40. *The Rotatory Dispersion of Organic Compounds. Part XXX. Campholic Aldehyde.*

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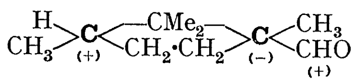
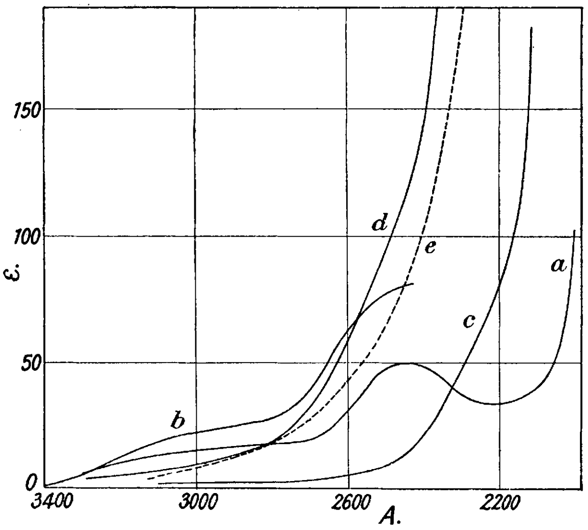
Measurements of the circular dichroism of camphor (Kuhn and Gore, *Z. physikal. Chem.*, 1931, *B*, **12**, 389) and of camphor-β-sulphonic acid (Lowry and French, J., 1932, 2654) have shown that the ultra-violet absorption band of the ketone is composite, since the optical activity is concentrated in the low-frequency half of the band. The maximum of circular dichroism is therefore displaced relatively to the maximum of absorption in the direction of *lower* frequencies from 2910 to 3020 A. in camphor, and from 2840 to 2900 A. in the sulphonic acid. Similarly in carvomenthone (Lowry and Lishmund, J., 1935, 709) the maximum of circular dichroism is displaced as in camphor by 110 A., from 2886 to 2995 A. The visual absorption band of camphorquinone (Part XXIX; J., 1936, 1156) is also composite, since the main optically active component is accompanied by two smaller inactive bands, one on either side of the principal band. On account of this symmetrical distribution of the components, the maximum of circular dichroism is slightly displaced in the direction of *higher* frequencies.

In the aldehydes, the evidence for complexity is much less clear than in the ketones. Thus, in a series of four open-chain aldehydic acetates (Part XXIII, J., 1933, 1179; Part XXV, J., 1935, 696) the maxima of absorption and of circular dichroism agreed within 10 A., the difference increasing to 30 A. only in the *ketonic* sugar, penta-acetyl μ-*d*-fructose; but the composite character of the absorption is indicated (as in camphorquinone) by the greater half-width of the absorption band, as compared with the band of circular dichroism, in every case except penta-acetyl μ-*d*-glucose. In these circumstances, it was desirable to study the behaviour of a simple aldehyde, containing only hydrocarbon radicals in addition to the aldehydo-group, and this was made practicable by the generosity of Prof. H. Rupe of Basel, who prepared for us a specimen of campholic aldehyde (inset).



The results are of considerable interest, because the circular dichroism was found to have the normal frequency of an aldehydic band, although the absorption curve showed only a step-out at this wave-length. It also appeared that the principal optically active band at 2995 A. was accompanied by a secondary band of similar sign at about 3200 A. The constants of this secondary band of circular dichroism were therefore calculated from the residual anomalies in the curve of rotatory dispersion. The subsidiary band discovered in other simple aldehydes by Schou (*Compt. rend.*, 1926, **182**, 965) also exists in campholic aldehyde, although completely hidden from view in a " step-out." It is also optically active, with the same sign as the main band, and in this respect differs from the aldehydic and ketonic sugars (*loc. cit.*).

FIG. 1.



a. Absorption spectrum of campholic aldehyde in cyclo*hexane.*
b. ,, ,, ,, ,, *chloroform.*
c. ,, ,, ,, *acid in alcohol.*
d. }*Absorption spectra of old* cyclo*hexane solutions of the aldehyde, after complete extraction of campholic*
e. } *acid.*

Absorption.—A freshly prepared solution of the aldehyde in *cyclo*hexane showed (i) a step-out, passing through a point of inflexion $\varepsilon = 15$ at 2950 A., (ii) an absorption band with a maximum $\varepsilon = 50$ at 2450 A., and (iii) an intense general absorption beyond 2100 A. (Fig. 1*a*). A solution in chloroform gave a similar curve (Fig. 1*b*) but the absorption was about 50% greater, and the curve was cut off by the absorption of the chloroform before the maximum was reached. The absence of the usual aldehydic band was also proved by the use of a hydrogen discharge lamp as a source of continuous ultra-violet radiation.

