

## Rotatory Dispersion of Aliphatic Aldehydes

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Michigan, basaltic flows is in course of publication by the Geological Society of America. The undue variations of certain results are owing to the inclusion of obviously unsuited material, to determine the influence of geological and physical factors on the result. Table II shows the progress in the present project of building a geological time scale by the examination of authenticated basic rocks from all geological horizons. The advantage of the helium method when once substantiated lies in the wealth of suitable material available. The results recorded here, interdigitate well with lead ratios in radioactive minerals. The helium determination has been described previously.<sup>18</sup> The thorium measurements are described in the immediately preceding article.<sup>9</sup> The age result probable error is calculated from the usual differentiation of Eq. (1) for  $t$  in the same article.<sup>9</sup> The uranium content is calculated from the equilibrium factor, uranium =  $2.94 \times 10^6$  Ra. The average radium content of all the basic rocks in the two tables is  $1.65 \times 10^{-13}$  g per g. This value may be somewhat low for a general basic rock average since the Keweenaw basalts

<sup>18</sup> Paneth and Urry, *Zeits. f. physik. Chemie* **A152**, 110 (1931).

are low compared to material from other sources. Thus the average Keweenaw content (27 specimens) is  $1.60 \times 10^{-13}$  g per g, somewhat higher than was given in the preliminary Keweenaw report—15 specimens averaging  $1.3 \times 10^{-13}$  g per g<sup>19</sup>—but lower than an average of  $1.9 \times 10^{-13}$  g per g for 20 non-Keweenaw basic rocks. The average thorium content of all the basic rocks is  $2.0 \times 10^{-6}$  g per g and the mean Th/U ratio 4.1. The individual ratios are often higher than has previously been supposed, a finding in agreement with the results of R. D. Evans (private communication). As a comparison, the radium contents of various suites of granites as given in the literature vary from 9 to  $17 \times 10^{-13}$  g per g.<sup>20</sup> Individual measurements with the present apparatus give results from 5 to  $20 \times 10^{-13}$  g per g for granites.

This research was made possible by the support of the American Philosophical Society. The Geological Society of America has generously contributed to the support of the routine analyses.

<sup>19</sup> Urry, "Radioactivity Measurements. I," *Proc. Am. Acad.* **68**, 125 (1933).

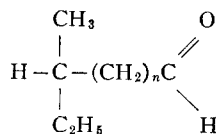
<sup>20</sup> Urry, "Radioactivity Measurements. II," *Proc. Am. Acad.* **68**, 137 (1933). See also Evans and Williams, *Am. J. Sci.* **22**, 441 (1935).

## Rotatory Dispersion of Aliphatic Aldehydes

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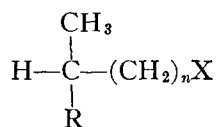
(Received October 11, 1935)

Rotatory dispersion curves of configurationally related aldehydes of the type



( $n$  being equal to 0, 1, 2, or 3) have been determined in the visible and the ultraviolet regions of the spectrum. Their analysis has shown first, that the band of the aldehydic group at  $\lambda 2950$  is rotatory active and that the sign of its contribution in the first member ( $n=0$ ) is opposite to that of the higher members and second, that the magnitude of that contribution varies periodically with the number of carbon atoms located between the aldehydic group and the asymmetric carbon atom.

PREVIOUS observations in this laboratory<sup>1</sup> have established the fact that in substances of the general type



(R = an alkyl or aryl group,  $n = 0$  or an integer, X = a chromophoric group with an absorption region situated in the near ultraviolet region of the spectrum) the change of the value of  $n$  from 0 to 1 brings about a change in the direction of rotation, this direction remaining constant for the substances with higher values of  $n$ . In the few cases<sup>2</sup> where no change of sign was observed, the analysis of the dispersion curve showed that the dispersion was anomalous, i.e., the sign of the rotation was opposed to that of the first contribution. These facts led to the belief that in all other cases, the observed changes of rotation were due to changes in the first contribution. Further, there was observed a periodicity in the values of the rotations of the individual members with the progressive increase in the value of  $n$ .

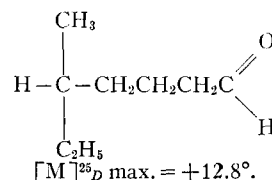
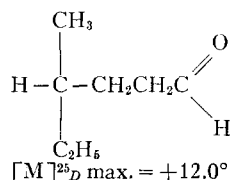
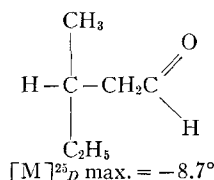
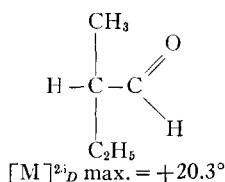
The group of substances thus far analyzed, however, was of a nature which did not permit direct measurement of the course of rotation within the region of the nearest absorption band. Hence the direction and value of its partial rotation were obtained by the analysis of the rotatory dispersion curve outside the band.

