[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY AND DEPARTMENT OF PHYSICS, INDIAN INSTITUTE OF SCIENCE]

The Optical Rotatory Dispersion of Terpenes

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The terpenes form an interesting series of optically active isomers, the rotatory dispersion of which has not been examined in detail. As they are colorless, measurements can be extended into the ultraviolet and information obtained regarding the natural frequencies of the electrons which determine the optical activity. The rotatory dispersions of pinene and limonene have been studied by Nutting[1] in the visible, and by Ingersoll[2] in the infra-red region of the spectrum. Darmois[3] investigated the dispersion of pinene up to 3130 Å. Recently, M. Servant[4] using alcoholic solutions of pinene found that the dispersion was anomalous in the region of 2800 Å.

A serious drawback to the use of the terpenes in an investigation of this nature is the great difficulty of obtaining them in a state of purity. The values for the rotation given in the literature vary, as will be shown later, in a marked manner and it is the exception rather than the rule to find *d*- and *l*-varieties of the same terpene with a rotation which is numerically the same. These discrepancies may be due either to (1) admixture with small quantities of the same terpene in an inactive form or of opposite sign, (2) admixture of other terpenes, or (3) as suggested by Simonsen, the existence of terpenes as an equilibrium mixture, the proportion of the constituents varying for reasons at present not understood. In case (1) dispersion results will be approximately correct, the error occurring only in the absolute magnitude of the rotation. Case (2) will be similar provided the quantity of impurity is small, while in case (3) the results will be very difficult to interpret.

In view of the above we have taken great pains to obtain our materials in as pure a condition as possible, but in spite of this it is evident that in some of the cases the final product cannot be regarded as quite satisfactory. The terpenes we have examined are *d*-pinene, *d*-limonene, *d*-camphene, *d*-Δ^3-carene, *d*-Δ^4-carene, *d*-α-thujene and *d*-sabinene. The report on the Raman spectrum of these terpenes will be published in the near future.

Experimental

Preparation of Materials

Pinene.—A sample of this terpene with $[\alpha]_D$ 51.14° was obtained in 2% yield by Thurber and Thielke[5] by regeneration from the active nitrosochloride. We did not succeed, however, in obtaining any product by this method, probably on account of the extremely low yields reported by these authors and consequently recourse was had to fractional distillation. A fairly pure sample of *d*-pinene of unknown origin was taken as the starting material; 500 g. was dried for a day over anhydrous magnesium sulfate and then subjected to fractional distillation over sodium at a pressure of 30 mm. using a Widmer–Schenck column nearly half a meter in length. Three such distillations, neglecting the head and tail fractions, gave the following fairly agreeing values for the rotation.

Fraction	1	2	3	4	5	6
Rotation	40.48	40.57	40.57	40.58	40.57	40.50

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(1) Nutting, *Phys. Rev.*, **17**, 1 (1903).
(2) Ingersoll, *ibid.*, **9**, 257 (1917).
(3) Darmois, *Ann. chim. phys.*, **22**, 281 (1911).
(4) Servant, *Compt. rend.*, **194**, 368 (1932).
(5) Thurber and Thielke, THIS JOURNAL, **53**, 1030 (1931).

Fraction 4 was used for the measurements. Its homogeneity was tested by freezing it in a bath of alcohol and liquid air, allowing nearly one-half to melt, pouring out the liquid and measuring the rotatory powers of the two portions. No difference could be detected.

The physical constants of this sample are given in Table I together with those recorded by other authors. All densities and refractive indices have been reduced to 25° making use of the temperature coefficients determined for our sample, 0.00084, 0.00038 per 1°, respectively.

TABLE I

PHYSICAL CONSTANTS OF *d*-PINENE

	B. p., °C.	d_4^{25}	n^{25}D	$[\alpha]_D$
1 Thurber and Thielke[5]	155–156	0.8549	1.4644	51.14
2 Gildemeister and Hoffmann[a]	154.5–155	.8550	1.4645	...
3 Dupont[b]	155–156	.8536	1.4601	48.08
4 Vèzes[c]	155–156	.8542	1.4634	48.4
5 Authors	62[d]	.8542	1.4645	47.89

[a] "Die ätherischen Öle," Dritte Auflage, 1928, Vol. I, p. 345. [b] *Ann. chim.*, [x] **1**, 257 (1924). [c] *Bull. soc. chim.*, [iv] **5**, 932 (1909). [d] 30 mm. (Rechenberg, "Ätherischen Öle" gives 62° (33 mm.)).

