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

BRANCHED-CHAIN FATTY ACIDS. XVIII. ULTRAVIOLET ABSORPTION SPECTRA OF SATURATED BRANCHED-CHAIN ACIDS[1]

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Ultraviolet absorption spectra appear to have been determined, among saturated fatty acids, only for normal isomers. It has been observed (1) that carboxyl gives a broad band at about 210 mμ, with ϵ of about 50. The size of the *n*-alkyl group attached to carboxyl has little effect on the absorption, but higher molecular weight acids absorb at slightly longer wave lengths. It would appear, however, since ultraviolet absorption is due to electronic excitation, that substituent alkyl groups near carboxyl might affect the absorption. It is known that an α-alkyl does affect the electron distribution in carboxyl, as evidenced, for example, by the change in dissociation constant of the acid which accompanies α-substitution. In the present report, it is shown that substitution of alkyl groups near carboxyl does have a significant effect on ultraviolet absorption, and the magnitude of the effect is sufficient to be of use in elucidation of structure of branched-chain acids.

TABLE I

ABSORPTION SPECTRA OF FATTY ACIDS

ACID	λ_{max}	ϵ_{max}
Stearic	210	48.5
Palmitic	210	50.2
6-Methyloctadecanoic	210	49.5
5-Methyloctadecanoic	209	53.3
4-Methyloctadecanoic	209	54.5
3-Methyloctadecanoic	211	53.8
3,3-Dimethyloctadecanoic	213	56.5
2-Methyloctadecanoic	213	67.2
2,2-Dimethyloctadecanoic	213	85.5
4-*n*-Butyl-4-ethylnonanoic	209[a]	70.5[a]
2-*n*-Butyl-2-ethylnonanoic	214	90.5
2,3-Dimethyloctadecanoic	213	144
2,3,4-Trimethylhexadecanoic	[b]	120[b]

[a] This curve is probably still rising at 208 mμ, the limit at which readings were obtained; *cf.* Fig. 2. [b] This curve does not exhibit a maximum. At 210 mμ, ϵ 120; *cf.* Fig. 2.

In Figure 1 are plotted representative absorption curves for methyl-substituted acids, and in Table I are given values of λ_{max} and ϵ_{max} for additional alkylalkanoic acids. The shape of the curves for all the methyloctadecanoic acids is the same as shown in Figure 1 for the 2- and 3-methyloctadecanoic acids. It will be noted

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that the absorption of palmitic and stearic acids is essentially the same, and the values are also in agreement with the curve which has previously been published

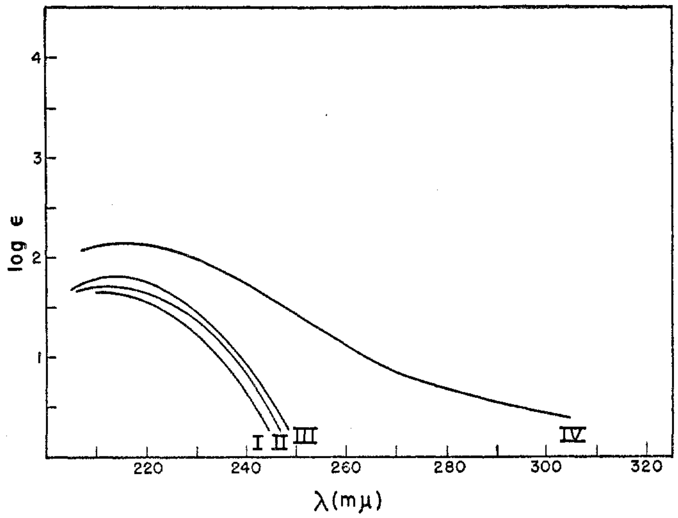


FIGURE 1. ABSORPTION SPECTRA OF METHYL-SUBSTITUTED FATTY ACIDS. I, palmitic acid (for reference); II, 3-methyloctadecanoic acid; III, 2-methyloctadecanoic acid; IV, 2,3-dimethyloctadecanoic acid.

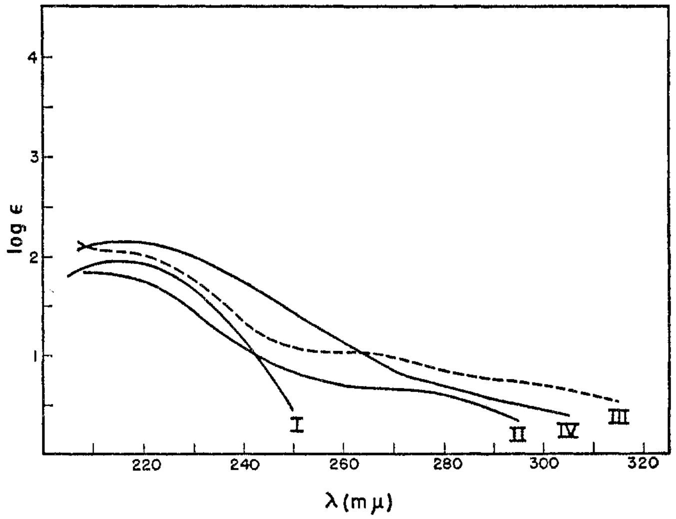
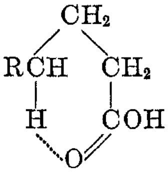


FIGURE 2. ABSORPTION SPECTRA OF POLYALKYLALKANOIC ACIDS. I, 2-*n*-butyl-2-ethyl nonanoic acid; II, 4-*n*-butyl-4-ethylnonanoic acid; III, 2,3,4-trimethylhexadecanoic acid; IV, 2,3-dimethyloctadecanoic acid.

for palmitic acid (2). It will also be noted that a 2-methyl substituent has a considerable effect in increasing the extinction coefficient, ϵ, whereas the 3-methyl substituent has a small effect. Substitution of two methyls at either the 2- or 3-

position increases the absorption considerably more than one methyl, and the effect of a group larger than methyl is only slightly greater than the effect of methyl. These observations are entirely consistent with the view that the effect of the substituent alkyl is an inductive one.

