

THE CHEMISTRY OF THE COFFEE-BEAN

I. CONCERNING THE UNSAPONIFIABLE MATTER OF THE COFFEE-BEAN OIL. PREPARATION AND PROPERTIES OF KAHWEOL*

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INTRODUCTION

Coffee has become a universal and almost indispensable beverage in the modern dietary; and according to government statistics, the importation of coffee into this country during the year 1931 amounted to 870,768 tons, which corresponds to a *per capita* consumption of 12 pounds. It is surprising in view of this extensive use of coffee that, outside of caffeine and some of its combinations, very little is known concerning many of the chemical compounds which are present in and make up the bulk of the coffee-bean. In order to secure more scientific and practical information on this subject, we have begun a systematic investigation in this laboratory of various at present unknown constituents of the coffee-bean. It is planned to include in this work not only the natural raw bean, but also the freshly roasted as well as the stale or aged roasted ground coffee. In this manner it is hoped to determine what chemical compounds are chiefly responsible for certain evident deteriorations in the quality of roasted coffee during storage or ageing.

The first part of the investigation is concerned with the nature and composition of the ether-soluble or fat constituents of the coffee-bean. This part of the work was first taken up because it seemed very probable that the staling of roasted coffee is due in part, at least, to oxidative changes of the unsaturated constitu-

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ents which are in the fat. The available published information on the nature of the coffee fat is meager and very incomplete. Certain constants of the coffee-bean oil have been determined and some attempts have been made to separate the fatty acids which are liberated when the fat is saponified.

The unsaponifiable matter which represented 10 per cent of the fat was a dark brown semisolid. It was very easily soluble in the common organic solvents but it was nearly insoluble in cold petroleum ether. As will be described in the experimental part of this communication, the material was separated into two principal fractions; namely, (1) a small amount of a phytosterol which was very similar to sitosterol, and (2) a large amount of a new, beautifully crystalline substance which possesses unusually interesting properties.

Phytosterols have been described previously by Juckenack and Hilger (1) and also von Noël (2), but the products isolated by these investigators had lower melting points and lower optical rotation than our product. The major part of the unsaponifiable matter referred to above as the second principal constituent is not a sterol, and as it has not previously been fully characterized, we have devoted some time to a study of its composition and reactions. Since this substance represents the principal constituent of the unsaponifiable matter and a not insignificant proportion of the coffee-bean oil, we propose to designate it by the name of kahweol from the arabic word "qahweh" meaning coffee.

Kahweol is strongly levorotary. It crystallizes readily from concentrated solutions but the crystal form varies with the solvent. From acetone it separated either in the form of very large colorless trigonal or pentagonal dense plates, while from methyl alcohol only massive colorless quadratic plates are obtained. From ether it crystallizes in very long, snow-white silky needles. It is easily soluble in glacial acetic acid and on the careful addition of water colorless prismatic needles are obtained which decompose, however, in a short time, giving a strong purple color.

Kahweol is extremely sensitive to atmospheric oxygen, light, heat, and especially to mineral acids, while it appears to be more indifferent to alkalis. In acid solutions or in the presence of traces of acid fumes, it very quickly turns purple in color. It is therefore very difficult, if not impossible, to keep the pure substance

for more than a few minutes or hours, at the most, in an unaltered condition. Even when pure colorless crystals of kahweol are placed in a sealed tube filled with carbon dioxide, the color changes to a deep yellow in less than 24 hours. When the substance is kept under ordinary conditions in a glass-stoppered bottle, it very rapidly changes to a yellow color and there is a constant increase in weight most probably due to the absorption of oxygen. These changes in physical appearance profoundly affect the melting point, solubility, and the optical activity. It is evident from what has been said about the sensitivity of kahweol that determinations of its physical constants must be made within a short time after it has been isolated. The freshly prepared substance, crystallized from ether and dried in a vacuum desiccator, melts at 143–143.5° to a clear oil and in methyl alcoholic solution gives a specific optical rotation of -204.5° .

