

## The Theobromine Content of Cacao-Beans and Cocoa.

BY RAYMOND V. WADSWORTH.

*(Read at the Meeting, March 1, 1922.)*

ANYONE searching through the published figures for the theobromine content of the cacao-bean would be bewildered by the different results recorded. In the ordinary text-books on cocoa and chocolate there is little help, even in the latest editions. The following average percentages have been recorded by various authorities: 0.82 to 1.34 per cent. (Winton, Silverman and Bailey<sup>12</sup>); 1 per cent. (Knapp<sup>24</sup>); 1.4 to 1.80 per cent. (Parry<sup>18</sup>); 1.5 per cent. (Wynter Blyth<sup>14</sup>); 2 per cent. (British Pharmaceutical Codex<sup>17</sup>); 0.9 to 3.0 per cent. (Whymper<sup>25</sup>).

When one considers any individual cacao-bean, the range of recorded percentages is almost as wide, though one would expect a much smaller

variation. Taking such beans as Trinidad and Caracas, the following results recorded by different workers, give an idea of the variations obtained:—

## TRINIDAD NIB.

Moisture Per Cent.	Cacao butter Per Cent.	Theobromine Per Cent.	Authority
6.20	51.57	0.4	Zipperer <sup>13</sup>
6.34	43.66	0.85	Ridenour <sup>7</sup>
3.09	48.28	0.91	Winton, Silverman and Bailey <sup>12</sup>
5.62	45.71	1.05	Eastes and Terry <sup>3</sup>
		1.44	Maupy <sup>10</sup>
4.72	53.57	1.94	Eastes and Terry <sup>3</sup>

## CARACAS NIB.

6.50	50.31	0.77	Zipperer <sup>13</sup>
5.13	51.45	1.03	Winton, Silverman and Bailey <sup>12</sup>
4.75	53.65	1.08	Eastes and Terry <sup>3</sup>
6.63	36.81	1.13	Ridenour <sup>7</sup>
		1.38	Maupy <sup>10</sup>
		1.43	Eminger <sup>9</sup>
		1.63	Wolfram <sup>13</sup>

It will be clearly seen from these figures that there is a need for either a revision of the percentages, or else some interpretation of the results—the latter never seems to have been attempted.

Many of the early workers obtained poor results simply on account of the methods then available for the estimation of theobromine, and it can be said that figures published before 1895—about which year both Eminger<sup>9</sup> and Kunze<sup>6</sup> published their methods—are of little more than historic value. It is interesting to record one or two early figures, remembering that it was only in 1841 that Woskresensky isolated the alkaloid:—

	Bell <sup>2</sup> (1881) Per Cent.	Zipperer <sup>4</sup> (1886) Per Cent.	Eastes & Terry <sup>3</sup> (1885) Per Cent.
Guayaquil cacao	0.54	0.33	1.74
Grenada cacao	0.91		1.42
Surinam cacao	0.78	0.50	1.42
Trinidad cacao	0.59	0.40	1.05, 1.94

Although many workers obtained below one per cent., others recorded percentages up to 4 per cent. (Payen<sup>2</sup>.)

The author has, in a previous paper<sup>26</sup>, criticised the present methods used for the estimation of theobromine, showing that not one of these would give accurate and concordant results. Consequently, all the figures published contain some error and need revising. To this task the present paper is intended as a contribution, and it is hoped that it may help to clear up the uncertainty, which so obviously exists, as to the amount of theobromine present in different cacao-beans, and provide an interpretation of the results obtained.

METHODS USED.—In a previous paper the author<sup>26</sup> has described a new method for the estimation of theobromine, depending upon the extraction of the alkaloid from the damp cacao mixed with magnesia, by means of tetrachlorethane, which gives accurate and concordant results. This method has been used in all the work recorded below.

