

African oil palms produce fruit throughout the year, but there is a peak season from July to October when an average of 68.3% of the fruit matures.

Composition of Palm Fruit

In order to determine the amount of fuel available for generating steam from the waste after processing of palm oil and palm kernels, six experimental pilot plant extractions, each of exactly one ton of fruit, were undertaken and weights recorded. Six tons of fruit bunches yielded 8,712 pounds of loose fruit which on processing yielded 2,400 pounds of crude pericarp oil, 1,854 pounds of pericarp waste, and 4,068 pounds of nuts containing 834 pounds of kernels and 3,225 pounds of shells. From the known b.t.u. value of the pericarp and shell waste it was calculated that five times as many boiler horse power

are available from the waste fuel as is required for the necessary processing steam.

Summary

The behavior of African oil palms in Honduras was studied with the view of establishing it as an economic crop in Central America. The highest yielding variety for this region was determined to be the Java variety. The influence of post-harvest handling of fruit on the formation of free fatty acids in palm oil was investigated. Actual plantation yields were obtained by processing plantation-produced fruit.

REFERENCE

1. Bunting, B., "The Oil Palm in Malaya," Malayan Planting Manual No. 1, Department of Agriculture, Kuala Lumpur, 1934.

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The Infrared Spectra of Saturated Fatty Acids With Even Number of Carbon Atoms From Caproic, C_6 (Hexanoic), to Stearic, C_{18} (Octadecanoic), and of Their Methyl and Ethyl Esters¹

ROBERT T. O'CONNOR, ELSIE T. FIELD, and W. SIDNEY SINGLETON,
Southern Regional Research Laboratory,² New Orleans, Louisiana

BEFORE many successful applications of infrared spectroscopy to fatty acid and vegetable oil chemistry can be made, extensive spectral data on a large number of pure reference compounds will be required. Heretofore the scant spectral data available on fatty acids, esters, and triglycerides have consisted either of measurements made over a very limited range of the infrared spectrum or have been obtained with compounds of undescribed purity.

Markley (12), reviewing the application of infrared spectrophotometry to fatty acid chemistry, refers to work of Barnes *et al.* (2), of McCutcheon *et al.* (13), and of Gamble and Barnett (7). Barnes and his co-workers (2) include, in a library of reference curves, infrared spectral data on several fatty acids and vegetable oils, measured however only over the region 5 to 13 microns. Some of their compounds were, admittedly, not of highest purity. McCutcheon *et al.* (13), investigating *cis* and *trans* isomers, measured only the region of the $C=C$ absorption band at about 6 microns. This vibration band, arising from $C=C$ stretching vibration, is very weak and is masked by the intense $C=O$ band at 5.8 microns. Gamble and Barnett (7) measured a few fatty acid esters and drying oils over the region 1 to 15 microns, but most of their curves include only the region 5 to 15 microns. These authors made some vibration band correlations with molecular structure. None of these studies reports any quantitative data.

To this brief list of studies of the infrared spectral properties of fatty acids should be added the work on deuterium-substituted fatty acids in the vapor phase by Herman and Hofstadter (8) and the more

recent work of Rao and Daubert (15), of Honn, Bezman, and Daubert (10), and of Lemon and Cross (11). These latter papers, in particular, indicate the possibilities of utilizing infrared spectral properties for analytical purposes.

After the work to be described in this communication was well under way, Shreve, Heether, Knight, and Swern presented infrared absorption data on a number of long chain saturated and mono-unsaturated fatty acids, methyl esters, and alcohols (19). Their data constitute the most complete study of the infrared spectral properties of fatty acids and esters which has yet been described. As a result of their observations, they have proposed an analytical method, based on infrared spectrophotometry, for the quantitative determination of *trans* isomers of mono-unsaturated acids and esters in the presence of the *cis* isomers and of saturated compounds (20). Comparisons of the method with the Twitchell lead salt-alcohol method for the determination of *trans* acids and esters have also been described (21).

To achieve a satisfactory degree of accuracy in quantitative analysis, measurements of infrared spectra will, very probably, have to be made on solutions of the material to be analyzed by the so-called differential analysis method (17). This method is the procedure universally employed for quantitative measurements in the ultraviolet region. With the infrared spectrophotometer adjusted to correspond to 100% and the beam passing through the solvent cell, the slit width and the gain are adjusted until a null reading is obtained on the output meter. Then the cell containing the absorbing specimen is shifted into the beam and the potentiometer is adjusted until a null reading is again obtained. The percentage transmission and/or optical density at the wavelength in question is read directly from the scale.

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²One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Most measurements of pure compounds however have been made either on pure liquids or on hydrocarbon mulls prepared from solids. Constants measured from the pure liquids are not strictly applicable for quantitative purposes to measurements made on solutions of various unknowns as the solvent may exercise considerable effect on the infrared spectral properties. Measurements from mulls cannot be applied to quantitative analyses as it is extremely difficult, if not impossible, to measure the thickness of the mull layer with sufficient accuracy. It is very desirable that the infrared spectra of pure compounds be obtained in the solvents which will be employed in applying such data to analytical purposes.