Kahweol is a highly unsaturated compound and its iodine number, determined by the Hanus method, gave results varying from 131 to 155, owing to the fact that there is a formation of an insoluble product in the determination and this formation does not take place with uniformity. With the Liebermann-Burchard reaction, it gives a bright red color which gradually changes to a permanent, deep, dull red. This coloration is so strong that even traces of kahweol, mixed with a phytosterol, will entirely mask the blue to green coloration which is given by sterols in the Liebermann-Burchard reaction.

Since kahweol is so sensitive and is so easily changed, it is practically impossible to obtain concordant results on analysis, and we have not been able to determine the composition of the pure substance with a desirable degree of accuracy. The only crystalline derivative that we have been able to prepare from kahweol is a monoacetyl compound. From the data at present available, obtained more or less indirectly, we believe that the substance possesses the formula $C_{19}H_{26}O_3$ and that it contains at least one hydroxyl group.

In order to secure a more stable form of kahweol, we tried to reduce it by catalytic hydrogenation but, unfortunately, the reduction does not proceed in a normal manner. In the reduction, about one-half of the total hydrogen is absorbed very rapidly, but after that the absorption is very slow; we have not been

able to obtain a reduction product which does not give an iodine number.

The iodine number which is obtained corresponds to approximately 1 atom of iodine, and this would indicate a substitution rather than addition on a double bond. The reduced kahweol apparently contains two hydroxyl groups, which would indicate that a carbonyl group in the original substance had been converted into a secondary alcohol. While the reduced kahweol is perfectly stable under ordinary conditions with respect to light and atmospheric oxygen, it is extremely soluble in most organic solvents, and hence it does not crystallize readily. The substance melts at 173–174°, and in methyl alcoholic solution the specific optical rotation is -67.8° . Values obtained on analysis were in agreement with the formula, $C_{19}H_{32}O_3$.

A product similar to kahweol has been isolated from coffee-bean oil by von Noël and Dannmeyer (3), and the opinion was expressed by these authors, due to a report by Schwarz and Sieke (4), that it possessed antirachitic properties, but further experiments did not substantiate this assumption. Through the kindness of Dr. A. F. Hess of New York, samples of kahweol were tested for antirachitic properties, but it was found to possess no activity whatever either before or after irradiation with ultraviolet light. Similar negative results were also obtained in The Fleischmann Laboratories by Dr. C. N. Frey. Kahweol has been tested by Dr. H. A. Mattill and H. S. Olcott for antioxygenic properties with negative results. This would indicate a possible absence of a phenolic hydroxyl group, since these investigators claim that most of the substances which they had examined and found to be antioxidants possessed a phenolic hydroxyl group.

It would seem that a substance which is so sensitive, as is kahweol, to reagents, light, heat, and oxygen, must possess some active physiological properties but, so far, all tests which have been made have given entirely negative results. Preliminary feeding experiments were also executed, through the kindness of Dr. L. B. Mendel, by Mr. W. E. Anderson, but no definite results have been obtained as yet.

EXPERIMENTAL

Preparation of Unsaponifiable Matter

The fat was first prepared by extracting freshly roasted, finely ground coffee-beans with petroleum ether¹ in a large Soxhlet extractor. The solvent used was the Mallinckrodt product with a boiling range of 30–60°. After complete removal of the solvent by distillation in a stream of CO₂, the fat was treated with 2 volumes of acetone to precipitate any phosphatides or other acetone-insoluble material. A very slight precipitate was obtained and filtered off, the acetone completely removed by distillation, and the remaining fat placed in a vacuum desiccator. This fat gave the following constants.

Iodine No. (Hanus).....	96.05
Saponification No.....	172.08
Reichert-Wollny “.....	0.866
Specific rotation in chloroform.....	$[\alpha]_D^{25} = -13.24^\circ$

For the saponification, 200 gm. of fat were refluxed in an atmosphere of nitrogen with 1000 cc. of 5 per cent alcoholic potassium hydroxide for 12 hours. About 200 cc. of alcohol were then distilled and the mixture of soaps was diluted with 4 liters of distilled water. The soap solution was extracted with ether eight times, with a total of 6 liters of solvent, in order to remove the unsaponifiable matter. After drying over anhydrous sodium sulfate, the solvent was removed by distillation. The remaining residue was subjected to a second saponification by refluxing with 300 cc. of 4 per cent alcoholic potash for 1 hour. The mixture was then diluted to 2 liters with distilled water, cooled, and extracted four times with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and distilled. A dark red semisolid was obtained which weighed 20.4 gm., which is equivalent to 10.2 per cent of the original fat. Especial care was taken to protect the unsaponifiable matter from air by using, as far as possible, an atmosphere of carbon dioxide.

