STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES.

PART IV. RAMAN EFFECT OF CEDRENE.

By Kichimatsu MATSUNO and Kwan HAN.

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Introduction.

In the present paper, the Raman effect of cedrene is reported, the constitution of which has been studied by Prof. K. Kafuku(1) and others(2) on the standpoint of the organic chemistry. The result of the Raman effect in the present investigation seems to provide an evidence for the organic chemists' idea regarding the constitution. The further discussion will be reported after studying the Raman spectra of the derivatives of cedrene and other terpenes, which are in the course of experiments.

Experimental.

The so-called "artificial cedrene" (b.p. 116–118°/10 mm., n_D^{30} 1.494) obtained by the dehydration of cedrol, was kindly supplied by Ass. Prof. T. Nozoe and Mr. K. Kuraoka. The Raman spectrum of this sample was taken by means of a spectrograph with two prisms. Six hours' exposure was enough for obtaining an intense Raman spectrum (Plate 1) in the total region of the visible part. The experiments were repeated by using a new sample obtained by dehydrating cedrol (m.p. 86°) supplied by Dr. Ichikawa of the Central Research Institute of Formosa. Using this new sample of cedrene, the Raman spectrum was obtained with a spectrograph of three prisms(3) by using a saturated solution of sodium nitrite as a filter (Plate 2). A longer exposure of 12–14 hours was required in this case. No difference was found in the above-mentioned two results. The data of the Raman spectrum are shown in Table I.

For the purification, the substances were dehydrated over calcium chloride, and then redistilled over metallic sodium in vacuum (b.p. 116–117°/10 mm., n_D^{30} 1.4943).

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(1) K. Kafuku, *J. Chem. Soc. Japan*, **55** (1934), 1235.

(2) Simonsen, "The Terpenes", Vol. II (1932), p. 530.

(3) This Bulletin, **9** (1934), 327.

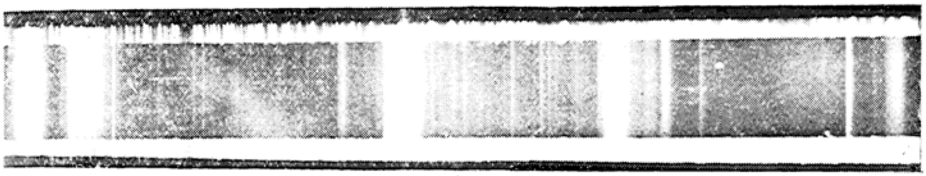

Plate 1. Raman Spectrum of Cedrene (I)

Plate 2. Raman Spectrum of Cedrene (II)

Table I. Raman Spectrum of Cedrene.

No.	ν(cm.$^{-1}$)	I	$\nu_0-\Delta\nu$(cm.$^{-1}$)	No.	ν(cm.$^{-1}$)	I	$\nu_0-\Delta\nu$(cm.$^{-1}$)
1	24560	4	q-2828(k-145)	25	23885	3	k- 820(i-631)
2	24525	½(d)	p-2828(k-180)	26	23855	2(d)	k- 850(i-661)
3	24474	4(d)	q-2914(k-231)	27	23787	2(b, d)	k- 918
4	24443	5(d)	k- 262(p-2910)	28	23763	3(d)	k- 942
5	24418	5(d)	q-2970	29	23737	2	k- 968
6	24391	5(b)	k- 314	30	23704	3(d)	k-1001
7	24381	½	p-2972	31	23680	½	k-1025
8	24362	½	k- 343(q-3026)	32	23666	3(b, d)	k-1039(i-850)
9	24314	2(b)	k- 391	33	23637	3(d)	k-1068
10	24293	1(b)	k- 412	34	23601	2	k-1104
11	24269	2(b, d)	k- 436	35	23579	4(b)	k-1126(i-937)
12	24250	2(b)	k- 455	36	23563	4(b)	k-1142
13	24211	2	k- 494	37	23537	3(b, d)	k-1168
14	24171	3	k- 534	38	23503	2	k-1202
15	24131	5	k- 574	39	23485	3(d)	k-1220
16	24116	2	k- 589	40	23465	3(d)	k-1240
17	24092	2	k- 613	41	23432	4	k-1273(i-1084)
18	24073	½	k- 632	42	23404	2	k-1301
19	24048	2	k- 657	43	23385 ?	0	k-1320
20	24006	2	k- 699	44	23354	4	k-1351
21	23973	5(d)	k- 732	45	23330	4	k-1375
22	23942	½	i- 574	46	23295	½(d)	i-1221
23	23925	5	k- 780(i-591)	47	23271	6	k-1434
24	23905	½	k- 800(i-611)	48	23257	6(b, d)	k-1448