In the present work infrared spectra have been obtained on the seven even-numbered carbon atom members of the homologous series of straight-chain, saturated, monobasic aliphatic fatty acids from caproic, C_6 (hexanoic), to stearic, C_{18} (octadecanoic), and on their methyl and ethyl esters from 1 to 12 microns. All measurements were made in chloroform by a null reading method, balancing the nonrecording instrument, a model IR-2 Beckman Infrared Spectrophotometer,³ with the solvent and then reading the value for the solution in rapid succession at every 0.05 micron throughout the spectral range and every 0.025 at points of sharp inflection.

The spectrophotometer was housed in a room maintained at about 74°F. and 20% relative humidity. In addition, the temperature of the instrument was maintained at 25°C. \pm 0.1° by a hydrocarbon circulating from a constant temperature bath. The same pair of 0.04 cm. matched cells was used throughout the work. The spectrophotometer was calibrated against various liquids of known infrared properties obtained from the National Bureau of Standards.

Quantitative data have thus been obtained, which, while dependent upon the slits and resolutions of the instrument used, are of high precision and can permit critical comparisons of intensities of one sample with any other at any wavelength. This method of differential analysis also eliminated any effect of background noise or interferences such as moisture.

Chloroform was selected as the solvent as it is quite transparent in the region of the infrared spectra investigated, the fatty acids and their esters are readily soluble in it, and it is frequently used in other studies of these compounds. Chloroform has the advantage over carbon disulfide for infrared measurements as it does not have a region of intense absorption between 1 to 12 microns whereas an intense maximum in the spectrum of carbon disulfide masks any absorption measurements in the important region 6-7 microns. Carbon disulfide is furthermore a dangerously toxic solvent (3) and not adaptable to studies where a large number of samples are to be measured.

The chloroform should be both chemically and optically pure, i.e., it should have the highest transmission to the infrared radiation obtainable. Chloroform has a strong absorption band at 8.2 microns and weaker bands at 4.2, 6.6-7.0, 9.3-9.5, and 10.8 microns (14). For purposes of comparison the best chloroform that has been purified in this laboratory has been measured against the empty cell. When compared in this manner, the transmission of the chloro-

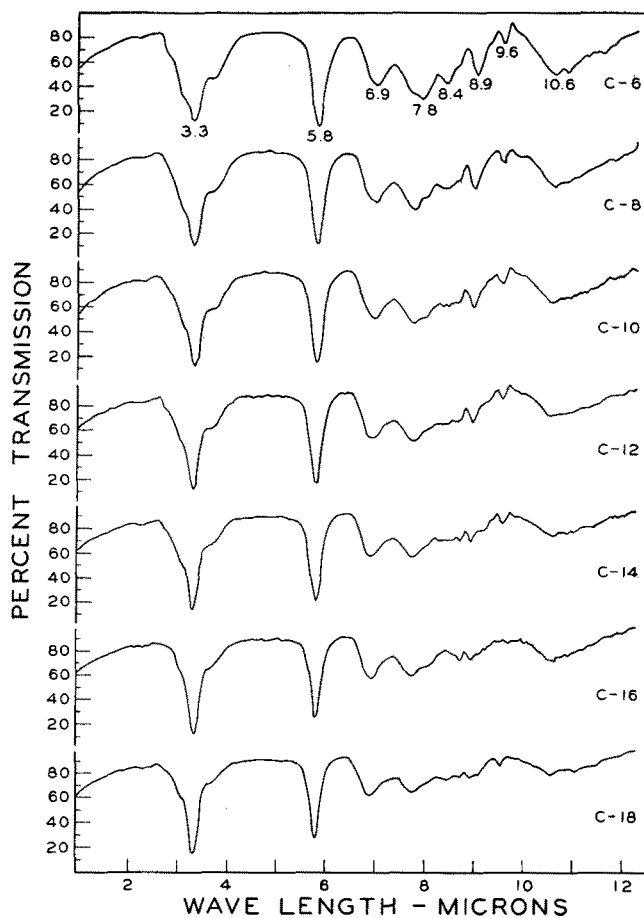


FIG. 1. Infrared spectra of fatty acids.
 C-6 Caproic C-10 Capric C-16 Palmitic
 C-8 Caprylic C-12 Lauric C-18 Stearic
 C-14 Myristic

form may at some wavelengths become greater than the 100%, due to reflectance losses through the air layer and at the interfaces of the empty cell used as the reference. The values suggested as minimum percentage transmission for chloroform to be used as a solvent for infrared measurements are 108, 100, 73, 102, 38, 10, 21, 84, 78, and 30 for wavelengths of 1.0, 3.0, 4.0, 6.0, 7.0, 8.0, 9.5, 10.0, 11.0, and 12.0 microns, respectively.

Preparation of Acids and Esters

The fatty acids were obtained from commercial products containing approximately 85-90% of the desired acid. Unsaturated impurities were removed by sulfonation and water washing. Esterification of the washed materials with the appropriate alcohol gave the methyl and ethyl esters. The esters were fractionally distilled and repeatedly recrystallized from acetone. A portion of each of the fatty acid methyl esters was converted to the appropriate acid. All products were dried over phosphorous pentoxide. The melting points and/or refractive indices of the fatty acids and their methyl and ethyl esters are given in Table I. A comparison of these data with available published values (12) indicates that the compounds obtained closely approached 100% purity.

Discussion

Spectra of the 7 acids and their methyl and ethyl esters are shown in Figures 1, 2, and 3 as plots of

³ Mention of names of firms or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms of similar products not mentioned.