Limonene.—Two hundred and fifty grams of a fairly pure sample of *d*-limonene, $(\alpha)_D$ 98.3°, was fractionated over sodium in the same column as before and the following fractions obtained after two distillations.

Fraction	1	2	3	4	5
Rotation	100.12	100.88	101.28	101.46	101.32

Fraction 4 was chosen for the measurements and had the constants shown in Table II.

TABLE II

PHYSICAL CONSTANTS OF *d*-LIMONENE

	B. p., °C.	d_4^{25}	n^{25}D	$[\alpha]_D$
1 Schimmel & Co.[a]	....	0.8417	1.4720	122.47
2 Von Braun and Lemke[b]	176–176.4	.8371	....	126.84
3 Authors	71 (20 mm.)	.8409	1.4725	120.73

[a] Gildemeister and Hoffmann, "Die ätherischen Öle," 3d ed., 1928, p. 318. [b] *Ber.*, **56**, 1562 (1923). The sample prepared by Von Braun and Lemke was made by treating the pure tetrabromide with magnesium in ethereal solution.

***d*-Camphene.**—Camphene was prepared synthetically by the action of potassium cresolate on *d*-pinene hydrochloride according to the method given by Pariselle.[6] Fractions obtained during the distillation of pinene were used for preparing the hydrochloride, which after recrystallization had $(\alpha)_D$ 35.22°. The camphene after washing a number of times with hot potash solution was distilled over sodium and recrystallized twice from pure alcohol. It was found to be free from chlorine and had the constants given in Table III.

TABLE III

PHYSICAL CONSTANTS OF *d*-CAMPHENE

	B. p., °C.	d_4^{60}	n^{25}D	$[\alpha]_D$
1 Aschan[a]	46–47	0.8446	1.4564	74.55
2 Wallach[b]	48–49	.8470	1.4572	84.9
3 Pariselle[6]	44–46	...	....	77.1
4 Brühl[c]	50	.8456	1.4533	...
5 Authors	46	.8450	1.4570	81.39

[a] *Ann.*, **398**, 299 (1913). [b] *Ibid.*, **357**, 80 (1907). [c] *Ber.*, **25**, 162 (1892).

***d*-Δ³-Carene.**—About 250 g. of the substance was isolated from a large amount of Indian turpentine and gave finally the following fractions.

Fraction	1	2	3	4	5
$(\alpha)_D$	11.54	12.40	12.48	12.10	11.60

Fraction 3 was used for the measurements. The nitrosate of this was prepared and found to melt with decomposition at 142°. The sample had the constants shown in Table IV.

TABLE IV

PHYSICAL CONSTANTS OF Δ³-CARENE

	B. p., °C.	d_4^{25}	n^{25}D	$[\alpha]_D$
1 Arbusov and Michailov[a]	173.3	0.8536	....	15.21
2 Dupont[b]	170	.8596	1.4675	16.23
3 Authors	60	.8575	1.4701	14.63
4 Simonsen[c]	168–169	.8589	1.4703	9.09

[a] *J. prakt. Chem.*, **127**, 1 (1930). [b] *Ann. chim.*, [x] **1**, 184 (1924). [c] *J. Chem. Soc.*, **117**, 570 (1920).

***d*-α-Thujene, *d*-Sabinene and *d*-Δ⁴-Carene.**—Samples of these substances had been isolated by Dr. Simonsen (to whom our best thanks are due), thujene from the gum oleoresin of *Boswellia Serrata*,[7] sabinene from the essential oil of *Cupressus Torulosa* (Don)[8] and *d*-Δ⁴-carene from the essential oil of a species of *Andropogon*.[9] As only about 50 cc. of each was available we could not subject them to as thorough a purification as the other terpenes but in every case they were distilled over sodium in an all-glass apparatus in an atmosphere of carbon dioxide and only the middle fraction was taken.

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(6) Pariselle, *Compt. rend.*, **176**, 1901 (1923).