Table I. (*Concluded*)

No.	ν(cm.$^{-1}$)	*I*	$\nu_0-\Delta\nu$(cm.$^{-1}$)	No.	ν(cm.$^{-1}$)	*I*	$\nu_0-\Delta\nu$(cm.$^{-1}$)
49	23251	6(b, d)	k-1454	85	22088	4(b, d)	e- 850(f-907)
50	23228	3(d)	k-1477	86	22065	½(d)	f- 930(e-873)
51	23195	2(d)	e+257	87	22026	5(b, d)	e- 912
52	23124	2(d)	e+186	88	22001	6 b, d)	e- 937
53	23080	3(b)	i-1436(e+142)	89	21973	5(b, d)	e- 965
54	23039	?	k-1666(hg)	90	21952	3(d)	e- 986?(f-1043)
55	22851	2(b, d)	e- 87	91	21937	5(d)	e-1001
56	22814 ?	0(d)	e- 124	92	21914	2	e-1024
57	22794	4(bb, d)	e- 144	93	21901	3	e-1037
58	22749	3(b, d)	e- 189	94	21874	6	e-1064(f-1121)
59	22701	½(d)	e- 237	95	21851	2	e-1087?(f-1144)
60	22680	4(b, d)	e- 258(f-315)	96	21831	6(d)	e-1107(k-2874)
61	22650	0	e- 288	97	21811	5(b)	e-1127
62	22630	4	e- 308	98	21795	6(b)	e-1143 (k-2914, f-1200)
63	22621	3	e- 317				
64	22598	1	e- 340	99	21771	6(b)	e-1167(k-2934)
65	22574	2	e- 364	100	21737	6(b)	e-1201(k-2968)
66	22549	3(b, d)	e- 389	101	21719	2	e-1219
67	22528	3	e- 410	102	21704	3(b, d)	e-1234
68	22501	2(d)	e- 437	103	21669	2(d)	k-3036
69	22485	2(d)	e- 453	104	21660	5	e-1278
70	22469	0(d)	f- 526	105	21641	5	e-1297(f-1354)
71	22447	3	e- 491	106	21608	2 dd)	e-1330
72	22406	5	e- 532	107	21588	5	e-1350
73	22388	½	e- 550(f-607)	108	21563	5	e-1375(f-1432)
74	22367	8	e- 571(f-628)	109	21504	8	e-1434
75	22351	4	e- 587	110	21486	8	e-1452
76	22327	4	e- 611	111	21465	6(bb)	e-1473
77	22308	2	e- 630	112	21292	½	e-1646
78	22282	3	e- 656	113	21272	10	e-1666
79	22240	3	e- 698	114	21106	2(b)	e-2832
80	22205	8(b, d)	e- 733	115	20063	2	e-2875(f-2932)
81	22158	8	e- 780	116	20020	6(b, d)	e-2918
82	22136	2	e- 802	117	19999	6(b)	e-2939
83	22119	6	e- 819	118	19971	6(d)	e-2967(f-3024)
84	22105	½	e- 833	119	19914	2(d)	e-3024

