, cocoa butter, chocolate paste, and cocoa powder (*1*). More than 130 million pounds of cocoa powder were consumed in the United States in 2004 (*2*). The remaining cocoa bean-derived ingredients, mainly chocolate liquor and cocoa butter, go into the manufacture of chocolate candy (*3, 4*). These ingredients are all products of the cocoa bean, which is botanically the seed of the fruit of the cacao tree, *Theobroma cacao* L. The cacao seed is borne in a fleshy, berry-like fruit, also known as the cacao pod (*5*). Cacao seeds are removed and typically fermented in heaps or boxes for 4−5 days, dried, and transported to processing facilities, where they are deshelled and roasted at 100−150 °C. The roasted cocoa beans are then usually ground into a suspension, called cocoa liquor or chocolate liquor, which contains cocoa butter and nonfat fine, brown particles. Cocoa powder is usually made by mechanically pressing the liquor to expel most of the cocoa butter, leaving a solid cake, which is then ground into the product that most people know as cocoa powder. Typical cocoa powders contain 10−12% residual cocoa butter, with the remainder being nonfat cocoa solids—the brown particulate matter of the seed (*3, 4*). The cocoa powder is where the vast majority of the chocolate flavor and the polyphenol antioxidants reside (*6−8*).

Cocoa nibs, chocolate liquor, and cocoa powder can be modified by a 180-year-old process of treatment with alkali, also known as Dutching (*3, 4*). This process darkens the cocoa ingredients, changes the taste by reducing bitterness, and increases the dispersability of cocoa powder for various

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applications such as beverages. By far most of the alkali-treated powders are used in nonconfectionery applications. Alkalized cocoa powder and alkalized liquor are not commonly used as major ingredients in the manufacture of chocolate confectionery (*3, 9, 10*), although there are several large brands of dark chocolate in the United States that use these ingredients (*11*).

Cocoa and dark chocolate increasingly have been associated with cardiovascular health benefits. These include increasing vasodilation (*12*) and coronary arterial output (*13*) as well as decreasing blood pressure (*14, 15*) and platelet aggregation (*16*). These combined effects, along with epidemiological studies that show lowering of blood pressure (*17*) and decreases in mortality due to cardiovascular disease (*17, 18*), suggest that cocoa powder and dark chocolate are associated with heart and circulatory benefits. These benefits are thought to be conferred, in part, by the flavanol antioxidants found in cocoa (*19, 20*).

The central issue with the use of alkalinized or Dutch processed ingredients is that phytonutrients, in particular polyphenol and flavanols, may be modified or destroyed at alkaline pH. In 1961, Robinson et al. (*21*) reported that alkalizing cocoa caused a shift in the ultraviolet spectrum of the sample not seen when a similar cocoa sample was roasted without alkalization. A U.S. patent (*22*) showed that an alkali-treated cocoa powder lost 81% of the amount of total procyanidins compared to a cocoa powder that had not been alkali treated. In 2006, Gu et al. (*7*) compared three commercially available natural cocoa powders to two commercially available alkalized cocoa powders, which had 78% less flavanols. A recent Spanish paper (*23*) describes decreases in epicatechin and catechin of 67 and 38%, respectively, as a result of the alkalization of cocoa powders. Finally, in a study simulating the alkaline conditions of the lower gut, Zhu et al. (*24*) showed that catechin, epicatechin, or procyanidin dimers were degraded by 85% at pH 7.4 after 24 h and by 100% at pH 9.0 after 4 h. Despite these reports that alkali processing destroys flavanols, very few data exist on the detailed flavanol content of commercial cocoa powders.

The objective of this study is to determine the effect of varying degrees of alkali processing on the physical and chemical characteristics of commercially available cocoa powders. Color and extractable pH are measured as well as antioxidant, polyphenol, and flavanol contents, including the flavanol polymers (i.e., procyanidins). Total polyphenols refer to a very broad class of compounds found in all plants, characterized by the presence of more than one phenol unit per molecule. Flavonoids, one subgroup of polyphenols, are further composed of flavanols, flavonols, flavones, flavonones, isoflavones, and anthocyanidins. The flavanols, sometimes called flavan-3-ols, include both monomeric forms, such as catechin and epicatechin, as well as polymeric chains of flavanol monomers, more technically called procyanidins. For purposes of this paper, both the monomeric and polymeric units are included as "flavanols." The results reported in this paper are discussed with respect to the previous studies on natural and alkali-processed cocoa powders and the role these ingredients may play in a healthy diet.