The method of procedure when examining cacao-beans was as follows:—The beans were carefully shelled by hand. The shell was ground to a powder, the particles of which were less than 0·04 inch, and immediately bottled for use. The nib was ground in a warm mortar until every particle was less than 0·005 inch. In the estimation of the fat a fine grinding is very necessary. After grinding, the liquid mass (which the ground nibs had become) was solidified by cooling. A portion of this was scraped finely with a knife, thus still further reducing the size of particles, and used for the estimation of the moisture and fat of the original nib. The remainder was roughly broken up and extracted for 24 hours in a Soxhlet with petroleum spirit (B.Pt. below 80° C.), which, it has previously been shown<sup>28</sup>, does not dissolve the theobromine. The extracted mass was dried, thoroughly mixed and bottled ready for use. In dealing with such large quantities (60–100 grms.) it was found that after 24 hours' extraction, between 4 and 14 per cent. of fat was still left in the material; consequently the fat percentage and the moisture content had both to be estimated for the purpose of calculating the results back to the original nib.

When examining manufactured cocoas and shells the material could be used without any preliminary de-fatting being necessary.

In the case of nibs and cocoas the fat percentage varies very considerably with the different samples; thus the only method of comparison is between the results calculated on the dry, fat-free material. The results below are for this reason expressed on the dry, fat-free material as well as on the original cocoas. With shell, where the fat percentage is small and varies little, the figures are given on the dry shell as well as the original.

All the samples analysed were commercial samples obtained through the usual channels, and not special plantation preparations. Thus the results can be taken to represent the commercial cacao-bean at present coming on to the market.

**THEOBROMINE PRESENT IN NIBS\* OF DIFFERENT ORIGIN.**—The order of arrangement in the following table is that of theobromine content on the dry, fat-free material, the nibs containing the highest percentage appearing at the top of the table. Under "remarks" are noted roughly the degree of fermentation and the colour of the cotyledons when cut through. These, it will be found, are the most important factors influencing the theobromine content of the bean. The terms "Forastero" and "Criollo" have been used in various ways. "Forastero" really means "foreign," whilst "Criollo" means "native." Thus, if this meaning is taken as a basis, the same kind of cacao would be Forastero to one man and Criollo to another, living, for instance, on a different island. The meaning, however, which it seems least confusing to accept, is that followed by van Hall<sup>20</sup>. He takes the Forastero cacao to be that which has a purple bean and is flattish, and the Criollo cacao to be that which has a whitish bean and is more plump. Both kinds, on fermentation, lose their original colours, but, whereas the Criollo becomes a beautiful light chocolate-brown, the Forastero becomes a deep black or purple-brown to very deep brown. Thus it is possible to distinguish by the

\* Shelled Cacao-Beans.

colour of the bean the approximate type. It has not been found possible, as yet, to separate the different kinds of Forastero cacaos with accuracy; this is due to the shape and colour of the bean varying so much according to the length of fermentation, and to the various effects of the season, whether it be wet or dry. So, for the purpose of the following figures, the separation is only made into Forastero and Criollo:—

## THEOBROMINE IN CACAO NIB.

(All from unroasted beans, *i.e.* cacao as marketed.)

