Analysis of Rotatory Dispersion Curves. II Configurationally Related Substituted Fatty Acids
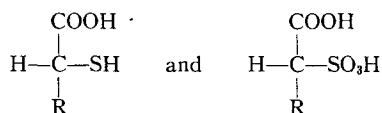
P. A. Levene and Alexandre Rothen

Analysis of Rotatory Dispersion Curves. II
Configurationally Related Substituted Fatty Acids

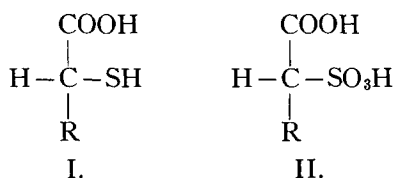P. A. LEVENE AND ALEXANDRE ROTHEN, *The Rockefeller Institute for Medical Research, New York*

The rotatory dispersion curves of substituted fatty acids of the types

$$\begin{array}{ccc}
\text{COOH} & & \text{COOH} \\
| & & | \\
\text{H—C—SH} & \text{and} & \text{H—C—SO}_3\text{H} \\
| & & | \\
\text{R} & & \text{R}
\end{array}$$

have been measured in the visible and ultraviolet regions. The results are in harmony with the rule previously reported that in members of homologous series, the total rotation of consecutive members may differ in sign, but the signs of the partial rotations remain constant.

THE present communication deals with the analysis of the partial rotations of members of two configurationally related homologous series of substances of the following types:

$$\begin{array}{cc}
\text{COOH} & \text{COOH} \\
| & | \\
\text{H—C—SH} & \text{H—C—SO}_3\text{H} \\
| & | \\
\text{R} & \text{R} \\
\text{I.} & \text{II.}
\end{array}$$

The members of the two series differ in the character of one substituent, namely, —SH and —SO$_3$H, respectively. These two groups differ in their chromophoric properties and it was of interest to inquire, first, into the direction of the partial rotations of each of these groups, and second, into the partial rotations of the remaining parts of the molecules which are identical in the members of both series.

A further point of inquiry was the effect of ionization of the carboxyl group on the partial rotations. In carboxylic acids of the type

$$\begin{array}{c}
\text{COOH} \\
| \\
\text{H—C—X} \\
| \\
\text{R}
\end{array}$$
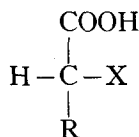
(where X=any functional group) ionization of the —COOH group was found to produce a marked effect on the value of the rotation of the substance measured in the visible part of the spectrum and frequently to produce a change in the direction of the rotation. It was desired to ascertain whether the ionization of the carboxyl group has a similar rotational effect on the substances of the two series.

Levene, Mori and Mikeska[1] have reported observations on the rotations for the sodium D line of four members of the normal series of 2-mercapto acids and of the four corresponding sulfo acids and certain of their salts. They found that all the members of the series of the mercapto acids rotate in one direction, whereas the rotations of the higher members of the series of sulfo acids were in the opposite sense from those of the lower, the change of sign occurring between the second and third member. On the other hand, the rotations of the salts of the higher mercapto acids were in the opposite direction from those of the lower, but the salts of the sulfo acids all rotated in the same direction.

The following four acids were made the subject of the present investigation.

Dextro 2-mercaptobutyric acid (1) and its *Levo* monosodium salt.
Dextro 2-mercaptocaproic acid (1) and its *Dextro* monosodium and *Levo* disodium salts.
Dextro 2-sulfobutyric acid (1) and its *Levo* disodium and *Levo* calcium salts.
Levo 2-sulfocaproic acid (1) and its *Levo* disodium salt.

Inasmuch as interpretation of the dispersion curves depends on a knowledge of the absorption curves, the latter were made the subject of special study.

The results of the study of the absorption and dispersion curves may be summarized as follows:

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[1] P. A. Levene, T. Mori and L. A. Mikeska, J. Biol. Chem. **75**, 337 (1927).

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ABSORPTION

Mercapto acids

The absorption curves of the two mercapto acids studied exhibit a definite maximum at 2400A. This band can safely be attributed to the SH group, inasmuch as 2-mercaptobutane has an absorption band in the same part of the spectrum, which is, however, slightly displaced towards higher frequencies (as is to be expected), and yet is still in a region of transparency for a simple aliphatic acid. The absorption curves of the sodium salts are less characteristic owing to the appearance of a strong second band (COO⁻) which overlaps the SH band and masks its maximum (see Fig. 1).

Sulfo acids

The absorption curves of the sulfo acids present a characteristic maximum at 2150A (see Fig. 2). This band is doubtless the first COOH band displaced towards lower frequencies by the proximity of COOH to SO_3H, since we ascertained that an ordinary alkylsulfonic acid (2-methylpropylsulfonic acid(1)), has practically no absorption at all in that region and absorbs much less than the corresponding aliphatic acid.

FIG. 2. Absorption curves of the sulfo acids and their sodium salts. The dotted curve is calculated.