MATERIALS AND METHODS

Cocoa Powder Samples. Twenty different commercial cocoa powders were obtained from five cocoa manufacturers. The brand names and product codes for these samples are summarized in **Table 1**. The products included natural cocoa powders with no alkalization as well as cocoa powders with various degrees of alkalization typically characterized as ranging from light, to medium, to heavy. In addition, the set of alkalized cocoa powders was purposely chosen to contain examples of both brown/black and red cocoa powders to assess the impact of these different processing steps on the antioxidant chemistries measured. All powders were analyzed for percent fat, color, pH, total polyphenols, antioxidant capacity (ORAC), flavanol monomers (catechin and epicatechin), and flavanol polymers (procyanidins). The measured pH of the cocoa powders was used as a guide for the degree of alkalization.

Table 1. Sources of the Cocoa Powders Used in This Survey

manufacturer	product code	product name	category
Blommer	7-15-06	Natural	natural
Blommer	7-15-06	Navajo	alkalized
ECOM-AMSA	AMSA-201005	AMSA Natural	natural
DeZaan	7-15-06	D-11-R	alkalized
DeZaan	7-15-06	D-11-B	alkalized
Gerkens-Brazil	NA-54	Bamboo	natural
Gerkens-Brazil	AL-70	Impact	alkalized
Gerkens-Brazil	RA-74	Bronze	alkalized
Gerkens-Brazil	RE-78	Marquise	alkalized
Gerkens-Brazil	BL-80	Midnight	alkalized
Gerkens-Holland	DP-70	Russet	alkalized
Hershey	2006	Hershey Regular	natural
Hershey	2006	Hershey Special Dark	alkalized
J. B. Cocoa	ZMC-100	Zamacon Natural	natural
J. B. Cocoa	ZMC-250	Zamacon Brown	alkalized
J. B. Cocoa	ZMC-360	Zamacon Red/Brown	alkalized
J. B. Cocoa	ZMC-530	Zamacon Dark Red	alkalized
J. B. Cocoa	ZMC-800	Zamacon Dark Brown	alkalized
J. B. Cocoa	ZMC-550	Zamacon Dark Red	alkalized
J. B. Cocoa	ZMC-900	Zamacon Black	alkalized

Fat, Color, and pH Analyses. Total fat of the cocoa powders was determined by Soxhlet extraction (*25*). The color of the cocoa powder samples was determined using a Hunter Tristimulus Colorimeter, model D25L DP-9000 unit (Reston, VA), equipped with a standard area 3.5 in. diameter viewing port. Fifteen grams of cocoa powder were placed in a glass sample cup for color measurement. Color was measured on three scales: the Hunter *L* scale measures degree of lightness (100 = light to 0 = black), the Hunter *a* scale measures red to green with true red equal to +100 and true green equal to −100, and the Hunter *b* scale measures yellow to blue with true yellow equal to +100 and true blue equal to −100. The extractable pH of the cocoa powders was determined by suspending 1 part powder in 9 parts deionized water at room temperature and measuring with an Orion pH (Orion Research, Inc., Cambridge, MA) calibrated at pH 4 and 10 on the day of use.

Antioxidant Capacity Analysis. Cocoa powder samples were analyzed in duplicate for antioxidant activity using oxygen radical absorbance capacity (ORAC), a widely used fluorescent method for assessing antioxidant capacity in biological samples. The current method is based on the inhibition of a peroxy radical induced oxidation initiated by the thermal based decomposition of 2,2′-azobis(2-methylpropanimidamide) (AAPH) using fluorescein as a fluorescent probe and Trolox as a standard substrate (*26, 27*). Cocoa powders (0.5 g) were extracted with 20 mL of 1:1 acetone/water containing 0.5% acetic acid by sonication at 50 °C for 10 min. The ORAC assay was conducted on a BioTek Synergy HT fluorescence plate reader using excitation and emission filters of 485 and 528 nm, respectively. ORAC values are expressed in micromoles of Trolox equivalents (TE) per gram of cocoa powder.

