

# RAMAN EFFECT IN SOME TERPENES.

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## INTRODUCTION.

Bhagavantam and Venkateswaran (*Nature*, 1930, **125**, 237) have found, in the optical isomers of pinene, appreciable differences in the relative intensities of some of the lines, especially the line corresponding to the infra-red wavelength of about  $74 \mu$  was particularly strong in the dextro while it was comparatively much weaker in the lævo form. The spectra of the dextro and lævo pinenes produced with ordinary and polarised light have been shown to be identical by A. Kastler (*C. R.*, 1930, **191**, 565), the differences found by Bhagavantam and Venkateswaran being attributed to impurities. The latter authors have recently published another paper (*Indian Journal of Physics*, 1932, **7**, 585) in which they obtained identical values for *l* and *d* pinene.

The purpose of the present investigation is to study a number of optical isomers having the empirical formulæ  $C_{10}H_{16}$  for their Raman Spectra, in order to settle the point of their identity.

As the last three substances were available only in very small quantities, a special tube, with fused flat ends, was designed and satisfactory results were obtained with 7-8 c.c. of the liquids. The physical constants of these substances and other optical properties are discussed in a paper by one of us (S. K. K. Jatkar) and Padmanabhan in a paper under publication in the *Journal of American Chemical Society*.

## RESULTS.

In the following tables, the results of the complete analysis of the Raman Spectra of all the eight isomers are given. In the case of dextro  $\Delta^3$ -carene, the results agree with those obtained by Dupont, Daure and Allard (*Bull. Soc. Chim.*, 1931, **49-50**, 1401) using the  $4358 \text{ \AA}$  of mercury as exciting line.

The Raman frequencies, with their intensities, are also graphically represented in Fig. 1.