The absorption curves of the sodium salts present a striking difference. The curve is displaced towards higher frequencies by about 150A, the maximum of the first band can no longer be seen and a continuous increasing absorption is observed as the wave-length becomes smaller. The fact that we have two bands overlapping each other and not one broad band is very well demonstrated by analysis of both absorption and dispersion curves. The striking change in the absorption is brought about by the ionization of the COOH group since the SO_3H group is already completely ionized in the free acid, as electrometric titration curves have shown.

ROTATION

Mercapto acids

Analysis of the dispersion curves and direct dichroism measurements have shown that the first SH band is strongly coupled and that its rotatory contribution is predominant, i.e., the total molecular rotation has the sign of the SH partial rotation due to anisotropy of the −SH band. The remainder of the rotation, the major
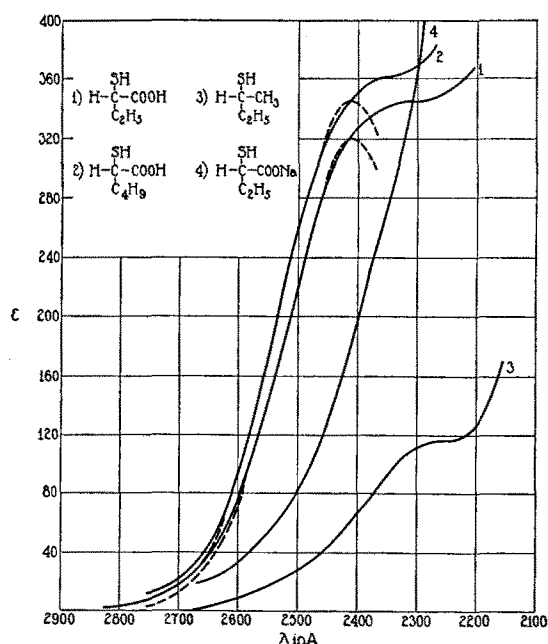
FIG. 1. Absorption curves of the mercapto acids and their sodium salts. The dotted curve is calculated.

part of which can be attributed to the anisotropy of the COOH group, is of opposite sign.

The dispersion curves may be expressed by two dispersion terms (of Drude formula) of opposite sign, the dispersion constants λ_1 being practically the same for both compounds and the same being true for the λ_2 (see Tables III and V).

Sulfo acids

It was stated above that the rotations of the higher members of this series, beginning with the third, are of opposite sign from those of the lower.

The change in sign is due not to the change in sign of the partial rotations of the corresponding anisotropic groups, but to the fact that the absolute magnitude of the second partial contribution is greater than that of the first for the higher members, as a result of which their dispersion is anomalous. (Dispersion curve of case 4, see Levene, Rothen and Marker, reference 2, page 664.) The analysis of the dispersion curves of the free acids shows (see Tables VIII and XI) that the total rotation may be expressed by two terms of opposite sign, the first term having a constant of dispersion corresponding to the first absorption band of the carboxyl group (2120A for 2-sulfobutyric acid (1), 2150A for 2-sulfocaproic acid (1)). In the case of 2-sulfobutyric acid the second term is negative and the dispersion constant λ_2 is less than zero, indicating clearly an anomalous course of this term. In the case of 2-sulfocaproic acid the second term is likewise negative and the value of λ_2 approaches zero, thus indicating a similar anomaly.

These observations are in harmony with the rule, deduced from previously reported observations, to the effect that in *members of homologous series the total rotations of consecutive members may differ in sign but the signs of the partial rotations remain constant.*[2] Recently, Kuhn[3] made similar observations on the configurationally related inorganic complex salts.

If we consider the sulfo acids in relation to the mercapto acids, we see that the change SH→SO$_3$H produces a great rotatory effect which

[2] P. A. Levene, Al. Rothen and R. E. Marker, Chem. Phys. 1, 662 (1933).
[3] W. Kuhn and K. Bein, Zeits. f. anorg. Chem. **216**, 321 (1934).

in small part may be due to the ionization of the group SO$_3$H. It may be mentioned, however, that the direction of the acid remains the same in an excess of mineral acid. The anisotropy of the carboxyl group is of opposite sign in the two series. In other words, the vicinal effect of the groups

$$\begin{array}{ccc} C_nH_{2n-1} & & C_nH_{2n-1} \\ | & & | \\ H-C-SO_3H & \text{and} & H-C-SH \\ | & & | \end{array}$$
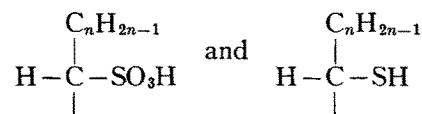
induces opposite anisotropies in the carboxyl group.