Total Polyphenol Assay. The total polyphenol colorimetric assay initially was developed as a method for the measurement of proteins based on the reagent's ability to react with hydroxyl constituents and later adapted by Singleton and Rossi (*28*) to measure phenolic compounds in wine. It is a widely used measure of reducing capacity. Cocoa powders were defatted with hexane, and the defatted cocoa powders (1.0 g) were then extracted with 10 mL of 70:29.5:0.5 acetone/water/acetic acid. The assay was conducted with 1 mL of sample extracts or gallic acid standards in 15 mL of water and 1.0 mL of Folin−Ciocalteu reagent for 10 min at room temperature followed by the addition of 20% Na_2CO_3 solution (3.0 mL) and incubation at

Table 2. Characteristics of the Cocoas Surveyed

ID	process category[a]	pH	% fat	color description[b]	color L^c	color a^c	color b^c
N-1	natural	5.39	11.01	light brown	40.3	10.8	14.5
N-2	natural	5.53	12.40	light brown	40.8	10.1	14.0
N-3	natural	5.60	11.20	light brown	38.8	9.7	12.7
N-4	natural	5.69	10.40	light brown	38.3	10.1	13.4
N-5	natural	5.76	10.43	light brown	38.1	9.9	12.9
L-1	light	6.77	11.80	brown	31.8	9.3	10.7
L-2	light	6.94	10.42	red/brown	35.1	10.6	12.1
L-3	light	7.00	10.50	red/brown	34.2	10.3	11.4
L-4	light	7.13	11.08	brown	33.2	10.0	10.9
M-1	medium	7.21	10.20	dark brown	33.6	10.3	11.5
M-2	medium	7.25	11.60	red/brown	31.1	10.7	10.3
M-3	medium	7.36	11.17	dark brown	27.2	8.2	7.9
M-4	medium	7.46	10.91	red/brown	30.2	10.9	9.7
M-5	medium	7.52	10.90	red/brown	29.1	11.9	9.7
H-1	heavy	7.69	11.50	dark red	25.6	10.9	7.6
H-2	heavy	7.81	12.70	black	22.9	6.2	5.2
H-3	heavy	7.82	10.00	black	17.8	3.6	2.7
H-4	heavy	7.92	11.00	black	15.9	1.7	−0.38
H-5	heavy	8.05	10.69	dark red	27.4	8.8	8.1
H-6	heavy	8.06	10.30	black	21.8	4.3	3.5

[a] Categories were based on measured pH ranges as described under Materials and Methods and do not necessarily reflect the manufacturer's designation. [b] Color descriptions refer to visual observation and do not necessarily reflect the manufacturer's color description. [c] Color values were determined using a Hunter Colorimeter as described under Materials and Methods.

40 °C for 20 min. Total polyphenols were calculated from absorbance at 755 nm and are expressed in milligrams of gallic acid equivalents per gram of cocoa powder.

Flavanol Analysis. Flavanols were measured by an HPLC method based on the separation of the flavanol monomers and polymers (procyanidins) by Gu and others (*29, 30*). The flavanol analyses were performed at Brunswick Laboratories (Norton, MA). Cocoa powders were defatted with hexane, and the defatted powders (1−2 g) were extracted with 5 mL of 70:29.5:0.5 acetone/water/acetic acid using sonication at 37 °C for 10 min. Sample extracts were clarified by centrifugation, filtered, and analyzed by HPLC using fluorescence detection with 276 nm excitation and 316 nm emission filters. Values for the flavanol monomers and individual polymeric forms ($n = 2-10$ and higher) in the defatted samples were corrected for percent fat so the flavanol values can be expressed in milligrams per gram of cocoa powder.

RESULTS AND DISCUSSION

Physical and Chemical Properties of Alkalized Cocoa Powders. In **Table 2** are shown extractable pH, fat content, and the color properties of the cocoa powders studied. The powders have been sorted top to bottom according to their extractable pH. The powders range from pH 5.39 for sample N-1, a natural cocoa powder, to pH 8.06 for a heavily alkalized cocoa powder (H-6). The natural cocoa powders all group in a narrow pH range from 5.39 to 5.76. The remaining cocoa powders have been arbitrarily grouped by pH ranges into lightly alkalized (pH 6.5−7.2), medium alkalized (pH 7.21−7.60), and heavily alkalized (pH ≥7.61). These designations are consistent with those previously reported (*31*) and closely correspond with the descriptions used by the manufacturers to characterize their alkalized cocoas. These pH groupings are used throughout the remainder of this paper.

