

# THE RAMAN SPECTRA OF *DEXTRO*, *LAEVO* AND RACEMIC FORMS OF BORNEOL AND CAMPHOR.

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## 1. Introduction.

PASTEUR'S principle of molecular dissymmetry postulates that enantiomorphous molecular configurations must give identical values for the magnitude of their scalar and vectorial properties, as the *dextro* and *laevo* forms of a compound are related to one another as an object is to its non-superposable *exact* mirror image. In several communications,<sup>1</sup> this identity was established as regards the magnitude of the rotatory power for many such pairs of isomers. In a subsequent communication,<sup>2</sup> the physical identity of the optically active and opposite forms was extended to several scalar properties, such as viscosity, density and refraction. In the present paper, which is a continuation of this series, dealing with work on the physical identity of enantiomers undertaken by one of us, we have extended the application of this principle to the Raman frequencies of the *d* and *l* forms of borneol and camphor. In this study, the racemic forms of these compounds are also included with the object of finding out whether the Raman spectrum of the racemic form is different from that of the *d* and *l* forms and thus throw any light on the mode of union of the *d* and *l* components in a racemate. The study of the viscosity-concentration graphs of the *d*, *l* and *dl* forms of camphor in ethyl alcohol as reported in an earlier paper,<sup>2</sup> showed that they diverge more and more apart with increasing concentration. For concentrations of about 3 per cent. and lower, the values of viscosity for the three forms are identical; but at higher concentrations the racemic form has higher viscosity than the *d* and *l* forms. The existence of the *dl* compound in the case of camphor in solution in ethyl alcohol above 3 per cent. concentration is thus clearly established. The racemic form of camphor in the solid state must be a true compound of the *d* and *l* components in equimolecular proportions. The study of its Raman spectrum in the solid state

as well as that of its opposite and active forms was thought to be of considerable interest. Since borneol is the secondary alcohol corresponding to the ketone, camphor, any differences in their Raman spectra must be ascribed to this change in the chemical structure of the molecule. A similar comparative study of the three forms of borneol is, therefore, also undertaken.

### 2. Experimental.

The technique of the complementary filters, devised by R. Anantha-krishnan,<sup>3</sup> for investigating crystals was employed. The pair of complementary filters used was a concentrated solution of iodine in carbon tetrachloride and an aqueous solution of sodium nitrite of suitable strength. The exciting line was  $\lambda$  4046 of the mercury arc spectrum. The Raman spectra were photographed on high speed golden isozenith plates and the duration of exposure was 96 hours in every case. A Fuess spectrograph of high light-gathering power was used in this work. The plates were measured by means of a Hilger cross-slide microscope in comparison with an iron-arc spectrum which was recorded in the centre of every picture.

### 3. Preparation and Purification of Materials.

The camphors and borneols were prepared and purified according to methods already given.<sup>4</sup> The melting points and rotatory power of the camphors were as follows :—

		m.p.	$[\alpha]_{\text{Hg } 5461}^{25^\circ}$	
<i>d</i> -Camphor	..	178°–179°	+ 59.61°	} for 33.3 per cent. solution in ethyl alcohol
<i>l</i> -Camphor	..	178°–179°	– 59.41	
<i>dl</i> -Camphor	..	178°	0.0	

The borneols used also gave correct values of the melting point and rotatory power.

The borneols and camphors at first gave a continuous background on the photographic plate, which masked many lines. On recrystallising the compounds three times from ligroin (b.p. 75°–90° C.), the background was sufficiently cleared.

### 4. Results.

Tables I and II record the frequency shifts of the Raman lines, visual estimates of their intensities, I and observed structural characters :—  
s = sharp, b = broad and d = diffuse.

TABLE I.

*Borneols.*

Exciting line 4046.5 A.U.  $\nu = 24705 \text{ cm.}^{-1}$

Time of exposure 96 hours each.

