



BIOCHEMICAL COMPONENTS OF COCOA AND THEIR BENEFITS ON HUMAN HEALTH

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Introduction

Cocoa, a small tree originated from Amazon basin of South America provides beans, which is the source for chocolates. The natives, Mayans and Aztecs used cocoa in preparation of a bitter drink called 'chocolatl'. They believed that, it gives energy, vitality and spiritual wisdom, and so it was given to men gone for battles, served in festivals, rituals and used in medicines. Linnaeus named cocoa as *Theobroma cacao*, derived from Greek words theo means 'God' and bromo, 'Drink'. The Spaniards add sugar into this Mexican 'chocolatl' to make it more palatable and acceptable among Europeans. In 1828, cocoa press was invented for separating butter from the beans, which led to manufacture of cocoa powder and solid chocolates. With the addition of milk and sugar it became the favourite food of the world. Cocoa and chocolates have lots of health benefits. Biochemical compounds, the polyphenols in cocoa have well known antioxidant biological activities and beneficial effects on cardiovascular system and also interact with the organoleptic traits of cocoa.

Cocoa beans

The cocoa pod contains 20 to 60 beans, embedded in white pulp. The beans are the main ingredient of chocolate, while the pulp is used in some countries to prepare a refreshing juice. Each seed consists of two cotyledons (the nib) and a small embryo, all enclosed in a skin (the shell). The cotyledons store the food for the developing plant and become the first two leaves of the plant when the seed germinates. The food store consists of fat, known as cocoa butter, which amounts to about half the weight of the dry bean. Another most noted active constituent is theobromine, a compound similar to caffeine and polyphenol

which constitute 10-12% of the whole bean's dry weight. The beans are fermented, which causes many chemical changes in both the pulp surrounding the beans and within the beans themselves. These changes cause the chocolate flavour to develop and the colour to change. The beans are then dried and despatched to processors as the raw material for the production of cocoa mass, cocoa powder and cocoa butter. The first stage of processing includes roasting the beans and shell removal. After roasting and deshelling an alkalising process can take place, to alter flavour and colour. All these processing procedures are important for the quality of the produce.

Nutritional aspects

Cocoa and chocolates are rich in minerals including magnesium, iron and highly concentrated source of energy. During the World War II soldiers were given with three chocolate bars a day because of its high nutritional value. One bar (41g) of chocolate provides 10-20% of recommended daily dietary value and the healthy components listed below are being absorbed readily by the body without wastage.

Calories	207
Carbohydrate	24.4 g
Fat	14.0 g
Fibre	2.20 g
Protein	1.60 g
Magnesium	46.0 mg

A growing number of clinical studies indicate that regular ingestion of polyphenol- rich cocoa exerts a range of effects potentially favourable to vascular health. There is recent evidence that the epicatechin content of cocoa is primarily responsible for its favourable impact on vascular endothelium.

Biochemical composition

The physics and chemistry of cocoa beans and cocoa products are very complex, changing throughout the development of bean, and depending on the type of processing it receives. Catechin, epicatechin and procyanidines are the main polyphenols present in cocoa contributing to bitterness and astringency of cocoa and these are the main polyphenols in fruits as well. These monomers can form links between C4 and C8, allowing them to assemble as dimers, oligomers, and polymers of catechins, the so-called procyanidins. Procyanidins are also known as condensed tannins, which, through the formation of complexes with salivary proteins, are responsible for the bitterness of cocoa. There are different products involved in the processing of cocoa to chocolate and their biochemical constituents contributed to the health benefits of cocoa.

1. Cocoa mass or liquor

Cocoa mass is produced by grinding the nib of the cocoa bean and the quality of the liquor depends on the beans used. Manufacturers often blend different types, Criollos, Forasteros and Trinitarios, beans to gain the required quality, flavour and taste. The cocoa liquor can undergo further roasting and alkalisation to alter the colour and flavour which will also alter its chemical composition. The cocoa mass contains 600 components and the major constituents are given below:

Composition of cocoa mass

Cocoa butter	54.5%
Protein	11.5
Fibre	3-10
Organic acids & aromas	9.5
Cellulose	9.0
Tannic acids & colour	6.0
Water	5.0
Mineral salts	2.6
Theobromine	1.2
Sugars	1.0
Caffeine	0.2

