[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

The Characteristics and Composition of Coffee Bean Oil

BY H. A. SCHUETTE, MILFORD A. COWLEY AND CHANG Y. CHANG

Almost a century ago[1] it was pointed out that the outer surface of the coffee bean is covered with a wax and that within the bean itself there is secreted an ether-soluble fatty oil. Except in one instance,[2] the presence here of two ether-soluble substances seems not to have been taken in account, however, for those[3] who have since that time contributed to our knowledge of the characteristics and composition of coffee oil have in reality reported data which are pertinent to the total ether extract of the bean, for wax and fat were not separated. Comparative data[2,3d–f] on the ether extracts of green and roasted beans are available, but none of any kind on the wax-free fatty oil appear to have been recorded heretofore. Data of the latter type, critically compared with the former, are herein presented.

No technical interest at present attaches to the recovery of coffee oil since the utilization of the bean itself for alimentary purposes is more profitable. If the observation[4] that it contains a highly active sterol which appears to be both therapeutically and prophylactically effective for rats fed upon a rachitogenic diet, is substantiated, then coffee oil might yet pass out of that class of fatty oils for which there is now only an academic interest.

I. Preparation of Materials

The oil used in this study was obtained in approximately 2.7% yield by petrolic ether extraction of green Santos beans after they had been dewaxed (yield of latter approximately 0.24%) with tetrachloroethane.[5] The removal of the wax was effected by washing the beans in 10-kg. portions in a wire screen drum which was made to revolve in a bath of the solvent.

The coffee oil obtained by this method of recovery was found to be of greenish-brown color and to possess an odor characteristic of the green bean. Steam distillation removed approximately 5% of a pungent volatile substance.

II. Analysis of Oil

(a) **Chemical and Physical Characteristics.**—The more important chemical and physical characteristics (Table I) were determined by the usual procedures.[6] Not only are new data on coffee oil hereby added, but some measure of comparison with the old made possible with the obvious limitation that in one instance the data are pertinent in fact to total ether extracts, in the other to a wax-free product. The effect of excluding the wax is seen in the increased iodine number and physical constants. The higher acid number is probably in part due to the fact that the oil was not immediately analyzed after recovery from the bean.

(b) **Unsaturated Acids.**—Treatment of the unsaturated acid fraction with bromine at −10° did not yield an ether-insoluble precipitate of hexabromide. The non-existence of linolenic acid in this oil was, therefore, indicated. Qualitative tests for linoleic and oleic acids were obtained.

The composition of this fraction, calculated by the mode of procedure of Kaufman[7] from the iodine and thiocyanogen numbers of the oil, is shown in Table II.

TABLE I

CHEMICAL AND PHYSICAL CHARACTERISTICS OF COFFEE BEAN OIL

	New data	Reported by others[2,3]
Specific gravity 25/25°	0.9653	0.9288–0.9512
Index of refraction, 25°	1.4790	1.4678–1.4778
Iodine number (Wijs)	100.72	79–97.8
Saponification number	195.53	149–195
Reichert–Meissl number	0.36	0–2
Polenske number	.40	.20–0.25
Acid number	7.05	2.1–7.9
Hydroxyl number	22.82[a]	0
Thiocyanogen number of unsaturated acids[b]	91.57	... ...
Saturated acids	33.60	... ...
Unsaturated acids	38.02	... ...
Iodine number of total fatty acids	94.11	79.7–90.5
Iodine number of unsaturated acids	153.61	... ...
Unsaponifiable matter, %	12.63	6.87–13.5
Iodine number of unsaponifiable matter (Wijs)	153.8	... ...

[a] Hydroxyl and acetyl numbers are practically alike in this zone. [b] Unsaponifiable-matter free.

---

[1] Robiquet and Boutron, *J. pharm. sci. access.*, **23**, 101 (1837); *Ann.*, **23**, 93 (1837).

[2] Meyer and Eckert, *Monatsh.*, **31**, 1227 (1910).

[3] (a) Rochleder, *Ann.*, **50**, 224 (1844); (b) De Negri and Fabris, *Z. anal. Chem.*, **33**, 569 (1893); (c) Hilger, *Forschungsb. Lebensm.*, **1**, 42 (1894); (d) Herfeldt and Stutzer, *Z. angew. Chem.*, **8**, 469 (1895); (e) Spaeth, *Forschungsb. Lebensm.*, **2**, 223 (1895); (f) Juckenack and Hilger, *ibid.*, **4**, 119 (1897); (g) Warnier, *Pharm. Weekblad*, **44**, 1080 (1907); (h) Anon., *Bull. Keuringsdienst van eet-en drinkwaren in Suriname*, 1919, *Olien en Vetten*, 1920, No. 31, 400; *C. A.*, **14**, 1229 (1920); (i) v. Noel, *Pharm. Zentr.*, **70**, 69 (1929); (j) Bengis and Anderson, *J. Biol. Chem.*, **97**, 99 (1932); (k) Heiduschka and Kuhn, *J. prakt. Chem.*, (n. s.), **139**, 269 (1934); (l) Bengis and Anderson, *J. Biol. Chem.*, **105**, 139 (1934).