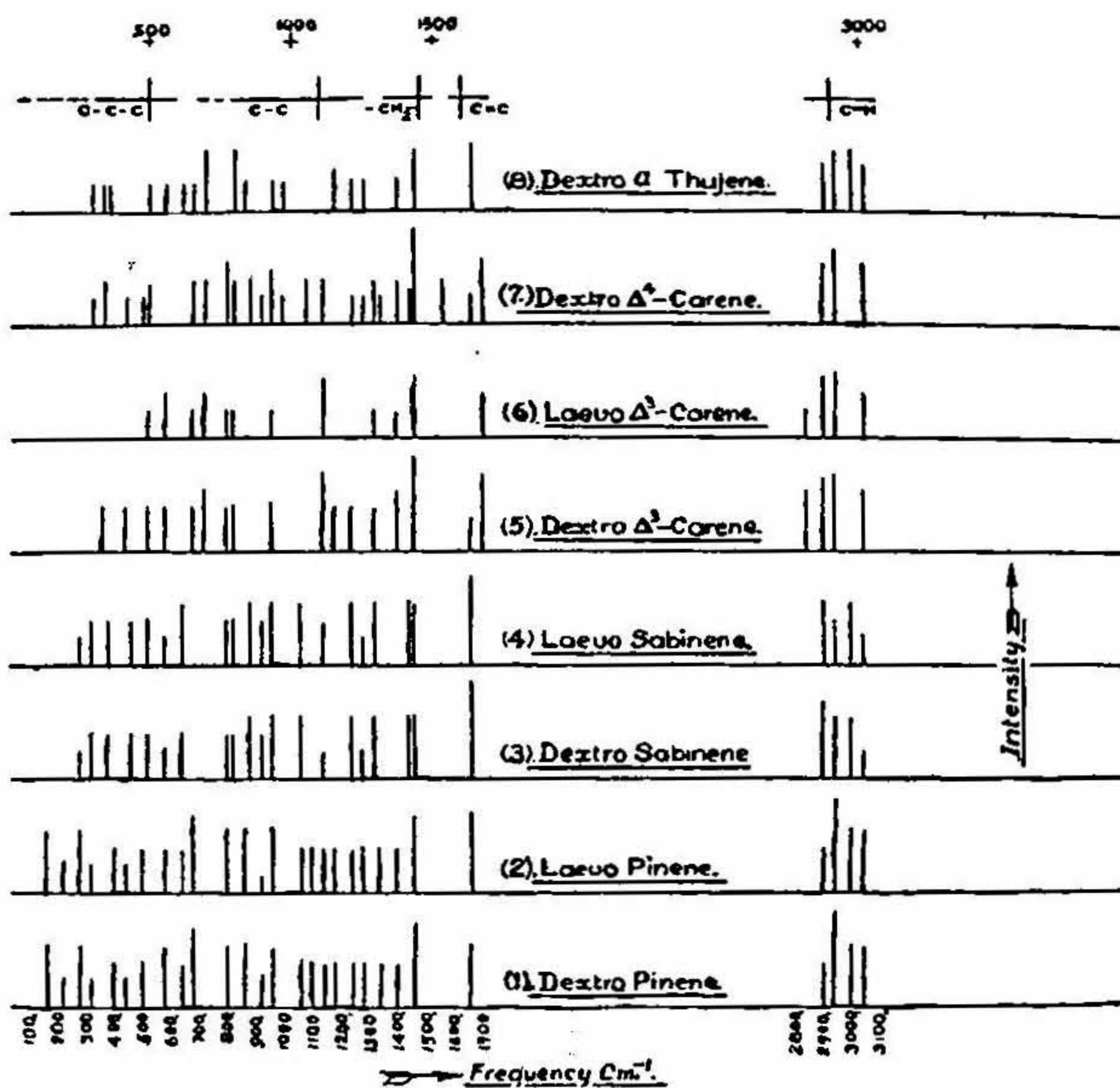


Fig. 1.

Terpenes.

TABLE I.

<i>d.a-Pinene. <math>\alpha_D = 47.1</math></i>		<i>l.a-Pinene. <math>\alpha_D = 44.3</math></i>		<i>d.a-Pinene. <math>\alpha_D = 47.1</math></i>		<i>l.a-Pinene. <math>\alpha_D = 44.3</math></i>	
Authors	Infra-red*	Authors	Infra-red	Authors	Infra-red	Authors	Infra-red
145(3) (a)	..	146(3) (a)	..	1086(2) (ae)	1083	1089(2) (aeh)	..
210(1) (a)	..	208(1) (a)	..	1127(2) (e)	..	1129(2) (e)	..
265(3) (abgh)	..	264(3) (abgh)	..	1173(2) (efh)	1170	1173(2) (efh)	1170
314(1) (a)	..	314(1) (a)	..	1222(2) (ae)	1235	1223(2) (ae)	1227
396(2) (a)	..	394(1) (a)	..	1268(2) (aeg)	..	1270(2) (aeg)	..
427(1) (ag)	..	431(1) (ag)	..	1330(2) (eh)	1325	1330(2) (eh)	1325
480(2) (aefgh)	..	481(2) (afgh)	..	1381(2) (ae)	1399	1382(2) (ae)	1374
574(3) (aceg)	..	574(2) (aceg)	..	1450(4) (aefh)	..	1449(4) (aefh)	1449
626(2) (abe)	..	625(2) (abe)	..	..	..	..	1587
669(4) (aceg)	..	671(4) (aceg)	..	1658(3) (agh)	1653	1657(4) (agh)	..
..	712	..	714	..	..	..	1695
..	758	..	758	..	..	..	1733
780(3) (aeg)	787	778(3) (aeg)	..	..	..	..	1818
846(3) (aefgh)	848	849(3) (aefh)	848	..	..	..	2083
..	877	..	877	..	2128	..	..
907(1) (ae)	..	905(0) (ae)	..	..	2703	..	..
954(3) (ae)	952	953(3) (ace)	943	2881(2) (e)	..	2885(2) (de)	..
..	990	..	990	2919(5) (adeg)	2907	2917(5) (adeh)	2924
..	1010	..	1016	2993(3) (efh)	..	2992(3) (eh)	..
1044(2) (eh)	..	1046(2) (eh)	..	3030(3) (aefh)	..	3032(3) (aeh)	..
				..	..	..	3774

\* W. W. Coblentz, *Investigations of Infra-red Spectra*, pp. 144-145.