¹ All solvents used in this work were freshly distilled, and the alcohol had been purified by distillation over potassium hydroxide.

Isolation of Kahweol

Since preliminary experiments had shown that it was difficult to prepare pure kahweol in large yields, an additional quantity of fat was saponified and more unsaponifiable matter collected.

The crude unsaponifiable matter, 39.9 gm., was dissolved in 40 cc. of hot acetone and the solution was diluted with cold petroleum ether until no further precipitate was produced. The precipitate which separated as an oil was quickly converted to a crystalline mass on shaking. This solid was filtered off, washed with cold petroleum ether, and designated as Crop I. The mother liquor and washings of 200 cc. deposited a large amount of fine, silky needles which were worked up separately as Crop II.

The material which was designated as Crop I was recrystallized from acetone and petroleum ether five times, yielding slightly colored, heavy, dense plates. Kahweol is very soluble in warm acetone. When the concentrated solution is cooled, large, dense, nearly colorless, pentagonal plate-shaped crystals separate. The mother liquor from these crystals, upon concentration and cooling, deposits large, dense, trigonal plate-shaped crystals. In order to decolorize the product, it was dissolved in warm ether, and to this solution was added a previously boiled suspension of norit in ether. The suspension was then refluxed a short while, filtered, and concentrated slightly. Beautiful colorless, fine needles separated which were dried in a vacuum and weighed 5.3 gm.

From the concentrated mother liquors of Crops I and II, another lot of crystals was isolated. These were dissolved in the ethereal mother liquor of Crop I. On concentration and cooling of this solution, no crystals separated, and the solvent was distilled off in a stream of CO_2 leaving a thick, yellow, resinous mass weighing 9.0 gm. The entire mass was crystallized from hot methyl alcohol in rhombic plates by cooling the orange-colored solution in a freezing mixture. This second lot weighed 5.45 gm., and on drying *in vacuo* showed a loss in weight of 10.16 per cent. This amount corresponds to about 1 molecule of methyl alcohol of crystallization which was calculated to be 9.58 per cent on an assumed molecular weight of kahweol of 302. It was evident by its behavior during crystallization that kahweol took on some solvent of crystallization and therefore appeared in the various crystalline forms. The crystals from acetone and methanol were

photographed and drawings made from the photographs are shown in Figs. 1, 2, and 3. In contrast to the others, the edges of the trigonal crystals were not straight but slightly irregular.

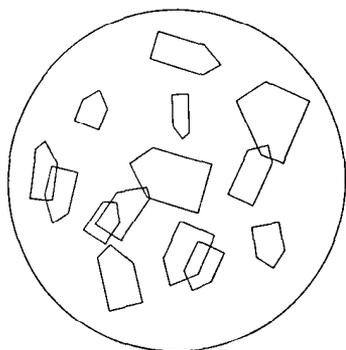


FIG. 1

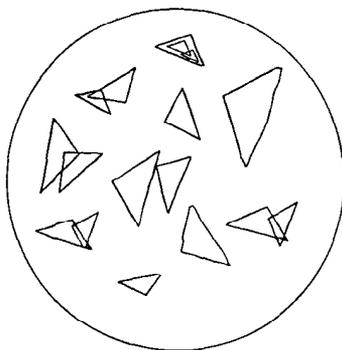


FIG. 2

FIG. 1. Kahweol from acetone. $\times 27.5$

FIG. 2. Kahweol from acetone mother liquor. $\times 27.5$

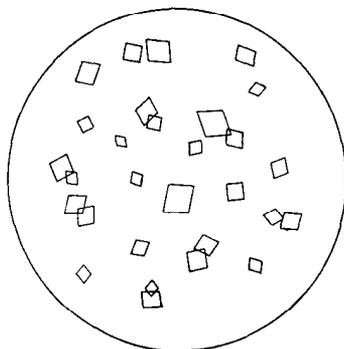


FIG. 3. Kahweol from methanol. $\times 27.5$

Kahweol has a satisfactory melting point, softening at 142° and melting to a clear orange-colored oil at $143\text{--}143.5^\circ$ showing a slight decomposition at the melting point. On cooling the melt does not crystallize but remains as a transparent resin. It is very sensitive to light, heat, and air. It turns yellow in color on exposure. It decolorizes bromine, gives no coloration in alcoholic