It was therefore desirable to analyze a group of substances of the same general type but with a chromophoric group which permitted the measurement of its rotation within the region of

the absorption band. The group  $-\text{C} \begin{array}{l} \nearrow \\ \searrow \end{array} \begin{array}{l} \text{H} \\ \text{H} \end{array}$  held

out the promise of presenting these advantages. The first absorption band of this group at 2950 Å is weak ( $E \approx 20$ ) well isolated without any overlapping, thus permitting calculation of its partial rotation from the experimental dispersion curve within the region of the absorption band.

Hence, the following series of configurationally related aldehydes of the above general type were prepared:



The mode of preparation of these substances has been described elsewhere.<sup>3</sup> The present communication deals with the analysis of the rotatory dispersion curves of the above four aldehydes. The results of the observations are summarized in Fig. 3. The ordinate represents the absolute magnitude of the partial rotation (which is proportional to the circular dichroism) of the band  $\lambda_{2950}$ , the abscissa the number of carbon atoms between the asymmetric center and the aldehydic group (the numerical value of  $n$ ).

It is evident that there is a periodicity in the

value of the rotatory component of the band  $\lambda_{2950}$ . This partial rotation is comparatively small in the third and fourth members ( $n = 2$  and 3). However, its magnitude in the fourth member is twice that of the third. Thus it is clear that the periodic variations of rotation with the increase of the numerical value of  $n$ , observed in the visible part of the spectrum are due to periodic variations in the partial contribution of the band  $\lambda_{2950}$ . These observations are significant for they add weight to the conclusions reached earlier regarding substances whose nearest absorption bands were not accessible to direct analyses.<sup>4</sup>

<sup>1</sup> P. A. Levene and R. E. Marker, J. Biol. Chem. **103**, 299 (1933).

<sup>2</sup> P. A. Levene, A. Rothen and R. E. Marker, J. Chem. Phys. **1**, 662 (1933).

<sup>3</sup> P. A. Levene and A. Rothen, J. Biol. Chem., **111**, 739 (1935).

<sup>4</sup> In an interesting and recent article, H. Hudson, M. L. Wolfrom and T. M. Lowry, J. Chem. Soc. 1179 (1933),

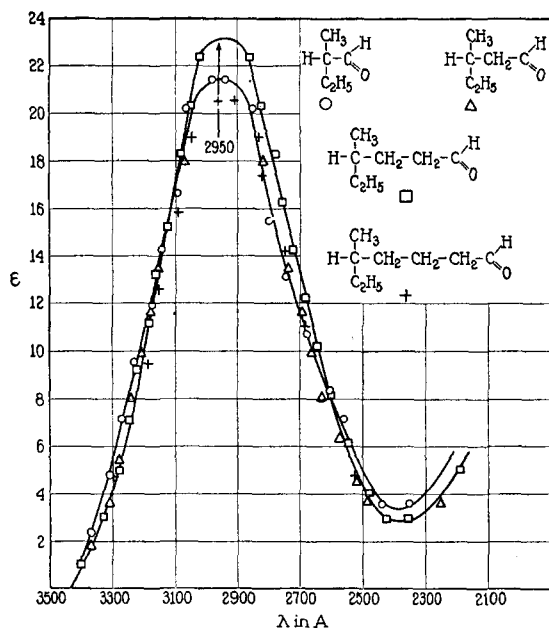


FIG. 1.

The physical basis of the observed changes in rotation still remains a matter of speculation. Among all the theories concerning optical activity, none is able to predict, first, that a change of sign occurs in the function  $(\varphi)_\lambda^* = f(n)$  when  $n$  is changed from 0 to 1; second, that for  $n > 1$  this function keeps the same sign but varies periodically with the successive values of  $n$  in magnitude only. It is possible to deduce from the mechanical model used by W. Kuhn<sup>5</sup> that a change of sign should occur when the distance between the two coupled oscillators increases, but the wave-length should be of the order of magnitude of interatomic distances, which is, of course, excluded in the case here considered. The more recent theory of Born<sup>6</sup> shows that one could expect a short periodicity in the function  $(\varphi)_\lambda = f(n)$  but no change of sign can be predicted.