(7) Simonsen, *Ind. For. Rec.*, **9**, 289 (1922).

(8) *Ibid.*, **10**, 1 (1923).

(9) *Ibid.*, **8**, 10 (1923).

d-α-**Thujene** has not been isolated by many workers and the values given by Simonsen must suffice for comparison.

	B. p., °C.	d_4^{30}	n^{30}D	$[\alpha]_D$
1 Simonsen	152–152.5 (699 mm.)	0.8277	1.4502	37.69
2 Authors	70.5 (47 mm.)	.8277	1.4501	38.84

Another fact indicating the purity of the sample is its high dispersing power which was also observed by Chugaev and Fomin[10] for a synthetic sample of *l*-α-thujene obtained by decomposition of thujyl xanthogenate. He obtained a ratio for $\alpha_{4861}/\alpha_{5893} = 1.94$, while the value for our sample was 1.96.

TABLE V

PHYSICAL PROPERTIES OF *d*-SABINENE

	B. p., °C.	d_4^{30}	n^{30}D	$[\alpha]_D$
1 Wallach[a]	163–165	0.8380	1.4655	80.17
2 Simonsen[8]	163–166 (702 mm.)	.8429	1.4676	65.2
3 Richter[b]	58–59 (18 mm.)	.8397	1.4646	88.0
4 Authors	66 (30 mm.)	.8430	1.4660	89.07

[a] *Ann.*, **350**, 163 (1906). [b] *Ber.*, **64**, 871 (1931).

d-Δ^4-**Carene.**—In the first paper on the isolation and properties of *d*-Δ^4-carene[11] Simonsen gives the values: b. p. 165.5–167° (707 mm.), d_4^{30} 0.8515, n^{30}D 1.474, $[\alpha]^{30}$D +62.2°. In a subsequent publication[12] he has isolated *d*-Δ^4-carene in a new species of *Andropogon*. After repeated fractionation he finds the first two fractions having the properties:

	B. p., °C.	d_4^{30}	n^{30}D	$[\alpha]_D$
A	164–167	0.8445	1.4705	65.16
B	167–192	.8465	1.4715	74.32

He detects Δ^4-carene in both the fractions and no other hydrocarbon could be identified. It appears to us that since the only other main constituent is *d*-piperitol $[\alpha]_D$ 46°, and limonene and phellandrene (substances of high specific rotation) were proved to be absent, fraction B is likely to be richer in Δ^4-carene than A. Our sample agrees in refractive index with fraction B, the rotation being still higher, *i. e.*, 82.64°, due, we believe, to greater purification. The constants are b. p. 64° (29 mm.), d_4^{30} 0.8441, n^{30}D 1.4717, $[\alpha]_D$ 82.64°.

Apparatus.—The readings in the visible spectrum were taken with the aid of a Lippich three-field polarimeter and those in the ultraviolet by an arrangement similar to the one described by Lowry,[13] the main feature of this method being that instead of measuring the rotation corresponding to a particular wave length as is done usually, it is the wave length corresponding to a predetermined angle of rotation that is measured.

In most of the experiments an iron arc was used as a source of light, but for camphene a spark between V-shaped iron electrodes was employed. Although the intensity was less than that of the arc, the light was steadier and more uniform and the resulting lines were easier to compare. Exposures had to be increased when the wave length approached the region of absorption and when necessary were prolonged up to fifteen minutes. The arc was focused by a quartz condenser onto a polarimeter with a quartz–calcite–fluorite optical system. The polarizer was of the two-field type with a fixed half-shadow angle of 5°. A quartz–fluorite achromatic doublet was used to focus the emerging light onto the slit of the spectroscope. For the first experiments a small quartz spectrograph giving a spectrum 6 cm. long was used. This was later replaced by a Hilger E 316 instrument with a dispersion of 40 Å./mm. at λ = 4000. The point at which the two spectra were of equal intensity was estimated visually with the aid of a traveling microscope. The accuracy with which this could be done depended upon several factors, the chief of which were the distribution and intensity of the spectral lines near the point of coincidence and the dispersion of the substance. In practice, deviations of more than 10 Å. from the mean were rarely encountered.

All the liquid terpenes were examined in a cell 2.5 cm. long, and camphene in the form of 30% alcoholic solution in a 10-cm. tube.