$\Delta\nu$: (87) (2b, d); (124) (0d) ?; 144 (4bb, d); 189 (3b, d); 237 (½d); 260 (4b, d); (288) (0); 308 (4); 317 (3); 340 (1); (364) (2); 389 (3b, d); 410 (3); 437 (2d); 454 (2d); 491 (3); 532 (5); (550) (½) ?; 571 (8); 587 (4); 611 (4); 630 (2); 656 (3); 698 (3); 733 (8b, d); 780 (8); 802 (2); 819 (6); (833) (½); 850 (4b, d); (873) (½d) ?; 915 (5b, d); 938 (6b, d); 965 (5b, d); (986) (3d) ?; 1001 (5d); 1024 (2); 1038 (3); 1066 (6); (1087) (2) ?; 1105 (2d); 1127 (5b); 1143 (6b); 1167 (6b); 1201 (6b); 1219 (2); 1237 (3b, d); 1275 (5); 1297 (5); 1325 (2dd); 1350 (5); 1375 (5);
1434 (8); (1646) (½) ?; 1666 (10); 2830 (2b); 2875 (2); 3030 (2d)
1452 (8)
1475 (6b, d)
2916 (6b, d)
2937 (6b)
2967 (6b)

Discussion.

The Raman spectrum of cedrene is the most complicated one. It contains one-hundred-nineteen lines. And some of the Raman lines are observed at the equal intervals. The mean interval between them is 25 cm.$^{-1}$, as shown below:

317		1101		1325	
	23		26		25
340		1127		1350	
	24				25
364		1143		1375	
	25		24		
389		1167			
	21				
410		1271			
	27		26		
437		1297			

According to the usual estimation, the lower frequencies may be ascribed to the deformation of the carbon linkages. And when we put

$$\omega_1 = 144,\quad \omega_2 = 308,\quad \omega_3 = 317,\quad \omega_4 = 364,\quad \omega_5 = 389,\quad \omega_6 = 410,\quad \omega_7 = 437,$$
$$\omega_8 = 454,\quad \omega_9 = 491,\quad \omega_{10} = 532,\quad \omega_{11} = (550),\quad \omega_{12} = 571,\quad \omega_{13} = 587,\quad \omega_{14} = 611,$$

we find that a number of the Raman lines higher than $\Delta\nu$ 630 cm.$^{-1}$ are two times as great as the above-mentioned frequencies as shown in Table II. These lines may be taken as the overtone of the corresponding lower ones.

Table II. The Frequencies Associated with the Overtone.

$\omega_{cal.}$	$\omega_{obs.}$	$\omega_{cal.}-\omega_{obs.}$	$\omega_{cal.}$	$\omega_{obs.}$	$\omega_{cal.}-\omega_{obs.}$
$2\omega_1 = 288$	(288)(0)	0	$2\omega_8 = 908$	915 (5b, d)	–7
$2\omega_2 = 616$	611 (4)	5	$2\omega_9 = 982$	(986)(3d) ?	–4
$2\omega_3 = 634$	630 (2)	4	$2\omega_{10} = 1064$	1066 (6)	–2
$2\omega_4 = 728$	733 (8)	–5	$2\omega_{11} = 1100$	1105 (2d)	–1
$2\omega_5 = 778$	780 (8)	–2	$2\omega_{12} = 1142$	1143 (6b)	–1
$2\omega_6 = 820$	819 (6)	1	$2\omega_{13} = 1174$	1167 (6b)	7
$2\omega_7 = 874$	(873)($\frac{1}{2}$)	1	$2\omega_{14} = 1222$	1219 (2)	3

From the result compared in Table II, it seems to be impossible to assign the intense lines of $\Delta\nu$ 733(8), 780(8), 915(5b, d), 1066(6), 1143(6b), and 1167(6b), simply as the overtone of the above-mentioned frequencies. Another origin must be taken into consideration.

As the usual assignment, the frequencies in the region of $\Delta\nu$ 733–1066 cm.$^{-1}$ may be attributable to the valency frequencies of the C–C bond. It will be noted that the organic chemists' picture(4) of the molecule indicates that:

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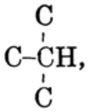
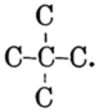
(4) Cf. (2).

(1) Cedrene is a tricyclic compound.

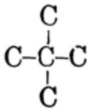
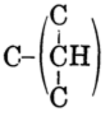
(2) There are carbon atoms holding one, two, three, and none hydrogen atoms, that is,  $\mathrm{C{-}\overset{C}{\underset{C}{C}}H}$, $-\mathrm{CH_2}-$, $-\mathrm{CH_3}$ and  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$.