A solution in *cyclo*hexane which had been kept for more than a year yielded a considerable extract of campholic acid, the absorption curve of which is shown in Fig. 1*c*; and when the whole of the acid had been extracted, it yielded a curve of general absorption, Fig. 1*d* or *e*, which we attribute to a condensation product of the aldehyde.

The absorption band at 2450 A. is abnormal in a simple aldehyde, since these usually exhibit a maximum at about 2900 A., but its origin is of no direct importance in the present research, since the circular dichroism is concentrated in the step-out, and there is no evidence that this band makes any substantial contribution to the rotatory power of the material. An analogy may be found in pulegone where the ketonic band at 2800 A. is replaced by a step-out (log $\varepsilon = 1{\cdot}625$ at 3210 A.) and a band (log $\varepsilon = 3{\cdot}8$ at 2430 A.), owing to conjugation, but curves (*c*), (*d*), and (*e*), which exhibit strong absorption only at wave-lengths less than 2450 A., lend little support to the view that the band is due either to oxidation or to condensation. Since no further material was available, we merely record the fact that a specimen of the aldehyde, which had been recently distilled in Basel into a glass tube and sealed up for transmission to Cambridge, gave the absorption curve shown in Fig. 1*a*, without prejudice to further enquiries as to the origin of the band.

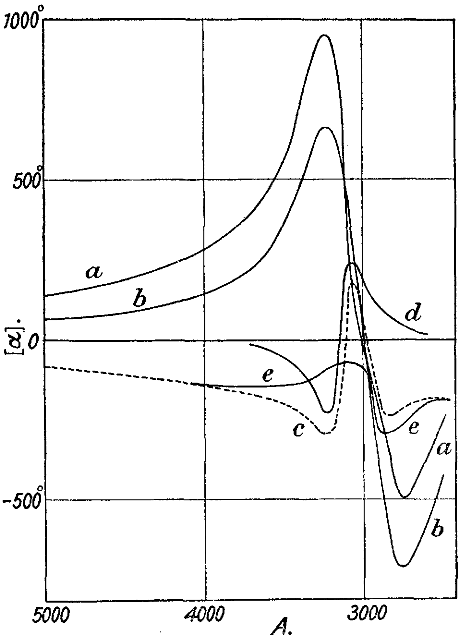
Circular Dichroism.—The circular dichroism reaches its maximum at 2995 A., with $(\varepsilon_l \sim \varepsilon_r)_{\text{max.}} = 0{\cdot}50$, and $\lambda' = 418$ A. The subsidiary band derived from the dispersion curve had the following parameters:

$\lambda_0 = 3140$ A., $(\varepsilon_l \sim \varepsilon_r)_{\text{max.}} = 0{\cdot}18$, $\lambda' = 160$ A.

Owing to the over-lapping of the two bands of similar sign, the curve is unusual in being steeper on the high-frequency side, but its components are more normal in shape.

The use of the subsidiary band gives a rotatory dispersion difference curve which is considerably nearer to the theoretical form, in that it does not cross the axis, behaviour which is quite impossible according to all theories for the analysis of dispersion from the activity of a simple band. There remains, however, in the final difference curve an anomaly which suggests the analysis to be not quite perfect. This is probably due to a second complicating subsidiary centred at 2940 A., since alteration of the primary –CHO contribution does little towards eliminating the anomaly. It should, however, also be mentioned that the extent of the maxima (Fig. 2*c*) is slightly exaggerated owing to the fact that the primary –CHO contribution should be calculated from the theoretical curve of simple circular dichroism. The difference, however, is slight, since the true extent of the subsidiary dispersion loop is about 170° as opposed to 240°, and the form remains unchanged.

FIG. 2.



a. *Observed rotations for campholic aldehyde.*
b. *Calculated carbonyl contribution.*
c. *Difference curve,* (a ~ b) *with sign reversed.*
d. *Calculated subsidiary component.*
e. *Final difference curve, showing third component.*

Rotatory Dispersion.—The rotatory dispersion was measured in two solvents, chloroform and *cyclo*hexane, in the regions of transparency and of absorption. The range of transparency high enough for Drude analyses was 6708—3768 A. with *cyclo*hexane as solvent, and 6708—3674 A. with chloroform. Three-constant, two-term equations were used to express the results, and the differences between the values for the two solvents were very slight. The value of λ_0 was in each case 2868 A. as compared with 2990 and 3000 A. from circular dichroism and absorption measurements respectively. The equations are of interest owing to their consisting of two terms of similar sign. This fact indicates directly that the predominant residual rotation as shown in Fig. 2 is not responsible for the induced activity of the aldehyde group, since these two terms could not under these conditions have the same sign. The results would indicate that the major part of the residual rotation is due to the asymmetric grouping in the γ position from the carbonyl group. The α asymmetric grouping is, however, responsible for the large induced dissymmetry, although the reason for the complexity of the curve may be found in the independent interaction of the two centres with the carbonyl group. The analysis by Drude's equation thus leads to the same general results as that by the more complete method, and the signs of the partial rotations are indicated on the formula above. A comparison shows campholic aldehyde to be analogous to menthone and carvomenthone (*loc. cit.*) in this respect.