Results

A large majority of the previous workers on the rotatory dispersion of organic compounds have had as their object the evaluation of the rotation and dispersion constants of a one term or two term Drude equation as the case may be.

$$[\alpha]_\lambda = \frac{K}{\lambda^2 - \lambda_0^2} \qquad [\alpha]_\lambda = \frac{K_1}{\lambda^2 - \lambda_1^2} + \frac{K_2}{\lambda^2 - \lambda_2^2}$$

k = rotation constant; $\lambda_1, \lambda_2, \lambda_0$ = dispersion constants

The values of the rotation and dispersion constants, deduced in most cases solely from the rotatory dispersion values, unsupported by independent evidence from absorption measurements, do not possess much significance. As far as the simple equation is concerned deviations are almost always observed when the limit of transmission is approached and when the dispersion constant is sometimes sought to be verified through absorption spectrum measurements, the agreement is often not satisfactory. Though it may be argued that the formulas were not meant to be applicable in those regions of the spectrum where absorption effects begin to make

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(10) Chugaev and Fomin, *Ber.*, **45**, 1293 (1912).

(11) Simonsen, *J. Chem. Soc.*, **121**, 2292 (1922).

(12) Simonsen, *Ind. For. Rec.*, (X) **8**, 8 (1924).

(13) Lowry, *Proc. Roy. Soc.* (London), **A81**, 472 (1908).

themselves felt, it also takes away from the calculated values of the rotation and dispersion constants their physical significance. When the two term equation is taken into account, it has been known that the two dispersion constants can be altered in an arbitrary manner without the agreement with the experimental values being impaired in any way provided the sum of the two is kept constant. Lowry (introductory paper, Faraday Society discussion on optical rotatory power, 1930) has stated that the distinction between simple and complex rotatory dispersion was introduced "for the purely utilitarian purpose of expressing the experimental results with the help of a minimum number of arbitrary constants from which deviations either large or small could be recorded."

We therefore thought it not worth while to subject our results to an algebraic analysis in order to devise a one term or two term Drude equation to suit them, but confined ourselves to seeing whether the dispersion was simple or complex by using the graphical method, *i. e.*, by plotting $1/(\alpha)$ and λ^2 on a graph and seeing whether a straight line was obtained or not. The intercept by the line on the axis of wave lengths gave a rough idea of the magnitude of the dispersion constant, *i. e.*, of λ_0^2. Greater importance was attached to the direct determination of this constant by a determination of the absorption spectrum, although all the substances here dealt with were found to have no band up to $\lambda = 2400$. The superiority of this method is already shown by the fact that in the case of Δ^3-carene the rotatory dispersion measurements indicated the position of the characteristic frequency at $\lambda = 2570$, hence showing that the rotatory dispersion was actually complex for this substance.

The following values were obtained by interpolation except those in the visible region, which were measured directly.

λ	α-Thujene	Δ^3-Carene	Δ^4-Carene	*d*-Pinene	*d*-Limonene	*d*-Sabinene	Camphene
5893	38.8	14.6	82.6	47.9	120.7	89.1	80.4
5780	41.1	15.3	88.0	49.9	126.3	92.6	85.5
5461	48.6	17.7	102.8	56.5	144.1	108.2	98.5
4358	109.2	33.3	182.5	96.2	234.9	171.5	182.3
4200	136.1	37.3	203.0	106.4	259.7	184.5	199.2
4000	165.3	44.3	232.6	120.5	298.5	200.0	231.5
3800	210.5	52.6	274.1	136.6	351.0	216.0	270.3
3600	274.0	64.5	327.7	160.5	408.2	238.1	324.7
3400	351.0	83.3	...	188.7	482.8	256.0	400.0
3200	488.0	111.1	...	227.3	578.0	261.0	517.3
3000	627.0	116.7	...	...	709.1	232.6	699.3

The actual experimental values are represented graphically in Fig. 1.

