

Analysis of Rotatory Dispersion Curves of Configurationally Related Fatty Acids

P. A. Levene, Alexandre Rothen, and R. E. Marker

Citation: *The Journal of Chemical Physics* **1**, 662 (1933); doi: 10.1063/1.1749348

View online: <http://dx.doi.org/10.1063/1.1749348>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/1/9?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Anomalous Sound Dispersion in the Fatty Acids](#)

J. Acoust. Soc. Am. **28**, 649 (1956); 10.1121/1.1908434

[Rotatory Dispersion of Configurationally Related Alkyl Azides](#)

J. Chem. Phys. **5**, 985 (1937); 10.1063/1.1749976

[Rotatory Dispersion of Configurationally Related Unsaturated Secondary Carbinols and Their Corresponding Chlorides](#)

J. Chem. Phys. **5**, 980 (1937); 10.1063/1.1749975

[Analysis of Rotatory Dispersions of Configurationally Related Halides](#)

J. Chem. Phys. **4**, 442 (1936); 10.1063/1.1749878

[Analysis of Rotatory Dispersion Curves. II Configurationally Related Substituted Fatty Acids](#)

J. Chem. Phys. **2**, 681 (1934); 10.1063/1.1749374



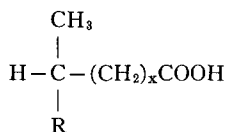
Analysis of Rotatory Dispersion Curves of Configurationally Related Fatty Acids¹

P. A. LEVENE, ALEXANDRE ROTHEN AND R. E. MARKER, *Laboratories of The Rockefeller Institute for Medical Research, New York*

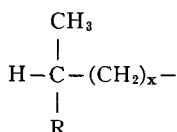
(THE CONTRIBUTION OF MR. MARKER WAS LIMITED TO THE PREPARATION OF SUBSTANCES)

(Received June 12, 1933)

The dispersion curves of fatty acids of the type



have been measured in the visible and in the ultraviolet regions with a view to establishing the sign and the magnitude of the contribution of the radicals



and $-\text{COOH}$ to the total rotation. The variables were R and x, the latter varying from 0 to 2. It was found that the increase of the chain of R had no effect on the sign of the contributions. The change of x from 0 to 1 or 2 resulted in a change of sign of the contribution of $-\text{COOH}$, leaving the sign of the other contribution unchanged. For 4 of the compounds it was possible to determine with precision the values of each of the two contributions.

THERE is comparatively little experimental material on rotatory dispersion extending far into the ultraviolet region of organic compounds and therefore no general rules correlating chemical structure with optical activity could be established to this date. Recently, Werner Kuhn² suggested a simple model on which the newer theories of rotatory dispersion were developed in a comparatively simple manner and he, in cooperation with Freudenberg, applied his theoretical conceptions in order to evaluate the contributions of the individual constituents of the molecule to the total rotation.³ The number of substances thus far analyzed in this manner is as yet small and the conclusions reached by Kuhn and Freudenberg in the case of isolated substances cannot as yet be generalized.

Kuhn has presented his theory in a number of publications and hence it need not be given here.

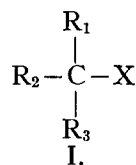
¹ For preliminary publication, see P. A. Levene and Alexandre Rothen, *J. Am. Chem. Soc.* **55**, 429 (1933).

² W. Kuhn and K. Freudenberg, *Hand und Jahrbuch der chemischen Physik*. "Drehung der Polarisationssebene des Lichtes." Leipzig (1932).

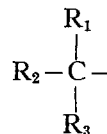
³ W. Kuhn and K. Freudenberg, *Ref. 2*, §26, p. 81.

For convenience of discussion, however, his terminology and his principal conclusions are recapitulated.

Given a simple molecule of the type



(where X is a group or an element with an absorption band in the visible or in the near ultraviolet and R₁, R₂ and R₃ are simple alkyl groups with absorption bands in the Schumann region) and discussing the rotatory contribution of X, Kuhn in his terminology refers to its anisotropy as *induced* anisotropy, whereas the function of the radical



which induces the anisotropy is referred to as the *vicinal* function.

Kuhn stresses the point that the rotatory power of a given molecule is the sum of at least two terms. His original dispersion formulae for each term were similar to the general Drude formulae. More recently Kuhn has proposed a new dispersion formula by using an exponential expression for the absorption curve which is in better agreement with experimental data than the classical "damping" formula. In the simplest case, therefore, the rotation of each molecule may be regarded as the algebraic sum of two contributions, that of the group with the absorption band nearest to the visible and that of the sum of the remaining groups.

Kuhn arrives at the following conclusions in regard to each of the two contributions:

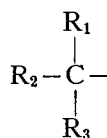
(1) The band in the visible or in the ultraviolet nearest to the visible (weak band) furnishes the major contribution to the rotation in the visible. (However, he reports individual cases in which this is not so.)

(2) The vicinal action of a group, in regard to the rotation in the visible, is due mainly to its strong Schumann bands.

(3) Small changes in the groups with the absorption bands in the more distant ultraviolet region do not alter the sign of the induced anisotropy of the nearest band.

(4) The value of the contribution of a group located at a certain distance from the asymmetric center and possessing an absorption band in the near ultraviolet is not greater than that of a simple alkyl group.

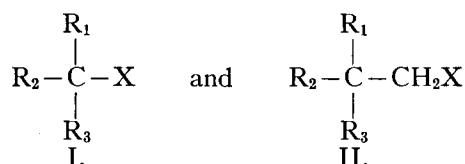
Kuhn himself was cognizant of the lack of precision in the majority of his conclusions. Thus, he emphasizes the difficulty of defining the type of change which is to be classified under the term "small change" and therefore the difficulty of predicting the sign of the induced anisotropy from the structure of the inducing groups. Likewise, the theory does not furnish information as to whether the identical radical



induces anisotropy-factors of the same sign regardless of the character of the group or the

atom with the weak absorption band. Furthermore, the rule of distance is expressed in very indefinite terms and states nothing of the possible changes with distance of the sign of anisotropy or of the possible alternation in the value of the anisotropy-factor of the group.

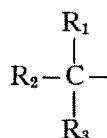
A more exact knowledge of the effect of the distance from the asymmetric carbon on the character of the induced anisotropy of a group would be of great assistance for the purpose of establishing the sign of the anisotropy-factor induced in different groups or elements by an identical radical. The reason is evident. Given the two substances



the first, on substitution of X by Y, may or may not preserve its original configuration, whereas the second one definitely does. Hence, a difference in the sign of the anisotropy of X and Y, if such should occur on substitution of X by Y in substance I, could be attributed to two alternative causes, either to differences in the absorption bands in X and Y or to a Walden inversion having taken place in the course of the reaction of substitution; in substance II, the change could be attributed only to the first-mentioned cause. If a precise knowledge of the effect of distance on the anisotropy of a group could be established, then from the effect of substitution in substances of type II, information could be obtained as to the effect of the identical substitution in substances of type I.

Fortunately, in certain substances of the general formulae I and II, it is possible to correlate their configurations by direct chemical methods without involving a reaction of substitution. In substances of this type it is possible to detect the existence or non-existence of change in sign of the factor of anisotropy of a given group when it is removed from the center of asymmetry by one or more carbon atoms. Should definite rules in this respect be discovered, it would be possible to correlate the configurations of substances of types I and II in cases where direct chemical methods are not available.

Such information would then be the basis on which the vicinal effects of one radical



on different groups or elements could be established.

These considerations led us to undertake a systematic study of the induced anisotropy in a given group as a function of its distance from the asymmetric center.