In the absence of any other explanation for the observed facts, we venture to suggest one

studied the rotatory dispersion of aldehydic sugars. They report a strong partial rotation of the band  $\lambda_{2900}$  which, in one case, is practically the only rotatory component of the rotation observed. But the presence, in those compounds, of three or four asymmetric carbon atoms renders interpretation more difficult.

\* The symbol  $(\varphi)_\lambda$  will be used to denote the partial rotatory contribution of the band  $\lambda$  due to the group X.

<sup>5</sup> W. Kuhn and K. Freudenberg, "Drehung der Polarisationsebene des Lichtes," *Hand- und Jahrbuch der chemischen Physik* (Leipzig, 1932), p. 47.

<sup>6</sup> M. Born, Proc. Roy. Soc. A869, 84 (1935).

which is in harmony with the deduction from Kuhn's mechanical model and with the theoretical consideration of Born<sup>6</sup> and others. The facts to be remembered are: First, that the configuration remaining constant, it is only the change of  $n$  from 0 to 1 which brings about inversion of sign of a given  $(\varphi)_\lambda$ , the sign remaining the same in all the other members of a homologous series. Second, there is no change in direction of rotation and no periodicity if  $X = \text{CH}_3$  so long as the length of the chain  $(\text{CH}_2)_n\text{CH}_3$  does not exceed that of R. Thus it is evident that the polar nature of X is a requisite for the phenomenon. On the other hand, it is known that the polar groups induce alternating polarities in the consecutive carbon atoms of the chain, which naturally is extended to the asymmetric carbon atom. Hence it is reasonable to assume that the dissymmetry of the asymmetric carbon atom will alter with the change of the electric charge of the neighboring carbon atom.

#### ANALYSIS OF THE ABSORPTION BAND

The absorption curves of the aldehydes may be seen in Fig. 1. It is apparent that the position of the band is identical in all four compounds, the intensity being of the same order of magnitude. The absorption curves can be expressed by an exponential equation based on a Maxwellian distribution.

TABLE I. Rotatory dispersion of dextro-2-methylbutanal-1 in heptane.

Concentration: 1.337M. Visible region:  $l = 40$  cm. U.V.:  $l = 5$  cm from 3640 to 3460Å, 1 cm for 3420Å, 0.1 cm for  $\lambda < 3420$ .

$\lambda(\text{Å})$	$\alpha^{25}$	$[\text{M}]^{25}_{\text{max.}}$	$[\text{M}]^{25}_{\text{max.}} = \frac{5.104}{\lambda^2 - 0.0932}$
5875.6	+5.140	+20.28	+20.25
5780.1	+5.369	+21.19	+21.19
5460.7	+6.315	+24.92	+24.92
4358.3	+13.37	+52.76	+52.76
4046.6	+18.30	+72.21	+72.36
3640	+3.98	+125	+130
3588	+4.48	+141	+144
3540	+4.99	+157	+159
3500	+5.49	+173	+174
3460	+6.00	+189	+188
3420	+1.35	+215	+215
3320-3070	+0.20	+325	—
2980	0.00	0	—
2930	-0.10	-160	—
2770	-0.35	-450	—
$\leq 2350$	-0.15	-240	—

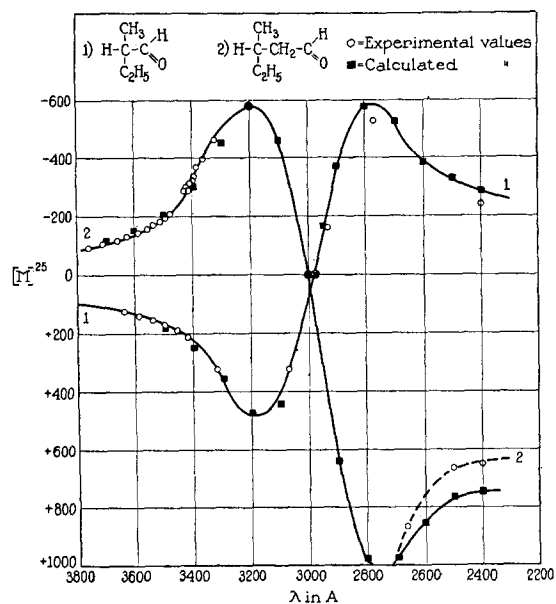


FIG. 2.

 TABLE II. Rotatory dispersion of *levo*-3-methylpentanal-1 in heptane.

