XXXI.—*The Rotatory Dispersive Power of Organic Compounds. Part IX. Simple Rotatory Dispersion in the Terpene Series.*

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In a paper on "The Form of the Rotatory Dispersion Curves," published in 1913 (T., **103**, 1067), it was shown:

(a) That the rotatory dispersion in a large number of simple organic compounds may be expressed by the formula

$$\alpha = k/(\lambda^2 - \lambda_0^2),$$

where k is the "rotation constant" and λ_0^2 is the "dispersion constant" of the substance.

(b) That this formula can be applied both to magnetic and to natural rotatory powers.

(c) That a very simple method of testing the form of the dispersion curves is to plot the reciprocals of the rotatory powers against the squares of the wave-lengths. When the simple dispersion formula is valid, the observations will plot out to a straight line.

The validity of this simple dispersion formula was established in several ways. Thus:

(1) Twenty-five hydrocarbons, alcohols, and acids for which the ratio $\alpha_{4358}/\alpha_{5461} = 1.636$ were grouped together, and their *magnetic* dispersion ratios were averaged for six different wave-lengths; these averages showed a remarkable agreement with the ratios calculated by means of the simple dispersion formula.

(2) In the same way the *optical* dispersion ratios of eight secondary alcohols, for which $\alpha_{4358}/\alpha_{5461} = 1.651$, were found to agree closely with ratios calculated by the simple formula.

(3) A few optical and magnetic rotations of larger magnitude showed a similar close agreement in individual cases, without the necessity for averaging which arises when the readings are small.

(4) In the case of α - and β -methyl glucosides, very concordant results were obtained when the two constants of the simple equation were calculated (a) from the mercury readings α_{4358} and α_{5461} , (b) from the cadmium readings α_{5086} and α_{6438} (Lowry and Abram, *Trans. Faraday Soc.*, 1914, **10**, 108).

These earlier observations showed that the simple dispersion formula can be applied very generally to compounds of simple structure, such as the optically active secondary alcohols, which contain only a single asymmetric carbon atom and also to com-

pounds such as the glucosides which contain several asymmetric carbon atoms associated with the simplest possible radicles, for example, hydrogen, hydroxyl, and the like. An opportunity has, however, occurred recently of testing the validity of this same simple formula in the case of a large number of optically active compounds in which these elements of simplicity in the molecular structure are conspicuously absent. The striking results of this further test form the subject of the present communication.

The new data now under consideration were provided by the observations of Prof. Rupe, who in continuation of earlier experiments on the "Influence of Constitution on the Rotatory Power of Optically Active Substances" (*Annalen*, 1903, **327**, 157; 1909, **369**, 311; 1910, **373**, 121; 1913, **395**, 87, 136; 1913, **398**, 372; 1914, **402**, 149) has published a series of measurements of the optical rotatory power of (1) twelve derivatives of methylenecamphor, (2) menthol and eleven of its esters, (3) myrtenol and eleven of its esters, (4) three hydrocarbons derived from citronellaldehyde, (5) camphor, pulegone, and carvone (*Annalen*, 1915, **409**, 327). Unlike the previous series of measurements, which were confined to observations with sodium light, the last series included, in the case of almost every compound, readings for four different wave-lengths in the visible region of the spectrum. It was therefore possible to study, not only the optical rotatory power of the various compounds, but also the character of their rotatory dispersion.

The four wave-lengths, selected from a continuous spectrum, were $\lambda = 6563$, 5898, 5463, and 4861, corresponding closely with the Fraunhofer lines: $C = 6563$, $D = 5893$, $F = 4861$, and the green mercury line Hg 5461. In order to preserve a convenient sequence of lettering, these four wave-lengths were described as C , D , E , and F ; but, as the symbol E has long been applied to the Fraunhofer line of wave-length 5270, the symbol Q is used below for the green (quicksilver) line in the series, which thus becomes C , D , Q , F .

The various substances were examined either in the pure state as liquids at 20° or dissolved in benzene at 20° , since this solvent was found to have no very great influence on the rotatory powers; several substances were examined both in the pure state and in solution.

When the experimental work was approaching completion, the data were handed over for detailed analysis to Dr. A. Hagenbach, Professor of Physics in the University of Basle. The important deductions which he was able to make are set out in a paper on "Rotatory Dispersion in Homologous Series" (*Zeitsch. physikal.*

Chem., 1915, **89**, 570). The chief points of this paper are as follows:

(1) The dispersion ratio α_p/α_o is practically constant in each series of closely-related compounds. Compounds which differ in any marked degree from the average are regarded as "relatively anomalous."

