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.

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(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).

The observations above quoted are mentioned to show that the fact of a steric hindrance to halogenation by neighboring negative groups has been recognized by several investigators.

Anomalous results in abnormally high halogen numbers have been reported by Ralls[3] for cholesterol in carbon tetrachloride solution. Others[4] have shown that the value of the iodine number is dependent upon the reaction time and excess of reagent.

With regard to thiocyanogen numbers Kaufmann, Barbour and Kimura[5] all state that while the iodine and thiocyanogen numbers of oleic acid are identical and equal to the theoretical value, for linolic acid only one of the two double bonds is saturated by thiocyanogen and only one of the three double bonds in the case of eleostearic acid.

More recently Gardner, Weinberger and Pribyl[6] working in this Laboratory, have emphasized the fact of steric hindrance in thiocyanogen addition especially in connection with their work on shellac. It was their work that suggested the present study of halogen and halogenoid addition to unsaturated compounds of different types.

The determinations reported here have been made, not of rate of reaction, but of amounts of halogen or halogenoid added in a given time under specified conditions, to see what generalizations might be drawn regarding the influence of negative groups near to the ethylenic bond upon the halogen addition process.

Experimental Method

The iodine numbers were found with the Hanus iodobromide solution in the usual way according to Scott.[7]

The thiocyanogen numbers were obtained by the method of Kaufmann.[8]

All solutions were kept in the dark and used only in diffused light. All vessels were dried in the oven at 110°. Burets and micro-burets standardized by the Bureau of Standards were employed. Blanks were run in all cases.

The iodine values were taken after one hour (occasionally two hours), the thiocyanogen values usually after forty-seven hours, though frequent determinations were made at around twenty-four hours.

The results reported here are generally the mean of five or six determinations which in all but a few cases checked one another very closely.

All our work goes to confirm the observation of Hugel and Krassilchick[9] that thiocyanogen numbers require upward of thirty hours. However, too long-continued reaction brings in an uncertain factor in the blank titer, since the solution is much less stable than iodine.

Discussion of Results

(1) Oleic and erucic acids contain one ethylenic linkage far removed from the carboxyl group. It is therefore to be expected that the latter will exert no repellent force upon the entering halogen.

The results obtained substantiate this expectation.

It appears then that with acids of sufficient purity the theoretical values for both iodine and thiocyanogen numbers will be found after one and forty-seven hours, respectively, provided the carboxyl is far removed from the ethylene bond, that is, the addition of 1 mole of halogen per mole of compound.

(2) Ricinoleic acid has the ethylene bond situated as in oleic acid, but it possesses an hydroxyl group. The mean iodine value, 119.87, is abnormally large, while the thiocyanogen value is near to the theoretical. Reference was made above to the work of Ralls on cholesterol in carbon tetrachloride solution where like results were reported. Gardner, Weinberger and Pribyl, who prepared the rincinoleic acid, also report a high iodine value. Evidently a reaction of the halogen with the alcoholic group has taken place in addition to the saturating reaction.

(3) Furoic and maleic acids are examples of unsaturated substances in which the influence of the near carboxyl groups might be expected to be strong.

The results reported are in accord with this prediction. In furoic acid not only is there one carboxyl group but conjugated double bonds. In maleic acid there are two carboxyl groups. The small values for furoic and nil values for maleic acid show the powerful repellent forces acting upon the halogen.

(4) Acrylic, α-crotonic (methylacrylic), and cinnamic (phenylacrylic) acids were chosen to demonstrate the effect, if any, of alkyl and aryl groups upon the halogen addition process. It was thought that the deterrant effect of the close carboxyl might be lessened by the substitution of methyl for hydrogen, and might be increased by the substitution of phenyl. These expectations

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(3) Ralls, THIS JOURNAL, **55**, 2083 (1933).

(4) See Rosenmund and Kuhnhenn, *Z. Unters Nahr. Genuss.*, **46**, 154 (1923); Dam, *Biochem. Z.*, **152**, 101 (1924).

(5) See Kaufmann, *Seifensieder-Ztg.*, **55**, 297 (1928); Barbour, *Oil and Fat Ind.*, **7**, 255 (1930); Kimura, *J. Soc. Chim. Ind. Japan*, **32**, 451 (1929).

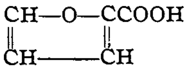
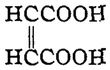
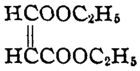
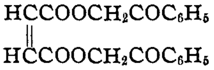
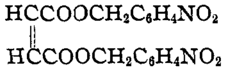
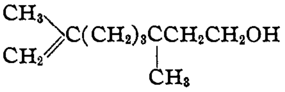
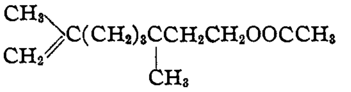
(6) Gardner, Weinberger and Pribyl, *Ind. Eng. Chem., Anal. Ed.*, **6**, 259 (1934).