Source: ICCO

2. Cocoa butter

Cocoa butter is the most valuable part of the bean, which affects the price paid for a particular mark or grade of cocoa beans. The fat or cocoa butter can be extracted from the bean in a number of ways. Each bean contains a significant amount of fat (40–50%) as cocoa butter. Pure press butter is extracted from the cocoa mass by horizontal presses. A solvent extraction process can be used to extract butter from the cake residue left after the expeller process; this type of butter must be refined. Cocoa butter obtained by pressing the cocoa nib exhibits the properties of brittle fracture below 20°C, a melting point about 35°C with softening around 30-32°C. Cocoa butter is composed of a number of glycerides. The quantity of fat and its properties such as melting point and hardness depend on the variety of cocoa and the environmental conditions.

To assess the suitability of varieties of cocoa for the processing industry, fat content was estimated in cocoa germplasm collections, hybrids and elite clones conserved at CPCRI, Regional Station, Vittal, by petroleum ether extraction method using Soxhlet apparatus and expressed in percentage. Among 44 collections of Nigerian origin 21 clones recorded more than 50 per cent fat which is considered as desirable character for industrial value of cocoa. Beans of the clone VTLCN-43 had the highest fat content of 55.27%. Among 11 Malaysian collections the fat content ranged from 40 to 55%. Among the local collections of Lalbaugh and Wynad the highest contents were only 45.79 and 38.69%. Among elite clones VTLC-1 had 55.74% fat under arecanut and VTLC-1 had the highest 52.7% when grown under coconut. Among 21 hybrids, 11 showed >50% fat. Fat content of clones differed significantly with locations and growing environments.

Clones and hybrids rich in fat content

Clone	Fat (%)	Clone	Fat (%)
VTLCN-5	51.67	VTLCM-1	50.60
VTLCN-6	50.33	VTLCM-3	52.10
VTLCN-13	54.45	VTLCM-4	52.20
VTLCN-14	51.32	VTLCM-6	50.00
VTLCN-16	53.20	VTLCM-8	55.00
VTLCN-17	51.11	VTLCM-9	53.00
VTLCN-18	51.60	VTLCM-10	52.10
VTLCN-25	52.53	VTLCC-1	55.74
VTLCN-26	51.00	VTLCP-1	52.70
VTLCN-32	51.53	VTLCH-3	52.10
VTLCN-34	50.67	VTLCP-1A	53.17
VTLCN-36	50.63	VTLCP-2	50.15
VTLCN-37	50.11	VTLCP-3	52.65
VTLCN-38	51.67	VTLCP-5	50.89
VTLCN-39	53.30	VTLCP-6	50.68
VTLCN-40	51.17	VTLCP-7	50.57
VTLCN-41	52.50	VTLCP-8	51.72
VTLCN-20	54.97	VTLCP-9	50.88
VTLCN-21	52.67	VTLCP-10	50.48
VTLCN-42	54.57	VTLCP-12	52.85
VTLCN-43	55.27	VTLCP-15	50.10

A comparative estimation of fat in open (sun drying) and oven dried beans were done in 14 elite clones. The fat content in beans dried in open ranged from 21.32 to 37.83% whereas, the beans dried in oven recorded a high percentage of fat ranged from 37.59 to 58.53%. Summer season beans showed lesser size and fat content than the monsoon beans. Some beans were collected from Andhra Pradesh and the fat estimates showed that the beans of coconut garden recorded a highest of 44.53% fat compared to beans of oil palm shade which has 40.06% fat. Tamil Nadu beans also showed lesser percentage of fat contents. We have assessed the fat contents of demonstration gardens in Karnataka and Kerala as well. Humid condition favours the size and ultimately the fat content of beans, but care should be taken to reduce the fungal attack during drying. It is observed that size of the bean is directly proportional to the fat content, so the dry bean size should be of more than 1 gram to get higher fat contents.