Salts of mercapto acids

The opposite rotations observed in the visible region for 2-mercaptobutyric acid (1) and its salt are easily understood, since the dispersion curve of the salt has been found to be anomalous. No change of sign of anisotropy occurs on passing from the acid to the salt, but only a decrease in the magnitude of the partial rotation of the SH group which for the salt becomes smaller than the second contribution for $\lambda > 4046.6$A. Although the dispersion curves of the monosodium salts of these acids seem distinctly different, they can be expressed with precision by two dispersion terms having the same constants λ_1 and λ_2, respectively (see Tables IV and VI). The change of sign between 2-mercaptocaproic acid (1) and its disodium salt is easily explained in the same way (see Tables V and VII). In short, the anisotropy of the SH band increases from the lower to the higher members of the series and is greater for the free acid than for its salts.

Salts of the sulfo acids

The striking differences between the absorption of the sulfo acids and their salts are also found in their rotatory behavior. The dispersion curves of the salts can be resolved into two terms of opposite sign, each of them being of the opposite sign to the corresponding term for the free acid (see Tables IX, X and XII). The constant λ_1 of *the first term* is about 100A smaller than the corresponding λ_1 of the first term for the acid. It is very probable that the constants λ_1 of the acid and salt correspond to two different electronic states, despite the fact that they are of almost the same magnitude.

Kuhn[4] arrived at analogous conclusions in a somewhat similar case when interpreting the dispersion curve of octyl nitrite. He assumed two different electronic states in the absorption band of NO_2 to explain two anisotropy factors of opposite sign in the same region of the spectrum.

The *second term* is strongly dispersive (λ_2 $-1924A$) in contrast to the anomalous second term of the acid.

Attention must be called to the fact that the dispersions of the thio and the sulfo acids were measured in different solvents. It is known that the direction of rotation of some substances changes with the change of solvent. However, this change was found to be due to the effect of the solvent on the numerical values of the individual partial rotations, the directions of the latter remaining unaltered.* In the special case of the thio-derivatives, the direction of rotation remains the same for both substances in ether or in water containing enough alcohol to effect the solution of the thio-derivatives.

SHAPE OF ABSORPTION CURVES

The absorption curves of the mercapto acids, the sulfo acids and their salts were analyzed and it was found that they could be expressed by an exponential equation based on a Maxwellian distribution (as was first done by V. Henri,[5] and since then by Kuhn,[6] Lowry[7] and others.[7] In accord with the recent work of Lowry,[4] we found that better agreement between experimental and calculated rotation values was obtained by using a wave-length scale instead of a frequency scale. Consequently, our absorption curves have been expressed in the wave-length scale. We give below the parameters of the absorption curves for the different compounds, as calculated from the equation

$$\epsilon = \epsilon_{max}.e^{-[(\lambda-\lambda_0)/\theta]^2}$$

(where $\theta = \lambda'/1.665$, λ' is the half-width of the

band and ϵ is the molecular extinction coefficient as defined in the *International Critical Tables*). Wave-lengths are expressed in microns to comply with the usual convention adopted in polarimetry. As may be seen from Figs. 1 and 2, only that part of the curve on the longer wave-length side of the origin λ_0 could be observed (see Table I).

TABLE I. *Absorption constants.*

Compound	Solvent	$\epsilon_{max.}$	λ_0	θ
2-Mercaptobutyric acid (1)	heptane	320	0.2410	0.0159
2-Mercaptocaproic acid (1)	heptane	345	0.2410	0.0172
2-Sulfobutyric acid (1)	water	147	0.2120	0.0172
Na salt of 2-sulfobutyric acid (1)	water	128	0.2025	0.0180
2-Sulfocaproic acid (1)	water	172	0.2150	0.0180
Na salt of 2-sulfocaproic acid (1)	water	128	0.2050	0.0180

TABLE II. *Circular dichroism.*†

Compound	λ in A	$(\epsilon_l-\epsilon_r)\lambda$	$(\epsilon_l-\epsilon_r)\lambda_{2410}$ Calc.	ϕ Calc. from dichroism data	ϕ Calc. from dispersion and absorption data
2-Mercaptobutyric acid (1)	2480	1.46±0.15	1.8₅	3700°	3600°
2-Mercaptocaproic acid (1)	2450	2.10±0.30	2.3	4600°	4680°
	2560	0.80±0.08			

It is interesting to note that in the case of the sodium salts of the two sulfo acids for which no maximum could be detected, the λ_0 which had to be chosen in order to represent correctly the first part of the absorption curve, had the same value as that found by dispersion measurements.

ROTATORY DISPERSION FORMULAE

According to Drude, the equation representing the rotation in the neighborhood of an active absorption band, has the form

$$[M] = \frac{A(\lambda^2-\lambda_0{}^2)}{(\lambda^2-\lambda_0{}^2)^2+\lambda'^2\lambda^2}.$$

The dispersion calculated from a simple term $A/(\lambda^2-\lambda_0{}^2)$ fixes the upper limit of the rotation. The rotation as we approach λ_ϕ (ϕ = maximum rotation) increases, although it never reaches the

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* See W. Kuhn, *Stereochemie* of K. Freudenberg, p. 416, 1933 and Levene-Rothen-Meyer, Science **80**, 101 (1934).