(7) Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1922, p. 1166.

(8) Kaufmann, *Z. Untersuch. Lebensm.*, **51**, 15 (1926).

(9) Hugel and Krassilchick, *Chimie & Industrie*, Spec. No. 203 (March, 1930).

EXPERIMENTAL RESULTS

Substance and formula	Calcd. I_2 and $(SCN)_2$ no.	Mean I_2 no. found	Mean $(SCN)_2$ no. found	Moles I_2/mole subs.	Moles $(SCN)_2$/mole subs.
Oleic acid $C_8H_{17}CH{=}CH(CH_2)_7COOH$	89.90	91.38	86.18	1.016	0.958
Erucic acid $C_8H_{17}CH{=}CH(CH_2)_{11}COOH$	75.0	75.0	73.0	1.000	.973
Rincinoleic acid $CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOH$	85.09	119.87	87.82	1.409	1.032
Furoic acid  $\begin{array}{l}\mathrm{CH{-}O{-}CCOOH}\\ \Vert \qquad\quad \Vert\\ \mathrm{CH{-}\!{-}\!{-}CH}\end{array}$	453.6	9.12	5.20	0.040	0.022
Maleic acid  $\begin{array}{l}\mathrm{HCCOOH}\\ \ \ \Vert\\ \mathrm{HCCOOH}\end{array}$	218.8	0.00	0.00	.000	.000
Acrylic acid $CH_2{=}CHCOOH$	352.4	1.77	.64	.005	.001
α-Crotonic acid $CH_3CH{=}CHCOOH$	295.0	7.01	.92	.023	.003
Cinnamic acid $C_6H_5CH{=}CHCOOH$	171.6	26.26	1.12	.151	.006
Esters of maleic acid					
Ethyl  $\begin{array}{l}\mathrm{HCCOOC_2H_5}\\ \ \ \Vert\\ \mathrm{HCCOOC_2H_5}\end{array}$	147.4	0.22	0.60	.001	.004
Phenacyl  $\begin{array}{l}\mathrm{HCCOOCH_2COC_6H_5}\\ \ \ \Vert\\ \mathrm{HCCOOCH_2COC_6H_5}\end{array}$	72.09	.63	2.70	.008	.037
p-Nitrobenzyl  $\begin{array}{l}\mathrm{HCCOOCH_2C_6H_4NO_2}\\ \ \ \Vert\\ \mathrm{HCCOOCH_2C_6H_4NO_2}\end{array}$	65.73	.00	1.00	.000	.015
Esters of cinnamic acid					
Ethyl $C_6H_5CH{=}CHCOOC_2H_5$	144.2	30.31	0.50	.210	.003
Phenacyl $C_6H_5CH{=}CHCOOCH_2C_6H_5$	95.40	11.82	1.05	.125	.011
p-Nitrobenzyl $C_6H_5CH{=}CHCOOCH_2C_6H_4NO_2$	89.67	8.98	1.79	.100	.019
Allyl alcohol $CH_2{=}CHCH_2OH$	437.3	Indef.	Indef.	Indef.	Indef.
Citronellol  $\mathrm{\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>\!C(CH_2)_3\underset{\underset{CH_3}{\vert}}{C}CH_2CH_2OH}$	163.6	162.4	173.8	0.992	1.062
Citronellol acetate  $\mathrm{\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>\!C(CH_2)_3\underset{\underset{CH_3}{\vert}}{C}CH_2CH_2OOCCH_3}$	140.1	133.3	114.1	0.952	0.815

were not fully realized. In all three acids the addition of halogen is far below the 1:1 mole ratio. The methyl substitution does, indeed, increase somewhat the amount of halogen added, but the effect of the phenyl substitution increases it still more, contrary to expectation. The iodine value of cinnamic acid is surprisingly high. The experimental result given, however, is the mean of five closely concordant determinations. It may be that the halogen substitutes in the phenyl group to some extent.

(5) To see the effect upon the negativity of carboxyl produced by ester formation, the ethyl, phenacyl, and *p*-nitrobenzyl esters of maleic and cinnamic acids were prepared and studied. The change from acid to ester does not alter largely the negativity of the group. In general the esters add halogen somewhat more than the acids.

(6) Allyl alcohol and citronellol were selected for study as illustrative of unsaturated alcohols. Citronellol acetate is also included in this section.

With allyl alcohol no definite iodine and thiocyanogen values could be obtained. Just as the end-point in titration seemed about to be reached with the next drop of $n/10$ thiosulfate a regeneration of iodine took place, coloring the entire solution blue again. This continued through the addition of 10–15 cc.