Using proprietary processes cocoa manufacturers can make a variety of alkali-treated cocoas. Alkali treatment involves adding any number of agents, most commonly sodium carbonate dissolved in water, directly to the powder, liquor, or cocoa nibs and then allowing the mixture to react. The mixture is cooled and dried, leaving the alkali in situ. Time, temperature, and concentration of the alkali are all variables that can affect the finished product. In the United States, food labeling requires that alkalized (Dutched) cocoa powders or liquors be declared as "cocoa [liquor] treated with alkali" (*32*). Labeling requirements differ in other parts of the world, thus making it difficult for consumers to determine whether natural or alkalized cocoa is used.

Most cocoa powder manufacturers indicate whether their cocoas have been lightly, medium, or heavily alkalized, or they describe the color. Representative samples of natural as well as a series of brown/black and red alkali-processed cocoa powders were selected for this study. The natural cocoas have a characteristic light to medium brown color. The brown/black cocoas show a range going from darker brown to black, whereas the red cocoas range from a red-brown to a brick-red. These brown/black and red cocoa powders are used to improve the flavor and appearance of various food products and are therefore important tools for food manufacturers.

In addition to the manufacturers' color descriptions, colors of all the cocoa powders used in this study were characterized by a Hunter Colorimeter using three scales of measurement: the L scale ranging from light to dark, the a scale for red to green, and the b scale for yellow to blue (**Table 2**). Using the L scale, the natural cocoas group together with the highest L values, whereas the powders that have undergone progressively more processing with alkali show a decrease in their L values. The results show that both the brown/black and red cocoas develop a darker color compared to the natural cocoas. The Hunter a scale results reveal that the natural cocoas and some of the lightly processed cocoas have a values between 8 and 11, but the heavily processed brown/black cocoa powders have a values in the 6.2−1.7 range, indicating they have lost their red component. The natural cocoas and the red cocoas have Hunter a color values in nearly the same range regardless of the level of processing. These results indicate that there are red color components in both natural and red alkalized cocoa powders. A ratio of Hunter a/b is used by some cocoa manufacturers to help define the degree of red, with higher a/b ratios denoting more red color (*33*). Further analysis of color values was not pursued in this study.

ORAC, Total Polyphenols, and Flavanols of Natural and Processed Cocoa Powders. Data shown in **Table 3** summarize the ORAC, TP, and flavanol composition, including the monomeric, oligomeric, polymeric, and total flavanols of the cocoa powders studied. **Figure 1** shows the relationship of cocoa powder pH compared to antioxidant activity (ORAC) and total polyphenols (TP). Of the powders tested, the natural cocoas show the highest levels of ORAC and TP. Antioxidant capacity, as measured by ORAC, was linearly correlated with pH ($R^2 = 0.8879$), with the natural cocoa powders (pH 5.3−5.8) having the highest ORAC values and the heavily processed cocoas (pH >7.60) having the lowest values (**Figure 1A**). A similar relationship was observed for TP (**Figure 1B**) with a slightly lower correlation coefficient ($R^2 = 0.8131$).

A comparison of total flavanols and pH (**Figure 2A**) shows that the natural cocoa powders tend to group with the highest total flavanols ranging from 22.86 to 40.25 mg/g. The lightly alkali processed powders range from 8.76 to 24.65 mg/g total flavanols, the medium alkali processed powders from 3.93 to 14.00 mg/g, and the heavily alkali processed powders from 1.33 to 6.05 mg/g total flavanols. Although there is clearly some overlap between the processing groups, overall the data show

Table 3. Antioxidant Activity (ORAC), Total Polyphenols (TP), and Flavanol Contents of Cocoas Surveyed