No.	<i>Lævo</i>			<i>Destro</i>			<i>Racemic</i>		
	$\nu$	$\Delta \nu$	I	$\nu$	$\Delta \nu$	I	$\nu$	$\Delta \nu$	I
1	24056	649	4s	24055	650	4s	24055	650	4s
2	23968	737	0	23968	737	0	23968	737	0
3	23945	760	0	23945	760	0	23945	760	0
4	23819	886 (?)	0	..	..		..	..	
5	23763	942	0	23763	942	0	23763	942	0
6	23733	972	1	23729	976	1	23727	978	1
7	23628	1077	1	23628	1077	0	23630	1075	0
8	23517	1188	0	23517	1188	0	..	..	..
9	..	..	..	23483	1222	0	23480	1225	0
10	23407	1298	$\frac{1}{2}$	23407	1298	$\frac{1}{2}$	23407	1298	$\frac{1}{2}$
11	23260	1445	2b	23265	1440	2b	23263	1442	2b
12	23227	1478	2b	23233	1472	2b	23232	1473	2b
13	21967	2738	0b	21967	2738	0b	21967	2738	0b
14	21828	2877	2b	21833	2872	1	21836	2869	1
15	21783	2922	2	21785	2920	2	21781	2924	2
16	21757	2948*	8b	21757	2948*	8b	21753	2952*	8b
17	21724	2981	1	21724	2981	2	21733	2972	2

Note 1.—\* Indicates that the line has also been excited by 4077 A.U.

Note 2.—There is a continuous spectrum superposed on the lines from 14 to 17.

TABLE II.

*Camphors.*Exciting line 4046.5 A.U.  $\nu = 24705 \text{ cm.}^{-1}$ 

Time of exposure 96 hours each.

No.	<i>Lævo</i>			<i>Dextro</i>			<i>Racemic</i>		
	$\nu$	$\Delta \nu$	I	$\nu$	$\Delta \nu$	I	$\nu$	$\Delta \nu$	I
1	24056	649*	4s	24055	650*	4s	24053	652*	4s
2	23848	857	2s	23855	850	1s	23851	854	0
3	23752	953	2s	23749	956	1s	23757	948	1
4	23462	1243	0	..	..		23462	1243	0
5	23282	1423	0	..	..		..	..	
6	23260	1445	$\frac{1}{2}$	..	..		..	..	
7	21837	2868	3b	21835	2870	3	21837	2868	3
8	21780	2925*	5	21785	2920*	4	21777	2928*	5
9	21742	2963*	6b	21737	2968*	6b	21733	2972*	6b

Note 1.—\* Indicates that the line has also been excited by 4077 A.U.

Note 2.—There is a continuous spectrum superposed on the lines 2868, 2925 and 2963  $\text{cm.}^{-1}$

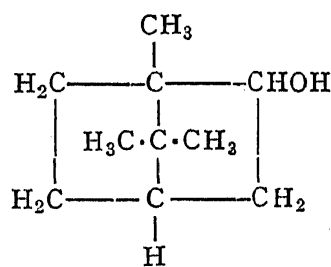
5. *Discussion of Results.*

Except for small variations in the spectra of the *dextro* and *lævo* forms of borneol and camphor, which are due to the difference in the quality of the photographs, no appreciable changes have been observed in the position, intensity and structure of the Raman lines in the two enantiomorphous forms of both these compounds. Similar results have been obtained by one of us<sup>5</sup> with the *d* and *l* forms of camphoric acid and its anhydride. Pasteur's principle of molecular dissymmetry, thus, stands firmly established with regard to this new property of matter, resulting from the interaction of molecules with light quanta.