With citronellol the iodine addition was complete, but the thiocyanogen value was somewhat high. It was noted, however, that in all these determinations the solutions were colored yellow and a precipitate, evidently polymerization products of thiocyanogen, had settled to the bottom. Decomposition of the thiocyanogen reagent goes on more rapidly in the presence of citronellol than in the blanks, and this doubtless accounts for the higher thiocyanogen values found.

The results with iodine do not show an attack upon the alcohol group. The mean iodine value for the acetate is nearly quantitative, but the thiocyanogen value is low.

Summary

Iodine and thiocyanogen numbers for unsaturated compounds of various types have been determined by the Hanus solution (one and two hours) and Kaufmann solution (forty-seven hours), respectively. The results are discussed in connection with the general question of the effect of negative groups in the vicinity of the ethylene bond in hindering the addition of the halogen and halogenoid. Such a hindrance is evident. The effect decreases with the distance of the negative group from the ethylenic linkage. Ester formation does not materially alter the negativity of carboxyl.

Thiocyanogen is much less reactive than iodine. At least thirty hours should be allowed for this reaction. Longer time of reaction than forty-eight hours leads to uncertainty of results due to progressive deterioration of the reagent.

In the case of alcohols high values may be found due to reaction with the alcohol group in addition to the reaction of saturation.

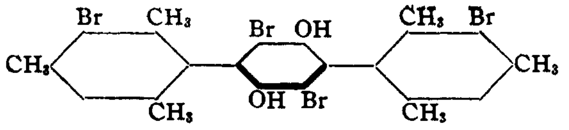
BROOKLYN, N. Y. RECEIVED JUNE 20, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

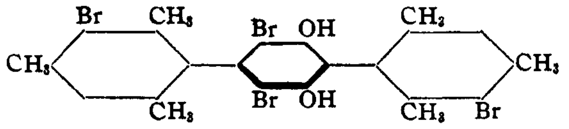
Stereochemistry of Diphenyls. XXXVI. Preparation and Resolution of Certain Substituted Dipyrrylbenzenes[1]

BY CHIN CHANG[2] AND ROGER ADAMS

By the isolation of the *cis* and *trans* forms of certain properly substituted diphenylbenzenes it was demonstrated that molecules containing two points of restricted rotation of the diphenyl type existed in the expected two diastereoisomeric forms. The *cis* and *trans* 3,6-di-(3-bromo-2,4,6-trimethylphenyl) - 2,5 - dibromohydroquinone (I and II) represent such a pair of diastereoisomers.[3]



I. *cis*



II. *trans*

Structural models clearly demonstrate that the *cis* form is racemic and the *trans* form meso, but all the attempts to confirm this by resolution of the *cis* and non-resolution of the *trans* resulted in failure, due, presumably, to the difficulty of introducing satisfactory salt-forming groups.

The investigation of compounds with two points of restricted rotation has been extended to the dipyrrylbenzenes. Previous results have established that phenylpyrroles may exist optically active and that the necessary conditions of substitution conform essentially to those in the diphenyl series. Moreover, it was demonstrated that the nitrogen atom plays no role in the optical activity. The preparation and study of various dipyrrylbenzenes, therefore, present several points of interest: (1) isolation of diastereoisomeric salts would confirm the correctness of the previous generalizations made concerning molecules with two points of restricted rotation; (2) dipyrrylbenzenes containing salt-forming groups can readily be produced and it would, therefore, be possible by a study of the resolution to distinguish the *cis* and *trans* modifications; (3) the *m*-dipyrrylbenzenes should be just as readily synthesized as the *p*-derivatives, whereas no method is available for the preparation of *m*-diphenylbenzene derivatives.

It is of interest that dependent on the type of substitution and whether the molecules are *p*- or *m*-diphenyl or dipyrrylbenzenes, the *cis* form may be either meso or racemic and the *trans* form either meso or racemic. Such possibilities have been discussed in detail elsewhere,[1] so that it is merely necessary to mention here that in a dipyrrylbenzene molecule of type III and IV the *cis* form is meso and the *trans* form racemic, whereas in the type V and VI the *cis* form is racemic and the *trans* form meso.

Compounds V and VI correspond exactly from a stereochemical viewpoint to Compounds I and II in the *p*-diphenylbenzene series.

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[1] For the previous paper see Chien and Adams, THIS JOURNAL, **56**, 1787 (1934). Also Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

[2] Submitted as part of a thesis for the Degree of Doctor of Philosophy at the University of Illinois.

[3] Shildneck and Adams, *ibid.*, **53**, 343, 2203 (1931); Browning and Adams, *ibid.*, **52**, 4098 (1930).