Phospholipid Concentration in Cocoa Butter and its Relationship to Viscosity in Dark Chocolate[1]

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Abstract

Fats extracted from chocolate liquor with a polar solvent, chloroform-methanol, was found to be 0.65% phospholipid. The evidence indicates that the phospholipids are associated primarily with the nonfat solids since concentrations were much lower in fat recovered with nonpolar solvents, hydraulic pressing and centrifugation. Seven of the 11 commercial cocoa butters analyzed had phospholipid concentrations between 0.05% and 0.13%. The highest concentration found was 0.57%. The reduction in viscosity caused by the addition of these butters, 14% by weight, to chocolate was related to the phospholipid concentration in cocoa butter. The higher the phospholipid level, the greater was the viscosity-reducing effect of the cocoa butter.

Introduction

Standardization and stabilization of viscosity in molten chocolate is essential if control is to be exercised over the amount of coating retained on confection centers during the enrobing process. The envelopment of all sugar crystals and nonfat cocoa particles with cocoa fat appears to be a necessary prerequisite for this control (1). While fundamental mechanisms are not clearly understood the several processes involved in the manufacture of chocolate coating (mixing, refining and conching) influence fluid properties, with final adjustment of viscosity being obtained by addition of cocoa butter as a terminal step.

Soybean lecithin is commonly added to chocolate coating as an aid in the control of viscosity. The advantages of lecithin involve not only a shortening of the time needed for manufacturing a coating but also result in a substantial savings in the amount of cocoa butter that has to be added. The effect of lecithin is to reduce the interfacial tension between cocoa fat and the nonfat particles thereby reducing the amount of cocoa butter needed for covering these particles (1).

The influence on viscosity of the naturally occurring phospholipids of cocoa beans has received little attention. Duck (2) proposed that the secondary reduction in viscosity taking place during conching is caused by a redistribution of the phospholipids. Unfortunately, this investigator did not have an opportunity to test his hypothesis. It has been observed by chocolate manufacturers that cocoa butters differ in respect to their ability to reduce viscosity in chocolate. Since cocoa beans are 0.3% to 0.5% by weight phospholipid (4, 5), it is not inconceivable that the variable effect of the added butter involves these polar lipids.

The study reported herein was undertaken to obtain information about the effect of cocoa bean phospholipids on viscosity. The degree of complexing to nonlipid solids was assessed using solvents of varying polarity, and phospholipid concentrations in several cocoa butters were determined and then related to viscosity reduction in chocolate.

Experimental Procedures

Samples

Conched and unconched dark chocolate coatings, chocolate liquor and cocoa butter were supplied by the Chocolate Manufacturers' Association of the USA. Cocoa butter and cocoa were also prepared in the laboratory by pressing 50 g quantities of chocolate liquor in a Carver hydraulic press equipped with heating plates (120 C). The sample was heated to 93 C before entering the press, where it was subjected to 15,000 psig pressure for 30 min. The press cake was pulverized to cocoa powder in a small laboratory mill (Chemical Rubber Co., Cleveland, Ohio).

Lipid Extraction

Lipid was extracted from 4 g of chocolate liquor, cocoa or cocoa butter by grinding in a mortar with 100 ml of chloroform-methanol as recommended by Folch *et al.* (3). Suspended cocoa fiber was removed from the extract by filtering through a short column of Celite 545 (Johns Manville, Pittsburgh, Pa.) Phosphorus was determined by the molybdenum blue method after digestion with hydriodic acid reagent as described by Saliman (6).

Information about free and bound phospholipids was obtained by comparing the effectiveness of chloroform-methanol (2:1), diethyl ether and hexane in extracting lipid phosphorus from Bahia chocolate liquor. The procedure followed was similar to that referred to above, except that 200 ml of solvent was used to extract a 5 g sample. These solvents were also used to extract the phospholipids from Bahia liquor which had been mixed in a small Hobart mixer for 72 hr at 60 C. The objective was to obtain information about the differences in phospholipid distribution between conched and unconched liquor by simulating the mechanical action of a commercial conche.

Ultracentrifugation

Tubes containing 20 g Bahia liquor were centrifuged at 20,000 rpm (32,000 × g) for 1 hr at 35 C in an IEC Model B-35 Centrifuge (International Equipment Co., Needham, Mass.). The lipid layer at the top of the tube was removed and analyzed for phosphorus.