METHODS OF ANALYSIS

The direct method of evaluation of the rotatory contribution of a given band of a given molecule consists in measuring its circular dichroism. This method is available when the band is situated in the visible or in the near ultraviolet region of the spectrum and when the ratio $(\epsilon_l - \epsilon_r)/\epsilon$ is sufficiently large to permit measurements of circular dichroism. (ϵ_l and ϵ_r are the extinction coefficients for left and right circular polarized light, respectively, $\epsilon_l - \epsilon_r$ = circular dichroism and ϵ = extinction coefficient of the band.)

When this method is not available, an estimation of the direction and in some instances of the numerical values of each rotatory contribution can be obtained from the dispersion curve of the given substance. For this analysis the assumption is made that, as a first approximation, the dispersion curve at some distance from an absorption band can be expressed by two simple Drude terms. Under the dispersion curve in this instance is understood the graph of the function $((1/\alpha), \lambda^2)$.

The curvature of this graph varies in a definite manner depending upon the relationship of the term $A_1/(\lambda^2 - \lambda_1^2)$ to $A_2/(\lambda^2 - \lambda_2^2)$ (members of the two Drude term equation) as was definitely shown by Hunter.⁴ It is evident that for very small intervals of the dispersion curve it is possible to find an expression $A_0/(\lambda^2 - \lambda_0^2)$ which can very nearly satisfy the right-hand term of the expression

$$[M] = A_1/(\lambda^2 - \lambda_1^2) \pm A_2/(\lambda^2 - \lambda_2^2).$$

⁴ H. Hunter, J. Chem. Soc. **125**, 1198 (1924).

The value of λ_0 and its variation with successive small wave-length intervals will provide the required information on the relative values of the four constants of the two Drude term formula.

Four combinations have to be considered in the discussion of the relationship of the dispersion curves to the relative values of the two terms. They are as follows:

Two terms of same sign (for long wave-lengths).

$$(1) \quad \lambda_1 > \lambda_2 [A_1/(\lambda^2 - \lambda_1^2)] > A_2/(\lambda^2 - \lambda_2^2)$$

$$(2) \quad \lambda_1 > \lambda_2 [A_1/(\lambda^2 - \lambda_1^2)] < A_2/(\lambda^2 - \lambda_2^2).$$

Two terms of opposite sign (for long wave-lengths).

$$(3) \quad \lambda_1 > \lambda_2 [A_1/(\lambda^2 - \lambda_1^2)] > A_2/(\lambda^2 - \lambda_2^2)$$

$$(4) \quad \lambda_1 > \lambda_2 [A_1/(\lambda^2 - \lambda_1^2)] < A_2/(\lambda^2 - \lambda_2^2).$$

Case 1

The resulting curve is practically a straight line for the long wave-lengths, the curvature becoming more pronounced for λ approaching λ_1 . The values of λ_0 lie in between λ_1 and λ_2 ($\lambda_2 < \lambda_0 < \lambda_1$) and are progressively shifted towards λ_1 for smaller wave-lengths.

Case 2

This is similar to 1 but the curvature is accentuated. The displacements of λ_0 are greater but we still have the condition $\lambda_2 < \lambda_0 < \lambda_1$.

Case 3

We have here the condition $\lambda_2 < \lambda_1 < \lambda_0$. On the small wave-lengths side we observe a displacement of λ_0 towards λ_1 . The curve in general will deviate from a straight line more than in cases 1 and 2. The apparent shift of λ_0 may be considerable when the whole spectrum is considered. Rotations in the visible region may lead to λ_0 values 1500A higher than that obtained from rotation in the ultraviolet. (The more so, the more nearly A_1 and A_2 approach the same magnitude.) (See Table XI.)

Case 4

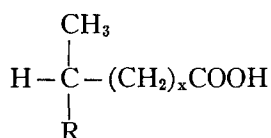
With decreasing wave-lengths, the curve shows first a minimum at λ_m ($\lambda_2 < \lambda_1 < \lambda_m$), then increases to $+\infty$, reappears at $-\infty$ and ap-

proaches zero for the smaller wave-lengths. (The rotation goes through a maximum, decreases, reaches a zero value and increases in the opposite direction.) The λ_0 values calculated from measurements in the long wave-lengths region are smaller than λ_2 ($\lambda_0 < \lambda_2 < \lambda_1$) and become negative for λ values approaching λ_m .

From this analysis it follows that the graph $((1/\alpha), \lambda^2)$ leads to information as to the direction of rotation of each of the two contributions and of their relative values.

STATEMENT OF THE SPECIFIC PROBLEM

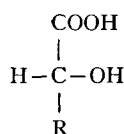
The present paper is concerned with the analysis of the series of disubstituted carboxylic acids of the general type



(x varied from 0 to 2 and R varied from C_2H_5 to $\text{C}_{10}\text{H}_{21}$). In Table I are given the maximum rotations of the members of several homologous series of configurationally related disubstituted carboxylic acids. The correlation was established by direct chemical methods.^{5, 6} In the series of acids given in Table I some are dextrorotatory and others are levorotatory. In those that have been studied, the carboxyl group was found to be anisotropic inasmuch as the rotatory dispersion curves of these substances were distinctly different from those of the optically active trisubstituted methanes. It is therefore warranted to regard the carboxyl group as furnishing one contribution to the rotation in the visible by the anisotropy of its absorption band or bands whereas the rest of the molecule furnishes the sum of the other contributions. A new group of bands characteristic for COOH has recently been located at 1750A, in addition to the

⁵ P. A. Levene and R. E. Marker, *J. Biol. Chem.* **91**, 77 (1931); **25**, 153 (1932); **98**, 1 (1932).

⁶ The configurations are related among themselves and have no bearing on the configuration of acids of the type

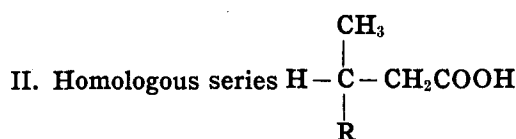


formerly known band at $\lambda = 2000\text{--}2100\text{A}$.⁷ This fact is important to bear in mind in order to explain the direction of the rotatory contribution of the carboxyl group in the series of acids given in Table I.

RESULTS OF THE ANALYSIS OF THE ROTATORY DISPERSION CURVES

I. Disubstituted acetic acids and their corresponding ethyl esters

In the case of the members of this homologous series, the dispersion curves may be expressed from the visible far into the ultraviolet region by a single Drude term, the λ_0 value being the same for all members and equal to 1850A. In the case of the propionic acid series, the λ_0 of the first member of the two term expression was found to be $\approx 2000\text{A}$, which corresponds to the position of the first absorption band of the carboxyl group. The λ_0 corresponding to the esters of the acetic acid series derivatives are even lower (1550 and 1480A for the ethyl esters of α -methylbutyric and α -methylvaleric acids, respectively). The only conclusion to be drawn is that their curves belong to the type described above under (1) or (2), i.e., two Drude terms of the same sign. The apparent validity of one Drude term to express the dispersion with a fair degree of accuracy over a considerable region of the spectrum (from 6000 to 2400A) is explainable on two alternate assumptions: first, that the contribution of the first band of the COOH or COOC_2H_5 ($\lambda \approx 2000\text{A}$) is very small in comparison with the contribution of the rest of the molecule; second, that not this band but the second band of the COOH group ($\lambda \approx 1750\text{A}$) furnishes the first contribution. This question could be solved by a study of the dichroism in the region of 2000A.



As compared with the series of disubstituted acetic acids, this series is more complex and more instructive. From Table I it will be seen

⁷ G. Scheibe, F. Povenz, and G. F. Lindstrom, *Zeits. f. physik. Chemie* **B20**, 283 (1933).

that in the visible region the rotations of the members of this series differ from those of the previous one in two respects: first, not all members of this series rotate in the same direction as is the case in the acetic acid series; second, the values of the rotations of the individual members of this series are lower than those of the corresponding members of the previous series. The analysis of the dispersion curve gives a ready explanation of both peculiarities.