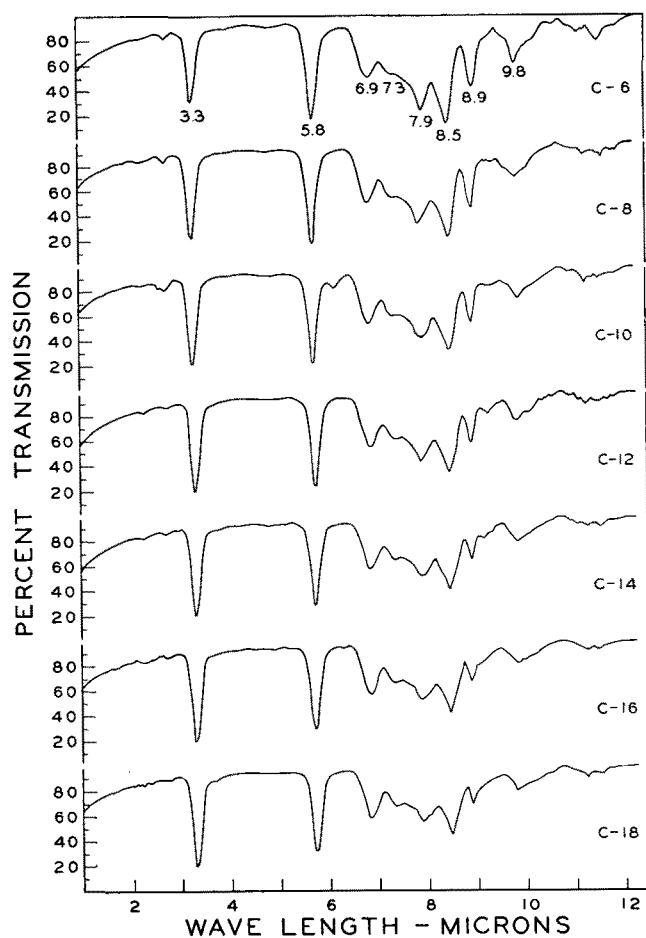


Fig. 2. Infrared spectra of methyl esters of fatty acids.

C-6 Caproic C-10 Capric C-16 Palmitic
C-8 Caprylic C-12 Lauric C-18 Stearic
C-14 Myristic

the percentage transmission of solutions containing approximately 20 g./l. against the wavelength in microns. These curves exhibit a number of pronounced absorption bands, the exact wavelength positions of maxima of which are indicated on each figure. The intensities of these bands, expressed as molecular extinction coefficients,⁴ are given in Table II. From a study of available infrared literature concerned with the generalities of frequency correlations and particularly from data on analogous compounds, most of these bands can be correlated with a feature of the molecular structure of the acid or ester.

⁴ ϵ (molecular extinction coefficient) = $O.D./cl$, where $O.D.$ is the optical density, c is the concentration in moles per liter, and l is the cell length in centimeters.

TABLE I

Melting Points and Refractive Indices of the Fatty Acids and Esters

	Fatty Acids		Methyl Esters		Ethyl Esters	
	Melting Point, °C. ^a	Refractive Index $n_D^{45^\circ C.}$ ^b	Melting Point, °C.	Refractive Index $n_D^{45^\circ C.}$	Melting Point, °C.	Refractive Index $n_D^{45^\circ C.}$
Caproic.....	1.4083	1.3960	1.3977
Caprylic.....	1.4191	1.4083	1.4077
Capric.....	28.8	1.4261	1.4152	1.4154
Lauric.....	43.2	1.4219	1.4216
Myristic.....	53.9	1.4272	1.4263
Palmitic.....	62.8-63.0	29.5	1.4310	1.4302
Stearic.....	69.5	38.3	1.4345	33.5	1.4340

^a Capillary tubes.

^b Abbé refractometer.

Band at 3.3 microns. This band arises from C—H stretching vibration and its wavelength position is quite consistent at 3.3 microns. The variation in wavelength for the 21 samples measured is only 0.02 micron from 3.30 to 3.32 microns.

The nonappearance of a band of observable intensity below 3.3 microns indicates the absence of any free O—H stretching vibration. Free O—H stretching would be expected to appear as a band at about 2.8 microns. Absence of any trace of this band in the spectra of the acids indicates that, even in the relatively dilute chloroform solutions measured, the hydrogen is bonded. The bonded O—H...O stretching vibration is unresolved from the C—H stretching vibration at 3.3 microns and the intensity of this band for the acids should be expected to be greater than for the esters. Reference to Table II shows that in all samples measured the band at 3.3 microns is more intense for the acids than for the esters.