(2) A similar statement may be made in reference to all the six ratios α_p/α_o , α_p/α_D , α_F/α_Q , α_Q/α_o , α_Q/α_D , α_D/α_o , as was shown by tabulating these ratios for (i) eight derivatives of methylene-camphor, (ii) menthol and seven of its esters, (iii) three hydrocarbons from citronellaldehyde.

(3) It follows, therefore, that if the dispersion law for one member of the series be given by the equation $\alpha = \phi(\lambda)$, the rotatory dispersion in every compound may be expressed by equations, such as:

$$\begin{aligned} [\alpha_1] &= C_1 \phi(\lambda). \\ [\alpha_2] &= C_2 \phi(\lambda). \\ [\alpha_3] &= C_3 \phi(\lambda). \end{aligned}$$

This proportionality of rotatory powers was demonstrated by tabulating the ratios α_2/α_1 , α_3/α_1 , α_4/α_1 , etc., in each of the three series of compounds.

Attempts were made to determine, mainly by graphical methods, the nature of the unknown function $\phi(\lambda)$. Thus, the equations of Biot,

$$\alpha = B/\lambda^2,$$

and of Stefan,

$$\alpha = A + B/\lambda^2,$$

were tested by plotting α against $1/\lambda^2$. Boltzmann's equation:

$$\alpha = A/\lambda^2 + B/\lambda^4 \quad \text{or} \quad \alpha\lambda^2 = A + B/\lambda^2,$$

was tested by plotting $\alpha\lambda^2$ against $1/\lambda^2$. In neither case was an exact linear law disclosed. The equations of Lommel, and the two-term equation which Drude used to express the rotatory power of quartz, could not be tested in this way; but the empirical equations:

$$\alpha = A + B/\lambda^n \quad \text{and} \quad \log \alpha = A + B/\lambda$$

were tested by plotting $\log \alpha$ against $\log 1/\lambda$ and against $1/\lambda$; subsequently, $\log \alpha$ was also plotted against λ , and α against $1/\lambda$ (*Annalen*, 1915, **409**, 349, 351), but again without disclosing any simple linear relation between these quantities. The nature of the function in the equation $\alpha = \phi(\lambda)$ thus remained still undiscovered. The present paper serves to supply this deficiency by showing that in almost every case the new dispersion data can be

expressed by a simple equation of the type first put forward by Drude.

The fact that Drude's equation was not used by Hagenbach, and in general failed during many years to secure the practical recognition which it deserves, may be accounted for in two ways. In the first place the equation was put forward, as an approximation only, in a very general form:

$$\alpha = \sum \frac{k_n}{\lambda^2 - \lambda_n^2},$$

containing an indefinite number of arbitrary constants. The arbitrary constants, λ_1^2 , λ_2^2 , λ_3^2 , . . . , in the denominator were deduced from measurements of refractive dispersion, and it was not even suggested that they could be derived (in a still more satisfactory way and often with much greater exactness) from the rotations themselves. In the second place, Drude demonstrated the validity of his equation only in one single case, namely, that of quartz, the equation for which took the form

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k}{\lambda^2}.$$

No data whatever were given for optically active liquids, and the magnetic rotatory dispersion in carbon disulphide and in creosote (!) was expressed by a different formula, also depending on measurements of refractive dispersion. The first extensive practical application of Drude's formula was therefore made less than six years ago in the second paper of the present series.

The easiest (although perhaps the least exact) method of testing the simple dispersion law, $\alpha = k/(\lambda^2 - \lambda_0^2)$, is to plot the reciprocals of the rotations against the squares of the wave-lengths. The dramatic effects which are produced by plotting $1/\alpha$ against λ^2 are shown by comparing the straight lines of Figs. 1 to 4 with the broken lines* or curves which were given by all other methods of plotting. It is specially remarkable that plotting α against $1/\lambda^2$ (Stefan's formula) should give curves, where plotting $1/\alpha$ against λ^2 (Drude's formula) gives very exact straight lines. These lines indicate clearly that, where half a dozen other relationships have failed, the simple Drude formula gives at once a satisfactory expression of the experimental data.†

* Hagenbach appears to have plotted his curves on the assumption that the "E" line used by Rupe was the Fraunhofer line ϵ_{5270} , and not the mercury line ϵ_{5461} .

† More exact data may perhaps compel the use of additional terms, as in the case of quartz, which requires one, two, or three terms, according to the range and accuracy of the data employed, but there are no indications of this in the data examined hitherto.