(a) *The case of the first member.* The curves expressing the dispersion of the acid and of its ester represent a typical example of case 4, above. The experimental values agree well with those calculated by a formula of this type (see Fig. 1, curves 1 and 2, Fig. 2, Table VII and Table VIII). The position of $\lambda_1(2050\text{\AA})$ corresponds to the known first absorption band of the COOH group. For λ_{5893} , for instance, the first contribution (COOH) in the case of β -

methylvaleric acid is 70 percent of the sum of the other contributions. The dispersion curve shows a typical abnormal course reaching a minimum ($\lambda_m=2860\text{\AA}$) which is followed for smaller wave-lengths by a sharp rise in the $1/[\alpha]$ values.

The value ($\lambda_m=2860\text{\AA}$) calculated for the position of the minimum of the dispersion curve is easily obtained by equating the first derivative of the dispersion equation to zero.

$$\frac{11.68}{(\lambda_m^2 - 0.034)^2} - \frac{8.088}{(\lambda_m^2 - 0.042)^2} = 0.$$

This is a good example to demonstrate that, although the dispersion in the visible region can be accurately expressed by one Drude term, the λ_0 value found (1120 \AA) has no significance since the dispersion in the ultraviolet definitely proves the presence of two terms of opposite sign, the value of the second term for the visible region being greater than that of the first.

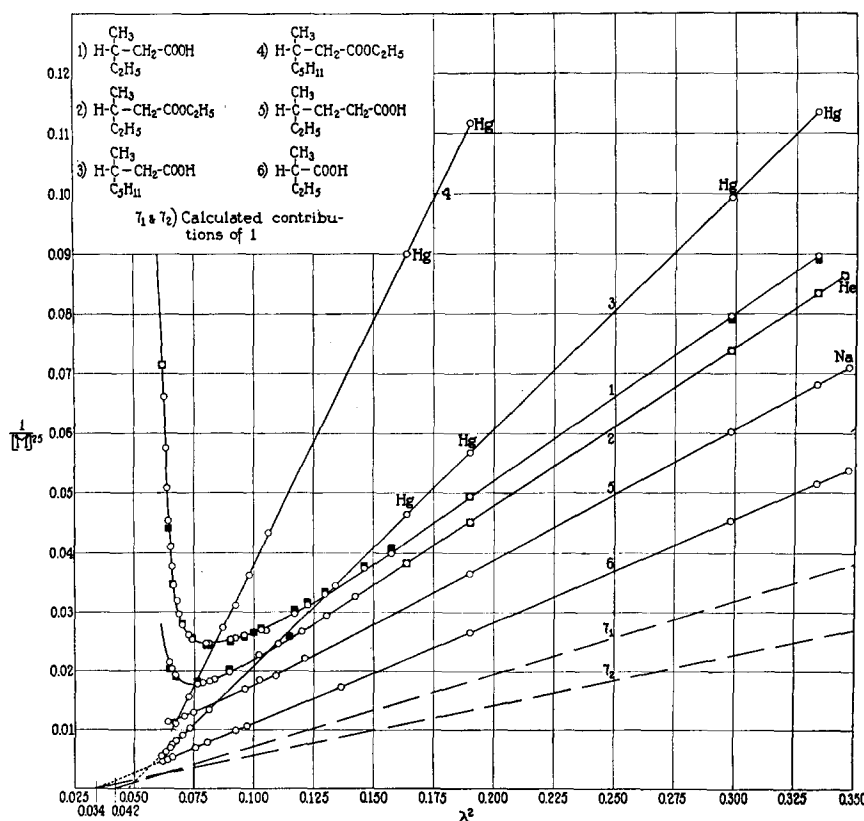


FIG. 1. Examples of the most characteristic dispersion curves. Circles represent experimental values, solid squares, calculated.

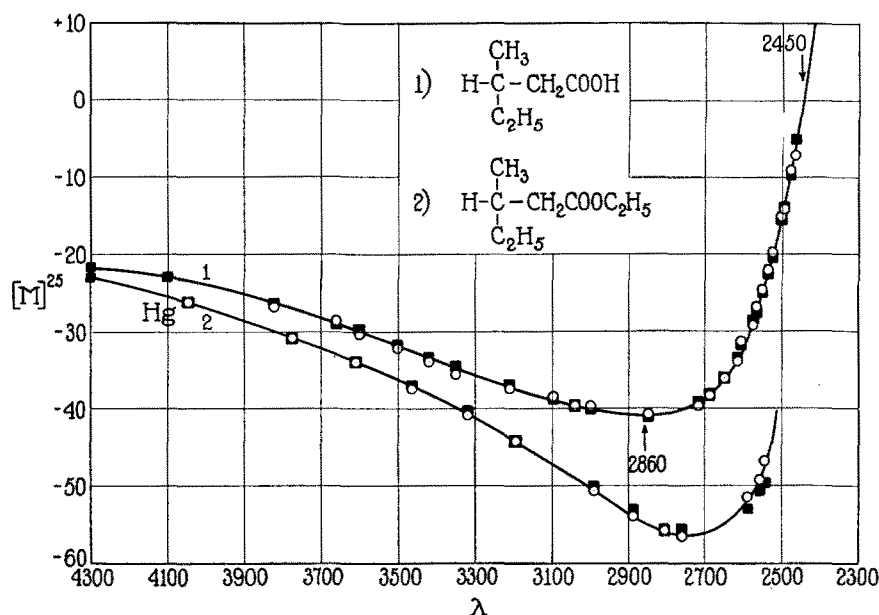


FIG. 2. Dispersions of two compounds exhibiting typical abnormality. Circles represent experimental values, solid squares, values calculated from a two Drude term formula (Tables VII and VIII).

The values calculated from a two Drude term formula valid for the ultraviolet region are about 0.5 percent higher than the experimental figures for $\lambda > 4500\text{\AA}$.

It will be seen from the comparison of the figures in the third and fourth columns of Table VIII that the rotations of the ester in the visible region, like those of the corresponding acid, can be represented within 0.1 percent by *one* Drude term. The λ_0 value has, of course, no physical significance. The values calculated from a two Drude term formula, valid for the ultraviolet region, may be seen in the fifth column. The magnitude of both terms has been indicated for the visible region to show how the observed rotation is but a small fraction of the rotation of each term.

The agreement between calculated and observed rotations is very good if we consider that for the small wave-lengths, the observed rotation is only one-tenth of the value of each Drude term.

(b) *The case of the higher members.* The character of the dispersion curves of these members is more pronounced in their esters. The curves belong to type 3. The ethyl ester of β -methylcaproic acid is a very good example of the limiting case in which the value of A_1 approaches

that of A_2 . For this substance, even in the visible region, the dispersion cannot be expressed by the one Drude term formula. The apparent λ_0 for the one Drude term formula is 3630\AA , calculated from the values $[M]_{5780}^{25}$ and $[M]_{4358}^{25}$, thus showing a striking shift from the position of the first absorption band. As expected, the rotatory dispersion curves present a strong convex curvature. Even in the visible, discrepancies as high as 20 percent are obtained between rotations calculated from a one Drude term formula and the observed value. (See Table XI.)

The low rotatory values observed in the visible region for this substance are due not to the low anisotropy factors of the absorption bands but to the fact that the two contributions are of opposite sign, the two constants A_1 and A_2 being nearly equal.