Kind of beans	Moisture Per Cent.	Butter Per Cent.	Theobromine On original material Per Cent.	On dry, fat-free substance Per Cent.	Remarks
Costa Rica (ordinary)	2.8	53.7	1.66	3.82	Very poorly fermented. Purple-brown.
Accra	2.7	52.7	1.69	3.80	All unfermented purple beans.
Costa Rica (fine)	3.18 2.9	56.4 56.9	1.53 1.12	3.77 2.78	Fermented. Purple to deep grey-brown.
Columbian	3.1	53.7	1.62	3.75	Very poorly fermented. Blackish-brown.
Lagos	2.7	53.0	1.56	3.51	Very poorly fermented. Blackish-brown.
San Domingo	2.9	52.2	1.51	3.36	Very poorly fermented. Purplish-brown.
Accra	1.6 2.9 2.5	53.3 54.6 52.7	1.52 1.41 1.42	3.38 3.32 3.17	Fermented. Purplish-brown.
Haiti	3.5	53.5	1.39	3.23	Poorly fermented. Blackish-brown.
San Thomé	2.7	54.8	1.36	3.20	Fermented. Purplish-brown.
Para	3.0	54.3	1.28	3.00	Poorly fermented. Blackish-brown.
Bahia	2.3	56.6	1.23	2.99	Fermented. Very deep brown.
Arriba	2.9 2.8	52.5 52.0	1.33 1.32	2.98 2.93	Poorly fermented. Deep browns and purples.
Caracas	2.5	52.7	1.32	2.95	Poorly fermented. Mixed. Mainly dark-brown.
Grenada	3.5	53.5	1.23	2.86	Fermented. Purple and browns.
Surinam	2.7	55.8	1.17	2.82	Fermented. Blackish-brown.
Cameroons	2.6	56.2	1.15	2.78	Highly fermented. Deep brown.
Machala	3.9 2.9	51.1 51.8	1.24 1.40	2.75 3.09	Poorly fermented. Deep brown and purple.
Trinidad	3.0	53.0	1.18	2.69	Fermented clayed beans. Deep browns and purples.
Ceylon	2.3	52.6	1.20	2.65	Fermented. Mixed browns and purples.
Jamaica	3.1 2.0	57.0 58.2	1.05 0.99	2.64 2.48	Fermented and unfermented. Mixed. Purples and browns.
Java	2.9	53.5	1.03	2.36	Poorly fermented. Washed. Light-brown to white.
Samoa	2.8	52.9	1.01	2.28	Light-brown beans.
Venezuela (clayed)	3.1	50.1	1.04	2.23	Do.
Do. (unclayed)	2.3	50.6	1.05	2.22	Do.

Expressed on the dry, fat-free material, it will be noticed that all the purple Forastero beans contain the highest percentage of theobromine, whilst all the light Criollo type of beans contain the lowest percentage. (H. C. Brill<sup>22</sup> found only a very slight difference in the theobromine content of Criollo and Forastero cacaos, and the latter, in his case, gave slightly the lower results.) From the figures given above there is no doubt that the light Criollo beans contain much less theobromine than the dark Forastero beans—a fact previously unrecognised.

There is also a distinct variation in the theobromine content of the nib of a particular bean; the three samples of Costa Rica vary by one per cent. and the Accra by 0.6 per cent. This difference is due, apart from the slight variation found in all natural products, to two causes:—*Firstly*: All the beans from one country are not of the same kind, the commercial samples being nearly always mixtures. If much cacao of the Criollo type is present, the alkaloid content is lowered, whilst if the whole is pure Forastero, it is raised. It is also highly probable that many trees now producing cacao are crosses between Criollo and Forastero, and this, for instance, is true of the Ceylon product. *Secondly*: The amount and type of fermentation influence the theobromine percentage considerably. From the table it will be seen that Accra unfermented cacao nib contains much more alkaloid than the fermented cacao nib. During fermentation theobromine is lost from the nib to a considerable extent. This conclusion is supported by other work of the author, in addition to that recorded here. It should be mentioned that Brill<sup>22</sup> says “during fermentation the theobromine shows no regular variation”; this is accounted for by the method used in the estimation, and it may be noted that his results are mainly very low. L. Nicholls<sup>19</sup> was also of the opinion that theobromine showed only a “very slight loss.” Other authors even claim an increase.

The maximum variation found in cacao-beans of all types and grades is between 0.99 and 1.69 per cent. of theobromine on the original nib, and between 2.22 and 3.82 per cent. on the dry, fat-free material.

For the cacao-beans which form the bulk of the world's production the average percentage would be 1.2 to 1.7 per cent. of theobromine on the original nib, and 2.8 to 3.8 per cent. of theobromine on the dry, fat-free material.