[4] W. Kuhn and H. L. Lehmann, Zeits. f. physik. Chemie **B18**, 32 (1932).

[5] V. Henri and J. Bielecki, Phys. Zeits. **14**, 516 (1913).

[6] W. Kuhn and E. Braun, Zeits. f. physik. Chemie **B8**, 281 (1930).

[7] T. M. Lowry and H. Hudson, Phil. Trans. Roy. Soc. **A232**, 117 (1933). H. Hudson, M. L. Wolfrom and T. M. Lowry, J. Chem. Soc. 1933, 1179.

† See the relations between circular dichroism, anisotropy factor and maximum rotation of an active band, Hand- und Jahrbuch der chemischen Physik, *Drehung der Polarisationsebene des Lichtes,* von W. Kuhn und K. Freudenberg. Leipzig, 1932, p. 79.

value calculated from a simple term. On the other hand, the main characteristic of Kuhn's[6] recent dispersion formula (written with a λ scale as used by Lowry[7])

$$[M] = \frac{\phi}{m}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^x dx + \frac{\theta}{2(\lambda+\lambda_0)}\right],$$

where m is the maximum value of the term inside the bracket, is that, for values of λ between $\lambda_{0+4\theta}$ and λ_ϕ the rotation increases more rapidly than if it were following a simple Drude term. Consequently, if a simple Drude term is used to express a dispersion over a wave-length interval which goes beyond the critical value $\lambda_{0+4\theta}$ then the value found for λ_0 is greater than the true value. We have found that, whenever sufficient precision was attained in the rotatory measurements in the neighborhood of the absorption

band, Kuhn's equation was more satisfactory than Drude's. This is very well illustrated in

TABLE IV. *Rotatory dispersion of levo monosodium salt of 2-mercaptobutyric acid (1) in water containing 25 percent CH_3OH.*

Concentration: 0.7043M
Visible region: $l = 20$ cm
U.V. region: $l = 5$ cm from 3500 to 3110, 0.5 cm from 2950 to 2780. Measurements on dextro form.

λ in A	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{5.150}{\lambda^2-0.062} - \frac{6.264}{\lambda^2-0.040}$
5780.1	−0.334	−2.37	−2.37
5460.7	−0.350	−2.48₅	−2.46
4358.3	−0.225	−1.60	−1.52
4046.6	0.00	0.00	0.00
3740	+0.15	+4.3	+3.45
3610	+0.25	+7.1	+6.0
3560	+0.35	+9.9	+7.3
3330	+0.65	+18.₅	+16.9
3245	+0.85	+24.₁	+23.1
3180	+1.05	+29.₈	+29.2
3110	+1.25	+35.₅	+37.9
2950	+0.25	+71	+72.6
2900	+0.35	+99	+91.0
2850	+0.45	+128	+116.0
2790	+0.55	+156	+159.6

TABLE III. *Rotatory dispersion of dextro-2-mercaptobutyric acid (1) in heptane.*

Visible region: Concentration 1.146₇M, $l = 20$ cm. U.V. region: Concentration 1.146₇ from 3990A to 3005A, 0.1147 from 2980 to 2770, $l = 5$ cm from 3990A to 2843A, 1 cm from 2768A to 2370A. Measurements on levo form. The figures in the last column ($[M]^{25}_{calc.}$) are calculated from the equation

$$[M]^{25}_{calc.} = \frac{\phi}{0.556}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx + \frac{\theta}{2(\lambda+\lambda_0)}\right] - \frac{19.578}{\lambda^2-0.043}.$$

$\phi = 3600°, \quad \lambda_0 = 0.245, \quad \theta = 0.01537, \quad \lambda_\phi = 0.2560.$

This equation reduces for $\lambda > 0.3065$ to

$$[M]^{25}_{calc.} = \frac{25.495_5}{\lambda^2-0.060} - \frac{19.578_4}{\lambda^2-0.043}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{19.1614}{\lambda^2-0.064} - \frac{13.2006}{\lambda^2-0.042}$	$[M]^{25}_{calc.}$
5892.6	5.605	24.440	24.40	24.41
5780.1	5.907₅	25.759	25.75	25.76
5460.7	6.947	30.293	30.29	30.31
4358.3	14.44	62.96	62.91	62.96
4046.6	19.19	83.67₆	83.67	83.59
3990	5.10	88.9₅	88.64	88.52
3815	6.10	106.₄	107.5	107.1
3690	7.10	123.₈	125.3	124.6
3593	8.10	141.₃	142.8	141.6
3518	9.10	158.₇	159.2	157.4
3445	10.10	176.₁	178.3	175.8
3340	12.20	211.₀	213.2	208.9
3260	14.10	245.₉	247.9	241.8
3197	16.10	280.₈	282.3	273.3
3145	18.10	315.₇	317.0	
3098	20.10	350.₆	354.6	339.1
3005	26.10	455.₂	455.2	
2980	2.80	488	490.5	
2950	3.10	541	539.0	
2908	3.60	628	621.7	630.
2870	4.10	715	716.2	740.
2855	4.35	759	760	
2843	4.60	802	799	825
2770	1.27	1102	1125	1215
	conc. 0.0115M			
2620	0.30	2600		2660
2560	0.30	2600		2730
2483				430
2370	−0.29	−5100		−4650
	conc. 0.057M			