For values of λ approaching λ_1 , the first term, $A_1/(\lambda^2 - \lambda_1^2)$, becomes predominant and the observed rotation practically represents the contribution of the first term. This is well demonstrated by a comparison of the dispersion of the ethyl ester of β -methylcaproic acid with that of the ethyl ester of β -methylcaprylic acid. (See Tables XI and XIV.)

$$\frac{[M]_{5780}^{25} \beta\text{-methylcaproic ethyl ester}}{[M]_{5780}^{25} \beta\text{-methylcaprylic ethyl ester}} = 0.173$$

and

$$\frac{[M]_{2600}^{25} \beta\text{-methylcaproic ethyl ester}}{[M]_{2600}^{25} \beta\text{-methylcaprylic ethyl ester}} = 0.918.$$

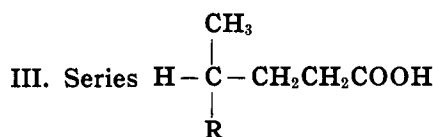
In other words, the anisotropy-factor of the COOC_2H_5 group of those two compounds is of the same order of magnitude although the rotation observed in the visible region is four times greater for β -methylcaprylic ethyl ester than for β -methylcaproic ethyl ester.

It is noteworthy that the calculated λ_1^2 of the first term of the two Drude term formulae, expressing the experimental dispersion curves of the β -methylcaproic and β -methylcaprylic esters is higher than the λ_1^2 found for β -methylvaleric acid (0.052 compared to 0.042). It is realized that too great significance should not be attached to this difference since it is possible to obtain a fair agreement of the experimental data by changing correspondingly in each formula the λ_0 values of both terms. Nevertheless, this difference does seem to be real. It should be noted here that results recently published⁸ show that a shift of the first band is observed (from about 2030Å to about 2130Å) when the absorption of acetic acid is compared with that of its ethyl ester.

As may be seen from Table XIII, the dispersion of β -methylcaprylic acid in the ultra-violet region may be well expressed by one Drude term with a λ_0^2 value (0.0484) noticeably higher than the λ_0^2 (0.0455) obtained from measurements in the visible region. In other words, the dispersion curve is not a straight line over the entire spectrum and the curvature is concave instead of convex as would have been expected for two terms of opposite sign. However, on account of the high value obtained for λ_0^2 it would appear that the first two terms do not have the same sign. It is possible that the second term departs strongly from a linear relation but there is also the possibility that the dispersion

due to a single band is greater than that required by a formula of the type $A/(\lambda^2 - \lambda_0^2)$.⁹ Nevertheless, the contribution of the first band undoubtedly has the sign of the observed rotation. This is the important fact which is revealed by our experiments.

(c) *Cause of the differences in rotation in the visible between the first and the higher members of this series.* From the foregoing considerations it is apparent that the differences in the direction of rotation in the visible between the first and the higher members is due not to the differences in the sign of the factors of anisotropy of the COOH absorption band of the respective members of the homologous series, but to the fact that in the case of the first member, the second contribution predominates in the rotation in the visible region of the spectrum whereas in the higher members the first contribution (the carboxyl) predominates.



All members of this series rotate in the visible part of the spectrum in the same direction. Rotatory dispersion measurements were made on one member only (see Table XV and Fig. 2, curve 5). The dispersion curve belongs to the same type as the first member of the preceding series. There is no doubt that a minimum could be detected if the curve could be extended sufficiently far into the ultraviolet.

From the values in the last three rows of Table XV it may be seen that this minimum must be very near 2530Å. (The value calculated from the equation in column 5 is 2500Å.) The absorption in this region, however, was too great to permit measurement of the rotation. As regards measurements in the visible region, the low value found for λ_0^2 (0.021) is the only indication that the dispersion is truly expressed by two terms of Drude of opposite sign, the one with the greater wave-length being smaller than the other (case 4).

Although there are two carbon atoms between

⁸ H. Ley and G. Arends, *Zeits. f. physik. Chemie* **B17**, 177 (1932).

⁹ W. Kuhn and K. Freudenberg, *Ref. 2*, pp. 76-79.

the asymmetric carbon atom and the carboxyl group, the anisotropy of the latter is still very important, its contribution being roughly 50 percent of that of the rest of the molecule.

In view of the fact that the direction of rotation is identical for all members of this homologous series, it is admissible to conclude that in all of them the two contributions are of opposite sign, the second contribution having the greater value for the visible and for the near ultraviolet regions.

GENERAL CONCLUSIONS

(1) In each of the three homologous series, acetic, propionic and butyric, the direction of rotation of each contribution remains constant in the entire series as long as R_1 is smaller than R_2 or *vice versa*, even in the case when the directions of rotation of individual members in the visible region of the spectrum are of opposite sign.

(2) The change of the distance of the groups COOH or COOC₂H₅ from the asymmetric center (by the introduction of CH₂ groups between the asymmetric carbon atom and the carboxyl group) has no effect on the direction of the second contribution which is furnished by the anisotropies of the bands located in the Schumann region. Kuhn has postulated that these groups contribute to the rotation in the visible principally by their vicinal effect and that this effect is not altered by small changes in their character. The direction of their own contribution, however, may change under these conditions. In the case of the substances here discussed, the direction of their contribution was not altered by the change of the distance of the anisotropic groups COOH or COOC₂H₅. Whether this is a general rule or applies only to the present series of substances, remains to be established.

(3) The change of the distance of the COOH or COOC₂H₅ groups from the asymmetric center brings about a change in the direction of the first contribution (carboxyl group) so that in the substituted acetic acids, the two contributions are of the same sign, whereas in the disubstituted propionic they are of opposite sign. Further increase in the distance of the COOH or COOC₂H₅ from the asymmetric carbon atom

by CH₂ does not alter the signs of either one of the two contributions characteristic of the disubstituted propionic acids.

(4) The change of sign of the first contribution (carboxyl group) on passing from the acetic to the propionic acid series may be due to one of two causes: either to change of sign of the anisotropy-factor of the identical absorption band or to the circumstance that in each series a different band of the COOH group is rendered anisotropic. As yet no decision can be made between the two possibilities.

(5) More precision will have to be introduced in the formulation of the distance rule of Tschugaeff and Kuhn¹⁰ inasmuch as the carboxyl group at considerable distance from the asymmetric carbon atom retains considerable anisotropy. It will be shown in a later publication that the same phenomenon holds for halides and for other groups or atoms with absorption bands in the near ultraviolet.

EXPERIMENTAL

Compounds

All the compounds were prepared as previously described.⁵ It was necessary, of course, to obtain them in the highest possible state of purity. It may be mentioned that, in general, compounds directly resolved (e.g., the acids used here) are of a high degree of purity, as a result of the numerous recrystallizations required for the resolution. The acids were purified through their sodium salts. All the final distillations were made in all glass apparatus and the substances carefully fractionated. At least two fractions were made in the last distillation and the product was used only if the indices of refraction were the same for both fractions. All the *acids* were titrated. Analyses for C and H on each substance gave figures in agreement with the calculated values within the limits of experimental error (± 0.1 percent).

The preparation of β -methylcaproic acid was duplicated. Both products had the same physical constants (n_D^{25} and δ_4^{25}) and exhibited the same dispersion. Titration was the most sensitive test, indicating that all our compounds, with the possible exception of α -methyldodecylic acid

¹⁰ W. Kuhn and K. Freudenberg, Ref. 2, §35, p. 111.

(accurate titration difficult), had a purity of at least 99.5 percent.

Solvent

N-Heptane was chosen for solvent, since it is the only hydrocarbon transparent in the ultra-violet region which is obtainable in large amounts in a pure state. The hexane, hitherto employed almost exclusively, is an ill-defined mixture of hydrocarbons. Before use, the *N*-heptane (obtained from California pine trees) was purified according to Henri.¹¹ After purification it had the following physical constants.

n_D^{25} 1.3850 δ^{25} 0.67943 B.P. 98.4°.