**THEOBROMINE PRESENT IN SHELLS OF DIFFERENT ORIGIN.**—The number of figures published of the theobromine content of cacao-shell are small. The general percentages recorded are as follows:—0.2 to 0.90 per cent. (Winton, Silverman and Bailey<sup>12</sup>; 0.76 per cent. (Eminger<sup>9</sup>); 1 per cent. (British Pharmaceutical Codex<sup>17</sup>); 1.0 to 1.4 per cent. (Knapp<sup>24</sup>); 0.4 to 2.0 per cent. (Whymper<sup>25</sup>). It will be seen that Whymper gives a wider range than any other authority, and, although he quotes no figures to support this higher percentage, the table below shows that even this range does not include all commercial shells.

The table below gives the results the author has obtained on a number of different commercial cacao-shells:—

# THEOBROMINE IN CACAO-BEAN SHELLS.

(Unroasted Beans.)

Shell from	Moisture Per Cent.	Theobromine On original material Per Cent.	On dry substance Per Cent.	Remarks.
Cameroons	12.3	2.61	2.98	Very loose shells. Very highly fermented.
Costa Rica	9.7	2.22	2.46	Well fermented.
(fine)	9.9	2.30	2.55	
Jamaica	12.5	2.15	2.46	Well fermented.
	14.0	2.00	2.33	
San Thomé	10.6	2.16	2.41	Well fermented.
Bahia	12.6	2.08	2.38	Well fermented.
Surinam	11.5	1.96	2.22	Well fermented.
Accra	11.2	1.63	1.84	Well fermented.
	10.5	1.53	1.71	
Samoa	11.3	1.36	1.53	Brittle shell. Pure Criollo.
Grenada	11.5	1.16	1.31	Well fermented.
	10.2	2.07	2.30	
Java	11.8	1.10	1.25	Washed loose shells. Pure Criollo
Accra	10.6	0.98	1.10	Fermented.
Venezuela	10.0	0.87	0.97	Pure Criollo.
	8.7	0.77	0.84	
		0.85	0.93	
Trinidad	9.2	0.74	0.81	
		0.78	0.86	
Haiti	10.5	0.65	0.73	Poorly fermented.
Machala	13.0	0.52	0.60	Poorly fermented.
	10.1	0.47	0.52	
Costa Rica (ord.)	9.7	0.51	0.56	Poorly fermented.
Columbian	13.3	0.44	0.51	Poorly fermented.
Lagos	9.2	0.40	0.44	Poorly fermented.
Ceylon	13.5	0.38	0.44	Washed.
Arriba	8.4	0.42	0.46	Poorly fermented.
	13.6	0.37	0.43	
Caracas	9.6	0.36	0.40	Slightly fermented.
San Domingo	9.1	0.34	0.37	Slightly fermented.
Para	13.1	0.23	0.26	Slightly fermented.
Accra	10.5	0.17	0.19	All unfermented.

It will be noticed that there is no difference between shells from Criollo and Forastero beans, and that no interpretation of the results can be made from this point of view. The Criollo tends to take its place in the middle of the Forastero. It will, however, be easily seen that shells from unfermented cacaos are always low in theobromine, whilst those shells which come from well-fermented beans always contain a much higher percentage. Thus the medium fermented Criollo occupies a middle position. The original shell of the cacao-bean, fresh from the pod, contains only about 0.17 per cent. of theobromine (as will be seen from

the last figure in the table), and the alkaloid present in the shell is brought there by sweatings from the nib during fermentation. Thus the highly-fermented samples contain much more than do those which have been but poorly fermented.