Constants of sample:  $\delta_D^{25}$  0.8010,  $n_D^{25}$  1.3989. Concentration 1.338M.  
Visible region:  $l=40$  cm. U.V.:  $l=10$  cm from 3970 to 3475 Å  
1 cm for  $a$ , 0.5 cm for  $b$ , 0.1 cm for  $c$ .

$\lambda(\text{Å})$	$\alpha^{25}$	$[M]^{25}_{\text{max.}}$	$[M]^{25}_{\text{max.}}$
			$= \frac{7.569}{\lambda^2 - 0.093}$
			$+ \frac{6.693}{\lambda^2 - 0.032}$
5875.6	-1.320	-8.67 <sub>9</sub>	-8.64
5780.1	-1.409	-9.26 <sub>4</sub>	-9.24
5460.7	-1.786 <sub>5</sub>	-11.74 <sub>6</sub>	-11.75
4358.3	-5.43	-35.7	-35.7
4046.6	-8.54	-56.1 <sub>5</sub>	-56.1
3885	-2.75	-72.3	-74.3
3850	-3.00	-78.9	-79.5
3710	-4.00	-105	-106
3660	-4.50	-118	-119
3630	-5.00	-131	-128
3590	-5.50	-144.5	-142
3555	-6.00	-158	-156
3535	-6.50	-171	-165
3510	-7.00	-184	-177
3492	-7.50	-197	-188
3475	-8.00	-210	-198
3430	-1.11 (a)	-292	
3420	-1.17 (a)	-323	
3395	-1.25 (a)	-329	
3360	-0.76 (b)	-400	
3320	-0.70 (b)	-460	
3200	-0.22 (c)	-580	
3000	-0.00 (c)	0.0	
2730	+0.43 (c)	+1100	
2660	+0.33 (c)	+870	
2500	+1.26 (b)	+670	
2400	+2.46 (a)	+650	

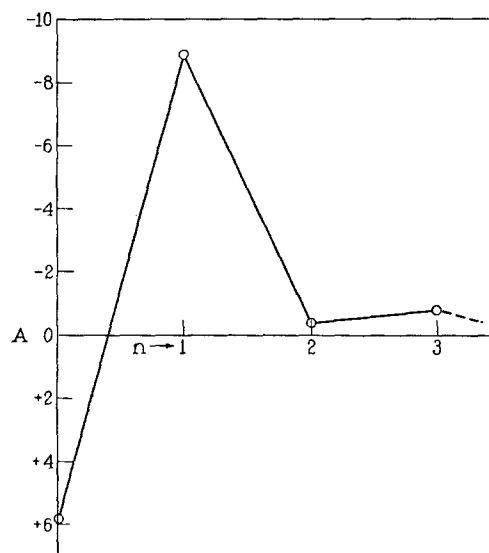


FIG. 3.

### ANALYSIS OF ROTATORY DISPERSION CURVE

The measurements of the rotatory dispersions may be found in Tables I, II, III, IV and on Fig. 2. The values found in the fourth column of the tables have been calculated, using in one case a one-Drude term, and in the others a two-Drude term formula. The constants of the formulas have been so chosen as to reproduce as well as possible the experimental data in the visible and very near ultraviolet regions. The agreement between experimental and calculated values is quite satisfactory especially if one considers that in the case of 3-methylpentanal-1 the two terms of opposite sign are of the same order of magnitude. The dispersion constants of the first terms come very close to the position of the absorption

 TABLE III. Rotatory dispersion of *dextro*-4-methylhexanal-1 in heptane.

Constants of sample:  $\delta_D^{25}$  0.8132,  $n_D^{25}$  1.4081. Concentration 1.016M.  
Visible region:  $l=40$  cm. U.V.:  $l=10$  cm for 3490 Å  
and 0.5 cm for 2350 Å.

$\lambda(\text{Å})$	$\alpha^{25}$	$[M]^{25}_{\text{max.}}$	$[M]^{25}_{\text{max.}}$
			$= \frac{0.371}{\lambda^2 - 0.087}$
			$+ \frac{4.114}{\lambda^2 - 0.036}$
5875.6	+0.800	+12.01	+11.87
5780.1	+0.819	+12.30	+12.30
5460.7	+0.930	+13.96	+13.93
4358.3	+1.54 <sub>0</sub>	+23.1 <sub>2</sub>	+23.12
4046.6	+1.82	+27.3	+27.37
3490	+0.60	+36	+37
2350	+0.20	+240	+228

TABLE IV. *Rotatory dispersion of dextro-5-methylheptanal-1 in heptane.*

Constants of sample:  $\delta_{25}^D$  0.8164,  $n_{25}^D$  1.4144. Concentration 0.616M.  
Visible region:  $l = 100$  cm. U.V.:  $l = 20$  for 3770 and 3580Å,  
5 cm for 3450Å, 1 cm for 2460Å.