General

All $[M]$ values (molecular rotations) indicated, correspond to substances completely resolved. The molecular rotations were calculated from the usual formula $[M] = 10\alpha/lc$ where c = concentration in mol per liter and l = length of the tube in decimeters. When substances not resolved to the maximum were used, the proper coefficient was applied in calculating $[M]$ from the experimental α . Maximum values for $\lambda = 5893$ have been published previously by Levene and Marker⁵ for all the acids presented in this communication. The absolute magnitudes of $[M]$ are only accurate to within a few percent but, of course, the dispersion measurements are of a much higher degree of accuracy (in the visible region from 0.1 percent to 0.01 percent, according to the magnitude of α).

All the $[M]$ values of the acids determined in heptane are 1 to 3 percent higher than in the homogeneous state.

Densities are expressed in g/ml (specific gravity 25/4 in vacuo).

Indices of refraction were determined with an Abbe refractometer accurately checked and are correct to ± 0.0001 . Wave-lengths are expressed in Angstrom units but to comply with the usual convention they are given in microns in the Drude equations and in Fig. 1.

Measurements in the visible region

Rotatory measurements in the visible region were made with a large Schmidt and Haensch

polariscope (Lippich type) reading to one-thousandth of a degree. The instrument was mounted on an optical bench permitting the use of 1-meter tubes. The half shadow angle adopted for all measurements was 3°. The apparatus was provided with a monochromator and color filter to eliminate the diffused light. All the measurements were carried out with monochromatic lights only. The sources were the following:

Hg arc (quartz lamp 6 amp.). Lines: 5790.7, 5769.6, 5460.7, 4358.3 and 4046.6. (For large values of α only, measurements were carried out with the lines 5790.7 and 5769.6 separately, the optical mean 5780.1 being used for most of the measurements.)

He arc. A hot cathode lamp, previously described, was found very satisfactory.¹² Lines: 6678.1 and 5875.6.

Na arc. The recently developed Osram sodium arc lamp was used. The line 5892.6 is much less intense than the yellow line obtained in the above-mentioned lamp.

To insure their correct position and thus eliminate the possibility of a shift of the zero of the apparatus, all these lamps were mounted on an optical bench.

Each α value given in the tables (for the yellow and green part of the spectrum) is the arithmetical mean of at least 20 readings, 10 for the empty tube and 10 for the tube when filled. The mean values of duplicate series of 10 readings agreed within 0.001°. When the angle to determine was very small, the mean values of duplicate series could be obtained within 0.0005 by exercising extra care. The zero position was determined for each wave-length separately. The shift of the zero position with wave-length could not be determined once and for all as it depended on the condition of strain of the glass and plates of the tubes. The rotation for 6678.1, 4358.3, 4046.6, were all photographically determined. The camera used for these determinations (see Fig. 3) consisted simply of a plateholder (6×9 cm) capable of vertical motion, by means of a rack and pinion in front of the eyepiece. No extra lens was necessary. In order to reduce the time exposure it was arranged that the images obtained were small (0.1 cm diam.); with Eastman plates No. 40, the time of exposure

¹¹ A. Castille and V. Henri, Bull. Soc. Chem. Biol. 6, 299 (1924).

¹² A. Rothen, Science 74, 204 (1931).

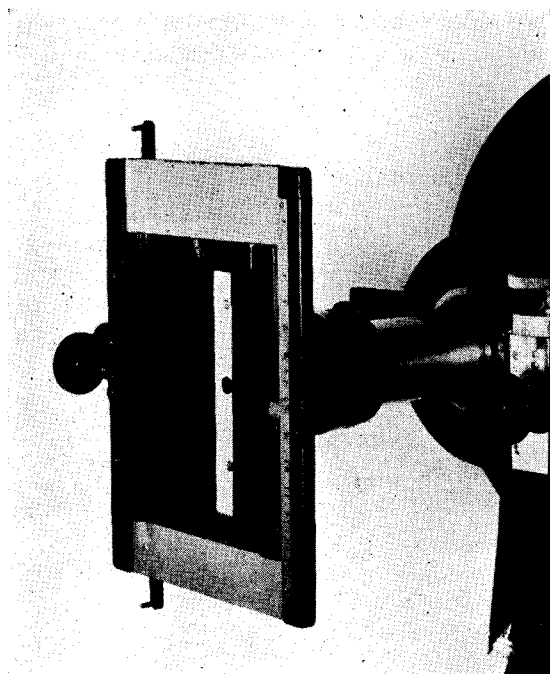


FIG. 3. Camera adjusted to the eyepiece of Schmidt and Haensch polariscope (Large Universal model)

corresponding to 4358.3 and 4046.6 was 10'' and 60'', respectively. For each determination a series of photographs was taken with settings of the analyzer 0.005° apart. The sensitivity obtained was 0.003° under the best conditions used. The photographs were examined with an ordinary binocular magnifying glass.

Temperature

All measurements were performed at 25°C. Water-jacketed tubes were used throughout. A thermostat (ca. 100 liters) in conjunction with a small pump ensured constant temperature of the polariscope tubes (25°C ± 0.02°). Variations greater than 0.02°C would have rendered useless all photographic measurements for heptane solutions in tubes 40 cm long, the variation in refraction thus produced being sufficient to outfocus the images on the photographic plate. The same temperature control was employed for measurements in the ultraviolet.

Measurements in the ultraviolet region

The apparatus used was of the type described by Kuhn.¹³ The Rochon prisms (polarizer and analyzer) had the following dimensions, 1.5 × 1.5

× 3 cm. The angle between the direction of polarization of the two halves of the polarizer was 6°. The image of the surface of the polarizer was focussed on the slit of a medium size Hilger spectrograph No. E316 by means of a quartz-fluorspar lens having a focal length of 27 cm. The analyzer was mounted on a graduated circle reading to 0.01°. A condensed spark between two tungsten-steel electrodes was used as the source of light.

In estimating the error $\Delta\lambda$ made in the reading of λ for which the two half spectra have the same intensity on the photographic plate, the expression $1/(\Delta\lambda) = k\delta\alpha/(\delta\lambda)$ may be used as a first approximation. When both the rotation and the dispersion of the tested compound have large values, the coefficient $\delta\alpha/(\delta\lambda)$ is large and hence the error $\Delta\lambda$ is reduced.

The apparatus was checked with 2 quartz plates calibrated by the Bureau of Standards ($\alpha_{5461}^{20} = 41.60^\circ$ and $\alpha_{5461}^{20} = 0.979$). The experimental values agreed well with the figures calculated from Lowry's equation.¹⁴ The figures obtained for the plate $\alpha_{5461}^{20} = 0.979$ (for which the readings were more difficult) were as follows:

$$\alpha_{2320} = \text{Found } 7.30 (\text{calc. } 7.28) \alpha_{2685} \\ \text{Found} = 4.90 (\text{calc. } 4.92).$$

$$\alpha_{2940} = \text{Found } 3.90 (\text{calc. } 3.93) \alpha_{3330} \\ \text{Found} = 2.90 (\text{calc. } 2.92).$$

As can be seen, the readings are correct to within a few hundredths of a degree.

TABLE I. Maximum molecular rotations of configurationally related aliphatic acids without solvent¹⁵ $[M]^{25}_{5892.6}$.