Fatty acid profile of cocoa varieties

Cocoa butter with free fatty acid content (ffa) of 1% or less together with acceptable flavour is the best indication of good quality beans prepared and stored properly. Prolonged storage may cause fat degradation and rise in ffa concentration. Type of fatty acids in 18 hybrids and 10 elite clones was assessed in freshly prepared beans at CPCRI. From the fatty acid profile it was clear that there are 11 fatty acids viz., lauric, myristic, palmitic, palmitoleic, stearic, oleic, linoleic, arachidic, eicosapentaenoic, behemic and lignoceric acids involved in quality of cocoa beans. The fatty acids palmitic, stearic, oleic, linolic and arachidic acids were present in all the accessions invariably. The percentage of stearic acid was the highest among all in a range of 30.50% in VTLCP-7 to 44.20% in VTLCP-1 followed by oleic, linolic and arachidic acids and these hybrids have high industrial and health values. Myristic acid was present in only one accession. The other fatty acids differed among the accessions in percentage of expression.

3. Cocoa powder

Cocoa powder is formed from cocoa mass. Presses are used to remove some of the fat and leave a solid material called cocoa press cake. These cakes are then crushed to form cocoa powder. The processing can be altered to produce cocoa powders of different composition and with different levels of fat. Composition of cocoa powder will vary depending on the roasting, alkalisation and pressing processes undertaken.

Biochemical composition of cocoa powder

Cocoa butter	11.0
pH (10% suspension)	5.7
Ash %	5.5
Water soluble ash %	2.2
Alkalinity of water soluble ash as K ₂ O in original cocoa %	0.8
Phosphate % (as P ₂ O ₅)	1.9
Chloride % (as NaCl)	0.04
Ash insoluble in 50% HCl	0.08
Shell % (calculated to unalkalised nib)	1.4
Total nitrogen	4.3
Nitrogen % (corrected for alkaloids)	3.4
Protein Nitrogen corrected for alkaloids x 6.25 %	21.2
Theobromine %	2.8

Fatty acid profile of cocoa hybrids

Fatty acids		VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	VTLC _P	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Lauric	C12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Myristic	C14:0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.12	-	-
Palmitic	C16	23.6	28	26.6	28.1	29.5	29.0	24.9	23.8	32.7	25.6	28.9	27.8	28.2	28.4	25.6	30.6	28.2	23.4
Palmitoleic	C16:1	-	-	-	0.23	-	0.29	-	0.20	-	0.18	-	-	-	0.22	0.25	-	0.24	-
Heptadecanoic	C17:0	-	-	-	0.32	-	0.28	-	0.39	-	0.35	-	-	-	0.18	0.28	-	0.31	-
Stearic	C18:0	44.2	39	41.3	39.5	38.0	35.6	39.4	42.1	33.8	40.5	37.8	37.9	38.5	35.5	40.1	37.8	37.9	43.6
Oleic	C18:1	29.0	27	28.6	28.7	28.3	30.3	32.7	28.9	29.3	29.3	29.7	30.7	30.1	30.7	28.5	27.6	28.9	29.8
Linoleic	C18:2	1.82	2.2	2.01	1.81	2.13	2.26	1.80	2.13	2.24	1.93	2.11	2.29	1.87	2.59	2.84	2.48	1.83	2.06
"Linolenic	C18:3	-	-	-	-	-	0.17	-	0.16	-	0.16	-	-	-	0.17	0.18	-	0.16	-
Arachidic	C20	1.31	1.5	1.42	1.29	1.45	1.17	1.18	1.53	1.31	1.28	1.34	1.33	1.28	1.42	1.49	1.46	1.16	1.08
Eicosapentaenoic	C20:5	-	-	-	-	0.39	0.27	-	0.19	0.71	0.22	-	-	-	-	0.21	-	0.44	-
Behemic	C22	-	0.3	-	-	0.26	0.19	-	0.24	-	0.20	-	-	-	0.24	0.25	-	0.17	-
Lignoceric	C24	-	-	-	-	-	0.36	-	0.36	-	0.20	-	-	-	0.54	0.23	-	0.47	-