TABLE V. *Rotatory dispersion of dextro-2-mercaptocaproic acid (1) in heptane.*

Visible region: concentration 0.6855M, $l = 20$ cm.
U.V. region: concentration 0.6855M from 3965A to 2703A, 0.2285M for 2665A, 0.114M from 2585A to 2550A, 0.0571M from 2380A to 2340A, $l = 5$ cm from 3965A to 2980A, 0.5 cm from 2920A to 2825A, 0.1 cm from 2785A to 2340A.

The figures in column 5 are calculated from

$$[M]^{25}_{calc.} = \frac{\phi}{0.554}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx + \frac{\theta}{2(\lambda+\lambda_0)}\right] - \frac{20.140}{\lambda^2-0.045},$$

where $\phi = 4680°, \lambda_0 = 0.245, \theta = 0.0132, \lambda_\phi = 0.255.$
This equation reduces for $\lambda > 0.3000$ to

$$[M]^{25}_{calc.} = \frac{28.415}{\lambda^2-0.060} - \frac{20.140}{\lambda^2-0.045}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25} = \frac{20.249}{\lambda^2-0.064} - \frac{11.973}{\lambda^2-0.042}$	$[M]^{25}_{calc.}$
5780.1	4.662	34.00₄	33.98	34.00
5460.7	5.447	39.73	39.73	39.75
4358.3	10.93	79.72	79.85	79.72
4046.6	14.34	104.5₉	104.3	104.3
3965	3.90	113.₈	113.3	112.8
3750	4.90	143.₀		
3590	5.90	172.₁	174.3	172.4
3482	6.85	199.₈		
3393	7.85	229.₀	232.4	228.3
3322	8.85	258.₂		
3215	10.85	316.₅	319.3	310.2
3170	11.85	345.₇	350.3	
3100	13.85	404.₁		
3070	14.85	433.₂	440.3	420.7
3042₅	15.85	462.₄	472.0	449.1
3020	16.85	491.₆	501.1	
2998	17.85	520.₈		474.8
2980	18.85	550.₀	560.7	526.8
2920	2.30	671	675.7	
2868	2.80	817	812.1	803
2825	3.30	948	964.4	965
2785	0.80	1170	1157	1173
2760	0.90	1310	1302	1330
2703	1.30	1900	1850	1940
2665	0.60	2620	2470	2500
2585	0.40	3510	6698	3650
2550	0.43	3800		3670
2380	−0.28	−4900		−5800
2340	−0.40	−7000		−6900

Tables III and V. The figures in columns 4 are calculated from a formula having two Drude terms, the constant λ_1 of the first term being 80A greater than the real value. Experimental and calculated rotations are in very good agreement over a considerable wave-length interval extending far beyond the critical value $\lambda_{1+4\theta}$ but, for values of λ approaching λ_ϕ, the calculated values have no longer any significance. For the near ultraviolet region, the figures found in columns 5 (which are calculated from a two term formula the first of which is a Kuhn term) do not check with the experimental values as well as do the figures in column 4, but are quite satisfactory for values of λ well within the band. Furthermore, the value of λ_1 of the Kuhn term is very near that found from absorption measurements for the head of this particular band. Part of the dispersion curve of the sodium salt of 2-sulfocaproic acid (1) may be seen in Fig. 3 (see Table XII). We have chosen this particular example since it illustrates very clearly how two different causes can produce an apparent shift of the value of λ_1 towards lower frequencies. The rotation from 5892.6A to 2822A of this salt, as well as that of the corresponding sulfobutyric acid, may be expressed within less than 0.5 percent by one Drude term. The value of the apparent λ_1 is 2186A, which is 136A higher than the value

TABLE VI. *Rotatory dispersion of dextro monosodium salt of 2-mercaptocaproic acid (1) in water containing 30 percent CH_3OH.*

Concentration: 0.3106M
Visible region: $l = 20$ cm
U.V. region: $l = 5$ cm

λ in A	α^{25}	$[M]^{25}$	$[M]^{25} = \dfrac{5.767}{\lambda^2-0.062} - \dfrac{3.848}{\lambda^2-0.040}$
5780.1	+0.504	+8.11	+8.11
5460.7	+0.587	+9.45	+9.51
4358.3	+1.21	+19.5	+19.4
4046.6	+1.59	+25.6	+25.6
3700	+0.60	+38.$_6$	+37.2
3450	+0.85	+54.$_7$	+52.5
3330	+1.10	+70.$_8$	+63.7