α -Methylbutyric acid*	-18.0	γ -Methylcaproic acid*	-13.6
Ethyl ester*	-22.9		
α -Methylvaleric acid*	-21.4	γ -Methylheptylic acid	-6.9
Ethyl ester*	-27.5		
α -Methylcaproic acid	-24.3	γ -Methylcaprylic acid	-4.1
α -Methylnonylic acid	-27.3	γ -Methylnonylic acid	-1.9
α -Methyldodecylic acid*	-27.5	δ -Methylheptylic acid	-11.1
β -Methylvaleric acid*	-10.4	δ -Methylcaprylic acid	-3.7
Ethyl ester*	-11.5		
β -Methylcaproic acid*	+3.6	δ -Methylnonylic acid	-1.7
Ethyl ester*	+0.69		
β -Methylheptylic acid*	+6.1	δ -Methyldodecylic acid	-0.6
β -Methylcaprylic acid*	+8.1	ϵ -Methylcaprylic acid	-12.2
Ethyl ester*	+4.1		

¹⁴ T. M. Lowry and W. R. C. Adams, Phil. Trans., Roy. Soc. **A226**, 391 (1927).

¹⁵ Rotatory dispersion curves have been determined only for compounds marked with an asterisk.

¹³ W. Kuhn, Ber. chem. Ges. **62**, 1727 (1929).

TABLE II. Rotatory dispersion of *levo*- α -methylbutyric acid in heptane.

Constants of sample: $\delta_4^{25} = 0.9340$, $n_D^{25} = 1.4038$. Visible region:¹⁶ Concentration 0.8543 *M*, $\delta_4^{25} = 0.7030$, $l = 40$ cm. U.V. region: Concentration 0.8563 *M*, $\delta_4^{25} = 0.7030$, $l = 10$ cm.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = -\frac{5.8110}{\lambda^2 - 0.03526}$ ¹⁷	λ	α^{25}	$[M]^{25}$	$[M]^{25} = -\frac{5.8110}{\lambda^2 - 0.03526}$
6678.1	-3.98 ₀	-14.1 ₆	-14.1 ₆	3040	-7.05	-100.0	-101.6
5892.6	-3.237	-18.62 ₁	-18.62 ₇	2980	-7.55	-107.1	-108.5
5780.1	-5.469	-19.44 ₆	-19.44 ₆	2880	-8.55	-121.3	-121.8
5460.7	-6.217	-22.10 ₄	-22.10 ₁	2832	-9.05	-128.4	-129.3
4358.3	-10.56 ₈	-37.56 ₄	-37.56 ₄	2745	-10.15	-144.0	-144.9
3690	-4.05	-57.4	-57.6	2571	-13.05	-186.6	-188.4
3540	-4.55	-64.6	-64.5	2529	-14.05	-200.8	-202.5
3410	-5.05	-71.7	-71.7	2505	-14.55	-206.4	-209.5
3290	-5.55	-78.8	-79.6	2490	-15.05	-215.0	-219.0
3115	-6.55	-92.9	-94.1	2380	-1.70	-241	-272
					(1 cm)		

TABLE III. Rotatory dispersion of *levo*-ethyl ester of α -methylbutyric acid without solvent.

Constants of sample: $\delta_4^{25} = 0.8689$, $n_D^{25} = 1.3973$. Visible region: $l = 10$ cm. U.V. region: $l = 5$ cm. Measurements on dextro form.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = -\frac{7.2843}{\lambda^2 - 0.02923}$	λ	α^{25}	$[M]^{25}$	$[M]^{25} = -\frac{7.2843}{\lambda^2 - 0.02923}$
5780.1	-2.880	-23.89	-23.89	3275	-5.65	-93.7	-93.4
5460.7	-3.264	-27.08	-27.08	3175	-6.15	-102.0	-101.8
4358.3	-5.46 ₈	-45.3 ₂	-45.3 ₂	3090	-6.65	-110.3	-110.0
4046.6	-6.56 ₀	-54.2 ₆	-54.1 ₆	3010	-7.15	-118.6	-118.7
3590	-4.40	-73.0	-73.1	2910	-7.90	-131.1	-131.4
3380	-5.15	-85.5	-85.7	2883	-8.15	-135.2	-135.2
3330	-5.40	-89.6	-89.2	2585	-2.45	-203	-194
					(1 cm)		

TABLE IV. Rotatory dispersion of *levo*- α -methylvaleric acid in heptane.

Constant of sample: $n_D^{25} = 1.4113$. Visible region: Concentration 0.7857₇ *M*, $\delta_4^{25} = 0.7031$, $l = 40$ cm. U.V. region: Concentration 0.8910₈ *M*, $\delta_4^{25} = 0.7066$, $l = 10$ cm.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = -\frac{6.7499}{\lambda^2 - 0.03496}$	$[M]^{25} = -\frac{6.770}{\lambda^2 - 0.03458}$	λ	α^{25}	$[M]^{25}$	$[M]^{25} = -\frac{6.7499}{\lambda^2 - 0.03496}$	$[M]^{25} = -\frac{6.770}{\lambda^2 - 0.03458}$
6678.1	-5.16	-16.4 ₁	-16.4 ₂	—	2835	-13.10	-147.0	-148.6	-147.8
5875.6	-6.837	-21.75 ₀	-21.75 ₅	—	2727	-15.10	-169.4	-171.2	-170.1
5780.1	-7.092	-22.56 ₁	-22.56 ₄	—	2644	-17.10	-191.9	-193.1	-191.5
5460.7	-8.060 ₈	-25.64 ₂	-25.64 ₂	—	2605	-18.10	-203.1	-205.2	-203.3
4358.3	-13.69 ₀	-43.55	-43.55	—	2574	-19.10	-214.1	-215.7	-213.6
3910	-5.10	-57.2	-57.2	-57.2	2540	-20.10	-225.6	-228.4	-226.0
3774	-5.60	-62.8	-62.8	-62.7	2513	-21.10	-236.8	-239.4	-236.8
3173	-9.10	-102.0	-102.7	-102.4	2488	-22.10	-248.0	-250.5	-247.7
2902	-12.10	-135.8	-137.0	-136.3	2420	-2.60	-280	-286	-282
						(1 cm)			

¹⁶ For all tables, under the term "visible region" we understand measurements made from 6678.1 Å. to 4046.6 Å., the rotations being observed with the large Schmidt and Haensch instrument. The term "U.V." comprises all measurements for $\lambda < 4046.6$ Å.

¹⁷ Lowry (Soc. 103, 1074 (1914)) gives 0.0375 for λ_0^2 from measurements in homogeneous state in the visible region.

TABLE V. Rotatory dispersion of levo-ethyl ester of α -methylvaleric acid without solvent.

Constants of sample: $\delta_4^{25} = 0.8643$, $n_D^{25} = 1.4032$. Visible region: $l = 10$ cm. U.V. region: $l = 5$ cm. Measurements on dextro form.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{8.9368}{\lambda^2 - 0.02225}$
5780.1	-2.714	-28.66	-28.66
5460.7	-3.192	-32.37	-32.38
4358.3	-5.257	-53.2 ₉	-53.2 ₉
4046.6	-6.21 ₀	-62.9 ₇	-63.1 ₈
3440	-4.58	-92.9	-93.0
3300	-5.08	-103.0	-103.1
3240	-5.33	-108.1	-108.0
3180	-5.58	-113.2	-113.3
3080	-6.08	+123.3	-123.1
2985	-6.58	-133.4	-133.1
2940	-6.83	-138.5	-139.2

 TABLE VI. Rotatory dispersion of levo- α -methyldecylidic acid in heptane.