Fatty acid profile of elite cocoa clones

Fatty acids		VTLCC 1	VTLCC 2	VTLCC 3	VTLCC 4	VTLCC 5	VTLCC 6	VTLCC 7	VTLCC 8	VTLCC 9	VTLCC 10
		%	%	%	%	%	%	%	%	%	%
Lauric	C12	-	-	0.24	0.16	0.15	-	-	0.24	-	-
Myristic	C14:0	-	0.09	0.18	0.15	-	-	-	0.19	-	-
Palmitic	C16	26.47	25.47	28.27	26.79	24.45	30.26	27.17	27.52	29.64	32.15
Palmitoleic	C16:1	0.29	0.24	0.22	0.23	0.19	0.21	-	0.20	-	-
Heptadecanoic	C17:0	0.24	0.19	0.21	0.18	0.34	0.36	-	0.33	-	-
Stearic	C18:0	37.51	39.79	37.27	38.15	40.01	37.62	41.01	38.63	39.67	35.65
Oleic	C18:1	31.67	30.15	29.66	29.73	29.54	27.58	29.68	27.30	27.00	29.61
Linoleic	C18:2	2.43	2.05	1.98	2.41	2.62	2.28	2.14	2.40	2.14	2.60
"Linolenic	C18:3	-	0.16	0.18	0.16	0.16	0.17	-	0.19	-	-
Arachidic	C20	1.18	1.29	1.17	1.22	1.19	1.29	-	1.45	1.55	-
Eicosapentaenoic	C20:5	-	0.10	0.40	0.24	0.46	-	-	0.64	-	-
Behemic	C22	0.21	0.21	0.20	0.21	0.18	0.22	-	0.26	-	-
Lignoceric	C24	-	0.25	-	0.37	0.71	-	-	0.66	-	-

Health benefits of cocoa

(i) Vasodilatation

The endothelium is a continuous, smooth, non thrombogenic surface of all blood vessels that exhibits a highly selective permeability in its healthy state. It synthesizes and releases a broad range of vasoactive substances. Functional impairment of the vascular endothelium in response to injury causes endothelial dysfunction associated with cardiovascular disease which is recognized as an early event in the development of atherosclerosis, and is associated with decreased bioavailability of the vasodilator nitric oxide.

Current evidence suggests that the consumption of cocoa and chocolate, rich in flavonoids, may provide protective vascular effects. In isolated rabbit aortic rings, cocoa extracts were shown to induce endothelium-dependent relaxation and to activate endothelial nitric oxide synthase. Oligomeric forms of the monomeric units, (-)-epicatechin and (-)-catechin, such as tetramers and higher, were associated with these effects. Additionally, a favorable balance in eicosanoid synthesis has been reported in cultured human aortic endothelial cells exposed to cocoa polyphenols and in human plasma samples from subjects 2 hours following the consumption of high-polyphenol chocolate (37 g). A decrease in the plasma leukotriene-prostaglandin

ratio was also found, which would result in more vasodilation, less platelet aggregation, and an anti-inflammatory profile. A significant rise in plasma epicatechin was also noted at the 2-hour time point following chocolate consumption.

It was concluded that the cardioprotective mechanisms, including vasodilation, is by the major polyphenols of cocoa, the epicatechin and catechin. These mechanisms may be related to increases in plasma epicatechin or catechin concentrations that signal the release of vasoactive substances from the endothelium, including nitric oxide and prostacyclin. Epicatechin has been shown to preferentially inhibit nitric oxide-related nitration and oxidation reactions without affecting nitric oxide synthesis and cyclic GMP signalling.

A recent clinical study has demonstrated an acute increase of brain perfusion following ingestion of polyphenol-rich cocoa. Moreover, long-term administration of cocoa polyphenol to aging rats is associated with preservation of youthful cognitive performance—raising the possibility that cerebral hypoxia (and/or suboptimal cerebrovascular nitric oxide production) might also play a role in the more modest fall-off in cognitive function associated with healthy aging. These considerations suggest that regular consumption of cocoa polyphenol might have important potential for promoting retention of youthfulness as human age.

(ii) Blood pressure effects

In healthy subjects, the effects of cocoa and chocolate on blood pressure have been differential. In untreated hypertensives, blood pressure lowering effect was noticed following 14 to 15 days of consumption of 100 g of dark chocolate. A recent report suggests that cocoa polyphenol may lower blood pressure by acting as an angiotensin I converting enzyme inhibitor, which also has antioxidant properties and can modulate nitric oxide production.