TABLE II.

<i>d.</i> Δ <sub>3</sub> -Carene α <sub>D</sub> = 9.3	<i>l.</i> Δ <sub>3</sub> -Carene. α <sub>D</sub> = 2.9	<i>d.</i> Sabinene. α <sub>D</sub> = 81	<i>l.</i> Sabinene. α <sub>D</sub> = 50	<i>d.</i> α-Thujene. α <sub>D</sub> = 39.2	<i>d.</i> Δ <sub>4</sub> -Carene. α <sub>D</sub> = 82.6
353(2) (ah)	..	(265)(1) (fg)	(264)(1) (fg)	(299)(1) (gh)	311(1) (ah)
424(2) (a)	..	316(2) (ade)	318(2) (ade)	(335)(1) (gh)	354(2) (ah)
513(2) (ah)	513(1) (h)	370(2) (a)	369(2) (a)	(372)(1) (afh)	415(1) (ae)
574(2) (aegh)	572(2) (aegh)	447(2) (a)	448(2) (a)	497(1) (abh)	485(1) (aegh)
683(2) (aegh)	684(1) (agh)	506(2) (abfgh)	500(2) (abfgh)	553(1) (agh)	517(2)(acefh)
719(3) (ae)	719(2) (ae)	569(1) (afg)	571(1) (afg)	(621)(1) (gh)	670(2) (aegh)
763(2) (ae)	760(1) (ae)	638(2) (aeh)	643(3) (aeh)	670(1) (ae)	704(2) (ae)
824(2) (aegh)	825(1) (aeh)	789(2) (ae)	788(2) (ae)	732(3) (ae)	758(3) (aeg)
939(2) (aeh)	941(1) (ae)	815(2) (aefh)	814(2) (aefh)	807(3) (aefgh)	831(2)(adeh)
1111(4) (a)	1109(3) (a)	868(3) (ae)	869(3) (ae)	843(1) (e)	862(3) (ae)
1162(2) (efh)	..	922(2) (ae)	920(2) (ae)	947(1) (aegh)	908(1) (ae)
1231(2) (e)	..	962(3) (aefh)	963(3) (aefh)	979(1) (ae)	958(3) (aeh)
1310(2) (aeh)	1312(1) (ah)	1035(3) (ae)	1037(3) (ae)	1168(2) (eh)	988(1) (e)
1372(3) (ae)	1382(1) (ae)	1112(1) (ae)	1111(2) (ae)	1210(1) (aef)	1067(2) (deg)
1437(5) (aefgh)	1439(3) (aefh)	1210(3) (ae)	1208(3) (ae)	(1274)(1) (gh)	1141(2) (e)
1641(1) (ah)	..	1273(1) (ae)	1278(1) (ae)	1382(1) (aeg)	1216(1) (e)
1683(4) (agh)	1685(2) (agh)	1310(3) (aegh)	1311(3) (aegh)	1445(3) (aefh)	1258(1) (eg)
2830(3) (eh)	2838(1) (e)	1426(3) (aeh)	1423(3) (aeh)	1642(3) (agh)	1304(2) (ae)
2877(4) (aeg)	2876(3) (ae)	1453(3) (aefh)	1456(3) (aefh)	2875(2) (aeg)	1333(1) (eh)
2920(4) (ae)	2917(3) (aef)	1652(5) (agh)	1653(5) (agh)	2910(3) (aeh)	1379(2) (aeg)
3008(2) (efh)	3008(2) (ef)	2877(4) (aeg)	2874(3) (aeg)	2980(3) (aeg)	1420(1) (e)
		2922(3) (aeg)	2924(2) (aeg)	3050(2) (efg)	1448(5) (aefh)
		2986(3) (e)	2994(3) (e)		1554(2) (a)
		3036(1) (e)	3046(1) (e)		1639(1) (ah)
					1670(3) (agh)
					2876(3) (ade)
					2918(4) (adeh)
					3005(3) (aeh)

## DISCUSSION.

*Frequencies due to definite bonds.*

The frequencies originating from various linkages are classified in the following table :

TABLE III.