$\lambda(\text{Å})$	$\alpha^{25}$	$[M]^{25}_{\text{max.}}$	$[M]^{25}_{\text{max.}} = -\frac{0.8158}{\lambda^2 - 0.087}$
			$+\frac{4.9102}{\lambda^2 - 0.036}$
5875.6	+1.596	+12.79	+12.72
5780.1	+1.643	+13.17	+13.17
5460.7	+1.856	+14.88	+14.86
4358.3	+2.99	+23.9 <sub>7</sub>	+23.97
4046.6	+3.47	+27.8 <sub>2</sub>	+27.81
3770	+0.80	+32	+31.5
3580	+0.90	+36	+33.5
3450	+0.20	+32	+33.6
2460	+0.30	+240	+230

band, with a slight displacement towards the red. The dispersion curves of the first two compounds ( $n=0$  and 1) are reproduced in Fig. 2. It was impossible to obtain a two-term formula representing accurately the experimental data over the whole wave-length range covered. The smallness of the angles observed as well as a gradual decrease in the rotations due to decomposition prevented any accurate determinations in the immediate neighborhood of the band. The calculated values have been obtained from a two-term formula, the first term being a Kuhn-Braun<sup>7</sup>-Lowry-Hudson<sup>8</sup> term. The general formula used was

$$[M]_{\text{max.}}^{25} = \frac{\phi\lambda_\phi}{m\lambda} \left[ e^{-[(\lambda-\lambda_0)/\theta]^2} \int_0^{(\lambda-\lambda_0)/\theta} e^{x^2} dx + \frac{\theta}{2(\lambda+\lambda_0)} \right] + \frac{B}{\lambda^2 - \lambda_1^2},$$

where:  $\phi = +500^\circ$ ,  $m = 0.560$ ,  $\lambda_\phi = 0.3166$ ,  $\lambda_0 = 0.2980$ ,  $\theta = 0.0207$ ,  $B = -0.798$ ,  $\lambda_1^2 = 0.036$  for levo 2-methylbutanal-1 and  $\phi = -700^\circ$ ,  $m = 0.560$ ,  $\lambda_\phi = 0.3180$ ,  $\lambda_0 = 0.2980$ ,  $\theta = 0.0223$ ,  $B = +8.07$ ,  $\lambda_1^2 = 0.036$  for dextro-3-methylpentanal-1. (To comply with the usual convention adopted in polarimetry, wave-lengths are expressed in microns.) As known,<sup>7</sup> the first term of this formula reduces to a simple Drude term  $A/(\lambda^2 - \lambda_0^2)$  for values of  $\lambda > 4\theta + \lambda_0$  where  $A = \phi\lambda_\phi\theta/m$ .

The following facts should be brought out: First, the center of the active part of the band is slightly displaced towards the red as compared to the absorption band; second, the active band does not spread over the entire width of the absorption band: The constants  $\theta$  determined from absorption measurements are very much larger than  $\theta$  determined to fit the dispersion formulas; third, the high value of the dispersion constants of the second terms for all compounds indicate that the second contribution is also located for the most part in the aldehydic group.

Experiments were attempted to determine directly the dichroism in the band  $\lambda 2950$ . As

expected, it could be detected only in the first two compounds. The measurements remained of a qualitative nature because of the small angles, but were, however, of the right order of magnitude.

## EXPERIMENTAL

The instruments used have been previously described<sup>9</sup> and the same precision is claimed. The method followed to determine the circular dichroism was that described by W. Kuhn.<sup>10</sup>

The compounds used were not resolved to the maximum. All observed  $\alpha$  values as given in the tables were multiplied by an appropriate coefficient to bring them to the maximum. The decrease of rotation due to decomposition was taken into account when the series of measurements extended over a long period of time.

<sup>7</sup> W. Kuhn and E. Braun, *Zeits. f. physik. Chemie* **B8**, 281 (1930).

<sup>8</sup> T. M. Lowry and H. Hudson, *Phil. Trans. Roy. Soc. London* **A232**, 117 (1933).

<sup>9</sup> P. A. Levene and A. Rothen, *J. Chem. Phys.* **2**, 681 (1934).

<sup>10</sup> W. Kuhn and E. Braun, *Zeits. f. physik. Chemie* **B8**, 445 (1930).