Viscosity Determination

Thirty grams of cocoa butter were added to 210 g of dark chocolate which had been sampled from a commercial batch prior to incorporation of cocoa butter for viscosity standardization. The mass was allowed to melt overnight in a laboratory oven adjusted to 54 C. After thorough mixing in a Hobart mixer, viscosity was measured with a Brookfield RVT viscosimeter using a No. 5 spindle at Speed 10 (Brookfield Engineering Laboratories, Inc., Stoughton, Mass.).

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TABLE I
Effect of Recovery Method on the Concentration of Phospholipids in Cocoa Butter

Recovery method	Phosphorus mg/100 g fat	Phospholipid, %
Solvent extraction		
Chloroform-methanol	25.8	0.65
Diethyl ether	8.3	0.21
Hexane	7.8	0.20
Hydraulic pressing	4.2	0.11
Ultracentrifugation	4.0	0.09

Instrument readings were converted to centipoise using the conversion table supplied with the instrument. Care was exercised to assure that all samples were mixed for the same length of time before measuring viscosity at 54 C.

Results and Discussion

To obtain a complete recovery of phospholipids, Parsons *et al.* (5) extracted cocoa beans with chloroform-methanol (3). No attempt was made to differentiate between the free and bound or complexed forms. Because of its potential usefulness in understanding the effect of the phospholipids on viscosity in chocolate, studies were undertaken to collect this information.

Results recorded in Table I show phospholipid recovery as affected by: (a) extracting with polar and nonpolar solvents; (b) hydraulic pressing to recover cocoa butter; (c) ultracentrifugation to surface a cocoa fat fraction from chocolate liquor. In every instance the phospholipids were found to be strongly associated with the nonlipid solids. Assuming complete recovery using chloroform-methanol, only 32% of the phospholipids was extracted with diethyl ether and 30% with hexane. The phospholipid concentrations in pressed cocoa butter and in fat recovered by ultracentrifugation were only about 15% of that in fat recovered with chloroform-methanol.

It had been anticipated that information about the migration of the phospholipids during conching might be obtained from analyses of pressed cocoa butters and of lipid extracts obtained using the solvents listed in Table I. Differences found among cocoa butters pressed from chocolate sampled at various stages of a commercial conching operation were minimal and provided no clear-cut evidence to support Duck's (2) claims. While the efficacy of diethyl ether and hexane relative to chloroform-methanol in extracting the phospholipids was not altered by conching, the amount of phospholipid extracted from conched chocolate by each of the solvents was slightly greater (approximately 10% more) than that recovered from unconched chocolate. The higher yields suggest that mechanical working in the conche does, indeed, have some effect on phospholipid binding. Additional work is needed to relate this change to the viscosity reduction which normally occurs during conching.

TABLE II
Phospholipid Content of Commercial Cocoa Butter

Sample	Phosphorus mg/100 g fat	Phospholipid,[a] %
Brazilian	0.5	0.01
Brazilian	2.4	0.06
Brazilian	5.0	0.13
Brazilian	5.0	0.13
Ivory Coast	3.4	0.08
Ivory Coast	4.1	0.10
Ghana	2.0	0.05
Ecuadorian	8.4	0.21
Mexican	23.0	0.57
Italian	0.4	0.01
German	3.1	0.07
Laboratory-pressed	4.2	0.10

[a] Calculated as grams lipid phosphorus/100 g × 25.

Laboratory-scale hydraulic pressing of chocolate liquors yielded cocoa butters with low levels of lipid phosphorus (5 mg/100 g fat). Using this figure it was calculated that 15% by weight cocoa butter would add 0.02% phospholipid to chocolate. While this might appear to be an insignificant amount, it cannot be precluded that its effect on viscosity in chocolate would be inconsequential. Typical formulas call for the addition of approximately 0.25% of commercial lecithin which contains a considerable amount of non-phospholipid material. Based on a lipid phosphorus analysis of a commercial lecithin used at the 0.25% level, the actual amount of phospholipid incorporated would only be about 0.12%. Thus, the amount needed for viscosity control is quite small and the contribution of trace amounts of phospholipid in the added cocoa butter cannot be completely ignored.

