243. *Studies of Rotatory Dispersion. Part XXIX. Absorption and Circular Dichroism of Camphorquinone.*

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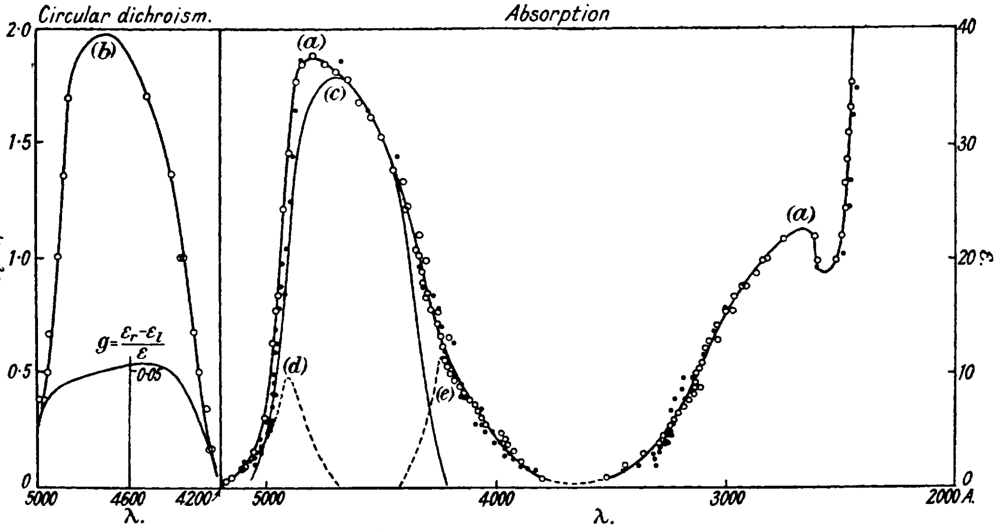
The optical properties of camphorquinone are of interest intrinsically, as well as on account of their close connection with the parent substance, camphor. These properties have already been investigated in some detail The rotatory dispersion was studied in benzene and in methyl alcohol by Lifschitz (*Z. physikal. Chem.*, 1923, **105**, 27), who followed the curve as far as the first maximum in the region of absorption. Solutions in toluene were investigated by Wedeneewa (*Ann. Physik*, 1923, **72**, 122), who plotted both maxima, and by Pfleiderer (*Z. Physik*, 1926, **39**, 663), who measured the magnetic as well as the optical rotatory dispersion. Lowry and Cutter (J., 1925, **127**, 614; see also Lowry and Richards, J., 1924, **125**, 2511) determined the rotatory dispersion at long wave-lengths in benzene, and Lowry and Gore (*Proc. Roy. Soc.*, 1932, *A*, **135**, 22) followed the curve right through the absorption band both in *cyclo*hexane and in the vapour state.

The absorption (Stewart and Baly, J., 1906, **89**, 496) was investigated in solution by Wedeneewa (*loc. cit.*), and by Lowry and French (J., 1924, **125**, 1921), who found optical evidence of two types of conjugation in the contrast between camphorquinone and methylenecamphor. It was examined in the vapour state by Purvis (J., 1923, **123**, 2518); and Lowry and Gore (*loc. cit.*) studied it both in *cyclo*hexane and in the vapour.

The only measurements of circular dichroism are those of Wedeneewa (*loc. cit.*); but her results do not appear to be of great precision, in part because the number of readings was too small, especially in the neighbourhood of the maximum. The curve which she plotted persists throughout the visible absorption band, but is very unsymmetrical, being much steeper on the side of longer wave-lengths. The maximum is shown as a sharp point, which is displaced from 4700 to 4900 A. with respect to the rounded maximum of visible absorption. Since great improvements have been made in the set-up of apparatus for the measurement of circular dichroism, it was of interest to reinvestigate the form of this curve for camphorquinone; at the same time the absorption curve was redetermined, in order to ensure that the data should be strictly comparable in every respect with those for the circular dichroism of the solutions. In each case the solvent used was *cyclo*hexane.

1. *Absorption.*—The absorption curve (*a*) (see figure) is very similar to that of Lowry and Gore, whose readings are shown by black dots. The wave-length of the maximum at 4780 A. in the blue region of the spectrum is identical with that of Lowry and Gore, but it is substantially greater than that given by Wedeneewa (4700 A.); its intensity $\varepsilon = 38{\cdot}8$ is about 1% less than the value, $\varepsilon = 39{\cdot}2$, deduced by Lowry and Gore from points rather more remote from the maximum. The absorption curve falls steeply on the side of longer wave-lengths, and less steeply on the side of shorter wave-lengths, but it does not show the small anomaly recorded by Wedeneewa. In the ultra-violet, the absorption is negligible from 3800 to 3400 A., but it then rises steeply, especially beyond 2400 A. A " step-out " recorded by Lowry and Gore in the range from 2900 to 2500 A. is now shown, by a fuller series of observations, to include an absorption band with a maximum, $\varepsilon = 23$ at 2650 A., followed by a shallow minimum $\varepsilon = 20$ at 2550 A. The " persistence " of this band, $\log \varepsilon_{\text{max.}} - \log \varepsilon_{\text{min.}} = 0{\cdot}06$ approximately, is very small when compared with that of the band in the visible, which has a persistence in the same units of about 1·6, but there can be no doubt of its real existence, since all the points plotted by Lowry and Gore fall on the continuous loop of curve (*a*).