This effect of fermentation has never previously been recognised. It helps us to understand the great variations which occur, and may help us to determine the approximate length of fermentation to which any particular sample has been subjected. When beans are very unevenly prepared, as in the case of the Accra cacao, it will be seen that the theobromine present in the shell varies very greatly (*e.g.* 0.19 to 1.84 per cent.); but where the bean is evenly prepared, the theobromine content is fairly constant, *e.g.* Trinidad cacao. If the bean is washed, as is so often the case in Ceylon, Java and Samoa, much of the alkaloid is washed away, and thus the fermentation of such beans cannot be judged in this way.

The maximum variation found in the shell of the cacao-bean of commerce is between 2.98 and 0.19 per cent. on the dry shell.

When shell is used for the commercial extraction of theobromine, it is obvious that well-fermented cacaos are to be desired.

**THEOBROMINE PRESENT IN GERMS.**—The germ is the radicle of the cacao-bean. So far as the author is aware, there is only one result published of the theobromine content of germs, that of Haussler<sup>20</sup>, whose figures are as follows:—Fat, 7.8 per cent.; theobromine, 1.88 per cent.

The germs used in the analysis given below were separated commercially from a blend of roasted cacao-beans, and consequently do not represent the analysis of germs from one particular kind of beans. It must be said, however, that, although the author has analysed many samples from different blends, the results have been practically the same in every case. From this it appears probable that the variation in the theobromine content of the germs is small.

	Fat Per Cent.	Theobromine On original material Per Cent.	On fat-free substance Per Cent.
Roasted cacao-bean germs	5.8	2.10	2.23

**EFFECT OF ROASTING ON THE THEOBROMINE CONTENT OF NIB.**—Most authorities are agreed that roasting of the cacao-bean has practically no effect on the theobromine content. The following are the results of the work of three authors on the subject:—

	Moisture Per Cent.	Butter Per Cent.	Theobromine Per Cent.
Weigman <sup>5</sup>			
Raw whole bean	7.93	45.57	1.49
Roasted whole bean	6.79	46.19	1.58
Zipperer <sup>13</sup>			
Raw shelled bean	7.11	51.78	0.45
Roasted shelled bean	6.71	49.24	0.43
Winton, Silverman and Bailey <sup>12</sup>			
Raw shelled bean	5.13	51.45	1.03
Roasted shelled bean, medium roast	3.71	51.65	1.02
„ „ high roast	3.11	51.50	0.95

Whymper<sup>25</sup>, however, disagrees with the above results, and gives the following figures which he obtained:—

	Theobromine Per Cent.
Raw bean	1.11
Roasted bean (120° C. 15 mins.)	0.77
"    "    (230° C. 8 mins.)	0.25

The author's results, given below, support the figures, showing that there is practically no loss of theobromine during the roasting of the bean. Whymper's results must be due to the method employed for the estimation. Such a loss would mean that manufactured cocoas must contain very little alkaloid, which, in the latter part of the paper, will be seen not to be the case.

#### LOSS OF THEOBROMINE FROM NIB DURING ROASTING.

Nibs from	Moisture Per Cent.	Cacao butter Per Cent.	UNROASTED.		Moisture Per Cent.	Cacao butter Per Cent.	ROASTED.	
			Theobromine On original material Per Cent.	On dry, fat-free substance Per Cent.			Theobromine On original material Per Cent.	On dry substance Per Cent.
Accra beans	2.9	54.6	1.41	3.32	2.1	54.8	1.47	3.42
	2.5	52.7	1.41	3.15	1.5	54.3	1.46	3.31
Arriba "	2.8	52.0	1.32	2.93	2.0	53.2	1.41	3.14
Machala "	2.9	51.8	1.40	3.09	1.6	52.9	1.37	3.00

EFFECT OF ROASTING ON THE THEOBROMINE CONTENT OF SHELL.—Very few figures are given for the loss of theobromine from shell on roasting. The figures quoted below are from Winton, Silverman and Bailey<sup>12</sup>:—

	Theobromine	
	Moisture Per Cent.	On original material Per Cent.
Raw	8.69	0.33
Medium roast	6.01	0.48
High roast	5.16	0.56

It will be noticed that there is a slight increase during roasting. The author's results, given below, support this, so far as shells having a low theobromine percentage go. In the case of those shells which contain a high percentage there is a slight loss due to roasting. The shell comes into contact with the greatest heat, and with some type of roasting is liable to get slightly charred. It consequently follows that there would be a distinct loss of matter by volatilisation, and shells containing a high percentage of theobromine would lose the alkaloid on their surface readily.