A marked exception occurs in the case of pulegone, which gives a smooth, full curve, and evidently shows "complex" rotatory dispersion. Diphenylmethylenecamphor, $C_{10}H_{14}O:CPh_2$, the dispersion ratios of which are much lower than those of all the related compounds, gives a curve; so also does menthyl β -phenylcinnamate, $C_{10}H_{19}O \cdot CO \cdot CH:CPh_2$, the rotatory dispersion of which must be complex, since the dispersion ratio, $\alpha_F/\alpha_G = 1.72$, falls below the

FIG. 1.

minimum value $\alpha_F/\alpha_G = \lambda_G^2/\lambda_F^2 = 1.818$, beyond which λ_0^2 would become negative and λ_0 an imaginary quantity; the fact that both these compounds contain the group $:CPh_2$ can at present only be regarded as a coincidence. All the other compounds appear, as a result of this rough graphical analysis over a narrow range of wave-lengths, to give simple rotatory dispersion.

A more exact test of the dispersion formula is given by numerical calculation. The following table shows that the specific rotations,

observed and calculated, of a series of typical compounds lie well within the range of possible experimental errors.

TABLE I.

Specific Rotations, Observed and Calculated.

Ethylidenecamphor,* $[\alpha] = 47.322/(\lambda^2 - 0.0829)$.

Obs.	136.37°	178.58°	219.31°	308.49°
Calc.	136.05	178.58	219.55	308.49
O—C	+0.32	±	−0.24	±

Hydroxymethylenecamphor,* $[\alpha] = 22.843/(\lambda^2 - 0.0874)$.

Obs.	66.53	87.66	108.57	153.41
Calc.	66.53	87.70	108.26	153.41
O—C	±	−0.06	+0.33	±

Benzylmethylenecamphor, $[\alpha] = 33.431/(\lambda^2 - 0.0887)$.

Obs.	97.87	129.00	156.26	226.50
Calc.	97.75	129.00	156.39	226.50
O—C	+0.12	±	−0.12	±

Menthol,* $[\alpha] = 15.068/(\lambda^2 - 0.0236)$.

Obs.	37.01	46.58	54.78	70.84
Calc.	37.01	46.47	54.82	70.84
O—C	±	+0.11	−0.04	±

Menthyl benzoate,* $[\alpha] = 29.364/(\lambda^2 - 0.0255)$.

Obs.	72.41	91.10	107.76	139.30
Calc.	72.46	91.10	107.59	139.30
O—C	−0.05	±	+0.17	±

Myrtenol, $[\alpha] = 14.700/(\lambda^2 - 0.0316)$.

Obs.	36.83	46.49	55.04	71.81
Calc.	36.83	46.48	55.09	71.81
O—C	±	+0.01	−0.05	±

Myrtenyl benzoate, $\alpha = 11.505/(\lambda^2 - 0.0341)$.

Obs.	29.01	36.67	43.51	56.90
Calc.	29.01	36.67	43.52	56.90
O—C	±	±	−0.01	±

* Dissolved in benzene.

In view of the fact that the readings for solutions in benzene were multiplied by ten to convert them into specific rotations, whilst the others were approximately doubled, the agreement shown above is practically perfect.

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Even clearer evidence of the validity of the simple dispersion formula is afforded by a study of the average dispersion ratios observed and calculated for groups of related compounds. Three such groups were averaged by Hagenbach, namely:

- (a) Eight derivatives of methylenecamphor (dissolved in benzene), $\alpha_F/\alpha_C = 2.310$.
 (b) Seven esters of menthol (pure or in benzene), $\alpha_F/\alpha_C = 1.920$.

FIG. 2.

Rotatory dispersion in menthol and its esters.

Notice curvature in the case of β -phenylcinnamate.

- (c) Three derivatives of citronellaldehyde (in the pure state), $\alpha_F/\alpha_C = 1.991$.

To these there are now added average ratios for:

- (d) Six derivatives of methylenecamphor (in the pure state), $\alpha_F/\alpha_C = 2.303$.

- (e) Menthol and seven esters (dissolved in benzene), $\alpha_F/\alpha_C = 1.911$.

(f) Myrtenol and eight esters (in the pure state), $\alpha_F/\alpha_C = 1.958$. The close agreement between the observed and calculated values of these ratios is shown in table II.

FIG. 3.

Rotatory dispersion in myrtenol and its esters.

TABLE II.