ID	ORAC (μmol of TE/g)	TP (mg/g)		flavanol fractions							total flavanols (mg/g)
				$N = 1$ (mg/g)	$N = 2$ (mg/g)	$N = 3$ (mg/g)	$N = 4$ (mg/g)	$N = 5$ (mg/g)	$N = 6$ (mg/g)	$N = 7-10$ (mg/g)	$N > 10$ (mg/g)
N-1	846	63.20	4.08	4.03	2.93	1.46	1.03	0.81	1.25	20.09	35.69
N-2	628	56.40	3.20	3.31	2.93	1.53	1.17	1.01	1.95	21.10	36.21
N-3	615	61.90	4.56	5.02	3.78	2.08	1.45	1.15	1.40	20.81	40.25
N-4	822	49.60	4.52	4.34	3.68	1.94	1.31	1.03	1.89	19.26	37.97
N-5	620	40.59	3.31	3.49	2.99	1.11	0.63	0.46	0.36	10.50	22.86
L-1	544	51.89	4.10	3.64	1.86	0.89	0.49	0.31	0.39	12.97	24.65
L-2	398	23.84	1.48	1.30	1.53	0.22	0.05	0.02	0.05	4.10	8.76
L-3	365	27.28	1.70	1.75	1.88	0.30	0.06	0.07	0.02	5.69	11.48
L-4	395	24.71	2.09	1.91	1.59	0.32	0.10	0.07	0.06	4.17	10.31
M-1	321	19.03	0.71	0.83	0.83	0.12	0.03	0.07	0.17	4.59	7.33
M-2	398	33.04	2.46	2.56	1.81	0.46	0.17	0.10	0.00	6.44	14.00
M-3	279	13.20	0.93	0.91	0.39	0.04	0.01	0.00	0.00	1.64	3.94
M-4	237	15.68	1.18	0.95	0.80	0.12	0.03	0.01	0.03	1.79	4.92
M-5	297	26.51	1.61	1.32	0.90	0.15	0.04	0.04	0.00	4.87	8.91
H-1	254	13.25	0.73	0.77	0.85	0.13	0.03	0.00	0.00	3.19	5.70
H-2	233	11.52	0.45	0.67	0.14	0.05	0.06	0.04	0.23	2.87	4.51
H-3	294	30.97	0.18	0.45	0.24	0.07	0.03	0.01	0.00	5.07	6.05
H-4	94	7.66	0.44	0.35	0.12	0.04	0.03	0.00	0.00	0.36	1.33
H-5	198	10.79	0.92	0.88	0.29	0.04	0.03	0.00	0.00	0.76	2.92
H-6	259	9.54	0.48	0.49	0.49	0.06	0.06	0.00	0.00	1.44	3.04

a linear relationship ($R^2 = 0.8934$) with the pH of the cocoa powders. Similar patterns are shown for the low molecular weight flavanol fractions (monomers to trimers), thought to be the most immediately absorbable in humans (*34*), with a correlation coefficient for monomers of $R^2 = 0.8013$ (**Figure 2B**), for dimers of $R^2 = 0.8375$ (**Figure 2C**), and for trimers of $R^2 = 0.9017$ (**Figure 2D**). In data not shown, the relationships between pH and $N = 4-6$ oligomers, $N = 7-10$ oligomers, and the $N > 10$ polymers also show linear relationships with $R^2 = 0.8448$, $R^2 = 0.7195$, and $R^2 = 0.8621$, respectively.

In **Figure 3** is shown the average and standard deviation of flavanol content of the types of cocoa tested, ranging from natural cocoas to lightly, medium, and heavily alkali-processed cocoas. Shown within each bar are the average contributions made to the total flavanol content by monomers (bottom), $N = 2-3$ (next higher), $N = 4-6$, $N = 7-10$, and $N > 10$ (at the

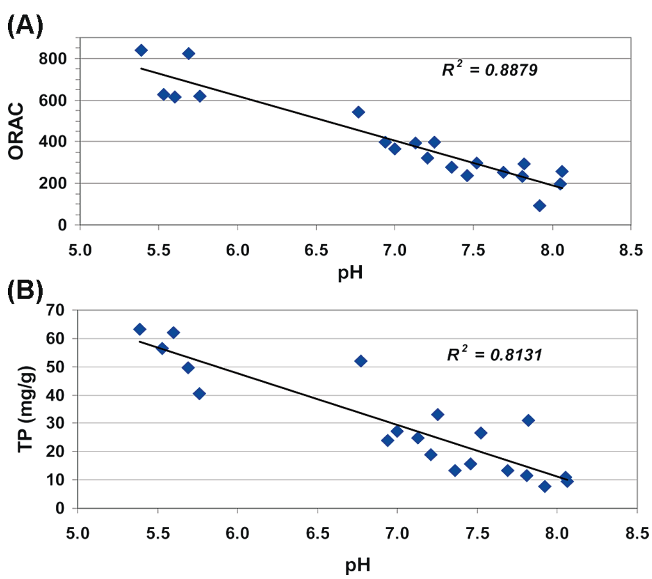

Figure 1. Relationship between pH and ORAC and total polyphenols in cocoa powders. All cocoa samples were measured for (**A**) ORAC (μmol of TE/g) and (**B**) total polyphenols (mg of gallic acid equiv/g) and plotted against pH. Correlation coefficients, shown as R^2 values, represent a linear equation.