solution with ferric chloride, and in the Liebermann-Burchard reaction gives a bright red color which changes in a few minutes to a deep dull red which remains permanent. Qualitative tests for nitrogen, halogen, sulfur, and ash were negative.

Attempts to obtain a molecular weight directly by Rast's (5) method were unsuccessful due to incomplete solubility in camphor.

Rotation—0.0660 gm. of substance dissolved in methyl alcohol and made up to 10 cc. gave in a 1 dm. tube a reading of -1.354° ; hence $[\alpha]_D^{21} = -204.54^\circ$.

Analysis—4.507 mg. gave 3.22 mg. H₂O and 12.40 mg. CO₂
 Found. H 8.00, C 75.04
 Calculated for C₁₉H₂₈O₃. " 8.61, " 75.50

It should be stated here that kahweol darkens on drying before analysis at 100° in a vacuum and in an atmosphere of nitrogen.

Some of the pure white, needle-like crystals were exposed to light and air at room temperature and almost immediately a yellowish tint was observed, which developed into a decided yellow color after several hours. At the end of 34 days, 0.3159 gm. gained 15.4 mg. or 4.87 per cent. On inspection of this exposed material it was found that the discoloration occurred on the surface first and gradually advanced towards the interior, since, upon disintegration of a few small masses after this long exposure, some colorless crystals were found.

An examination of this exposed substance also revealed a change in melting point and optical rotation as well as solubility. The melting point was now indefinite, as the substance darkened at 120° and fused to minute globules which effervesced slightly at 142° but did not completely decompose with effervescence before 200°.

Rotation—0.0750 gm. of substance dissolved in methyl alcohol and made up to 10 cc. gave in a 1 dm. tube a reading of -1.253° ; hence $[\alpha]_D^{21} = -167.06^\circ$.

From the above determination it is evident that a diminution of 37.48° in rotation had occurred. Moreover, the exposed kahweol was incompletely soluble in chloroform whereas the fresh substance dissolved completely, although on standing, a deep green color would develop with a precipitation of a dark green flocculent solid.

In order to ascertain some facts as to the constitution of this interesting product, attempts were made to prepare a few derivatives. Owing to its high unsaturation, the derivatives were in preference prepared from the reduced kahweol. However, an acetylation of kahweol was successfully executed.

Acetylation of Kahweol

With the method of Verley and Bölsing (6), 0.4437 gm. of kahweol was treated with 20 cc. of acetic anhydride-pyridine mixture on a steam bath for 15 minutes. After cooling and addition of 25 cc. of water, the clear yellow solution was titrated with sodium hydroxide. Fine needle-like, prismatic crystals separated out. A difference of 1.55 cc. of 0.855 N sodium hydroxide was obtained between the titration of a blank and the actual determination.

Analysis—1.55 cc. 0.855 N NaOH = 0.079515 gm. $C_2H_4O_2$
 Found. $C_2H_4O_2$ 17.92
 Calculated for $C_{19}H_{26}O_3 \cdot COCH_3$. “ 17.44

This would indicate that a monoacetyl derivative had been formed. The crystals were filtered off, thoroughly washed with water, and dried *in vacuo* overnight. The weight was 0.46 gm., and the substance melted at 132–134° to a clear orange-colored oil. The Liebermann-Burchard reaction gave the same color as the original kahweol.

The acetyl product crystallized very satisfactorily from dilute alcohol in long, slender, needle-like prisms and from 95 per cent alcohol in long, slender plates of pale salmon color. After two recrystallizations the substance sintered at 125°, softened to a turbid oil at 133–134°, and melted to a clear oil at 142–144°. A remelt occurred at 136–137°. On drying at 110° *in vacuo* the substance lost 2.84 per cent in weight. Calculated on a basis of $C_{21}H_{28}O_4 \cdot \frac{1}{2}H_2O$, the theoretical loss would be 2.55 per cent.