(3) The molecule includes more possibly a 1-methyl-cyclopentene-(1) than a 1-methyl-cyclohexene-(1) ring.

From these points of view, let us compare, in the first place, the Raman spectrum of cedrene with those of the other simple paraffine molecules which have been observed by Kohlrausch and Köppl(5). As shown in Table III, in the paraffine series, the frequencies of ca. $\Delta\nu$ 840 and 890 cm.$^{-1}$ are found in the normal compounds, while the corresponding shifts in their isomerides are ca. $\Delta\nu$ 780 and 950 cm.$^{-1}$. It is also found that $\Delta\nu$ 1335 cm.$^{-1}$ disappears in the normal compounds, and $\Delta\nu$ 1066 cm.$^{-1}$ does in the iso-compounds.

Table III. Raman Frequencies of the Normal- and Iso-Praffines.

C_nH_{2n+2}	a	b	c	d	e	f	g	h	i	j	k	l
C_4H_{10} (*n*)	298	—	825	(873)	895	—	1058	1006	—	1299	—	1447
C_5H_{12} (*n*)	—	—	841		895	1027	1066	1110	—	1301	—	1446
C_6H_{14} (*n*)	269	—	822	863	889	1026	1069	1112	—	1302	—	1446
C_7H_{16} (*n*)	256	—	845		886	1021	1069	1113	1169	1300	—	1445
C_4H_{10} (*i*)	335	427	(789)	832	954	(1029)	—	1120	1168	1298	1334	1454
C_5H_{12} (*i*)	(366)	424	773	826	953	(1030)	—	1123	1167	(1295)	1337	1453

In the second place, let us consider the Raman spectrum of tetramethyl-methane which was studied by the above authors(7) and Rank.(6) Kohlrausch and Köppl(7) have ascribed ω_1 732(10), ω_2 332(4b), ω_3 921 (7b), and ω_4 416(1) in tetramethyl-methane to the vibration frequencies of the  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$ linkage, while ω_1 795(9), ω_2 371(4b), ω_3 965(4b) and ω_4 437(1) in iso-butane to the  $\mathrm{C{-}\left(\overset{C}{\underset{C}{C}}H\right)}$ linkage. From the fact that

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(5) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, (B) **24** (1934), 377.

(6) D. H. Rank, *J. Chem. Phys.*, **1**, (1933), 572.

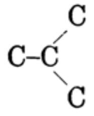
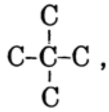
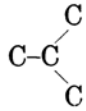
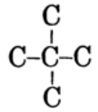
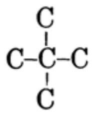
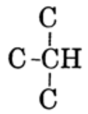
the above-mentioned Raman lines are also observed in the other isomerides of paraffines and their derivatives having the valency bond of  or  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$, as shown in Table IV, and the fact of the disappearance and the displacement of the frequencies in the normal compounds of the paraffine series as shown in Table III, we may ascribe the frequencies in the regions of 732–795 and 915–965 cm.$^{-1}$ to the valency frequencies of the  or  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$ linkage.

Table IV. Raman Frequencies Possibly Associated with the  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$ or  $\mathrm{C{-}\overset{C}{\underset{C}{C}}H}$ Linkage.

Molecule	ω_1	ω_2	ω_3	ω_4
Tetramethyl-methane(7)	732 (10)	333 (4b)	921 (7b)	416 (1)
Tertiary butylcarbinol(8)	744 (9)	333 (2b) 350 (2b)	933 (4)	407 (½)
Tertiary amylcarbinol(8)	714 (4) 726 (3)	350 (2)	903 (2) 931 (2)	405 (0) 441 (½)
Isobutane(7)	795 (9)	371 (4b)	965 (4b)	437 (1)
Isopentane(9)	762 (5) 796 (4)	366 (1)	906 (2) 948 (2)	469 (4)
Isobutyl alcohol(9)	782 (2)	361 (½)	953 (3b)	494 (4)
Isobutyl amine(9)	792 (5b)	363 (2b)	952 (3)	480 (4b)
Methyl-isopropylcarbinol(8)	757 (2b) 786 (3)	358 (1)	930 (3) 954 (2)	462 (½) 496 (½)
2,5-Dimethyl-hexane(10)	778 (2)	313 (2)	962 (3br)	444 (4b)

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(7) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, (B) **26** (1934), 219.
(8) K. W. F. Kohlrausch and F. Köppl, *Monatsh.*, **63** (1933), 269.
(9) H. Kopper, R. Seka and K. W. F. Kohlrausch, *Monatsh.*, **61** (1932), 403.
(10) John W. Murry, *J. Chem. Phys.*, **2** (1934), 618.