The racemic forms of borneol and camphor give the same Raman lines as the *d* and *l* forms of the respective substances. This result agrees with the fact that the Raman lines due to the vibrations of atoms in the individual molecules of the optically active forms are, in the first approximation, unaffected by the intermolecular forces binding the *d* and *l* molecules forming the racemate. The viscosity measurements<sup>2</sup> at different concentrations of the racemic camphor have definitely indicated that for concentrations above 3 per cent. in ethyl alcohol, the *d* and *l* components form a loosely-bound complex molecule (*dl*) which dissociates into its constituents at lower concentrations. From this it may be concluded that the binding force between *d* and *l* components of the racemate is small and therefore, any intermolecular oscillations arising from this binding could, at best, give only weak Raman lines of low frequency. The sodium nitrite solution in the path of the scattered rays renders frequencies up to about 600\* from 4046 A.U., very weak. Due to this and also to the presence of a continuous spectrum in this region, any frequency of this order could well have escaped detection in the present investigation.

The following remarks on the relation between chemical constitution and the characteristic Raman frequencies of the compounds may be made.

(a) *Borneols* :



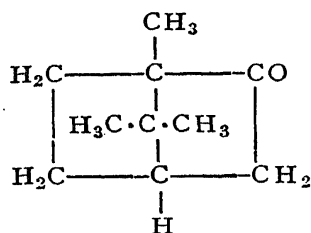
On an average about seventeen frequencies have been recorded in Table I for the borneols. Out of these, five lines at 2738, 2877, 2922, 2948 and 2981 belong to the valence oscillations and two at 1445 and 1478 to the deformation oscillations of the CH groups. The lines at 886, 942, 972, 1077, 1188 and 1222 may be due either to ring structure or to the C—C vibrations. The line at 649 is the strongest and sharpest line in that region and presumably arises from the symmetrical oscillations of the tetrahedral

group  $\begin{array}{c} \text{C} \\ | \\ \text{C} - \text{C} - \text{C} \\ | \\ \text{C} \end{array}$ . The weak line at 1298 is exactly double this frequency

and has, therefore, to be taken as its harmonic.

\* The figures given in this paper indicate wave numbers per cm.<sup>-1</sup>

(b) *Camphors* :



The structural formula of borneol differs from that of camphor in that the secondary alcohol group  $\text{CHOH}$  has been replaced by a carbonyl group  $\text{C} = \text{O}$ . In Table II, only nine frequencies have been recorded. The three lines at 2868, 2925 and 2963 must be ascribed to  $\text{C}-\text{H}$  valence vibrations. Two of these (2868 and 2925) are also present in borneol. In spite of the fact that long exposures have been given and the  $\text{C} \leftrightarrow \text{H}$  vibrations have been recorded strongly, the  $\delta(\text{CH})$  frequencies have appeared only feebly in *laevo* camphor. In the *dextro* and racemic forms, their presence could not be detected. This comparative weakness of the  $\delta(\text{CH})$  frequencies in camphor for equal intensities of the  $\text{C} \leftrightarrow \text{H}$  lines in both borneol and camphor is rather surprising.

There are four low frequencies, namely, 649, 857, 953 and 1243 in camphors. Of these, the line at 649 is also found in borneol and is evidently due to the 'neopentyl' group as indicated for the latter. The other three frequencies differ from those of borneol in that region as may be expected from the difference in their molecular structure. The Raman shifts characteristic of the  $\text{C} = \text{O}$  linkage in camphor could not be detected as it falls in the region of  $\lambda 4358$  of the mercury arc spectrum. The line due to  $\text{OH}$  in borneol has also not been recorded. From the complexity of the molecular structure of these two compounds, we should expect many more lines than have been recorded here and a detailed investigation of these substances in the state of solution would be of great interest.

### 6. Summary.

1. The Raman spectra of the *d*, *l* and *dl* forms of borneol and of camphor have been studied in the crystalline state. The spectra of *dextro* and *laevo* forms in both cases are identical, thus supporting Pasteur's Law of Molecular Dissymmetry.

2. The Raman spectra of the *dl* forms of borneol and camphor are also the same as those of their optically active isomers. This supports the view already derived from measurements of viscosity that the *d* and *l* components in a racemic compound are very loosely bound.

3. The most intense shifts in these compounds are those associated with C—H vibrations.

4. An intense and sharp line occurs at about  $650\text{ cm.}^{-1}$  in both camphor and borneol and is ascribed to the neopentyl group.

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