When the rather voluminous data on the infrared spectra of simple alcohols are examined, the postulation that O—H bonding produces a shift in absorption maxima sufficient to cause the 2.8 micron O—H band to become unresolved from the 3.3 micron C—H band appears to be somewhat questionable. The free O—H stretching vibration of these compounds is reported as a band at 2.75 to 2.80 microns with hydrogen bonding causing a shift to 2.90 to 3.00 microns. However Herman and Hofstadter (8) have shown that monomeric acetic and propionic acids (with free

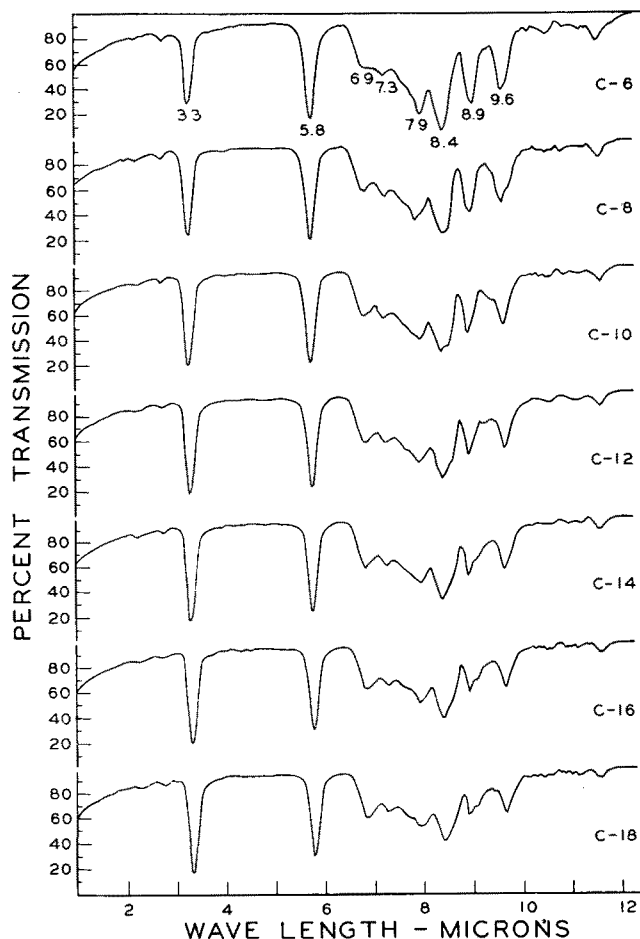


Fig. 3. Infrared spectra of ethyl esters of fatty acids.

C-6 Caproic C-10 Capric C-16 Palmitic
C-8 Caprylic C-12 Lauric C-18 Stearic
C-14 Myristic

TABLE II
Infrared Absorption Spectral Data for Chloroform Solutions of Specified Saturated Fatty Acids
and Their Methyl and Ethyl Esters

Compound	Mol. Wt.	Wavelength of Absorption Bands										
		3.3 μ			5.8 μ			6.9 μ			7.3 μ	
		λ	ϵ	ϵ per C-H ¹	λ	ϵ	$\frac{\epsilon}{0.05 M^2}$	λ	ϵ	ϵ per C-H ¹	λ	ϵ
		1	2	3	4	5	6	7	8	9	10	11
Fatty Acid												
Caproic.....	116.15	3.30	126.60	7.05	5.80	142.86	209.99	6.98	46.46	2.59		
Caprylic.....	144.21	3.30	158.63	7.27	5.80	154.30	210.55	6.98	56.24	2.31		
Capric.....	172.26	3.32	185.60	7.23	5.80	163.60	210.10	6.95	58.55	2.28		
Lauric.....	200.31	3.30	214.33	7.22	5.80	180.28	216.33	6.90	64.10	2.16		
Myristic.....	228.36	3.30	248.91	7.40	5.78	191.82	216.94	6.90	68.51	2.04		
Palmitic.....	256.42	3.32	274.37	7.30	5.78	202.57	215.39	6.92	79.49	2.11		
Stearic.....	284.47	3.32	304.38	7.32	5.80	210.51	219.04	6.90	79.65	1.92		
Methyl Ester												
Caproate.....	130.18	3.30	79.62	4.25	5.75	117.61	180.02	6.90	39.05	1.85	7.35	42.96
Caprylate.....	158.24	3.30	117.10	4.70	5.75	125.01	180.39	6.88	50.64	2.03	7.35	50.64
Caprate.....	186.29	3.30	143.40	4.98	5.75	139.68	182.52	6.88	59.60	2.07	7.35	50.28
Laurate.....	214.34	3.32	167.19	5.11	5.78	145.75	182.19	6.90	62.16	1.90	7.35	49.30
Myristate.....	242.39	3.32	193.91	5.29	5.75	155.13	181.79	6.88	67.87	1.85	7.35	53.33
Palmitate.....	270.45	3.30	216.36	5.33	5.75	159.57	183.91	6.88	73.02	1.80	7.35	54.09
Stearate.....	298.50	3.30	232.83	5.22	5.75	164.18	185.07	6.88	77.61	1.74	7.35	53.73
Ethyl Ester												
Caproate.....	144.20	3.30	99.50	4.32	5.78	124.01	185.95	6.85	40.38	1.75	7.25	47.59
Caprylate.....	172.26	3.30	125.75	4.68	5.78	136.09	187.76	6.85	46.51	1.73	7.25	55.12
Caprate.....	200.31	3.30	152.22	4.95	5.75	146.19	188.24	6.85	52.07	1.69	7.25	54.07
Laurate.....	228.36	3.30	178.12	5.14	5.78	150.72	187.26	6.85	57.09	1.65	7.28	54.81
Myristate.....	256.41	3.30	200.00	5.18	5.78	158.97	189.74	6.85	61.54	1.59	7.28	56.41
Palmitate.....	284.47	3.32	227.58	5.34	5.78	164.99	182.06	6.85	65.43	1.54	7.28	56.89
Stearate.....	312.52	3.32	246.89	5.30	5.78	171.89	187.51	6.85	71.88	1.54	7.28	56.25

¹ ϵ per C-H group. See text. ² ϵ for solutions containing exactly 0.05 M acid or ester per liter. See text.