#### LOSS OF THEOBROMINE FROM SHELL DURING ROASTING.

Shell from	Moisture Per Cent.	UNROASTED.		Moisture Per Cent.	ROASTED.	
		Theobromine On original material Per Cent.	On dry substance Per Cent.		Theobromine On original material Per Cent.	On dry substance Per Cent.
Accra beans	11.2	1.63	1.84	6.9	1.51	1.62
	10.5	1.53	1.71	5.0	1.61	1.69
Arriba beans	8.4	0.42	0.46	3.4	0.61	0.63
Grenada beans	10.2	2.07	2.30	5.0	2.1	2.21
Machala beans	10.1	0.47	0.52	3.3	0.55	0.57



THEOBROMINE CONTENT OF COMMERCIAL COCOAS.—Previous results published vary greatly, as in the case of the cacao-bean. The following is an average example:—

Moisture Per Cent.	Van Houten's Cocoa		Authority
	Fat Per Cent.	Theobromine Per Cent.	
4.53	29.78	0.69	F. Yapple <sup>8</sup>
	29.66	2.00	C. Girard <sup>15</sup>
	1.99–2.23		A. Kreutz <sup>16</sup>

From the results already given on cacao nibs it will be seen that the greatest bulk of cacao coming on the market (*i.e.* from the Gold Coast, Ecuador, San Thomé and Brazil) contains above 2.8 per cent. of theobromine, on dry, fat-free material. It follows that the majority of manufactured cocoas must generally contain a minimum of 3 per cent. (on the dry, fat-free substances) allowing for a blending of the different varieties. It will be seen from the following table that the analyses bear out this expectation:—

#### THEOBROMINE IN COCOAS.

Name of Maker and Country of manufacture	Name of cocoa	Moisture Per Cent.	Fat Per Cent.	Theobromine	
				On original material Per Cent.	On dry, fat-free substance Per Cent.
Mazawattee (England)	Dee & Ess	6.9	31.7	2.18	3.55
Cailler (Switzerland)	Pure soluble	7.4	27.6	2.29	3.52
Van Houten & Zoon (Holland)	Rova	7.4	27.6	2.25	3.46
Cadbury (England)	Bournville	6.4	28.6	2.22	3.42
Fry (England)	Pure breakfast	4.1	28.0	2.32	3.42
Lipton (England)	Lipton's	5.9	25.0	2.35	3.40
Caley (England)	Fleur de Lys	6.1	32.8	2.05	3.36
Peradeniya Choc. Co. (Ceylon)	Peradeniya	4.9	40.5	1.81	3.32
Lyons (England)	Lyons'	4.5	25.2	2.32	3.30
Cadbury (England)	Essence	6.7	26.0	2.20	3.27
Bishop & Co. (America)	Bishop's	4.4	21.9	2.34	3.18
Rothwell (England)	Welco	7.3	23.3	2.20	3.17
Rowntree (England)	Elect	4.5	26.0	2.20	3.17
Armour (America)	Veribest	5.8	21.7	2.29	3.16
Horne & Sutton (England)	Digestive	6.3	26.6	2.12	3.16
Barber & Co. (England)	Essence	6.3	27.4	2.08	3.14
Peters (Switzerland)	Breakfast	5.9	20.5	2.25	3.06
Fry (England)	Concentrated	6.9	30.4	1.90	3.03
Watford Mfg. Co. (England)	Delecta	6.0	27.4	2.00	3.00
Co-op. Wholesale Sy. (England)	Essence	6.7	27.7	1.89	2.88
Caley (England)	Mella	4.6	31.1	1.62	2.52
W. Baker & Co. (Canada)	Breakfast	4.6	25.6	1.76	2.52
Van Houten & Zoon (Holland)	Pure soluble	6.0	25.0	1.65	2.39