top). Compared to natural cocoas, which averaged 34.6 mg/g ± 6.8 total flavanols, the light alkali-processed cocoas had 39.8% as much total flavanols (13.8 ± 7.3 mg/g), the medium alkali processed cocoa had 22.5% as much total flavanols (7.8 ± 4.0 mg/g), and the heavily alkali processed cocoa had 11.2% as much total flavanols (3.9 ± 1.8 mg/g). The pattern of flavanols in each category appears to be about the same with respect to the level of monomers, oligomers, and polymers, which decrease proportionately as the level of processing increases from natural cocoa powders to the heavily alkali processed cocoas. The monomeric flavanols comprise about 10% of the total flavanol content, whereas the sum of the monomers, dimers, and trimers comprises approximately 30% of the total flavanols in each type of cocoa studied.

The average level of total flavanols in the natural cocoas compared to brown/black cocoas and red cocoas subjected to light, medium, and heavy alkalization is shown in **Figure 4**. Each bar represents the average of those cocoa samples in a particular color set and degree of alkalization as defined previously in this paper. The brackets indicate the range of values for the samples averaged. The data show that alkalization causes a progressive reduction in flavanol content that is evident in both red and brown/black cocoas. Therefore, the various manufacturing methods used to obtain either the red cocoas or the brown/black cocoa powders affect flavanol content in a similar and predictive way.

This is the first comprehensive study of the effect of alkaline processing on cocoa powders. Alkalized or Dutch-processed powders are an important tool in the formulation of numerous food products such as cocoa beverages and baked products. Because of the interest in beneficial cardio-vascular-active flavanols and other compounds, it is important to characterize their loss in these ingredients. The average level of total flavanols found in the five commercially available, natural cocoas studied here (34.6 ± 6.8 mg/g) compares favorably with earlier studies; Gu et al. (*7*) found 40.8 ± 8.3 mg/g total flavanols in two natural cocoa powders, Miller et al. (*8*) found 21.8 ± 2.3 mg/g in three natural cocoas, and Fisher and Hollenberg (*20*) reported 30 mg/g (3000 mg/100 g) for cocoas made by the Kuna Indians and 40 mg/g (4000 mg/100 g) in a flavanol-rich cocoa powder.