TABLE II (Continued)

Compound	Wavelength of Absorption Bands														
	7.8 μ		8.4 μ		8.7 μ		8.9 μ		9.6 μ		10.4 μ			10.6 μ	
	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	α	λ	ϵ
	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Fatty Acid															
Caproic.....	7.80	70.85	8.40	46.46	8.60	44.14	8.98	41.81	9.55	16.26	10.3	26.71	0.23	10.60	39.49
Caprylic.....	7.80	70.66	8.40	43.26	8.70	41.82	8.98	43.26	9.58	17.31	10.3	23.07	0.16	10.60	36.05
Capric.....	7.80	70.61	8.45	43.05	8.70	41.33	8.98	43.05	9.55	20.67	10.3	24.11	0.14	10.58	37.89
Lauric.....	7.80	70.11	8.45	44.07	8.60	40.06	8.95	42.07	9.55	19.43	10.3	26.04	0.13	10.50	34.05
Myristic.....	7.80	70.79	8.45	43.39	8.70	41.10	8.92	43.39	9.55	20.32	10.3	27.40	0.12	10.55	36.54
Palmitic.....	7.80	71.80	8.45	43.59	8.70	41.02	8.95	43.59	9.55	18.46	10.3	28.21	0.11	10.62	41.03
Stearic.....	7.75	71.12	8.45	42.67	8.70	42.67	8.90	42.67	9.55	20.77	10.3	28.45	0.10	10.55	39.82
Methyl Ester															
Caproate.....	7.95	82.01	8.48	110.65			8.98	57.28	9.85	26.04	10.3	10.4	0.08		
Caprylate.....	7.90	82.23	8.50	107.60			8.98	56.97	9.85	26.90	10.3	7.9	0.05		
Caprate.....	7.95	81.95	8.48	108.02			8.95	55.87	9.88	27.94	10.3	13.0	0.07		
Laurate.....	7.90	83.59	8.48	107.17			8.92	53.59	9.85	27.86	10.3	8.6	0.04		
Myristate.....	7.90	79.99	8.48	106.65			8.92	53.33	9.85	26.66	10.3	9.7	0.04		
Palmitate.....	7.90	81.14	8.48	110.88			8.90	51.39	9.85	25.96	10.3	8.1	0.03		
Stearate.....	7.90	83.58	8.48	110.44			8.90	53.73	9.80	26.87	10.3	9.0	0.03		
Ethyl Ester															
Caproate.....	8.00	110.03	8.42	119.69			9.05	72.10	9.62	62.00	10.3	8.7	0.06		
Caprylate.....	7.88	89.58	8.42	118.86			8.95	72.35	9.62	62.01	10.3	6.9	0.04		
Caprate.....	7.95	88.11	8.40	120.16			8.92	72.09	9.65	62.08	10.3	8.0	0.04		
Laurate.....	7.90	89.06	8.40	121.03			8.92	73.08	9.65	61.66	10.3	6.9	0.03		
Myristate.....	7.95	89.74	8.40	123.08			8.90	71.79	9.65	61.54	10.3	5.1	0.02		
Palmitate.....	7.92	88.19	8.40	122.32			8.92	71.12	9.65	62.58	10.3	5.7	0.02		
Stearate.....	7.92	90.63	8.40	125.01			8.88	71.88	9.65	62.50	10.3	9.4	0.03		

O—H groups) have bands at 2.75 microns while the dimers (bonded O—H...O group) exhibit bands at 3.2 microns. Similarly these same authors studied the deuterium substituted acids and showed that the free O—D stretching vibration of the monomer gave rise to a band at 3.75 microns; the bonded O—D...O vibration of the dimer resulting in a band at 4.35 microns. This work adequately demonstrated that hydrogen bonding of these carboxylic acids causes a shift in absorption maxima of about 0.4 to 0.6 microns, sufficient to cause the hydrogen bonded O—H...O band to be unresolved from the C—H stretching band at 3.3 microns. Davies (5), studying the infrared absorption of organic hydroxyl compounds in the 3-micron region, included data on lauric acid which somewhat supports the conclusion that bonded O—H...O and C—H stretching vibrations are unresolved at about 3.3 microns. For the homologous series the intensities of the bands are quite constant. The partial molecular extinction coefficients (obtained by multiplying the molecular

weight of the C—H groups involved in the 3.3 micron stretching vibration by the extinction coefficient at 3.3 microns and then dividing by the number of C—H groups in the molecule) are seen (Table II, column 3) to be reasonably constant, with average values of 7.26 for the acids and 4.98 and 4.99 for the methyl and ethyl esters, respectively. Careful examination of these values, particularly for the esters, reveals that there is a slight but consistent increase in the value of the extinction coefficient per C—H group with molecular weight. As all of these measurements were made from solutions containing close to 20 g. of ester per liter, the molar concentration of the longer chain compounds is considerably less than for the shorter chain esters. Increase in intensity of the band with decrease in molar concentration might indicate some type of association involving perhaps only one of the more active of the 14 to 40 C—H groups in these esters. (Further evidence of association involving an active C—H group will be discussed later.)