Constant of sample: $n_D^{25} = 1.4403$. Visible region: Concentration 0.8489 M , $\delta_4^{25} = 0.7240$, $l = 20$ cm. U.V. region: Concentration 0.8573 M , $\delta_4^{25} = 0.7244$, $l = 10$ cm. Measurements on dextro form.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{8.6638}{\lambda^2 - 0.03446}$
6678.1	-3.57 ₀	-21.0 ₂	-21.0 ₅
5875.6	-4.733	-27.87 ₇	-27.87 ₉
5780.1	-4.909	-28.91 ₄	-28.91 ₄
5460.7	-5.580	-32.86 ₆	-32.85 ₁
4358.3	-9.46 ₀	-55.7 ₂	-55.7 ₂
3890	-6.40	-74.6	-74.1
3665	-7.40	-86.3	-86.7
3510	-8.40	-98.0	-97.6
3248	-10.40	-121.3	-122.0
3180	-10.90	-127.1	-130.0
3120	-11.40	-133.0	-138.0
2670	-2.00	-233	-235
	(1 cm)		
2630	-2.10	-245	-249
	(1 cm)		

 TABLE VII. Rotatory dispersion of levo- β -methylvaleric acid in heptane.

Constant of sample: $n_D^{25} = 1.4140$. Visible region: Concentration 0.8598 M , $\delta_4^{25} = 0.7060$, $l = 40$ cm. U.V. region: Concentration 0.8598 M for first 8 measurements, 0.8616 M for the others. $l = 20$ cm for $\lambda 3820$ to 3040 , 10 cm for $\lambda 3210$ to 2500 , 5 cm for $\lambda 2495$ to 2464 , 1 cm for last two measurements.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{3.5876}{\lambda^2 - 0.01254}$	$[M]^{25} = \frac{8.088}{\lambda^2 - 0.042}$	λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{8.088}{\lambda^2 - 0.042}$
6678.1	-2.84 ₈	-8.27 ₂	-8.27 ₈	-8.33	2650	-3.10	-36.0	-35.9
5780.1	-3.837 ₆	-11.15 ₇	-11.15 ₇	-11.23	2615	-2.90	-33.7	-33.1
5460.7	-4.322 ₁	-12.56 ₆	-12.56 ₀	-12.64	2605	-2.70	-31.3	-32.2
4358.3	-6.95 ₅	-20.22	-20.22	-20.22	2575	-2.50	-29.0	-28.8
3820	-4.60	-26.7	-26.5	-26.5	2568	-2.30	-26.7	-27.8
3660	-4.90	-28.5	-28.9	-28.9	2550	-2.10	-24.4	-25.2
3600	-5.20	-30.2	-29.8	-29.8	2535	-1.90	-22.0	-22.6
3500	-5.50	-32.0	-31.5	-31.5	2525	-1.70	-19.7	-20.8
3420	-5.80	-33.7	-32.9	-32.9	2500	-1.30	-15.1	-15.3
3350	-6.10	-35.5	-34.1	-34.1	2495	-0.60	-14	-14.0
3040	-6.70	-39.0	-39.5	-39.5	2478	-0.40	-9.0	-9.4
3210	-3.20	-37.1	-36.7	-36.7	2464	-0.30	-7.0	-5.0
2690-3100	-3.30	-38.3	-38.1	-38.6	2395	+0.55	+64	+26
2720-3000	-3.40	-39.5	-39.2	-40.1	2300	+0.10	+120	+120
2850	-3.50	-40.6	-41.1	-41.1	conc. 0.086 M			

TABLE VIII. Rotatory dispersion of levo-ethyl ester of β -methylvaleric acid without solvent.

Constants of sample: $\delta_4^{25} = 0.8644_3$, $n_D^{25} = 1.4040$. Visible region: $l = 10$ cm. U.V. region: $l = 5$ cm, $l = 1$ cm for last 3 measurements.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{3.7826}{\lambda^2 - 0.01911}$	$[M]^{25} = \frac{11.614}{\lambda^2 - 0.0420}$	λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{11.614}{\lambda^2 - 0.0420}$	$[M]^{25} = \frac{15.364}{\lambda^2 - 0.0373}$
				$+ 38.30_1$ $- 49.89_4$	3775	$- 9.20$	$- 30.7$	$- 30.5$	
5875.6	$- 6.947$	$- 11.58_3$	$- 11.59_9$	$- 11.59_3$	3610	$- 10.20$	$- 34.0$	$- 33.7$	
				$+ 39.76_1$ $- 51.76_6$	3465	$- 11.20$	$- 37.3$	$- 36.9$	
5780.1	$- 7.193$	$- 11.99_3$	$- 12.00_8$	$- 12.00_8$	3320	$- 12.20$	$- 40.7$	$- 40.5$	
				$+ 45.33_2$ $- 58.88_9$	3195	$- 13.20$	$- 44.0$	$- 43.9$	
5460.7	$- 8.129$	$- 13.55_4$	$- 13.55_4$	$- 13.55_7$	2990	$- 15.15$	$- 50.5$	$- 49.9$	
				$+ 78.50_0$ $- 100.65$	2887	$- 16.15$	$- 53.8$	$- 52.8$	
4358.3	$- 13.28$	$- 22.14$	$- 22.14$	$- 22.15$	2850	$- 16.40$	$- 54.7$	$- 53.7$	
				$+ 95.39_7$ $- 121.51$	2805	$- 16.65$	$- 55.6$	$- 55.7$	
4046.6	$- 15.66$	$- 26.11$	$- 26.15$	$- 26.11$	2760	$- 16.90$	$- 56.4$	$- 55.4$	
					2590	$- 3.10$	$- 51.7$	$- 52.8$	
					2558	$- 2.95$	$- 49.2$	$- 50.5$	
					2545	$- 2.80$	$- 46.7$	$- 49.3$	

TABLE IX. Rotatory dispersion of dextro- β -methylcaproic acid in heptane.¹⁸

Constant of sample: $n_D^{25} = 1.4220$. Visible region: Concentration $0.8678 M$, $\delta_4^{25} = 0.7090$, $l = 100$ cm. U.V. region: Concentration $0.8556 M$, $\delta_4^{25} = 0.7086$, $l = 10$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{1.2580}{\lambda^2 - 0.02845}$
6678.1	2.62	3.02	3.01 ₃
5875.6	3.441	3.965	3.972
5780.1	3.572	4.116	4.116
5460.7	4.049	4.666	4.664
4358.3	6.76 ₀	7.79 ₀	7.79 ₀
4046.6	3.22 (40 cm)	9.28	9.30
3260	1.40	16.4	16.2
3050	1.70	19.9	19.5
2980	1.75	20.5	20.8
2765	2.30	26.9	26.2
2680	2.50	29.2	29.0
2610	2.70	31.5	31.7
2570	2.85	33.3	33.4
2390	0.45 (1 cm)	53	43.9

¹⁸ The low value found for λ_0^2 and the absence of any appreciable curvature seem to indicate that the first two rotatory contributions have the same sign.

TABLE X. Rotatory dispersion of dextro sodium salt of β -methylcaproic acid in water.

Visible region: Concentration $0.7663 M$, $\delta_4^{25} = 1.024_3$, $l = 40$ cm. U.V. region: Concentration $0.7663 M$, $\delta_4^{25} = 1.024_3$, $l = 5$ cm. Measurements on levo form.

λ	5780.1	5460.7	4358.3	2730	2590	2500
α^{25}	0.810	0.916	1.51 ₀	0.60	0.70	0.80
$[M]^{25}$	2.92 ₄	3.30 ₈	5.45	17.3	20.2	23.1
$[M]^{25} = \frac{9.096}{\lambda^2 - 0.023}$	2.92 ₄	3.30 ₈	5.45	17.6	20.6	23.0

In fact, it is possible to express the experimental results almost within the limits of error, by a formula such as

$$[M]^{25} = \frac{0.286}{\lambda^2 - 0.042} + \frac{0.983}{\lambda^2 - 0.022}$$

in which λ_1^2 has the same value (0.042) found for the lower homologue.

This would be an important exception in the homologues of the propionic acid series. These results induced us to repeat the dispersion measurements on another preparation of this acid. Measurements on both samples agreed very well.