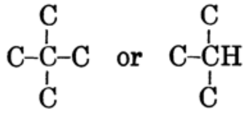

Table V. The Vibration Frequencies Associated with the $\mathrm{C{-}\overset{\displaystyle C}{\underset{\displaystyle C}{C}}{-}C}$ or $\mathrm{C{-}\overset{\displaystyle C}{\underset{\displaystyle C}{C}}H}$ Linkage.

Molecule	ω_1	ω_2	ω_3	ω_4
Isobutane	785 (9)	371 (4b)	965 (4b)	437 (1)
Cedrene	780 (8) 733 (8)	389 (3b, d) 317 (3)	965 (5b) 915 (5b, d)	427 (2d) 410 (3)
Tetramethyl-methane	732 (10)	332 (4b)	921 (7b)	416 (1)

Table VI. The Valency Frequencies of the Carbon Bonds.

Cedrene	α-Pinene		β-Pinene(12)	Sabinene(13)
	V.B.(11)	M.H.(13)		
733 (8)	—	—	—	729 (1d)
780 (8)	774 (2)	774 (6)	786 (5)	786 (5)
802 (2)	—	—	—	—
819 (5)	816 (0)	818 (2)	—	808 (4d)
850 (4b, d)	844 (2)	844 (7)	850 (5)	—
(873)(½)	878 (0)	885 (2)	879 (5)	882 (2d)
915 (5b, d)	904 (1)	908 (4)	—	916 (6d)
938 (6b, d)	931 (0)	933 (2)	—	930 (1)
965 (5b)	949 (3)	954 (5d)	942 (4)	953 (6b)
986 (3)	—	—	—	989 (3)

It may, therefore, be possible to assign the frequensies of $\Delta\nu$ 733, 780, 915, and 965 cm.^{-1} in cedrene as due to these linkages in the cedrene molecule. The vibration frequencies associated with the linkage in question in cedrene are compared also with those in iso-butane and tetramethyl-methane as shown in Table V. It is interesting that the relation of the intensities of these lines in the latter are similar to that in the former. As to the other Raman lines in the region of 802–850 cm.^{-1}, they may be attributable to the $-CH_2-CH_2-$ linkage of the ring.

Further, let us compare the Raman lines which are possibly associated with the valency frequencies of the carbon linkages in cedrene with those

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(11) S. Venkateswaran and S. Bhagavantam, *Ind. J. Phys.*, **7** (1933), 585.
(12) G. Dupont, P. Daure and J. Allard, *Bull. soc. chim.*, **49** (1932), 1401.
(13) The details will be published shortly in this Bulletin.

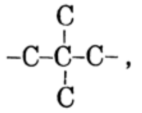
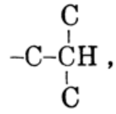
in the other terpenes, such as α-pinene, β-pinene, and sabinene, which have been known to have the carbon linkages of  $-\mathrm{C}-\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}-\mathrm{C}-$,  $-\mathrm{C}-\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\mathrm{H}$, $-\mathrm{CH_2}-$ and $-\mathrm{CH_3}$ (Table VI). The frequencies of $\Delta\nu$ 780, 873, and 965 cm.$^{-1}$ in cedrene are also found in α-pinene, β-pinene, and sabinene. The frequencies of $\Delta\nu$ 819, 915 and 938 cm.$^{-1}$ appear in cedrene, α-pinene, and sabinene, but not in β-pinene. The frequency of $\Delta\nu$ 850 cm.$^{-1}$ appears in cedrene, α-pinene, and β-pinene, but not in sabinene. The fact that all the shifts between $\Delta\nu$ 733 and 986 cm.$^{-1}$ in cedrene are found also in α-pinene, β-pinene, or sabinene seems to give a verification of the organic chemists' idea regarding the constitution of cedrene.