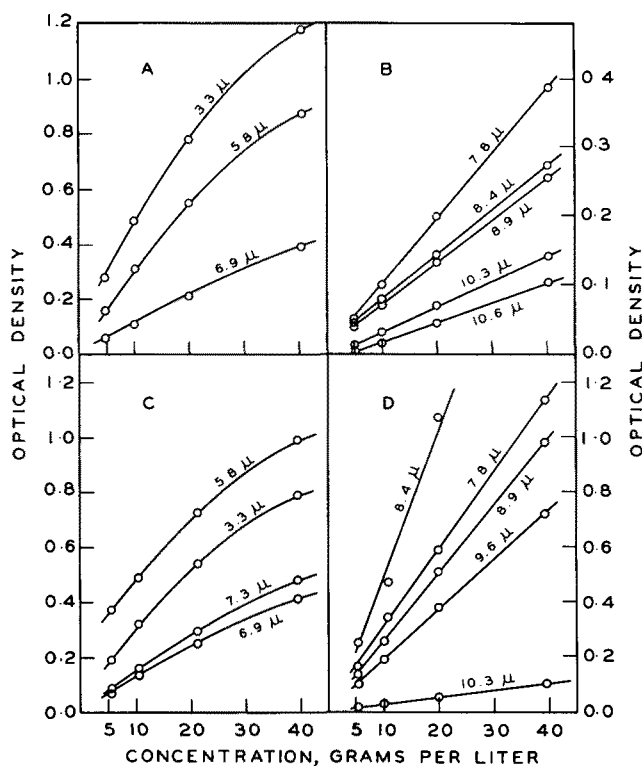


FIG. 4. Beer's law relationships of specified infrared. Absorption bands of stearic acid (A and B) and of ethyl caproate (C and D).

In Figure 4 are shown the results of some studies of the Beer law relationships for the various bands for a selected acid (stearic) and a selected ester (ethyl caproate) over the concentration range 5-40 g./liter. From examination of Figure 4A and C it will be seen that the C—H stretching vibration does not follow the Beer law for either acids or esters. The complication due to unresolved O—H...O bands could be advanced to explain the failure of the acids to follow the Beer law. Failure of the esters to obey this relationship may be construed as additional evidence for association involving a C—H bond.

Band at 5.8 microns. This band is attributable to C=O stretching vibration. The wavelength position of the band in chloroform solution varies slightly, but consistently, the acids exhibiting maxima between 5.78 and 5.80 microns and the esters at shorter wavelengths, between 5.75 and 5.78 microns.

As each of the samples measured contains one C=O group, the molecular extinction coefficients for a homologous series might be expected to be constant. As shown in Table II, column 5, the molecular extinction coefficients increase regularly with increase in molecular weight. Beer's law does not apply to solutions of these compounds (Figure 4A and C). The concentrations of the solutions measured were all close to 20 g. per liter. This would mean that the molar concentration is considerably less for the longer chain molecules. Increase in molecule extinction coefficient with decrease in molar concentration might indicate association of some sort. Considered with the failure of the C—H stretching vibration band to follow Beer's law an association involving an active C—H and the C=O groups might be postulated.

To test the hypothesis that the failure to obey Beer's law is due to association, chloroform solutions

of the saturated acids and esters, exactly 0.05 molar, were prepared and their infrared absorption measured from 5.6 to 5.8 microns. The results of these measurements, shown in column 6 of Table II, tend to support the hypothesis. The molecular extinction coefficients obtained from measurements of solutions of equal molar concentrations are constant with average values of 214.04, 182.27, and 186.96, and variations from these averages of $\pm 1.53\%$, $\pm 0.73\%$, and $\pm 0.89\%$ for the acids and their methyl and ethyl esters respectively. These slight variations are attributable to small differences in the purities and to experimental errors while measuring the extinction coefficients of the various samples.

The molecular extinction coefficients of the infrared band at 5.8 microns could, if established very accurately with highly pure compounds, for a single value of molarity of a chloroform solution be used as criteria of purity for subsequent preparations of these materials. Failure of these compounds to obey Beer's law however means that any attempts to use the measured intensity at 5.8 microns to calculate the concentrations of C=O bonds in unknown mixtures would be likely to be unsatisfactory.

Band at 6.9 microns. This band is attributed to C—H bending vibration. The wavelength position of maxima is found at 6.85 microns in the spectra of all ethyl esters. Methyl esters exhibit bands at slightly longer wavelengths, 6.88 to 6.90 microns, and the acids at still longer wavelengths, 6.90 to 7.00 microns.

Partial molecular extinction coefficients, when divided by the number of C—H groups in each compound, reveal "extinction coefficients per C—H group" which are approximately constant for the three homologous series (Table II, column 9). The intensities of these bands at 6.9 microns are somewhat less than the C—H stretching vibration band, and the accuracy is consequently somewhat less. The slight effect of any association involving a C—H bond is not apparent, and the deviation from the Beer law is very slight, Figure 4A and C.