It is surprising, however, that a methyl substituted in the 4- or 5-position has as large an effect as one in the 3-position, whereas a substituent in the 6-position has no effect. This small effect of the substituent in the 3-, 4-, and 5-positions is regarded by us as real, for it has been verified in numerous determinations. The effect in the 4- and 5-positions cannot be described as an inductive effect *unless* the carboxyl may be considered as near these positions. This would be the case if, at a given time, a certain fraction of the molecules of acid were in the form of a *quasi* ring, as shown in Formula I. This would place the 3-, 4-, and 5-carbons at similar distances from the chromophore. As a matter of fact, Smith and McReynolds (3) have used the concept of such a *quasi* ring to correlate numerous facts observed in connection with the esterification of acids, the saponification of esters, and the ionization constants of acids. The present observations of absorption spectra add further credence to this theory.



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The concept of the *quasi* ring may be used to adequately explain certain anomalies observed in the spectra of the polysubstituted acids. For example, it will be noted in Figure 1 and Table I that 2,3-dimethyloctadecanoic acid gives more absorption at longer wave lengths than the other methyl-substituted acids, and has a much larger ϵ_{max} than either 2,2- or 3,3-dimethyloctadecanoic acid. This seems reasonable if it be remembered that the steric interference of the 2,3-dimethyl substitution is considerably relieved in the *quasi* ring form; therefore a larger fraction of the molecules would be in this form. It must be recognized that the chromophore in 2,3-dimethyloctadecanoic acid is a weak one, and small amounts of impurities might give large effects in the absorption curves; however, we are fortunate in having available two samples of this acid, prepared by entirely different synthetic routes (4). The absorption spectra of the two samples were very similar and nearly identical in the essential features mentioned above.

Other effects, which may be correlated on the basis of the existence of the *quasi* ring, are found in the curves of Figure 2. Although 4-methyloctadecanoic acid gives a curve of the normal type, 2,3,4-trimethyloctadecanoic acid gives an anomalous curve which does not have a maximum in the region near 210 mμ but begins to turn up in the region below 215 mμ. This, again, is explicable on the assumption that the steric effect of the substituents at the 2- and 3-positions increases the fraction of molecules existent as *quasi* rings. 2-*n*-Butyl-2-ethylnonanoic acid gives a curve of the normal type, with relatively high ϵ, whereas 4-*n*-butyl-4-ethylnonanoic acid gives a curve which continues to rise as far as 208 mμ. In this latter instance, the absence of hydrogens on the γ-carbon rules out such a formulation as in Formula I, and this may be responsible for the extinction coefficient being no higher. The anomalous shape of the curve may possibly arise from the proximity of the large γ-substituents to carboxyl, even in the open-chain form.

From these observations, it would be predicted that large alkyl substituents as remote from carboxyl as the δ-position might exert some steric hindrance on the carboxyl group. This is presently being investigated in this laboratory, and it will be shown in a future paper in this series (XXIII) that 2,3,4-trimethylhexadecanamide is hydrolyzed considerably more slowly than is 2,3-dimethyloctadecanamide, in spite of the fact that 4-methyloctadecanamide is not appreciably more hindered than stearamide.

Since it would be expected that solvation might have an effect on the percentage of molecules existing as *quasi* rings, it should be of interest to examine the spectra of branched-chain acids in a non-polar solvent such as hexane.

Spectra were determined on a Beckman Model DU quartz spectrophotometer. Comparisons were made in the usual manner against the solvent at 100% transmission, down to about 215 mμ. Below that point, comparisons were made against the solvent at 10% transmission. Since comparisons in the latter manner were less accurate, all data in critical regions were checked several times, and a frequent check on dark current was maintained. For accurate data in this region, it is mandatory that the slit width be kept constant. Curve III, Figure 2, was checked at least five times on several samples of acid. The readings at 10% transmission were always extended to overlap the readings at 100% transmission. Readings at 10% transmission were taken at 1 mμ intervals. Concentrations were approximately 5×10^{-3} molar, in 95% ethanol.

Branched-chain acids used for these determinations were pure samples whose syntheses have been described in earlier papers in this series. Stearic and palmitic acids were commercial samples purified by fractional distillation of the esters and recrystallization of the acids to constant melting point. The equivalent weights of all acids used were in excellent agreement with the theoretical values.

SUMMARY

It is shown that substituent alkyl groups in fatty acids exert an influence on the ultraviolet absorption band of carboyxl, even when these groups are as remote from carboxyl as the δ-position. The data may be correlated on the assumption that fatty acids exist to some extent in the form of a *quasi* ring. Substituents in the α- and β-positions increase the amount of acid present as a *quasi* ring.

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