CONCLUSIONS.—The theobromine content of the nib of the cacao-bean varies with the amount of fermentation to which the bean has been subjected, and also with the variety—Criollo or Forastero—to which it belongs. The maximum variation due to all these causes has been found to be between 0.9 and 1.7 per cent. on the original shelled cacao-bean, or between 2.2 and 3.9 per cent. on the dry, fat-free material. The lower limit represents the light Criollo bean, and the higher the dark, unfermented Forastero.

The variation of the theobromine percentage in the shells of the cacao-bean is much greater than in the nib, being between 0.19 and 2.98 per cent. on the dry shell, the lower figure here representing the unfermented cacao-shell, and the higher the shells from very thoroughly fermented cacaos.

The germ, as commercially separated from roasted cacao-beans, contains 2.1 per cent. of theobromine.

During roasting there is practically no loss of theobromine either from the nib or shell.

Manufactured cocoas of commerce contain a much higher percentage of theobromine than is usually accepted. It will be found that they generally contain between 2.0 and 2.3 per cent. of theobromine on the original cocoa, and between 3.0 and 3.6 per cent. on the dry, fat-free material.

The work was carried out in Messrs. Cadbury Bros. Research Laboratory, and the author wishes to thank the firm for their permission to publish these results.

#### REFERENCES.

1. 1859. Mitscherlich, *Der Kakao und die Schokolade*.
2. 1881. Bell, J., *Analysis and Adulteration of Food*, Part I.; 79.
3. 1885. Eastes and Terry, *Pharmaceutical Journal*, [iii.], **15**, 764.
4. 1886. Zipperer, P., *Untersuch. über Kakao*, p. 56.
5. 1889. Weigman, König: *Chemie der menschl. Nahrungs-und Genussmittel*, I., 1019.
6. 1894. Kunze, W. E., *ANALYST*, **19**, 194 (*Zeitsch. Anal. Chem.*, **33**).
7. 1895. Ridenour, *American J. Pharm.*, **67**, 202.
8. 1895. Yaple, F., *Chem. Zeit.* [Rep.], **21**, 240.
9. 1896. Eminger, A., *Apoth. Zeit.*, p. 716.
10. 1897. Maupy, V. L., *ANALYST*, **22**, 191; (*J. Pharm. Chim.*), **5**, 329.
11. 1902. Dekker, J., *Rec. Trav. Chim.*, **22**, 143.
12. 1902. Winton, Silverman and Bailey, *Conn. Experimental Station Report*, 268-287.
13. 1902. Zipperer, P., *Manufacture of Chocolate*, **54**, 34.
14. 1903. Wynter-Blyth, A., *Foods*, 367.
15. 1909. Girard, C., *Int. Cong. Appl. Chem.* (Sec. 8, C. 185).
16. 1909. Kreutz, A., *ANALYST*, **34**, 20 (*Zeitsch. Nahr. Genuss.*), 1908-16, 579.
17. 1911. British Pharmaceutical Codex.
18. 1911. Parry, E. J., *Foods and Drugs*, Vol. I., 22.
19. 1913. Smith, H. H. (Ed.), *Fermentation of Cacao*, 238.
20. 1913. van Hall, C. J. J., *Cocoa*, p. 71 *et seq.*
21. 1914. Haussler, E. P., *Arch. Pharm.*, 252, 82; *ANALYST*, **39**, 308.
22. 1917. Brill, H. C., *Philippine J. Science*, **12**, [A], 9-15.
23. 1920. Wadsworth, R. V., *ANALYST*, **45**, 133.
24. 1920. Knapp, A. W., *Cocoa and Chocolate*, 163-168.
25. 1921. Whympster, R., *Cocoa and Chocolate*, 140, 395, 410.
26. 1921. Wadsworth, R. V., *ANALYST*, **46**, 32.