Band at 7.3 microns. This band arises from symmetrical deformation vibration of the methyl group. In the chloroform solutions measured the band is not observed in the spectra of the acids, but it is quite pronounced in the spectra of all methyl and ethyl esters. Evidently only the —CH₃ group adjacent to the C=O group of the ester is active at this wavelength or any contribution of the methyl group at the end of the long chain acids and esters is negligible.

The wavelength of the maxima of the band is between 7.25 and 7.28 microns for all ethyl esters and 7.35 microns for all methyl esters. As each of the compounds measured contains only one —CH₃ group in the ester portion of the molecule, the extinction coefficient for homologous series might again be expected to be constant. However as with the C=O stretching vibration at 5.8 microns, Table II, column 11, reveals a steady increase in the molecular extinction coefficients for solutions all containing about 20 g. per liter. Thus further evidence of association of the methyl and ethyl esters is obtained, and additional evidence is indicated that this association involves the —CH₃ group of the ester. The band does not follow the Beer law (Figure 4C).

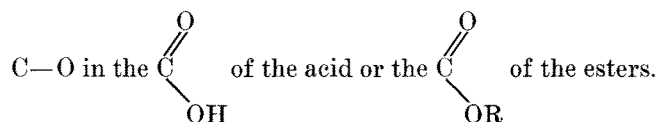
Bands at 7.7-8.0 and at 8.5 microns. These bands arise from C—O vibrations. In the chloroform solu-

tions all series of compounds exhibit two bands, one considerably weaker than the other in the spectra of the acids, but both of about the same intensity in the spectra of the esters:

Acids.....	7.75-7.80 microns (strong)
Methyl esters.....	7.90-7.95 microns (strong)
Ethyl esters.....	7.88-8.00 microns (strong)

Acids.....	8.40-8.45 microns (weak)
Methyl esters.....	8.48-8.50 microns (strong)
Ethyl esters.....	8.40-8.42 microns (strong)

These bands arise from stretching vibrations of the

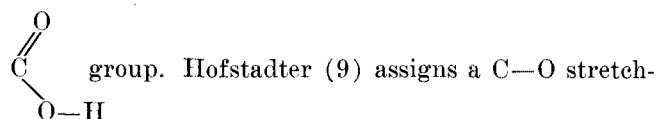


The exact frequency of the C—O stretching vibration changes somewhat with molecular environment.

Unlike the C=O stretching vibration the intensity of the C—O band is quite constant at both 7.7-8.0 microns and at 8.5 microns, as shown by the molecular extinction coefficients given in Table II, columns 13 and 15. Figure 4, B and D, gives evidence that Beer's law is applicable to these bands. Evidently association of these molecules, which appears to affect the C=O and the —CH₃ group, does not similarly affect the C—O group.

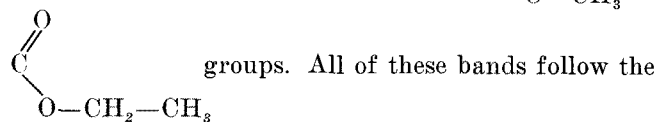
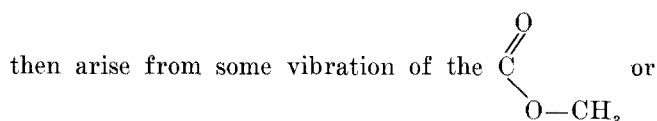
Band at 8.7 and 8.9 microns. The spectra of the acids exhibit bands of about equal intensity at 8.7 and 8.9 microns. Only the band at 8.9 microns is seen in the spectra of the esters. It is of some importance probably that this band is considerably more intense in the spectra of the ethyl esters than in that of the methyl esters. This observation indicates that the 8.9 band arises, in part at least, from a vibration involving the ester group and the vibration is more intense in the ethyl than in the methyl radical.

The bands at 8.7 microns in the spectra of the acids are probably attributable to a C—O stretching of the



ing vibration to a band at about 8.7 microns.

Randall *et al.* (14) assign an unsymmetrical stretching vibration of the C—C—O group to a band about 9.0 microns, and this may be the weaker component of an unresolved band observed at 8.9 microns. The stronger component of this unresolved band must



Beer law, as shown in Figure 4, C and D.

Band at 9.6 microns. In the spectra of all ethyl esters a distinct band is seen with maxima between 9.62 and 9.65 microns. This band is not observed in the spectra of either the acids or the methyl esters. The only absorption observed in the spectra of the acids in this region is a weak band at 9.55-9.58 mi-

rons. Similarly in the spectra of the methyl esters, only a weak inflection is observed at 9.80-9.88 microns. If either of these absorptions occurs in the spectra of the ethyl esters, it is probably covered by the strong 9.6 band.

Thus the band at 9.6 microns appears to offer an opportunity to distinguish an ethyl ester from a methyl ester by observation of infrared spectra. The band arises obviously from a vibration involving the ethyl ester group. Its intensity follows Beer's law (Figure 4, D).

Band at 10.3 microns. A band, observed in the infrared spectra of monounsaturated fatty acids at 10.3 microns (in chloroform solution), has become one of the most useful in the application of infrared spectra to fatty acid chemistry. Rasmussen *et al.* (16) were probably the first to suggest that the band is characteristic of the trans form of the C=C group. Sheppard and Sutherland (18) have assigned this band to a deformation vibration of a hydrogen atom directly attached to a carbon atom in an ethylenic type of double bond. The more symmetrical cis isomer reveals no band at 10.3 microns. Anderson and Seyfried (1) first suggested that this band might be used for quantitative measurement of the trans C=C isomer in the presence of the cis C=C group; and Shreve, Heether, Swern, and Knight (20) presented a quantitative method for the determination of the trans isomer in the presence of the cis isomer and of saturated compounds, based on infrared absorption at 10.3 microns.