TABLE XI. Rotatory dispersion of dextro ethyl ester of β -methylcaproic acid without solvent.

Constants of sample: $\delta_4^{25} = 0.8627$, $n_D^{25} = 1.4100$. Visible region: $l = 10$ cm. U.V. region: $l = 5$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{1.7008}{\lambda^2 - 0.05288}$	$[M]^{25} = \frac{1.6665}{\lambda^2 - 0.01951}$	λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{1.7008}{\lambda^2 - 0.05288}$	$[M]^{25} = \frac{1.6665}{\lambda^2 - 0.01951}$
5780.1	0.211	0.751	0.753		2935	3.70	26.3	26.1	
5460.7	0.264 ₅	0.941	0.953		2910	4.00	28.4	27.9	
4358.3	0.74 ₀	2.63	2.63		2854	4.60	32.7	32.6	
4046.6	1.06 ₅	3.78 ₇	3.78 ₇		2835	4.90	34.8	34.5	
3400	1.40	9.95	9.77		2790	5.60	39.8	39.6	
3300	1.60	11.3	11.7		2770	6.00	42.7	42.2	
3240	1.80	12.8	13.1		2750	6.40	45.5	45.1	
3210	2.00	14.2	14.0		2710	7.20	51.2	51.8	
3155	2.20	15.6	15.6		2700	7.60	54.0	53.7	
3092	2.50	17.8	17.9		2667	8.60	61.2	60.9	
3050	2.80	20.0	19.7		2630	10.10	71.8	70.8	
3010	3.10	22.1	21.7		2605	11.10	78.9	79.0	

 TABLE XII. Rotatory dispersion of dextro- β -methylheptylic acid in heptane.

Constant of sample: $n_D^{25} = 1.4243$. Visible region: Concentration 0.8481 M , $\delta_4^{25} = 0.7105$, $l = 40$ cm. U.V. region: Concentration 0.8535 M , $\delta_4^{25} = 0.7109$, $l = 10$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{1.9022}{\lambda^2 - 0.04665}$	$[M]^{25} = \frac{1.996}{\lambda^2 - 0.04916}$	λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{1.996}{\lambda^2 - 0.04916}$
5875.6	0.814 ₅	6.35 ₃	6.37 ₁		3150	1.30	40.3	39.9
5780.1	0.848	6.61 ₈	6.61 ₈		3095	1.40	43.4	42.8
5460.7	0.972	7.58 ₇	7.56 ₃		3035	1.50	46.5	46.5
4358.3	1.70 ₀	13.2 ₇	13.2 ₇		3000	1.60	49.6	48.9
3660	0.70	21.7		23.5	2920	1.80	55.8	55.3
3590	0.80	24.8		25.0	2860	2.00	62.0	61.2
3430	0.90	27.9		29.1	2810	2.20	68.2	67.0
3370	1.00	31.0		31.0	2765	2.40	74.4	73.1
3280	1.10	34.1		34.2	2680	2.80	86.9	88.1
3215	1.20	37.2		36.8	2540	4.20	130.0	130.0

 TABLE XIII. Rotatory dispersion of dextro- β -methylcaprylic acid in heptane.

Constants of sample: $\delta_4^{25} = 0.8984$, $n_D^{25} = 1.4290$. Visible region: Concentration 0.8629 M , $\delta_4^{25} = 0.7138$, $l = 40$ cm. U.V. region: Concentration 0.8629 M , $\delta_4^{25} = 0.7138$, $l = 5$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{2.5458}{\lambda^2 - 0.04554}$	$[M]^{25} = \frac{2.438}{\lambda^2 - 0.04836}$	λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{2.438}{\lambda^2 - 0.04836}$
5875.6	2.830	8.492	8.495		2850	3.10	74.4	74.2
5780.1	2.940	8.822	8.822		2765	3.60	86.4	86.8
5460.7	3.358	10.07 ₆	10.07 ₆		2643	4.60	110	113
4358.3	5.875	17.62 ₉	17.62 ₉		2597	5.35	128	128
4046.6	7.180	21.54 ₅	21.53 ₇		2550	6.10	146	146
3510	1.35	32.4		32.6	2538	6.35	152	152
3330	1.60	38.4		39.0	2524	6.60	158	159
3110	2.10	50.4		50.4	2515	6.85	164	164
2957	2.60	62.4		62.4	2505	7.10	170	169
					2485	7.60	182	182

TABLE XIV. Rotatory dispersion of dextro ethyl ester of β -methylcaprylic acid without solvent.

Constants of sample: $\delta_4^{25} = 0.8595$, $n_D^{25} = 1.4189$. Visible region: $l = 10$ cm. U.V. region: $l = 5$ cm. Measurements on levo form.

$[M]^{25} = \frac{1.3143}{\lambda^2 - 0.0529}$					$[M]^{25} = \frac{1.3143}{\lambda^2 - 0.0529}$			
λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{1.2066}{\lambda^2 - 0.05523}$	$-\frac{0.1087}{\lambda^2 - 0.019}$	λ	α^{25}	$[M]^{25}$	$-\frac{0.1087}{\lambda^2 - 0.019}$
5780.1	1.928 _s	4.327	4.327	4.329	2755	12.15	54.5	55.2
5460.7	2.216	4.972	4.966	4.969	2725	13.15	59.0	59.6
4358.3	3.99 ₂	8.956	8.956	8.954	2697	14.15	63.5	64.2
4046.6	4.95 ₀	11.106	11.119	11.106	2678	15.15	68.0	67.8
3256	5.15	23.1		23.5	2652	16.15	72.5	73.3
3130	6.15	27.6		27.8	2635	17.15	77.0	77.4
3030	7.15	32.1		32.3	2620	18.15	81.4	81.3
2948	8.15	36.6		37.0	2603	19.15	85.9	86.2
2885	9.15	41.1		41.6	2590	20.15	90.4	90.4
2832	10.15	45.5		46.4	2561	4.65	104	105
2792	11.15	50.0		50.6		(1 cm)		

TABLE XV. Rotatory dispersion of levo- γ -methylcaproic acid in heptane.

Constant of sample: $n_D^{25} = 1.4213$. Visible region: Concentration 0.8312 M , $\delta_4^{25} = 0.7080$, $l = 40$ cm. U.V. region: Concentration 0.8520 M , $\delta_4^{25} = 0.7087$, $l = 20$ cm and 10 cm.

λ	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{4.593}{\lambda^2 - 0.02172}$		$[M]^{25} = \frac{3.825}{\lambda^2 - 0.042} - \frac{8.395}{\lambda^2 - 0.032}$	
5892.6	-1.213 ₅	-14.10	-14.11	-14.11	-14.10	-14.10
5780.1	-1.265 ₅	-14.70	-14.70	-14.70	-14.70	-14.70
5460.7	-1.429 ₅	-16.61	-16.61	-16.61	-16.61	-16.61
4358.3	-2.35 ₀	-27.30	-27.30	-27.30	-27.30	-27.30
3480	-2.00 (20 cm)	-45.3	-46.2	-46.2	-45.9	-45.9
3220	-1.20 (10 cm)	-54.4	-56.9	-56.9	-55.1	-55.1
3095	-1.30 (10 cm)	-58.9	-62.0	-62.0	-60.5	-60.5
2900	-3.00 (20 cm)	-68.0	-72.3	-72.3	-70.3	-70.3
2830	-3.20 (20 cm)	-72.5	-80.3	-80.3	-74.2	-74.2
2730	-3.40 (20 cm)	-77.1	-87.0	-87.0	-79.8	-79.8
2530	-1.95 (10 cm)	-88.5	-108.6	-108.6	-88.5	-88.5