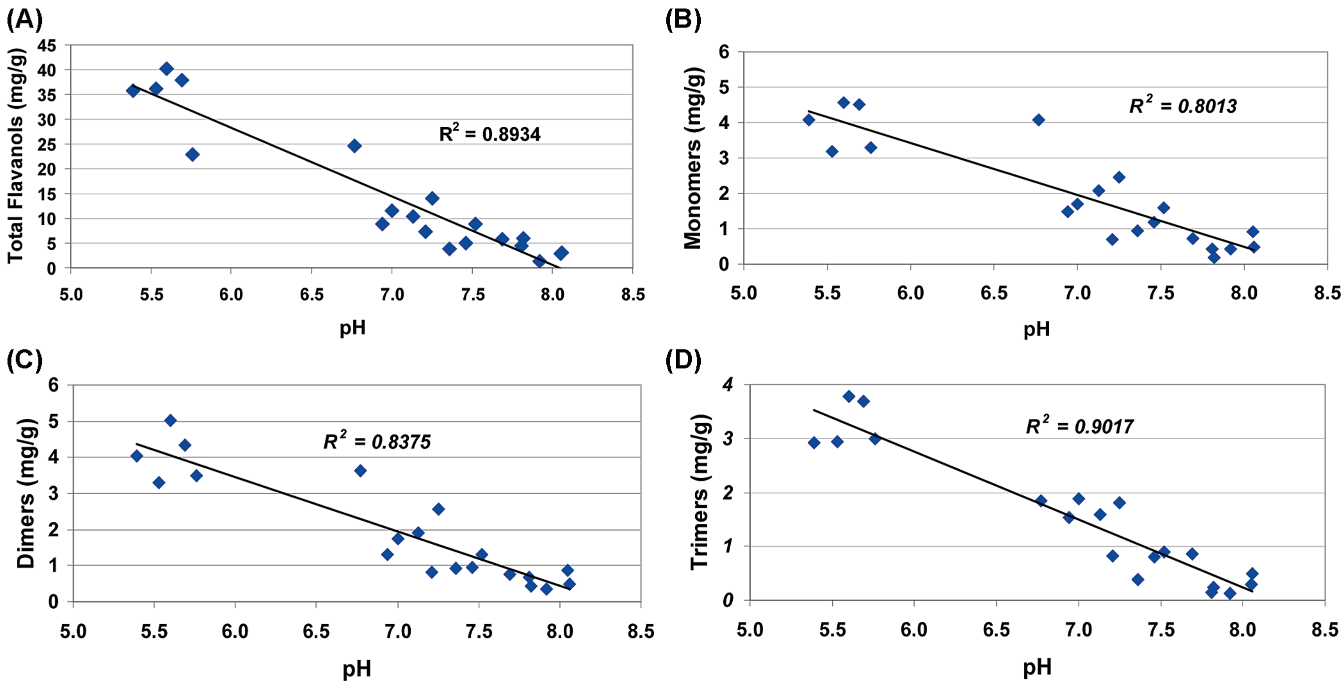

Figure 2. Relationship between pH and total flavanols, monomers, dimers, and trimers in cocoa powders. Cocoa powders were measured for pH and plotted against total flavanols (**A**), flavanol monomers (**B**), flavanol dimers (**C**), and flavanol trimers (**D**), all expressed as mg/g of sample. Correlation coefficients, shown as R^2 values, represent a linear equation.

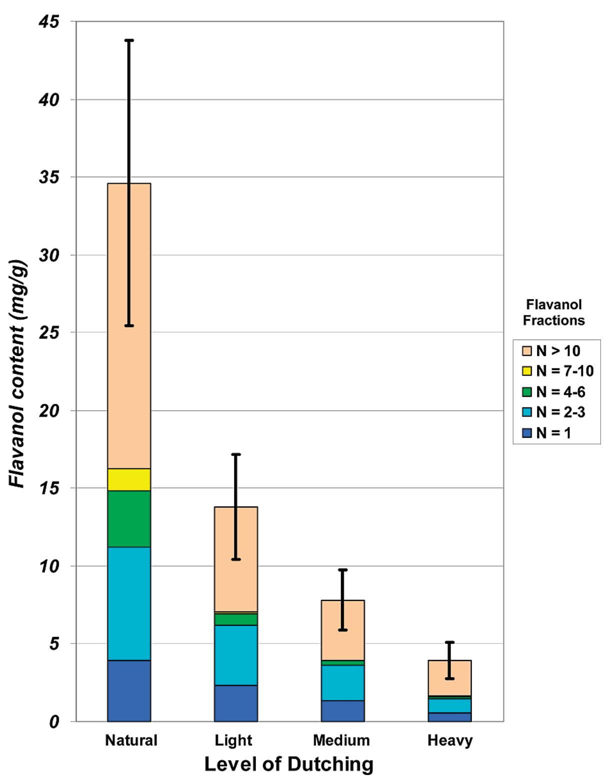

Figure 3. Average flavanol content of natural and Dutched cocoa powders. Cocoa powders samples were grouped into natural and lightly, medium, and heavily alkalized (Dutched) sets, and their flavanol contents in mg/g of sample as shown in **Table 3** were averaged. Within each bar, the average flavanol contents for several oligomer classes of flavanols are shown including $N = 1$, $N = 2-3$, $N = 4-6$, $N = 7-10$, and $N > 10$. The error bars represent the standard deviation for the total flavanol content of each group of samples.