Dispersion Ratios, Observed and Calculated.

		α_F/α_C	α_F/α_D	α_F/α_Q	α_Q/α_C	α_Q/α_D	α_D/α_C	
(a)	{ Obs.	2.310	1.751	1.415	1.633	1.237	1.319	$\lambda_0^2 =$
	{ Calo. ...	2.310	1.752	1.418	1.629	1.236	1.318	0.0879
(b)	{ Obs.	1.920	1.529	1.294	1.488	1.181	1.259	$\lambda_0^2 =$
	{ Calc.	1.921	1.529	1.294	1.484	1.181	1.257	0.0250
(c)	{ Obs.	1.991	1.561	1.313	1.515	1.188	1.274	$\lambda_0^2 =$
	{ Calc. ...	1.992	1.569	1.316	1.513	1.191	1.269	0.0401
(d)	{ Obs.	2.303	1.756	1.423	1.619	1.234	1.312	$\lambda_0^2 =$
	{ Calc. ...	2.303	1.748	1.417	1.626	1.234	1.318	0.0871
(e)	{ Obs.	1.911	1.521	1.289	1.482	1.180	1.256	$\lambda_0^2 =$
	{ Calc. ...	1.911	1.522	1.292	1.479	1.179	1.255	0.0227
(f)	{ Obs.	1.958	1.550	1.306	1.499	1.186	1.264	$\lambda_0^2 =$
	{ Calc. ...	1.958	1.550	1.306	1.499	1.186	1.264	0.0334

This agreement is nearly as close as in the case of the data by which the validity of the simple Drude formula was first established, and even the largest differences are usually less than the average errors of the individual ratios. The "simple" character of the rotatory dispersion could therefore only be called in question if data were available of greater exactness or over a wider region of the spectrum.

A further opportunity of testing the validity of the simple dis-

FIG. 4.

Rotatory dispersion in derivatives of camphor pulegone and carvone.

Notice curvature in the case of pulegone.

persion law is provided by the inclusion in a more recent paper by Prof. Rupe (*Helv. Chim. Acta*, 1918, **1**, 452) of dispersion data for four samples of camphylcarbinol,

a compound containing three asymmetric carbon atoms as com-

ponents of a complex ring system. The agreement between the observed and calculated rotations is shown in table III.

TABLE III.

Rotatory Dispersion in Camphylcarbinol.

First sample, $[\alpha] = 15.980 / (\lambda^2 - 0.10220)$.

	$\lambda = 6563$	5898	5463	4861
Obs.	48.64°	65.24°	81.57°	119.17°
Calc.	48.64	65.05	81.43	119.17
O—C	±	+0.19	+0.14	±

Second sample, $[\alpha] = 15.213 / (\lambda^2 - 0.10223)$.

Obs.	46.31	62.11	77.67	113.48
Calc.	46.31	61.93	77.53	113.48
O—C	±	+0.18	+0.14	±

Third sample, $[\alpha] = 15.252 / (\lambda^2 - 0.10239)$.

Obs.	46.45	62.22	77.74	113.90
Calc.	46.45	62.13	77.79	113.90
O—C	±	+0.09	-0.05	±

Fourth sample, $[\alpha] = 16.10 / (\lambda^2 - 0.10304)$.

Obs.	49.13	65.73	82.44	120.82
Calc.	49.13	65.76	82.39	120.82
O—C	±	-0.03	+0.05	±

It will be observed that the sample having the highest rotatory power, which was also probably the purest, gives a remarkably close agreement, the differences being in opposite directions and amounting only to a few hundredths of a degree, or about 1 part in 2000. This exact agreement suggests that the simple dispersion law may be of value as a test of purity, and that deviations from it may in some cases justify a further examination of the chemical composition of the material used for the measurements.

It is of interest to notice the chemical character of the compounds to which the "simple" dispersion formula has now been applied. They are as follows:

1. Methylene camphors.

2. Menthol esters.

3. Myrtenol esters.

4. Hydrocarbons from citronellaldehyde.

Nearly all are complex ring compounds or loaded with double bonds. The fact that the simple formula applies to compounds of such complex structure is remarkable evidence of the broad and sound basis on which the formula rests.