While lipid phosphorus levels were always low and did not vary greatly among cocoa butters recovered from chocolate liquor under carefully controlled pressing conditions in the laboratory, a much higher concentration was found in a commercial sample of butter. This raised a question concerning the wisdom of applying data collected on laboratory-derived samples to what actually occurs in a large commercial process. Analysis of another commercial sample of butter yielded a phospholipid concentration similar to laboratory-pressed cocoa butter. This indicated that phospholipid levels in cocoa butter might be affected by variables such as equipment used, press temperature and the type of bean from which butter was recovered. Therefore, several samples of cocoa butter were supplied by a chocolate manufacturer and the concentrations of phospholipids found in these samples recorded (Table II). The only information provided about the samples was their identification with respect to type of bean or exporting country, or both.

Phospholipid concentration exceeded 0.13% in only two of the 12 samples and in eight samples phospholipid levels were within a relatively narrow range between 0.05% and 0.13%. However, the fact that concentrations as high as 0.57% were found indicates that abnormal cocoa butters occasionally will be found and could conceivably affect viscosity when used in chocolate coating.

To determine if the phospholipid level in butter could be related to the viscosity of chocolate, butters representing a wide range of phospholipid concentrations were added to a chocolate paste taken from a commercial refiner before final standardization with cocoa butter. In addition to the commercially derived butters, a laboratory-pressed butter and a cocoa fat sample obtained by extraction of chocolate liquor with chloroform-methanol were included in the trials. The latter was to represent a fat containing essentially all of the extractable phospholipids of chocolate liquor. Analyses of the pressed and solvent-extracted fat from this liquor yielded phospholipid concentrations higher than expected (0.23% and 0.97% respectively). An inquiry to the manufacturer of this liquor revealed that soybean lecithin had been added which would account for the high values found. Although the original intent was to use liquor which contained only natural cocoa bean phospholipids, a repeat of the experiment using pressed butter and solvent-extracted fat from regular liquor was not attempted because it was not expected that conclusions drawn from the data would be any different. In a sense the selection of the liquor containing the added lecithin was fortuitous, since it extended the range of phospholipid concentrations studied. As shown in Table III, the higher the phospholipid concentration in cocoa butter the greater was its viscosity-reducing effect when added to dark chocolate coating.

The data reported herein show that the naturally occurring phospholipids of cocoa beans do, indeed, affect the viscosity of chocolate. The finding that phospholipid concentration influenced the viscosity of chocolate suggests that phosphorus analyses of butters purchased for use in chocolate could be helpful in predicting a butter's behavior. Conditions selected to yield cocoa butter containing a maximum level of natural cocoa bean phospholipids could reduce the amount of butter needed for viscosity standardization and make the chocolate manufacturer less dependent on added lecithin.

While the moisture level in chocolate liquor is very low (about 1%), slight variations may affect the recovery of cocoa butter by hydraulic pressing. Commercial experiences indicate that recovery is facilitated when a small amount of water is added to the liquor or when liquor is from lightly roasted cocoa beans. Little information is available on the effect of small variations in moisture on phospholipid recovery. The authors have measured lipid phosphorus in cocoa butter pressed from unroasted cocoa beans which contained 5% moisture, and the values found were not greatly different from those recorded for butter pressed from chocolate liquor having 1% moisture. However, before moisture's role can be properly ascertained roasting and grinding variables will have to be accounted for. The approach logically is to add varying amounts of moisture to aliquots from the same batch of liquor followed by hydraulic pressing and analysis for lipid phosphorus.

TABLE III
Viscosity of Chocolate as Affected by Cocoa Butters Containing Varying Levels of Phospholipids

Butter sample	Cocoa butter		Viscosity centipoise
	mg P/100 g	% Phospholipid,	
Italian	0.4	0.01	21,500
Brazilian	5.0	0.13	17,200
Laboratory-pressed	9.2	0.23	16,600
Mexican	23.0	0.57	13,400
Solvent-extracted	38.6	0.97	12,600

Extraction of fat with solvent is not widely practiced on a commercial scale; when used, it is believed that nonpolar hexane is the solvent. More polar solvents should yield fat with a greater phospholipid content thereby enchancing the viscosity-reducing effect of cocoa butter. The data further suggest that phosphorus analyses could be employed to differentiate between hydraulically pressed and solvent-extracted cocoa fat.

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