Cocoa-containing foods are likely to be responsible for the reduction in blood pressure and the improvement of endothelial function. Consumption of flavan-3-ol-rich chocolate or cocoa is shown to increase arterial and peripheral vasodilation, whereas this effect is less or absent after consumption of flavan-3-ol-low chocolate or cocoa. An increased activity of nitric oxide is likely to play a major role in this process. This is supported by the observation that polymeric procyanidins increased endothelial nitric oxide synthase activity in cultured endothelial cells. The lower cardiovascular mortality risk associated with cocoa intake could not be attributed to the lower blood pressure observed with cocoa use.

(iii) Modulator effect of cocoa on platelet dysfunction

Platelet dysfunction is another hallmark of atherosclerotic vascular disease. Interestingly, in addition to providing antioxidant vitamins, certain fruits and vegetables may also protect against thrombosis because of their high polyphenol content. Several studies have demonstrated platelet inhibitory properties of cocoa. Cocoa reduces ADP/collagen-activated, platelet-related primary hemostasis within hours of ingestion. These effects were explained, at least in part, by a reduction in the ADP-induced expression of the activated conformation of glycoprotein IIb/IIIa surface proteins. Furthermore, similar to low-dose aspirin, *ex vivo* catechin and epicatechin reduce glycoprotein IIb/IIIa expression, thereby exerting antiplatelet effects. In healthy volunteers, consuming 100 g dark chocolate reduced platelet aggregation, an effect not seen after ingestion of white chocolate or milk chocolate. Cocoa decreases not only platelet aggregation but also adhesion. In young healthy smokers, dark chocolate reduces platelet adhesion as assessed by a shear stress-dependent platelet test. Similarly, stearic acid, a saturated fat commonly found in chocolate, reduces mean platelet volume, an index of platelet activation, in humans.

(iv) Inflammation and immune function effects

Inflammation and increased oxidative stress promote endothelial dysfunction and atherogenesis. Nitric oxide normally inhibits nuclear transcription factor (NFkB), which binds to the promoter regions of genes coding for pro-inflammatory proteins such as cytokines and adhesion molecules. In endothelial dysfunction may be manifested decreased bioavailability of nitric oxide. Excess intracellular ROS in oxidative stress also activates NFkB. Cocoa flavonoids may prevent activation of NFkB and subsequent cytokine transcription by diminishing intracellular ROS.

(v) Effects on insulin resistance

Cocoa polyphenol influence directly insulin resistance and in turn, reduce the risk for diabetes. Cocoa may induce pancreatic β -cell regeneration and stimulate insulin secretion, have a hypoglycemic effect, and improve glucose tolerance. The vasodilatory effects of cocoa can also improve insulin sensitivity mediated by endothelial function. Sustained consumption of cocoa over long periods may effect insulin resistance to a greater degree than single doses of cocoa product.

(vi) Chocolate and women health

Chocolate cravings among teenage girls and women around the world are common. Studies at Europe confirmed the link between this food and female health and proved that estrogen levels

and biological needs cause cravings in women and chocolate become their persistent companion. Chocolates having the perfect combination of sugar and fat boosted a potential brain chemical serotonin which brought about the feeling of calmness and general mood stability. Fat release endorphins which energized the mind and lifted the spirit. Thus chocolate provide an exclusive positive biological, physiological and psychological experience especially in women. Chocolate is considered as a symbol of love and devotion and it was found out that phenylethylamine in cocoa triggers euphoric feelings like those associated with falling in love. Polyphenol chocolate (2000 mg/ 100g) shakes and ice creams are being sold in handy packs for young working women and housewives in Japan.

Conclusion

The investigations on the biochemical components, antioxidant, vasodilatory, blood-pressure lowering, anti-platelet, and anti-inflammatory effects of cocoa and chocolate provide exciting new evidence into the potential vascular benefits of polyphenol- rich foods. Balance and moderation are important in a healthy diet and must be considered in chocolate consumption also, which is high in calories and fat. Dark chocolates with more of cocoa solids play a major role in present day diet and these foods represent plentiful sources of polyphenol when relished in moderation with a healthy and active lifestyle will be good for our heart and general health.



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