TABLE VII. *Rotatory dispersion of levo disodium salt of 2-mercaptocaproic acid (1) in water containing 20 percent CH_3OH.*

Concentration: 0.236M
Visible region: $l = 20$ cm
U.V. region: $l = 5$ cm

λ in A	α^{25}	$[M]^{25}$
5780.1	−0.244	−5.17
5460.7	−0.269	−5.70
4358.3	−0.255	−5.40$_5$
4046.6	−0.15	−3.18
3480	+0.35	+30
3350	+0.60	+51

TABLE VIII. *Rotatory dispersion of dextro 2-sulfobutyric acid (1) in water.*

Concentration: 0.8630M
Visible region: $l = 40$ cm
U.V. region: $l = 5$ cm from 3670A to 2835A, $l = 1$ cm from 2620A to 2535A
Measurements on levo form.

λ in A	α^{25}	$[M]^{25}$	$[M]^{25} = \dfrac{3.0656}{\lambda^2-0.045} - \dfrac{2.1733}{\lambda^2+0.030}$
5875.6	1.535	4.446	4.419
5780.1	1.600	4.635	4.635
5460.7	1.894	5.486	5.486
4358.3	3.89	11.27	11.27
4046.6	5.04	14.60	14.60
3670	0.90	20.8	21.0
3580	1.00	23.2	23.1
3500	1.10	25.5	25.3
3280	1.45	33.6	33.2
3160	1.70	39.4	39.1
3050	2.00	46.3	46.2
2975	2.25	52.1	52.1
2900	2.55	59.1	59.3
2835	2.80	64.9	67.0
2620	0.90	104	107.6
2585	1.00	116	118.0
2535	1.10	127	136.1

TABLE IX. *Rotatory dispersion of levo disodium salt of 2-sulfobutyric acid (1) in water.*

Concentration: 0.6517M
Visible region: $l = 40$ cm
U.V. region: $l = 5$ cm from 3450 to 2522A, 0.5 cm from 2500 to 2370A, 0.1 cm for (2335 and) 2320A.
Measurements on dextro form. The figures in the last column are calculated from the equation

$$[M]^{25}\text{calc.} = -\frac{\phi}{0.562}\frac{\lambda\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx + \frac{\theta}{2(\lambda+\lambda_0)}\right] + \frac{28.640}{\lambda^2-0.037}.$$

$\phi = 5140°,\qquad \lambda_\phi = 0.219,\qquad \lambda_0 = 0.2025,\qquad \theta = 0.0180.$

for $\lambda > 0.2750$ this equation reduces to

$$[M]^{25} = -\frac{36.039_5}{\lambda^2-0.041} + \frac{28.640}{\lambda^2-0.037}.$$

| λ in A	α^{25}	$[M]^{25}$	$[M]^{25} = -\dfrac{7.4323}{\lambda^2-0.05385}$	$[M]^{25}$calc.
5892.6	−6.605	−25.337	−25.333	−25.369
5780.1	−6.923$_5$	−26.560	−26.560	−26.560
5460.7	−7.947	−30.486	−30.417	−30.486
4358.3	−14.26	−54.70	−54.61	−54.70
4046.6	−17.63	−67.63	−67.63	−67.64
3780	−2.70	−82.9	−83.5	−83.2
3680	−2.95	−90.5	−91.1	−90.8
3585	−3.20	−98.2	−99.5	−98.8
3510	−3.45	−105.9	−107.2	−106.2
3445	−3.70	−113.5	−114.6	−113.2
3330	−4.20	−128.9	−130.3	−128.0
3235	−4.70	−144.2	−146.3	−142.9
3155	−5.20	−159.6	−162.7	−157.8
2840	−8.80	−270.1	−277.7	−253.0
2745	−10.80	−331.4	−345.7	−302.4
2680	−12.80	−392.8	−413.5	
2620	−15.60	−478.7		
2595	−16.80	−515.0		−492
2540	−19.80	−607.6		−598
2522	−20.70	−635.3		−644
2500	−2.30	−705.8		−706
2480	−2.55	−782.6		
2455	−2.80	−859		−862
2418	−3.30	−1013		−1038
2398	−3.80	−1166		
2370	−4.40	−1350		−1384
2320	−1.00	−1535		−1834
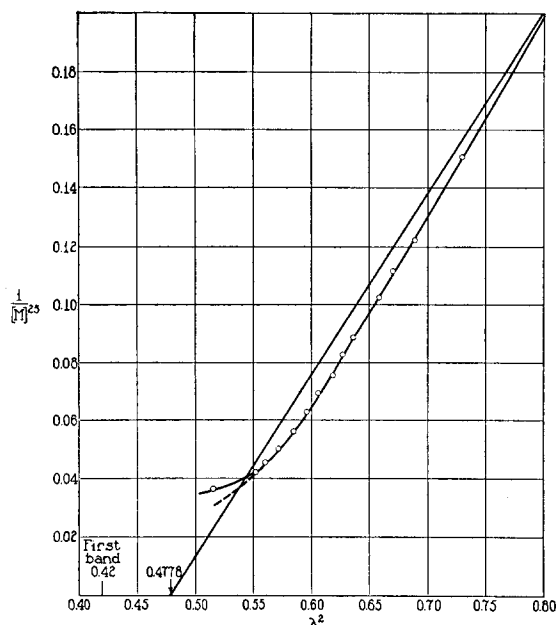
FIG. 3. Dispersion curve of the sodium salt of sulfocaproic acid. The dotted curve is calculated.