Analysis—3.808 mg. gave 2.65 mg. H_2O and 10.30 mg. CO_2
 Found. H 7.79, C 73.76
 Calculated for $C_{19}H_{26}O_3 \cdot COCH_3$. “ 8.20, “ 73.25

The analysis indicates an empirical formula of $C_{21}H_{27}O_4$ as against the assumed formula of $C_{21}H_{28}O_4$.

For a further check on the acetyl content of this derivative, 0.1339 gm. was treated with an excess of 0.1 N alcoholic potassium hydroxide with gentle refluxing for $\frac{1}{2}$ hour. The excess alkali was titrated with standard sulfuric acid and a consumption of 4.04 cc. of 0.1 N alkali for saponification was found.

Analysis—4.04 cc. 0.1 N KOH = 0.02424 gm. $C_2H_4O_2$
 Found. $C_2H_4O_2$ 18.11
 Calculated for $C_{19}H_{25}O_3 \cdot COCH_3$. “ 17.44

Reduction of Kahweol

5 gm. of kahweol were dissolved in 200 cc. of alcohol, 0.2 gm. of platinum oxide which had been prepared according to the method of Voorhees and Adams (7) was added, and the suspension was shaken with hydrogen. At the start, the absorption of gas was rapid but after 500 cc. were absorbed, the action was markedly retarded. The mixture was warmed and in the course of 30 minutes an additional 400 cc. of hydrogen were taken up. The catalyst now began to separate out, so the suspension was filtered; the filtrate was shaken with fresh platinum oxide and hydrogen. Within an hour 200 cc. more of hydrogen were slowly absorbed, when the catalyst again separated. The suspension was filtered and the alcohol distilled off under diminished pressure, leaving a thick, resinous, faintly yellow residue which would not crystallize on standing overnight. A Liebermann-Burchard reaction still gave a pronounced yellowish orange color.

The resinous material was dissolved in 200 cc. of absolute alcohol, 0.1 gm. of platinum oxide was added, and the hydrogenation was repeated. There was a slow but distinct absorption of gas and, after a treatment of an hour, during which warming and strong shaking were resorted to, 150 cc. more of hydrogen were taken up, making a grand total of 1250 cc. of gas which were absorbed. Since further absorption was not evident, although the catalyst was in colloidal suspension, the hydrogenation was interrupted. The catalyst was removed by treatment with norit, the filtrate concentrated in a vacuum to a small volume and chilled in a freezing mixture, but since no crystals separated, the concentrated solution was evaporated almost to dryness with CO_2 . On continued scratching, crystallization was finally effected. The mass was placed in a vacuum desiccator for 48 hours, after which time

a hard white cake weighing 6.0 gm. was obtained. Part of this increase in weight is due to alcohol of crystallization.

The solid cake was treated with 25 cc. of ether and with stirring a semicrystalline product resulted. After the substance had been filtered off, washed with ether, and dried *in vacuo*, it weighed 4.3 gm. The melting point was 170–172°; the melted substance did not crystallize on cooling.

The mother liquor yielded 1.9 gm. of a nearly colorless residue when evaporated to dryness in a current of carbon dioxide.

All attempts to crystallize the ether-insoluble reduced product from single or mixed solvents proved unsuccessful. A solution of the substance in acetone, when mixed with petroleum ether, deposited a white amorphous product which contained a few prismatic crystals. The reduced kahweol softened at 165–166° and melted to an opaque oil at 171–172° which cleared at 175°. An iodine number was obtained with the Hanus method, and no insoluble iodide was evident as was the case with kahweol. This value was 33.63 corresponding to but 1 atom of iodine.

Rotation—0.0985 gm. of dried substance dissolved in methyl alcohol and made up to 10 cc. in a 1 dm. tube gave a reading of -0.668° ; hence $[\alpha]_D^{23} = -67.81^\circ$.