Absorption and circular dichroism of camphorquinone. (a) *Absorption.* (b) *Circular dichroism.* (c) *Optically active absorption band (calc.).* (d) *and* (e) *Residual absorption bands.* (g) *Dissymmetry factor.*

2. *Circular Dichroism.*—The curve (*b*) of circular dichroism differs in almost every respect from that of Wedeneewa. Thus: (i) The maximum, $\varepsilon_r - \varepsilon_l = 1{\cdot}95$ at 4700 A., is smoothly rounded instead of being sharp. (ii) Its wave-length, instead of being displaced from 4700 to 4900 A., is shifted slightly in the opposite direction from the maximum of absorption, from 4780 to 4700 A. (iii) The curve of circular dichroism is steeper on the side of longer wave-lengths, but is much less unsymmetrical than that of Wedeneewa. Moreover, it does not flatten out as it approaches the axis on the side of shorter wave-lengths, but falls instead rather precipitately, as if a reversal of sign were impending. Attempts to detect circular dichroism in the range from 2965 to 4200 A., however, gave only negative results, so that this reversal could not in fact be observed.

3. *Dissymmetry Factor.*—The dissymmetry factor, $g = (\varepsilon_r - \varepsilon_l)/\varepsilon$ [curve (*g*)], rises progressively in the centre of the band from 4900 to 4300 A., in approximate proportion to the frequency, as is required by theory for a band which includes only one component;

but it falls off on either side as the absorption becomes more feeble. This conclusion was established with some difficulty, since the circular dichroism was not at all easy to measure on the side of longer wave-lengths, on account of the fewness and weakness of the lines available in this region. Under these conditions, the readings of circular dichroism tended to extend to longer wave-lengths than the readings of absorption, and the dissymmetry factor rose abruptly as the absorption became small. The absorption curve was therefore checked by reading lines of the cadmium and the copper arc, and the circular dichroism was read for the only strong line (Cd 5086) which appeared to be available in this region. In these circumstances we are convinced that the dissymmetry factor, as now plotted from our revised readings of the plates, is substantially correct, and that the anomaly referred to above was due to errors in the earlier readings of circular dichroism.

4. *Analysis of Absorption Curve.*—Measurements of circular dichroism have already established the complexity of the principal absorption band of camphor (Kuhn and Gore, *Z. physikal. Chem.*, 1931, *B*, **12**, 389) and of camphor-β-sulphonic acid (Lowry and French, J., 1932, 2655), since, in each of these compounds, circular dichroism is developed only on the long-wave-length side of the ketonic band, which must therefore include also an optically inactive component of shorter wave-length. In the present instance, no similar concentration of circular dichroism was observed, but the form of the absorption band differs so completely from that of the curve of circular dichroism as to leave little doubt of its complexity. In order to test this, we used our curve of circular dichroism to calculate a theoretical absorption curve (*c*) on the assumption that the whole of the absorption at $\lambda = 4500$ A. was due to the optically active component and that the factor g was proportional to the frequency. These assumptions enabled us to recognise the existence of two optically inactive bands as indicated by the broken lines curves (*d*) and (*e*). Other analyses would be possible, if we had assumed that only a part of the absorption at 4500 A. was due to the optically active absorption band; but the existence of *three* components is clearly established, since there is an obvious surplus of absorption on either side of the main band; and the form of the subsidiary bands (*d*) and (*e*) is so normal that we are ready to accept our first analysis as substantially correct.

EXPERIMENTAL.

The camphorquinone (Kahlbaum) was purified by sublimation. After drying in a desiccator over-night, it melted sharply at 198°. The *cyclo*hexane had been purified by distillation and freezing, and was transparent in the range of wave-lengths covered by the experiments.

The absorption in the visible spectrum was measured with a Nutting spectrophotometer and a filament-lamp as a source of a continuous spectrum. The wave-lengths were read off from a drum, the calibration of which was checked against lines of the mercury arc. Measurements of absorption were, however, also made with the line spectra of cadmium and copper, in order to ensure that the curves of absorption and circular dichroism were not displaced by any error of wave-length. In the ultra-violet a Spekker photometer was used, with a tungsten-steel spark as a source of light.

The circular dichroism was measured with the apparatus used by Lowry and Hudson (*Phil. Trans.*, 1933, *A*, **232**, 177) in the investigation of the xanthates. In the ultra-violet, a rhomb of fused silica and a quartz spectrograph were used; but the dichroism of the visual band was observed with a rhomb of Uviol glass, and a spectrograph with two glass prisms; a few plates were taken, however, with a single prism of glass. The iron arc was the principal source of light, but has very few lines in the region of maximum circular dichroism. Attempts to use a brass arc, and a spark between uranium electrodes, were not satisfactory. On the other hand, the lines from an enclosed cadmium arc were found to be very suitable for use with this apparatus, although only one of them was of suitable wave-length to be of value in the present instance.

SUMMARY.

(*a*) The absorption and circular dichroism of camphorquinone have been measured in solutions in *cyclo*hexane.

(*b*) The curve of circular dichroism resembles a parabola, with a smoothly-rounded maximum, $\varepsilon_r - \varepsilon_l = 1{\cdot}95$ at 4700 A., but it is definitely steeper on the side of longer wave-lengths.

(*c*) The visual absorption band rises to a maximum, ε = 38·8 at 4780 A., but a second band of very small persistence was discovered in the ultra-violet with a maximum ε = 23 at 2650 A.

(*d*) The principal component of the visual absorption is the optically active band, of which the circular dichroism was recorded; but the form of the absorption curve is much less regular, and can only be interpreted by assuming the presence of optically inactive components on either side of the main component. These inactive components are shown tentatively with maxima ε = 9·4 at 4900 A., and ε = 11·4 at 4230 A.

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