TABLE X. *Rotatory dispersion of levo calcium salt of 2-sulfobutyric acid (1) in water.*

Concentration: 0.33076M, visible region $l=40$ cm, U.V. region $l=10$ cm from 3980 to 2520A, 5 cm for 2340 and 2320A, 0.1 cm for 2270 and 2250A.

Measurements on dextro form.

The figures in the last column are calculated from the equation

$$[M]^{25} = -\frac{\phi}{0.562}\frac{\lambda\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx+\frac{\theta}{2(\lambda+\lambda_0)}\right]+\frac{32.355}{\lambda^2-0.037}.$$

$$\phi=5760°, \qquad \lambda_\phi=0.2190, \qquad \lambda_0=0.2025, \qquad \theta=0.0180.$$

for $\lambda > 0.2750$ this equation reduces to

$$[M]^{25} = -\frac{40.346}{\lambda^2-0.041}+\frac{32.355}{\lambda^2-0.037}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=-\dfrac{8.0476}{\lambda^2-0.0542}$	$[M]^{25}$calc.
5780.1	−3.804	−28.75	−28.75	−28.75
5460.7	−4.367	−33.01	−32.98	−33.36
4358.3	−7.85	−59.3₃	−59.29	−59.33
4046.6	−9.72	−73.4₇	−73.47	−73.42
3980	−2.55	−77.1	−77.2	−77.2
3670	−3.30	−99.8	−100.0	−99.4
3540	−3.80	−114.9	−113.2	−112.1
3410	−4.30	−130.0	−129.7	−127.8
3300	−4.80	−145.1	−147.1	−138.4
3220	−5.30	−160.2	−162.7	−158.4
3155	−5.80	−175.3	−177.5	−171.9
3045	−6.80	−205.6	−209.0	−199.4
2965	−7.80	−235.8	−238.8	−224.6
2896	−8.80	−266.0	−271.3	−250.8
2830	−9.80	−296.3	−311.0	−281.2
2753	−11.80	−356.7	−372.9	
2688	−13.80	−417.2	−446.1	
2600	−17.80	−538.1		−534
2565	−19.80	−598.6		−611
2540	−21.80	−659.1		−670
2520	−23.80	−719.5		−723
2340	−2.80	−1690		−1800
2320	−3.30	−1995		−2200
2270	−0.70	−2120		−2600
2250	−0.80	−2420		−2775

TABLE XI. *Rotatory dispersion of levo 2-sulfocaproic acid (1) in water.*

Concentration: 0.6830M, visible region $l=40$ cm, U.V. region $l=10$ cm for 3560 and 3270A, 5 cm, for 3450A, 1 cm for 2700A, 0.1 cm for 2400A.

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=\dfrac{3.0626}{\lambda^2-0.0462}-\dfrac{6.5309}{\lambda^2-0.007}$
5892.6	−2.465	−9.023	−9.022
5780.1	−2.548	−9.326	−9.328
5460.7	−2.809	−10.282	−10.275
4358.3	−3.93	−14.38	−14.39
4046.6	−4.26	−15.59	−15.61
3560	−1.10	−16.1	−16.5
3450	−0.53	−15.5	−16.2
3270	−1.00	−14.6	−14.9
2700	+0.20	+2.9	+15.6
2400	+0.22	+32	+102.2

TABLE XII. *Rotatory dispersion of levo disodium salt of 2-sulfocaproic acid (1) in water.*

Concentration: 0.2572M, visible region $l=40$ cm, U.V. region $l=10$ cm from 3790 to 2520A, 1 cm from 2520 to 2350A, 0.1 cm for 2270.