[4] V. Noel and Dannmeyer, *Strahlenther.*, **32**, 769 (1929); Lendrich, *Volksernahr.*, **5**, 310 (1930); *C. A.*, **25**, 4633 (1931); Schwarz and Sieke, *Arch. Hyg.*, **104**, 65 (1930).

[5] Grateful acknowledgment is made to C. A. Tarnutzer for his assistance in the preliminary studies which led to the development of the technique used in removing the wax, and for the actual recovery of the oil itself.

[6] Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., 1930, 3d ed., pp. 314–330.

[7] Jamieson, "Vegetable Fats and Oils," Chemical Catalog Co., Inc., New York, 1932, pp. 346–347.

Qualitatively these data support the substance of an earlier report[2] to the effect that linoleic acid is the principal unsaturated acid of coffee oil, but quantitatively there is no agreement in this instance even as to the order of magnitude thereof, for the oleic acid content was stated to be 2% as against 50% for the former.

TABLE II

COMPOSITION OF THE UNSATURATED ACID FRACTION

Acid	Fraction, %	Oil, %
Oleic	32.48	12.36
Linoleic	67.52	25.66

(c) **Saturated Acids.**—The methyl esters of the saturated acids were separated into four fractions, the first half having a boiling point range of 143 to 155° (3 mm.), the latter 157 to 176° (2 mm.). The mean molecular weights of the respective fractions as calculated from saponification and iodine numbers—the latter serving as a basis for correcting each for the presence of unsaturated acids—indicated the existence in this oil of acids in the C_{14} to C_{20} group. They were subsequently identified by their melting points and neutralization equivalents.

TABLE III

COMPOSITION OF THE SATURATED ACID FORMATION

Acid	Fraction, %	Oil, %
Myristic	6.52	2.19
Palmitic	60.04	20.17
Stearic	27.16	9.13
Arachidic	6.28	2.11

Others have reported the palmitic acid content of the ether extract of the coffee bean as being, in one instance, 25 to 28%;[2] in another, 29%,[31] whereas recently this value has been placed at 23.60%[3k] and 28.1–33.4%,[31] respectively. Until this year, the only information on the stearic acid content of this oil was that it is present "in small quantity."[3c] Recently published data now lend an interpretation to this statement in quantitative terms, *viz.:* 1.05%[3k] and 4.4–7.4%,[31] respectively. "Daturic" acid, however, has been claimed to exist in this oil to the extent of 1.5%[2] and 3.0%,[31] respectively. The addition of myristic and arachidic to the list of coffee oil acids is new.

Summary

The important physical and chemical constants and the approximate percentage composition of a sample of wax-free (Santos) coffee oil have been determined. Palmitic (20,1%) and linoleic (25.6%) were found to be the predominating acids. They are accompanied by myristic (2.2%), stearic (9.1%), arachidic (2.1%) and oleic (12,3%) acids.

Inasmuch as the constants of coffee oil which are to be found in the literature pertain to the total ether extract of the bean, a comparison of the data herein reported with the former has no meaning by way of verification. It is apparent, however, that the presence of the wax affects some of the constants, for the upper limits of the iodine number, refractive index and specific gravity have been raised.

MADISON, WISCONSIN RECEIVED JUNE 18, 1934

[CONTRIBUTION FROM THE LABORATORY OF THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Addition of Iodine and Thiocyanogen to Unsaturated Compounds[1]

BY B. P. CALDWELL AND F. A. PIONTKOWSKI

Introduction

The determination of iodine numbers of fats and oils has long been practiced in analytical laboratories and needs no comment here. The study, too, of the rate of halogen addition to unsaturated compounds has occupied the attention of many chemists.[2]

Sudborough and Thomas recognized the highly catalytic character of the reactions studied by them, and explained their discordant velocity constants as possibly due to the presence of unknown catalysts. Nevertheless, their work is sufficiently informative to indicate a quick rate of addition of bromine to oleic acid in carbon tetrachloride solution, and to elaidic acid, whereas crotonic (methylacrylic) and cinnamic (phenylacrylic) acids both have very much smaller velocity constants for the reaction. They observed that the addition of bromine to unsaturated acids is a comparatively slow process, but that the speed of reaction is greater, the farther removed the ethylenic bond is from the carboxyl group.

Böeseken and Blumberger stated that when a benzene nucleus is attached near the double bond the rate of iodination is slow.

---

(1) This paper is from a portion of a thesis submitted by F. A. Piontkowski to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

(2) See Hugo and Bauer, *Ber.*, **37**, 3317 (1904); Sudborough and Thomas, *J. Chem. Soc.*, **97**, 715, 2450 (1910); Herz and Myline, *Ber.*, (a) **39**, 3816 (1906); (b) **40**, 2898 (1907); Barrett and Lapworth, *Proc. Chem. Soc.*, **23**, 18 (1907); Hoffmann and Kirmreuther, *Ber.*, **42**, 4481 (1909); Böeseken and Blumberger, *Rec. trav. chim.*, **44**, 96 (1925).