Rotatory Dispersion of Campholic Aldehyde in cyclo*Hexane at* 20°.

(a) $c = 16{\cdot}6525$ g./100 c.c.; $l = 2$ dm. (b) $c = 16{\cdot}6127$ g./100 c.c.; $l = 2$ dm.

$$[\alpha] = 18{\cdot}454/(\lambda^2 - 0{\cdot}08225) + 8{\cdot}346/\lambda^2.$$

λ.	$[\alpha]$, obs.	$[\alpha]$, calc. — $[\alpha]$, obs.	Soltn.	λ.	$[\alpha]$, obs.	$[\alpha]$, calc. — $[\alpha]$, obs.	Soltn.
6438	75·64°	0·03°	a	4358	215·29°	0·00°	a
5893	93·68	0·00	a	4356	215·80	−0·15	b
5780	98·34	−0·08	a	4167	248·91	1·08	b
5461	113·49	−0·35	a	4095	266·96	−1·19	b
5086	136·92	−0·04	a	3996	290·64	0·00	b
4800	160·73	0·07	a	3867	336·19	−6·12	b
4678	173·64	−0·41	a	3768	375·32	−7·56	b
4673	174·11	−0·31	b				

Rotatory Dispersion of Campholic Aldehyde in Chloroform at 20°.

$$[\alpha] = 18{\cdot}276/(\lambda^2 - 0{\cdot}08227) + 7{\cdot}985/\lambda^2.$$

(a) $c = 13{\cdot}368$ g./100 c.c., $l = 2$ dm.; (b) $c = 12{\cdot}740$ g./100 c.c., $l = 2$ dm.; (c) $c = 12{\cdot}270$ g./100 c.c., $l = 1$ cm.; (d) $c = 1{\cdot}44$; (e) $c = 0{\cdot}720$; (f) $c = 0{\cdot}530$; (g) $c = 0{\cdot}510$; (h) $c = 0{\cdot}246$ g./100 c.c., $l = 1$ cm.

λ.	$[\alpha]$, obs.	$[\alpha]$, calc. — $[\alpha]$, obs.	Soltn.	λ.	$[\alpha]$, obs.	$[\alpha]$, calc. — $[\alpha]$, obs.	Soltn.
6708	67·33°	0·12°	a	6497	72·35°	0·35°	a
6438	74·22	0·04	a	6362	76·52	−0·13	a
6104	84·35	0·05	a	5893	91·99	0·00	a
5782	96·38	0·01	a	5780	96·49	−0·01	a
5700	100·09	−0·20	a	5536	107·80	−0·23	a
5472	111·30	−0·25	a	5461	111·77	−0·35	a
5218	125·37	0·09	a	5209	126·10	−0·01	a
5153	129·91	−0·13	a	5105	133·26	−0·18	a
5086	134·50	0·00	a	4934	145·40	0·79	a
4810	157·08	−0·03	a	4800	157·50	0·55	a
4722	165·80	−0·10	a	4680	169·64	0·45	a
4678	170·00	0·30	a	4554	184·50	0·06	b
4358	212·25	−0·49	a	4549	184·6	0·65	b
4271	224·8	1·46	b	4070	266·0	1·47	b
3876	322·8	−0·73	b	3872	323·4	0·00	b
3756	373·9	−6·53	b	3713	393·7	−10·82	b
3674	413·2	−7·31	b				

Region of absorption.

λ.	$[\alpha]$, obs.	Soltn.	λ.	$[\alpha]$, obs.	Soltn.
3739	369·3	c	3670	411·0	c
3517	513·8	c	3459	584·0	c
3450 3125	597	e	3426 3425	649·5 653	c d
3406	690·0	c	3382	730·0	c
3355 3144	806	e	3347 3134	800	d
3250 3180	901	e	3220 3091	950 302	f f
3067	157	g	3018	0	ef
2936	−157	g	2853	−302	g
2860	−320	e	2787	−470	g
2770	−497	e	2540	−320	h
2755	−500	g			

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