The figures in the last column are calculated from the relation

$$[M]^{25}=-\frac{\phi}{0.562}\frac{\lambda\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx+\frac{\theta}{2(\lambda+\lambda_0)}\right]+\frac{21.271}{\lambda^2-0.037}.$$

$$\phi=5290°, \qquad \lambda_\phi=0.2210, \qquad \lambda_0=0.2050, \qquad \theta=0.0180.$$

for $\lambda > 0.2770$ this expression reduces to

$$[M]^{25}=-\frac{37.437}{\lambda^2-0.042}+\frac{21.271}{\lambda^2-0.037}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=-\dfrac{16.197}{\lambda^2-0.04778}$	$[M]^{25}$calc.
5892.6	−5.560	−54.04	−54.09	−54.09
5780.1	−5.820	−56.57	−56.57	−56.57
5460.7	−6.649	−64.63	−64.68	−64.69
4358.3	−11.725	−113.97	−113.93	−113.97
4046.6	−14.37	−139.7	−139.7	−139.7
3790	−4.35	−169.1	−169.0	−168.8
3720	−4.60	−178.8	−178.8	−178.6
3600	−5.10	−198.3	−198.0	−197.7
3490	−5.60	−217.7	−218.8	−218.3
3410	−6.10	−237.2	−236.4	−235.6
3327	−6.60	−256.6	−257.5	−256.4
3265	−7.10	−276.0	−275.4	−273.9
3150	−8.10	−314.9	−314.8	−312.5
3055	−9.10	−353.8	−355.6	−352.7
2980	−10.10	−392.7	−394.8	−389.2
2920	−11.10	−431.6	−432.1	−424.6
2868	−12.10	−470.4	−469.8	−460.0
2822	−13.10	−509.3	−508.4	−495.8
2761	−15.10	−587.1	−569.3	
2702	−17.10	−664.8	−642.0	
2625	−21.10	−820.4	−766.7	−805
2590	−23.10	−898.1		
2567	−25.10	−975.9		−940
2541	−27.10	−1053.6		
2520	−29.10	−1131.4		
2520	−2.90	−1128		−1110
2504	−3.10	−1205		
2487	−3.40	−1322		
2460	−3.70	−1438		−1395
2445	−4.10	−1594		
2415	−4.60	−1788		1720
2390	−5.10	−1983		1954
2365	−5.60	−2177		
2350	−6.10	−2372		2390
2270	−0.70	−2720		3330

found from absorption measurements. This shift is due to our having neglected a second term of opposite sign. Now, for values of λ smaller than the critical value $\lambda_{0+4\theta}$ the dispersion becomes still greater and λ_1 seems shifted still further towards lower frequencies. This second shift is produced because the rotation increases accord-

ing to a Kuhn term and not a Drude term. In fact, the dispersion curve may be fairly well represented by two terms of opposite sign, the first one being a Kuhn term with a value λ_1 equal to that found from absorption measurements.

CIRCULAR DICHROISM

In the case of the mercapto acids, measurements of circular dichroism were made by the method used by Kuhn.[8] Because of experimental difficulties, our results are not very accurate. However, the order of magnitude of the circular dichroism found for the SH band is quite in accord with the maximum partial rotation contributed by that band as calculated from the dispersion curves. Our results are summarized in Table II.

EXPERIMENTAL

Compounds

The compounds were obtained by the methods previously described by Levene, Mori and Mikeska,[1] with the exception of 2-sulfobutyric acid (1) which was prepared and resolved according to Backer.**

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[8] W. Kuhn and E. Braun, Zeits. f. physik. Chemie **B8**, 445 (1930).
** The values of the molecular rotations given are not to be taken as maximum rotations since no attempt was made to resolve the compounds to the maximum, hence no special precaution was taken to determine precisely the *absolute* rotations, as the main purpose of this work was to obtain accurate dispersion measurements. However, the *ratio* of the rotations of the acids to those of their respective salts must be considered as characteristic of the compounds,

All the compounds were carefully analyzed. Titrations indicated that the mercapto acids were at least 99.8 percent pure. The analyses of the sulfo acids were performed on their Ba salts.***

Apparatus

The instruments described in a previous article[2] were used to determine the rotatory dispersions in the visible and the ultraviolet regions. The same general procedure was followed and the same precision is claimed. Absorption measurements were carried out with a Hilger sector photometer in conjunction with a Hilger quartz spectrograph model E316.

Unless otherwise indicated, wave-lengths are expressed in microns in all formulae employed.

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since the same source of material was used to determine the dispersion of the acids and their salts. Backer and Boer [H. J. Backer, J. H. de Boer, Rec. trav. chim. **43**, 297 (1924)] had previously resolved 2-sulfobutyric acid (1). The value they obtained for the maximum rotation of the calcium salt was $[M]_{5892} = -25.3°$, as compared to our own value $[M]^{25}_{5892} = -27.46°$. (Their value has been recalculated from their own function $[M] = f(c)$ for the concentration at which we made our measurements.) The dispersion data given by these authors for a short wave-length interval are in accord with our own measurements. We determined accurately the following ratio

$$\frac{[M]^{25}_{67801} \text{ Ba salt}}{[M]^{25}_{67801} \text{ acid}} = -6.28°,$$

which is not in accord with the value $-3.27°$ recorded by Backer. Furthermore, the dispersion of this acid as given by Backer is completely different from our own curve. These discrepancies induced us to repeat our measurements but we found that our results were readily duplicated.
*** We are indebted to Dr. G. M. Meyer of this department for the preparation of a sample of 2-mercapto-butyric acid (1).