<i>Analysis</i> —3.805 mg. gave 3.54 mg. H ₂ O and 10.34 mg. CO ₂	
3.835 “ “ 3.57 “ “ “ 10.45 “ “	
Found.	H 10.41, C 74.12
	“ 10.42, “ 74.31
Calculated for C ₁₉ H ₃₂ O ₃ .	“ 10.47, “ 74.02

The above analyses indicate an empirical formula of C₁₉H₃₂O₃ and molecular weight of 308.

The ether-soluble fraction of 1.9 mg. was dissolved in 15 cc. of chloroform and treated with petroleum ether until a permanent cloudiness was apparent. On scratching, crystallization began and on standing overnight, a small amount of colorless, prismatic crystals had separated on the sides and bottom of the flask. These were filtered off and the filtrate was concentrated *in vacuo* to a faintly yellow, glassy mass. There was no tendency to solidify in crystalline form. A treatment with 50 cc. of absolute ether yielded a small amount of insoluble matter which was removed by filtration and the clear filtrate was concentrated. On stand-

ing overnight, a small amount of solid had separated. The clear ether solution was decanted and concentrated, when a colorless glassy mass was obtained. This was placed in a vacuum desiccator and on evacuation, the substance suddenly solidified to a nearly colorless mass of shining, thin filaments weighing 1.8 gm. This material on rubbing presented an appearance of crystalline particles, but it could not be separated in crystalline form from any solvent.

The iodine number by the Hanus method was 121.65 but this value is only approximate, since there was a formation of an insoluble product in the reaction.

Rotation—0.1006 gm. of substance dissolved in methyl alcohol and made up to 10 cc. in a 1 dm. tube gave a reading of -0.593 ; hence $[\alpha]_D^{23} = -58.94^\circ$.

Acetylation of Reduced Kahweol

For acetylation, 1.0 gm. of the ether-insoluble fraction was refluxed for 2 hours with 25 cc. of acetic anhydride and 2 gm. of fused sodium acetate. On cooling the mass was diluted with water, when an oily material, which would not crystallize, separated. It was extracted with ether; the ether extract was washed with water and dilute sodium bicarbonate and finally with water until the washings were neutral in reaction. The orange-yellow-colored extract was treated with norit, filtered, and evaporated to dryness to a thick, yellow, oily substance weighing 1.5 gm. This was placed in a vacuum desiccator overnight and formed a clear transparent resinous mass weighing 1.4 gm.

This derivative was very soluble in acetone, methyl alcohol, ethyl alcohol, chloroform, ethyl acetate, benzene, and glacial acetic acid, but would not crystallize. Petroleum ether seemed to soften the substance but did not dissolve it completely.

Since this derivative could not be crystallized, the crude substance was saponified for the purpose of determining the number of acetyl groups.

Analysis—0.2065 gm. substance required 11.65 cc. 0.1 N KOH to saponify. 11.65 cc. 0.1 N KOH = 0.0699 gm. $C_2H_4O_2$.

Found.	$C_2H_4O_2$, 33.85
Calculated for $C_{19}H_{30}O_3 \cdot (COCH_3)_2$.	“ 30.61

The value obtained would indicate the presence of two acetyl groups signifying the presence of two hydroxyl groups in the reduced kahweol.

Further corroboration on the presence of two hydroxyl groups was sought in the preparation of a naphthyl isocyanate derivative.

Naphthyl Isocyanate Derivative of Reduced Kahweol

In a small flask, 0.5 of reduced kahweol and 1.0 gm. of naphthyl isocyanate were mixed and heated over a low flame to nearly the boiling point. Complete solution ensued. On cooling, a transparent resinous mass remained which would not crystallize. It was warmed up again and on scratching, crystallization was effected. The mass was treated with absolute alcohol in which almost complete solution took place. A slight amount of insoluble matter was removed by filtration and water was gradually added to the clear filtrate until the solution was cloudy. On standing, an oily substance separated on the bottom of the flask. The clear supernatant liquor was decanted and the residue, after it had been dried in a vacuum desiccator, weighed 0.82 gm. This material could not be crystallized from organic solvents. It was therefore purified by dissolving in alcohol, treating with norit, filtering, and precipitating by the gradual addition of water, when an amorphous solid separated.

After drying *in vacuo*, this derivative softened at 118° and melted to a slightly turbid oil at 128°.