*Raman frequencies due to different bonds.*

Substance	$-\text{CH}_2-$	$\text{C}=\text{C}$	Aliphatic $\text{C}-\text{H}$	$\text{H}-\text{C}\leq\text{H}_2\text{C}=\text{C}$
(1) <i>d</i> -Pinene ..	1450	1658	2881, 2919, 2993	3030
(2) <i>l</i> -Pinene ..	1449	1657	2885, 2917, 2992	3032
(3) <i>d</i> -Sabinene ..	1426 1453	1652	2877, 2922, 2986	3036
(4) <i>l</i> -Sabinene ..	1423 1456	1653	2874, 2924, 2994	3046
(5) <i>d</i> . $\Delta^3$ - Carene ..	1437	1641 1683	2830, 2877, 2920	3008
(6) <i>l</i> . $\Delta^3$ - Carene ..	1439	1685	2838, 2876, 2917	3008
(7) <i>d</i> . $\Delta^4$ - Carene ..	1420 1448	1554 1639 1670	2876, 2918	3005
(8) <i>d</i> . $\alpha$ -Thujene ..	1445	1642	2875, 2910, 2980	3050

In all the eight isomeric compounds, three frequencies of the  $\text{C}-\text{H}$  linkage are present with the mean values of 2875, 2915 and 2975. In the dextro and lævo  $\Delta^3$ -carenes, a smaller frequency of 2830 is also present. All the compounds except the sabinenes contain the  $\text{H}-\text{C}\leq$  linkage which is shown by a frequency at 3025. In the sabinenes the frequency 3035 is due to the  $\text{CH}_2=\text{C}$  grouping.



A frequency of the mean value of 1650, characteristic of a C=C linkage is present in all the compounds. In the dextro  $\Delta^3$ -carene and dextro  $\Delta^4$ -carene, this is split up into two and three components respectively.

The  $-\text{CH}_2-$  linkage frequency of 1450 is shown by all the isomers, in some it is accompanied by a component of a smaller value.

In pinenes, the  $-\text{CH}_2-$  linkage shows the rotational spectra of hydrogen around the carbon, consisting of eight sharp lines the distances of which from the 1450 line can be represented approximately by the relation given by Bonino and Cella (*Nature*, 1930, **126**, 915),

$$\Delta\nu = B(4m - 4).$$

By putting  $B = 6.15$  and  $m =$  the even series, namely, 2, 4, 6, 8, etc., the calculated values of these rotational frequencies agree fairly well with the observed ones. Our values are in agreement with those recently reported by Bonino and Cella (*Mem. Accad. Italia Chim.*, 1931, **2**, No. 4-5-51; *C.A.*, 1932, **26**, 2656).

It is quite peculiar that this characteristic band in the pinenes is absent in the rest of the isomers. Recently, Bhagavantam and Venkateswaran (*loc. cit.*) have reported several faint lines in this region. These are due to sabinene which is the usual impurity in pinene. The probable explanation of the occurrence of the large number of frequencies in this region is the existence of different kinds of C-H linkages in the compounds due to the double bond as in cyclohexene, the apparent regular spacing in pinene being fortuitous.

*Smaller shifts.*—The very large number of frequencies in the region 200–1300 which are due to the carbon linkages, show that with increasing number of carbon atoms, spectra too complex for analysis are obtained. In a series of isomers these shifts vary owing to the changes in the structure which fact may be useful in identifying a particular compound.



TABLE IV.