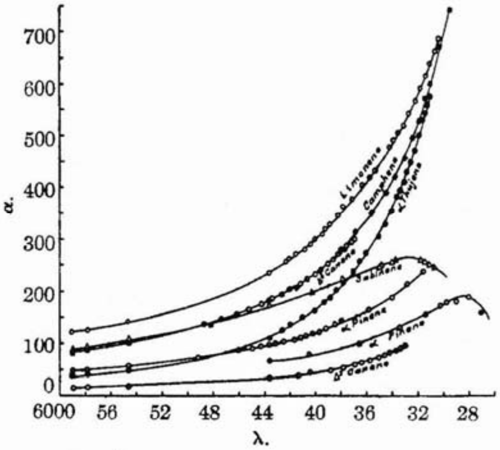

Fig. 1 —Rotary dispersion of terpenes.

Discussion of Results.—It was observed that the relation between $1/(\alpha)$ and λ^2, the square of the wave length, is linear for all the terpenes examined except α-thujene and sabinene, showing that the molecular rotation can be expressed in most cases by the single term Drude equation

$$[\alpha]_\lambda = \frac{A}{\lambda^2 - \lambda_0^2}$$

The values of the constants A and λ_0 are

	A	λ_0
Pinene	14.81	1900
Limonene	37.33	1950
Δ^3-Carene	4.08	2580
Δ^4-Carene	25.27	2290
Camphene	23.9	2370

The values for pinene approximate to those found by Darmois.[3] The limit of his measurements was $\lambda = 3130$. Servant,[4] who examined the rotation as far as $\lambda = 2657$ in alcoholic solution by giving prolonged exposures with the mercury arc, obtained the values:

Values	4358	4046	3650	3341	3132	3021
(α), min.	−65	−77.5	−99	−130	−155	−172
Values		2967	2893	2804	2698	2651
(α), min.		−177	−180	−188	−158	−147

These are given in the lower curve for α pinene in Fig. 1.

Darmois was unable to examine limonene in the ultraviolet as the absorption was too great. This must be attributed to some impurity in his material as we found no difficulty in taking readings as far as λ 3000. Possibly some oxidation had occurred, as we observed that transparency in the ultraviolet was improved by filling the apparatus with carbon dioxide prior to distillation and by subsequent exclusion of air.

In the case of α-thujene a straight line was not obtained on plotting $1/(\alpha)$ and λ^2, indicating that at least two frequencies are involved in the rotatory dispersion. This is also evident from its abnormally high dispersion ratio $\alpha_{4358}/\alpha_{5461} = 2.28$, in the absence of any absorption band up to λ 2400. The high dispersion of the substance was also noticed by Chugaev and Fomin[10] for the synthetic hydrocarbon in the visible region.

Sabinene has been found to be definitely anomalous, the rotation attaining a maximum value at λ 3300. The occurrence of anomalous rotatory dispersion in hydrocarbons is very rare and sabinene along with nopinene[3] form the only instances known so far. Since an examination of these two substances for absorption by the Hartley–Baly method failed to show any band, the anomalies are not due to the Cotton effect but to the superposition of two rotations of opposite sign and unequal dispersion, the characteristic frequencies being in the extreme ultraviolet. The two rotations can be attributed either to two different molecules or to two optically active portions of the same molecule. If the first assumption is made it follows that the substances are not homogeneous but are mixtures of at least two different substances. Unfortunately neither sabinene nor nopinene yields any crystalline derivative from which the parent hydrocarbon can be regenerated, so that only physical methods of separation are available to test this conclusion. Further work regarding the nature of the anomalous rotatory dispersion of these two substances has already been taken up and will form the subject of a future communication.

Thanks are due to Dr. H. E. Watson for his helpful guidance during the course of the work.

Summary

1. The rotatory dispersion of the following isomeric hydrocarbons has been measured in the visible and in the ultraviolet: *d*-α-pinene, *d*-limonene, *d*-Δ^3-carene, *d*-Δ^4-carene, *d*-α-thujene, *d*-sabinene and *d*-camphene.

2. The absorption spectra of these substances by the Hartley–Baly method showed that none of these substances had any band up to λ 2400.

3. The high tension spark between iron electrodes is suggested as a source of light for ultraviolet spectropolarimetry superior in many respects to the arc.

4. It was found that pinene, Δ^3-carene, Δ^4-carene, limonene and camphene have simple dispersion while thujene possesses complex dispersion and sabinene anomalous dispersion.

5. The limitations of the Drude formula as calculated from rotatory dispersion measurements are mentioned.

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