## DISCUSSION.

Mr. A. W. KNAPP said that the point which specially interested him in the paper was the number of figures given by Mr. Wadsworth which proved that during fermentation the amount of theobromine in the nib decreased, because it appeared to be generally accepted by all save himself that during fermentation the amount of theobromine increased. This opinion had largely resulted from the theory that the bean, when taken from the pod, contained a glucoside which, during fermentation, split up into theobromine, dextrose and cacao-red. The glucoside theory was founded on very slender evidence, and Mr. Wadsworth's figures showed that it was in need of revision. The defence, which would be made by those who believed that the glucoside existed, would be that Mr. Wadsworth's process not only estimated the free theobromine, but also decomposed the glucoside and estimated the combined theobromine thus set free. Some analysts were so convinced of the presence of the glucoside, that they recommended that the cacao products should be treated with acid to hydrolyse it, before attempting to estimate the total theobromine. In Mr. Wadsworth's process treating with acid was unnecessary, which threw doubt on the glucoside theory. Another suggestion which had been made was that the theobromine originally existed in combination with tannin; such a compound would be readily decomposed by the magnesia used in Mr. Wadsworth's process. Mr. Wadsworth's figures showed that the theobromine found in cacao-shell came almost entirely from the interior, and this suggested a purely physical explanation of the distribution of the theobromine during fermentation. The bean, during fermentation, became permeated with liquid, and this distributed the theobromine evenly through the cotyledons and shell of the bean, and when the beans were subsequently dried, they dried naturally from the outside, with consequent concentration of theobromine in the shell. This would explain why, in a fully fermented bean, Mr. Wadsworth actually found more theobromine in the shell than in the nib. He thought Mr. Wadsworth's figures might help the botanist in the difficult matter of classifying the cacao from different countries. He noted that the author did not support Mr. Whymper's figures showing the loss of theobromine on roasting. The author actually obtained an increase, which he presumed proceeded entirely from the loss of volatile matter. The figures given in the paper for theobromine in cocoa were higher than those commonly accepted, and made one wonder why cocoa was not usually considered at least as stimulating as coffee.

Mr. CHASTON CHAPMAN asked whether the results given by the author related solely to theobromine, or included caffeine and any other bases that might be present in small quantity. If the numbers related to theobromine alone, he was rather surprised to see such high results.

Mr. CRIBB said that he had always felt considerable doubt whether cacao-shell really contained any alkaloid, and asked if Mr. Wadsworth considered the presence of theobromine in the shell from unroasted and unfermented beans as definitely proved. He also enquired whether the specimens of shell which yielded unusually low theobromine figures were derived from "earthed" beans.

Mr. WADSWORTH, referring to the question of the acid treatment giving a higher result than treatment by the ordinary method, said that estimations were made with an entirely unfermented bean, which would naturally contain the highest amount of glucoside; when examined without previous treatment the amount was 3·76 per cent. on the dry, fat-free material, when submitted to acid treatment it was 3·80 per cent.—a difference of 0·04 per cent. With “Arriba” beans the difference was:—Without acid, 3·0; with acid, 2·98 per cent. The figures obtained by his method represented the whole of the theobromine present, not only free theobromine, and did not represent the caffeine. Regarding the question of theobromine in unfermented shell, he had examined in England specially preserved unfermented beans direct from the plantation, and they always contained approximately 0·2 per cent. of theobromine. Time had, of course, elapsed in which changes might have occurred in the beans, but he thought that probably a small amount was always present. As to the earthing of beans, he considered it made very little difference in the percentage of theobromine. Heavily earthed beans contained, in the shell, 0·77 per cent., or 0·85 per cent. when corrected for the amount of earth.

---