Characteristic Wave-lengths.—In Drude's simple equation, the rotatory dispersion is defined completely by the "dispersion constant" λ_0^2 ; this is the square of a wave-length, which is that of a hypothetical absorption band, usually in the ultra-violet region of the spectrum. This wave-length defines the whole course of the dispersion curve, and is independent of the particular wave-lengths used to determine it; thus the value of λ_0^2 may be deduced equally well from the mercury ratio $\alpha_{4358}/\alpha_{5461}$, from the cadmium ratio $\alpha_{5086}/\alpha_{6438}$, or from the ratio α_F/α_C derived from the data now under discussion. A preliminary study of these data by Prof. Rupe had, however, disclosed the fact that, in the case of the methylene-camphors, $\alpha_F/\alpha_C = \alpha_D$, whilst in the case of the citronellaldehyde hydrocarbons, $\alpha_F - \alpha_C = \alpha_D$, that is, for each series there is a "characteristic wave-length," λ_a (*Zeitsch. physikal. Chem.*, 1915, **89**, 581), for which the rotation is equal to the difference between the rotations for the *F* and *C* lines. This wave-length is not a fundamental constant of the dispersion curve like the λ_0^2 of Drude's equation, since it depends on the two standard wave-lengths, for example, *F* and *C*, which are selected as determining the difference; but it usually lies within the limits of the visible spectrum and affords a picturesque method of setting out the essential features of the dispersion curve. By assuming the validity of Stefan's formula, Hagenbach showed that this wave-length can be deduced from the expression

$$\frac{1}{\lambda_a^2} = \frac{\alpha_C}{\alpha_F - \alpha_C} \left\{ \frac{1}{\lambda_F^2} - \frac{1}{\lambda_C^2} \right\} - \frac{1}{\lambda_0^2},$$

or, taking in all the four rotatory powers,

$$\frac{1}{\lambda_a^2} = \frac{\alpha_F - \alpha_C - \alpha_E}{\alpha_C - \alpha_D} \left\{ \frac{1}{\lambda_C^2} - \frac{1}{\lambda_D^2} \right\} - \frac{1}{\lambda_E^2}.$$

Drude's equation, on the other hand, which is the one that actually fits the curves, gives for the "characteristic wave-length" the expression

$$\lambda_a^2 = \frac{\lambda_C^2 - (n-2)\lambda_F^2}{(n-1)^2} = \frac{0.4307 - 0.2363(n-2)}{(n-1)^2},$$

where n is the dispersion ratio α_F/α_C . Thus, for the citronellaldehyde hydrocarbons, for which $n=2.00$, this equation gives $\lambda_a^2 = \lambda_C^2$, as was observed experimentally when it was found that $\alpha_F - \alpha_C = \alpha_D$.

Constant Rotatory Dispersion in Homologous Series.—In the compounds now under consideration, new radicles are introduced into the molecule at points which are separated from the asymmetric carbon atoms by a considerable chain, including in every case either an oxygen atom or a double bond. A constant dispersion ratio is therefore observed from the beginning, and any substance of which the rotatory dispersion differs largely from the average of the series is noteworthy and exceptional. The only conspicuous exceptions amongst some thirty-six compounds under consideration in the present research were found in two substances containing the group :CPh₂. These have now been shown to differ from the others also in giving complex instead of simple dispersion curves, so that the rule appears to apply without exception to all compounds showing simple rotatory dispersion.

A different state of affairs prevails, however, in the secondary alcohols of Pickard and Kenyon, which have a "growing chain" attached directly to the asymmetric carbon atom. The dispersion is here always simple, but the dispersion constant varies in the different series, and only assumes a steady value in each series when the "growing chain" of carbon atoms has definitely established itself as the heaviest radicle attached to the asymmetric carbon atom (Lowry, Pickard, and Kenyon, T., 1914, **105**, 101). The lowest homologues usually show an exceptionally high rotatory dispersion, but this is not accompanied by any change in the type of the dispersion curve, and is therefore entirely distinct from the "anomalous rotatory dispersion," of which an exact definition was given in a former paper of the present series (T., 1915, **107**, 1195). It would be a real misfortune if substances which are perfectly normal in their rotatory dispersion were to be regarded even as "relatively anomalous" whenever they happen to differ slightly from their homologues, and it is hoped that this unnecessary and misleading description will be abandoned.

Summary.

It is shown that the simple dispersion formula

$$\alpha = k/(\lambda^2 - \lambda_0^2)$$

can be applied to express the rotations produced by a large number of compounds of the terpene series, including (*a*) derivatives of methylenecamphor, including camphylcarbinol, (*b*) menthol and its esters, (*c*) myrtenol and its esters, and (*d*) hydrocarbons derived from citronellaldehyde. Pulegone, and two compounds containing the group :CPh₂, show complex rotatory dispersion.

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