No band is observed in the spectra of the saturated fatty acids and esters at 10.3 microns. The specific extinction coefficients (α)⁵ are given in column 24 of Table II to show that they are sufficiently constant to permit an average value to be used as a correction for the absorption of saturated compounds when measuring the intensity of the trans C=C band, as proposed by Shreve *et al.* (20). The data of Table II, column 24, also show that the esters have considerably less absorption at 10.3 microns than the corresponding acids. Determination of trans C=C components might be made somewhat more accurately in a mixture of esters than in the fatty acids. Absorption at 10.3 microns in the spectra of both saturated fatty acids and esters follows Beer's law (Figure 4, B and D).

Band at 10.6 microns. A band at 10.50 to 10.60 microns is observed in the spectra of all the saturated acids and is completely absent in the spectra of the esters. Davis and Sutherland assigned to a band at 10.6 microns a vibration of the OH group in and out of the plane of the carbonyl group (6). Colthup (4) assigns a band at about 10.6 microns to an out of plane OH—O vibration of the dimer acid only. The band follows Beer's law (Figure 4B) and affords another opportunity to differentiate between an acid and an ester by infrared.

The use of infrared spectra to distinguish among saturated fatty acids, methyl esters, and ethyl esters is summarized as follows:

a) The appearance of the symmetrical deformation vibration band of the methyl group in the chloroform solutions at 7.3 microns is evidence for the presence of an ester. Acids exhibit only a weak inflection in chloroform solution at this wavelength.

⁵ α (specific extinction coefficient) = $O.D./cl$, where $O.D.$ is the optical density, c is the concentration in grams per liter, and l is the cell length in centimeters.

b) A band at 8.6 to 8.7 microns is observed in the spectra of the acids but not in that of the esters.

c) A band at 9.6 microns is exhibited by all ethyl esters but not by methyl esters, nor by saturated acids, thus affording an opportunity to distinguish between methyl and ethyl esters.

d) A band at 10.5-10.6 microns is seen in the spectra of the acids, but not in the spectra of the esters.

Summary

Infrared spectra from 1 to 12 microns have been obtained for 7 of the homologous series of monobasic, straight-chain, saturated fatty acids of even carbon atom content from C_6 to C_{18} and of their methyl and ethyl esters.

Infrared data are presented as plots of the percentage transmission against the wavelength in microns on a linear wavelength scale for each compound, and the exact wavelength positions of maxima of the 11 most prominent bands are tabulated.

Correlations of each of these bands with molecular structure are given.

Methods for distinguishing the acids from the esters and of differentiating an ethyl ester from a methyl ester by observation of infrared spectra are described.

An explanation, supported by earlier work with deuterium-substituted compounds, is given to account for the nonappearance, in the spectra of the fatty acids of any absorption attributable to either the free O—H group or the bonded O—H . . . O group.

Evidence has been accumulated which indicates an association of some sort of the esters and that this association probably involves the carbonyl and the methyl groups.

Data are presented to show which of the bands in the infrared spectra do and which do not follow Beer's law.

The tabulation of the absorption bands with their intensities and a correlation of each with molecular structure should be helpful to future studies of the applications of infrared spectra to fatty acid chemistry.

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Oxygen-Absorption Apparatus for Measuring Induction Periods of Fats¹

I. R. HUNTER, Western Regional Research Laboratory,² Albany, California

WORK in this laboratory on the separation of an antioxidant material from defatted rice bran has prompted the development of an apparatus for the automatic determination of the induction period of fats by the oxygen-absorption method. The usefulness of this method for indicating susceptibility of fats to oxidative rancidity has been established by previous investigators. It has been applied successfully to studies on the stabilization of fats by antioxidants (1, 2, 3). The method consists in maintaining a sample of the fat in an oxygen-filled glass chamber at a constant temperature until a predetermined amount of the gas is absorbed.

The present apparatus is distinguished by the use of a modified glass syringe, which responds to contraction in oxygen volume and opens an electrical circuit after the calculated amount of absorption. The

entire apparatus is sufficiently compact that several can be operated in a single constant-temperature bath.

As illustrated in Figure 1, the unit consists primarily of the reaction flask (A) and the syringe (B) modified by replacing the tip with an inner standard-taper $19/38$ ground-glass joint (C). The flask is made from a 250-ml. Erlenmeyer by attaching an outer ground-glass joint with a lip (D) for holding a mercury seal (J); side arms (E) carrying 2-mm. stopcocks are attached to the flask about 1 cm. below the neck. The plunger of the syringe has an opening (F) so that plunger weights can be equalized by the addition of mercury or shot (H). The flask is made gas-tight by lubricating the stopcocks with a silicone stopcock grease and the hypodermic with a silicone oil having a viscosity of 150 centistokes. As an added precaution against leakage, a mercury seal is placed in the lip of the flask.

The electrical system comprises a lever-operated microswitch (G) and an ordinary electric clock modified so that the time of stopping during a 96-hour

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² Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.