Analysis (Dumas Method)

0.2045 gm. substance gave 7.8 cc. N at 22° and 754 mm.

0.2037 " " " 7.8 " " " 22° " 752 "

Found. N 4.36, 4.38

Calculated for $C_{19}H_{32}O_3 \cdot (C_{10}H_7NCO)_2$. " 4.33

Here again the analysis indicates the presence of two hydroxyl groups in the reduced kahweol.

One further determination of hydroxyl content was carried out by the Zerevitinov (8) method with the following results.

Analysis—0.1214 gm. substance gave 18.0 cc. CH_4 at 25° and 740 mm.

0.1910 " " " 29.4 " " " 25° " 742 "

Found. OH 10.10, 10.52

Calculated for $C_{19}H_{30}O \cdot (OH)_2$. " 11.04

The values obtained in all these determinations point towards the presence of two hydroxyl groups in the reduced kahweol leaving 1 oxygen atom unaccounted for. This second hydroxyl group most probably was formed through the reduction of a carbonyl group present in the original kahweol.

Isolation of Sitosterol

Crop II, described in an early section of the experimental part, was recrystallized from petroleum ether by chilling the warm saturated solution in a freezing mixture. This product was slowly soluble in hot methyl alcohol but dissolved completely on long heating. On cooling the methyl alcohol solution, fine colorless needles separated out. The sterol was then recrystallized twice from alcohol from which it separated in very thin plates weighing 0.68 gm.

The mother liquors were combined, concentrated, and cooled. The crystals which had separated were filtered off, washed with cold methyl alcohol, and recrystallized twice from this solvent, giving 0.44 gm. which proved to be identical with the first fraction.

The substance gave a blue color changing to a deep green in the Liebermann-Burchard reaction. It melted sharply at 138–139° to a clear oil, solidifying at 127–126° and remelting at 138°.

Rotation—0.1349 gm. of dried substance dissolved in 10 cc. of chloroform in a 1 dm. tube gave a reading of -0.480 ; hence $[\alpha]_D^{21} = -35.58^\circ$.

Analysis—3.855 mg. gave 4.06 mg. H₂O and 11.79 mg. CO₂
 3.943 “ “ 4.18 “ “ “ 12.08 “ “

Found. H 11.79, 11.86, C 83.41, 83.55
 Calculated for C₂₇H₄₆OH. “ 11.91, C 83.93

4.042 mg., 4.135 mg. dried in nitrogen with a partial vacuum lost 0.187 mg., 0.192 mg.

Found. H₂O 4.63, 4.64
 Calculated for C₂₇H₄₆OH·H₂O. “ 4.45

A Rast molecular weight determination was made with the following result.

Analysis—0.225 mg. substance + 2.934 mg. camphor gave $\Delta = 7.5^\circ$
 Found. Mol. wt. 409
 Calculated for C₂₇H₄₆OH·H₂O. “ “ 404

The properties and composition of the substance indicate that it is similar to the usual sterols found in plants.

SUMMARY

1. The unsaponifiable fraction of the fat, extracted from freshly roasted coffee, contains a highly unsaturated, strongly optically active, and sensitive product which we designate by the name kahweol, together with one or more sterols.

2. The composition of kahweol corresponds approximately to the formula $C_{19}H_{26}O_3$. The substance apparently contains one hydroxyl group and it melts at 143–143.5°; $[\alpha]_D^{21} = -204.5^\circ$.

3. Catalytic reduction of kahweol leads to a compound having the composition $C_{19}H_{32}O_3$ in which two hydroxyl groups are present. Reduced kahweol melts at 175°; $[\alpha]_D^{23} = -67.81^\circ$.

4. The phytosterol isolated is similar to sitosterol. It was analyzed for $C_{27}H_{46}OH \cdot H_2O$; it melted at 138–139°, and the specific optical rotation was -35.58° .

We desire to express our thanks to Professor L. B. Mendel, Dr. A. F. Hess, Dr. C. N. Frey, Dr. H. A. Mattill, and to Mr. W. E. Anderson for carrying out certain biological experiments and to Professor H. T. Clarke of Columbia University in whose laboratory the micro analyses were made. We are also indebted to the Standard Brands Incorporated for financial assistance.

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