The Phosphatides and Oil in Unroasted and Roasted Coffee Beans

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IT IS a well known fact that coffee beans contain a rather high amount of oil, which does not diminish appreciably on roasting, but it is also known that the oil undergoes some changes on roasting. It has even been mentioned in the literature that the total quantity of oil is larger after roasting than before it. This may be due to the loss of water (20%) on roasting or the formation of ether soluble substances which are included with and calculated as oils (1).

There is, however, no mention of the phosphatides of these coffee oils, either from green or roasted coffee, nor is there a reference to any changes which these phosphatides might undergo during the roasting process. The first step was, therefore, to find the amount of phosphatides in green coffee beans and subsequently to investigate what happens to them during roasting.

TABLE I

Type of coffee	Light petrol. extract	Phosphatides in the oil	Alcohol-benzene extract	Phosphatides in extract	Caffeine in alcohol-benzene extract
	Green coffee				
	%	%	%	%	%
Kenya	10.43	2.50	0.91	16.0	0.86
Brazil	6.05	1.47	2.44	3.9	0.65
Cameroon	9.47	2.50	1.17	9.7	0.74
Uganda	5.03	1.16	1.02	13.0	1.36
Madagascar	8.30	1.80	0.63	5.2	1.39
	Roasted coffee				
Kenya	13.13	.....	1.23	3.0	1.44
Brazil	9.38	0.40	2.50	.....	1.04
Cameroon	13.57	.....	1.43	.....	1.05
Uganda	8.88	.....	2.00	0.5	1.65
Madagascar	9.4	0.20	1.16	1.1	2.24

The experiments were carried out on five different types of coffee: Madagascar, Kenya, Cameroon, Brazil, and Uganda. The tests on the green and roasted beans were always carried out with beans from the same sample. The coffee was extracted in the usual way, at first repeatedly with light petroleum. When all the oil had been removed in this manner the residue was extracted with alcohol-benzene (20-80) which has proved the best solvent for the extraction of those phosphatides (and oils) which are "bound" to proteins or carbohydrates and which cannot be extracted by any of the usual fat solvents. The light petroleum and alcohol-benzene extracts were analyzed for phosphatides. In case of the latter the material had to be purified since this solvent mixture always extracts some carbohydrates. In this particular case most (if not all in some cases) of the caffeine was extracted also and could be isolated in nearly white crystals. The alcohol-benzene extract was separated into its various components in the following way:

Extraction with ether removed the phosphatides and fatty matter. The insoluble residue was extracted with chloroform which removed the caffeine and a small amount of waxy material, leaving the carbohydrates in the residue. The caffeine was freed from the wax by recrystallization from water. This method therefore gives a quantitative estimation of the oils and phosphatides, caffeine, and wax. For each of these extractions 200 grams of roasted or green beans were used. The following tables give the results.

IT CAN be seen that all the types of green coffee contain phosphatides. What is remarkable is their high percentage in the light petroleum extract. The usual amount of phosphatide in solvent extracted oils is on the average no higher than 0.5% whereas in this case we have amounts varying from 1.16 to 2.5%. This is the highest percentage of phosphatides in any oil extracted by ordinary solvents. It was therefore to be expected that the alcohol-benzene extraction would yield a further quantity of phosphatides, and it can be seen that in some cases very high amounts were obtained. One point, however, is not easily explicable. Nearly all previous investigators state that fresh green coffee contains much higher quantities of oil, i.e. 10-13% (1). In this case the extraction was carried out for a long time and the beans were crushed once more between extractions to facilitate the penetration of the solvent without, however, increasing the amount of extract.

TABLE II

Characteristics of Oil From Kenya Coffee

	Unroasted	Roasted
Acid value	9.3	23.06
Ester value	185.6	176.15
Saponification value	194.9	199.21
Corrected for unsap.		
Acid value	9.54	23.6
Ester value	190.4	180.7
Sap. value	199.94	204.3
Iodine value	91.9	85.1
Total insoluble non-volatile fatty acids	89.42%	89.02%
Iodine value	81.7	81.04
Mean molecular weight	289.6	288.2
Unsaponifiable matter	2.25%	2.52%
	Crystalline. Characteristic phytosterol reaction and micro-crystalline appearance of acetate.	Crystalline. Characteristic phytosterol reaction and micro-crystalline appearance of acetate.

The roasted beans had in all cases lost nearly all their phosphatides, and in cases where a small amount had escaped destruction, it was only a trace of the original amount. This seems to prove that the roasting destroys the phosphatides although it cannot be said whether this has any effect on the taste or flavor of the coffee extract. I can confirm on the other hand that the amount of oil, or rather light petroleum extract, in roasted beans is considerably higher than in unroasted ones. This is no doubt partially due to the loss of about 20% of water (and other products). But the observed increase is in some cases much higher than could be expected from this source alone. The alcohol-benzene extracts also show an increase which is, however, not so considerable as the light petroleum one.

[1] Koenig: Die Menschlichen Nahrungs und Genussmittel. Vol. I, page 1116, 1933.