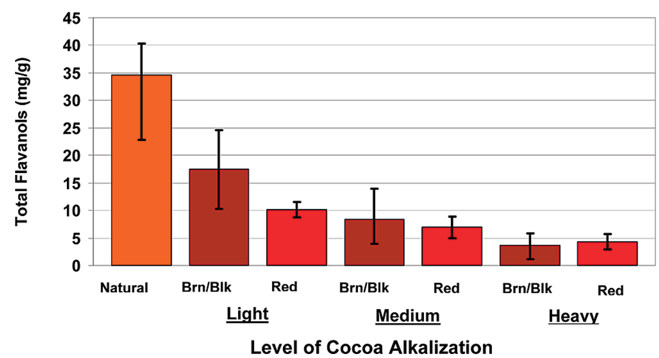

Figure 4. Total flavanols for brown/black and red Dutched cocoas. Cocoa powder samples were grouped into natural and lightly, medium, and heavily alkalized (Dutched) samples that were classified as either brown/black or red. The total flavanol contents, expressed in mg/g of sample, were averaged and are shown for natural cocoas (tan bars), brown/black cocoas (brown bars), and red cocoas (red bars). The brackets for each bar represent the range of values for each group of samples.

The USDA Proanthocyanidin database (*35*), which includes only $N = 1-10$ flavanols for cocoa powder, reports an average of 13.73 mg/g with a range of 0.77−53.1 mg/g, although it is not clear whether the USDA included alkalized (Dutched) processed powders in their samples. The content of flavanols from $N = 1-10$ for the natural cocoa powders in this survey (**Table 3**; **Figure 3**) averaged 16.2 ± 2.9 mg/g, which is in good agreement with the USDA value.

The alkalized cocoas reported by Gu et al. (*7*) had total flavanol levels of 8.95 mg/g ranging from 7.0 to 10.3 mg/g, which roughly corresponds to the level found here for the medium alkali processed cocoas. By contrast, Fisher and Hollenberg (*20*) claim that brand-name cocoa powders purchased from grocery stores in mainland Panama were devoid of flavanol content, and several commercially available cocoa powders from the American marketplace contained <5% of the flavanol content (about 2.0 mg/g) compared to a flavanol-rich cocoa powder containing 40 mg/g of total flavanols. These latter values of commercial cocoas are uncharacteristically low for natural cocoa powders and inconsistent with data reported by Gu et al. (*7*) and Miller et al. (*8*) or in this study. The reason for the discrepancy is difficult to discern because the analytical methods were not clearly described, but the low values for commercial cocoa powders reported by Fisher and Hollenberg (*20*) are more representative of a heavily alkalized sample. From the growing body of evidence presented here and in the literature cited, it can be concluded that most commercially available, natural cocoa powders contain anywhere from 2 to 4% by weight of total flavanols.

The results shown here are also contrary to the belief that alkalization or Dutch processing destroys all flavanols (*19, 20*). Instead, about 40% of the natural level of flavanols is retained on average for lightly Dutched powders, and an average of 22% is retained in even moderately alkali processed cocoa powders. This predictable and gradual loss of flavanol antioxidants during the cocoa alkalization process has positive implications for the food manufacturer. From the results reported in this study, it is now possible to balance the benefits of high flavanol contents in natural and in lightly to moderately alkalized (dutched) cocoas with improvements in color, flavor, and functionality to design food products that can satisfy more consumers. It also dispels the misconception that all Dutched cocoas are devoid of beneficial flavanols and antioxidant capacity.

In fact, cocoa powder is one of the richest dietary sources of flavanols (on a weight basis) identified thus far, exceeded only by a few food ingredients such as buckwheat hulls, sorghum, and cinnamon (*35*). Despite the losses caused by light and medium alkali processing, as defined here by extractable pH, both the light and medium alkali-processed cocoas are still in the top 10% of measured foods with detectable flavanols in the USDA database. Nonetheless, compared to natural cocoa powder, alkali treatment or Dutching does substantially reduce the level of flavanols in cocoa powders and represents an important processing step during which losses can occur. Foods that contain cocoa powder and alkalized cocoa ingredients are common in the diet, contributing one of the most favorite flavors to ice creams, confections, baked goods, and beverages. In estimating dietary consumption of flavanols from cocoa, care should be taken to correct for the amount of alkali-treated cocoa powders consumed.

Finally, even for products that are labeled with “cocoa powder processed with alkali”, a 20-fold difference was observed between the lightest alkalized powder (24.56 mg/g) and the most heavily alkalized powder (1.33 mg/g). This makes an ingredient statement almost meaningless as a tool to predict the total level of flavanols in the final product. To assist consumers in making healthier food choices, there is a need for more detailed data on the flavanol content of finished products.

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