*Classification of frequencies of all the isomers.*

<i>d</i> -pinene	<i>l</i> -pinene	<i>d</i> -sabi- nene	<i>l</i> -sabi- nene	<i>d</i> . $\Delta^3$ - carene	<i>l</i> . $\Delta^3$ - carene	<i>d</i> . $\Delta^4$ - carene	<i>d</i> . $\alpha$ - thujene	Vibra- tor
139(3)	140(3)							C-C-C
204(1)	202(1)							
259(3)	258(3)	258(1)	258(1)					
308(1)	308(1)	311(2)	312(2)			305(1)	292(1)	
				347(2)		348(2)	328(1)	
		364(2)	363(2)				366(1)	
390(2)	388(2)							
421(1)	425(1)			418(2)		410(1)		
474(2)	475(2)	441(2)	442(2)			479(1)		
		500(2)	500(2)	507(2)	506(1)	511(2)	491(1)	
568(3)	568(2)	563(1)	565(1)	568(2)	566(2)		547(1)	
620(2)	619(2)	632(2)	637(3)				614(1)	
662(4)	665(4)			677(2)	678(1)	664(2)	664(1)	
				714(3)	713(2)	699(2)	726(3)	
774(3)	772(3)	784(2)	783(2)	757(2)	754(1)	752(3)		
		809(2)	808(2)	818(2)	819(1)	825(2)	801(3)	
840(3)	843(3)						837(1)	
		862(3)	863(3)			856(2)		
901(1)	899(0)	917(2)	915(2)			902(1)		
949(3)	948(3)	958(3)	958(3)	934(2)	935(1)	952(3)	941(1)	
						982(1)	973(1)	
1038(2)	1040(2)	1030(3)	1031(3)					
1081(2)	1084(2)					1061(2)		
1121(2)	1123(2)	1107(1)	1106(2)	1106(4)	1104(3)	1135(2)		
1167(2)	1167(2)			1156(2)			1162(2)	
1217(2)	1217(2)	1205(3)	1203(3)	1225(2)		1210(1)	1204(1)	
1262(2)	1264(2)	1268(1)	1273(1)			1252(1)	1268(1)	
		1304(3)	1306(3)	1305(2)	1306(1)	1299(2)		
1324(2)	1324(2)					1327(1)		
1376(2)	1377(2)			1367(3)	1377(1)	1374(2)	1377(1)	
		1421(3)	1418(3)			1414(1)		
1445(4)	1444(4)	1449(3)	1450(3)	1432(5)	1434(3)	1442(5)	1440(3)	
						1549(2)		
1653(3)	1652(4)	1647(5)	1648(5)	1636(1)	1680(2)	1634(1)	1637(3)	
				1678(4)		1665(3)		
				2825(3)	2833(1)			
2876(2)	2880(2)	2872(4)	2869(3)	2872(4)	2872(3)	2871(3)	2870(2)	
2914(5)	2912(5)	2917(3)	2917(2)	2916(4)	2912(3)	2913(4)	2905(3)	
2988(3)	2986(3)	2981(3)	2989(3)				2975(3)	
3025(3)	3027(3)	3031(1)	3041(1)	3003(3)	3003(2)	3003(3)	3045(2)	

A careful study of the shifts of all the isomers shows that the frequencies 145 and 845 are characteristic of pinenes, 370 and 868 of sabinenes, 353 and 719 of  $\Delta^3$ -carenes. Further the  $\Delta^4$ -carene can be distinguished from the  $\Delta^3$ -carenes by the presence of additional frequencies 758, 958 and 1067 in the former compound.

The shifts in Table IV are  $5 - 6 \text{ cm}^{-1}$  less than those given in Table I owing to the vacuum correction not being applied.

## COMPARISON OF THE DEXTRO AND LAEVO FORMS.

The Raman frequencies of the dextro and lævo forms of the pinene and the sabinene are identical in value and also in intensity, within the limits of experimental error. The absence of some frequencies in lævo  $\Delta^3$ -carene and the difference in the intensities of the frequencies of dextro and lævo forms are due to the substance lævo  $\Delta^3$ -carene being not sufficiently pure. This latter fact explains the cause of faint lines obtained by Bhagavantam and Venkateswaran in lævo pinene, the commercial samples of which show rotations as low as  $22^\circ$ .

### SUMMARY.

1. The spectra of the dextro and lævo forms of a series of isomeric terpenes are shown to be identical.

2. The structural changes among the isomers are shown in smaller shifts which may be useful in identifying these compounds in essential oils.

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