Finally, it was necessary to establish whether the phosphorus content obtained by the two methods of extraction were genuine phosphatides. The quantities obtained were naturally rather small but it was possible to refine some of the crude material by repeated precipitation with acetone from ether solution. Of this refined material 0.092 grams gave 3.39% P, an indication that the substance is nearly a pure plant phosphatide. Another sample, not so highly refined, was analyzed for phosphorus and nitrogen to establish the P:N ratio. The waxy, brown ether soluble substance contained 1.81% P and 0.95% N, showing that it was only of about 50% strength. The P:N ratio of 1.1:1 is a very satisfactory result considering the small quantities of material available.

It was not originally intended to go further into the question of caffeine extraction, but as it was relatively easy to extract, it was considered worthwhile to investigate the question further, especially as the usual caffeine extraction is rather tedious and frequently gives rise to colored products. The caffeine extracted with alcohol-benzene crystallizes out in faintly yellow crystals in a nearly pure state. The yields of caffeine in Table 1 correspond to the figures of many previous authors. Only in one case was the residual caffeine left after the alcohol-benzene extraction investigated. After the usual light petroleum and alcohol-benzene extraction a sample of unroasted Cameroon coffee was treated in the usual way for the extraction of caffeine and only yielded 0.18% of caffeine. It therefore seems probable that the alcohol-benzene would remove all the caffeine if the extraction were carried out long enough.

Conclusion

Fresh green coffee beans contain a rather high percentage of phosphatides in the light petroleum extract as well as in the subsequent alcohol-benzene extract. Nearly all these phosphatides are destroyed by roasting. By using alcohol-benzene as a solvent the major portion—if not all—of caffeine is extracted also and can easily be isolated in a pure state.

I desire to express my thanks to Charles M. Caines who has been conducting a good deal of the analytical work.

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Report of the Committee on Analysis of Commercial Fats and Oils

Fat Stability Test

The Committee has not done any collaborative work on the fat stability test during the past year. However, some work has been going on in one of the laboratories, investigating some of the variables involved in the test. There is nothing definite to report at this time.

Unsaponifiable Matter

A group of samples was prepared by adding known quantities of various types of unsaponifiable matter to coconut oil. Coconut oil was used because of its natural low content of unsaponifiable matter. These samples were submitted to a subcommittee who determined the unsaponifiable matter by several selected methods. The results are shown in Table 1.

TABLE 1

Laboratory	Method	% Unsaponifiable Matter in Refined Coconut Oil				
		Refined Coconut Oil	Plus 2% Cholesterol	Plus 2% Lanolin	Plus 2% Lecithin	Plus 1% Denaturing Oil
1	Kerr-Sorber (a)	0.60	0.68	2.46	1.85	1.12
2	Kerr-Sorber (a)	0.27	1.98	1.19	0.33	0.90
3	Continuous (b)	0.27	2.10	0.83	0.35	0.70
4	Continuous (b)	0.32	2.20	1.21	0.23	0.38
5	S. P. A. (a)	0.25	2.17	1.28	0.34	0.78
6	S. P. A. (a)	0.28	2.19	1.35	0.28	0.25
2	S. P. A. (a)	0.55	2.49	1.50	0.62	0.61
5	F. A. C. (b)	0.19	2.07	1.06	0.26	0.84
6	F. A. C. (b)	0.20	1.92	1.03	0.26	0.44

(a) Ethyl ether.
(b) Petroleum ether.

Attempts to use ethyl ether with the continuous and F.A.C. methods were generally unsatisfactory, due to the formation of emulsions.

In the case of the original oil all methods gave results within reasonable agreement. When unsaponifiable matter was added, there was a tendency for the SPA method to yield the highest results although there was little to choose between it and the continuous method. Denaturing oil is not completely recovered by any method.

A comparison was made between vacuum and air oven drying. The results appear in Table 2:

TABLE 2

Sample	% Unsaponifiable Matter After Drying in	
	Air oven at 101-103°C. for 15 minutes	Vacuum oven at 70°C. for 30 min. and an absolute pressure of about 112 mm. of Hg.
Refined coconut oil	0.19	0.19
Refined coconut oil	0.25	0.25
Plus 2% cholesterol	2.07	1.95
Plus 2% cholesterol	2.18	2.17
Plus 2% lecithin	0.25	0.25
Plus 2% lecithin	0.37	0.30
Plus 2% lanolin	1.06	1.01
Plus 2% lanolin	1.28	1.28
	Air Oven at 101°C. for 15-20 minutes	Vacuum oven at 56°C.. and an absolute pressure of 4 mm. Hg. to constant weight
Soap	0.66	0.72
Brown grease	2.00	2.40
Light grease	0.86	0.91
Brown grease	1.88	1.90
Yellow grease	0.70	0.70
Yellow grease	0.96	0.93

Further work will be done on drying methods with special reference to the recovery of denaturing oils because it is probably at this point that this material is lost. Further work will also be done on the comparison of methods.