Table VII. Comparison of the Raman Frequencies in Cedrene, 1-Methyl-cyclopentene-(1) and 1-Methyl-cyclohexene-(1).

Methyl-cyclopentene		Cedrene	Methyl-cyclohexene (Godchot, etc.)(15)	Methyl-cyclopentene		Cedrene	Methyl-cyclohexene (Godchot, etc.)(15)
(Godchot, etc.)(15)	(Piaux)(16)			(Godchot, etc.)(15)	(Piaux)(16)		
—	—	308	—	—	928	938	—
333	325	317	—	—	—	965	—
		340		—	—	(986)?	990
—	—	364	—	—	1008	1001	—
—	—	389	—	1017	1026	1024	—
—	—	410	—	—	—	1038	—
437	432	437	437	—	—	1066	1069
—	—	454	—	1083	—	(1087)?	1087
—	—	491	495	—	—	1105	—
—	—	532	—	—	1133	1127	—
578	578	571	—	—	1148	1143	1152
—	—	587	588	—	—	1167	—
—	—	611	618	—	1207	1201	—
—	—	630		—	—	1219	—
—	648	656	—	1278	1259	1275	1266
—	—	698	695	—	1295	1297	1309
—	—	733		1336	1333	1325	1367
—	790	780	758	—	—	1350	—
—	—	802	—	1385	1383	1375	—
—	821	819	821	1445	1439	1434	1445
—	851	850	859		1465	1452	
879	881	(873)?	—			1475	
—	903	915	—	1660	1658	1666	1675

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(14) The details will be published shortly in this Bulletin.

(15) Marcet Godchot, Etienne Canales, and Germaine Cauquil, *Compt. rend.*, **197** (1933), 1408.

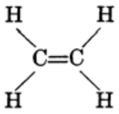
(16) Leon Piaux, *Compt. rend.*, **199** (1934), 67.

The facts that almost all the Raman lines observed in cyclohexane occur also in decahydro-naphthalene and decahydro-acenaphthene(14) and that many of the Raman lines of cedrene coinside with those of 1-methyl-cyclopentene-(1) and 1-methyl-cyclohexene-(1) (Table VII) give an another evidence of the organic chemists' constitution of cedrene.

The most intense line at $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is attributable to the inner vibration of the C=C bond. This frequency is generally influenced rather remarkably by the adjacent atoms or atom groups of the bond in the molecule. The frequency of $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is compared with that in the other molecules which have the C=C linkage, as shown in Table VIII.

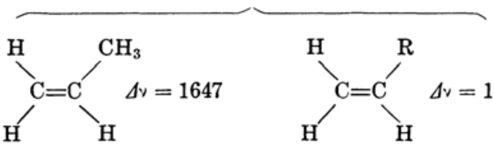
From the results we may summarize that the Raman frequency due to the C=C linkage indicates a constant value for each type of the molecules. And by the substitution of a methyl or methylene group for a hydrogen atom attached to the double bond of the carbon atoms the frequency is increased about 20 cm.$^{-1}$, with an exception of cyclopentene in which it is increased about 40 cm.$^{-1}$, as shown below:

I



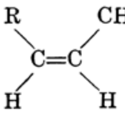
$\Delta\nu = 1620$

II



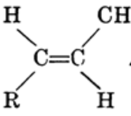
$\Delta\nu = 1647$ $\Delta\nu = 1642$

III



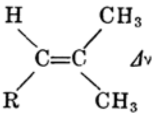
$\Delta\nu = 1658$

III′



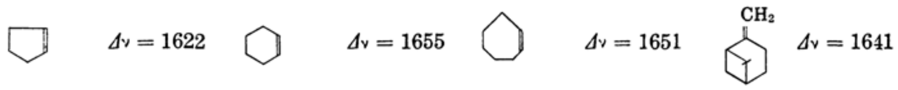
$\Delta\nu = 1673$

IV



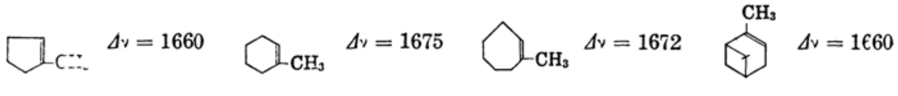
$\Delta\nu = 1679$

V



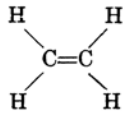
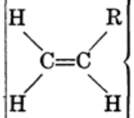
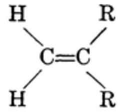
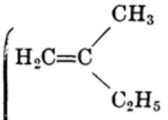
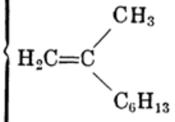
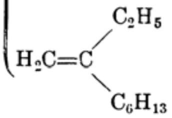
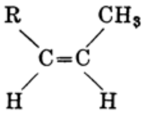
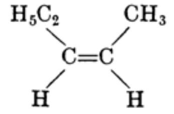
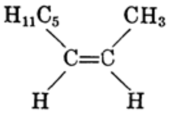
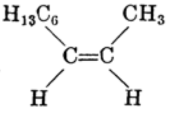
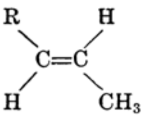
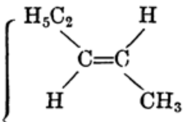
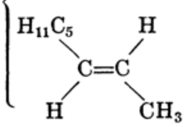
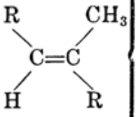
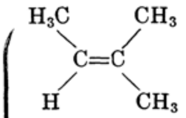
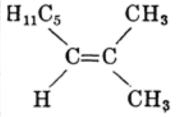
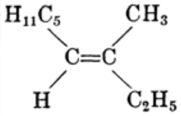
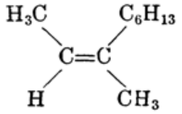
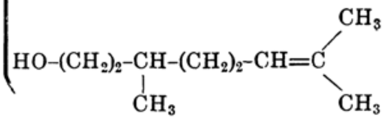
$\Delta\nu = 1622$ $\Delta\nu = 1655$ $\Delta\nu = 1651$ $\Delta\nu = 1641$

VI



$\Delta\nu = 1660$ $\Delta\nu = 1675$ $\Delta\nu = 1672$ $\Delta\nu = 1660$

Table VIII. Raman Frequencies Associated with the C=C Bond.

	$H_2C{=}CH_2$	1620(17)
	$H_2C{=}CH{-}CH_3$	1647(17)
	$H_2C{=}CH{-}CH_2OH$	1646(17)
	$H_2C{=}CH{-}CH_2Cl$	1640(17)
	$H_2C{=}CH{-}CH_2{-}C_6H_5$	1642(17)
	$H_2C{=}CH{-}C_nH_{2n+1}$ $(n=2-8)$	1642(17)
		1652(19)
		1647(18)
		1646(18)
		1658(20)
		1658(20)
		1658(20)
		1674(20)
		1673(20)
		1679(21)
		1677(18)
		1670(18)
		1672(18)
	 $HO{-}(CH_2)_2{-}\underset{CH_3}{CH}{-}(CH_2)_2{-}CH{=}C(CH_3)_2$	1675(27)

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(17) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 495.
(18) B. Gredy, *Compt. rend.*, **195** (1932), 313.
(19) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 480.
(20) M. Bourguel, B. Gredy, and L. Piaux, *Compt. rend.*, **195** (1932), 129.
(21) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 474.

Table VIII. (*Concluded*)

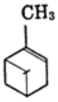
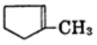
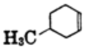
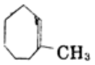
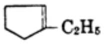
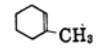
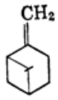
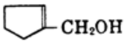
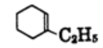
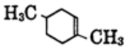
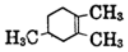
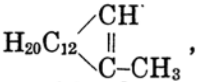
	1622$^{(22)}$		1655$^{(22)}$		1651$^{(22)}$		1660$^{(25)}$
	1660$^{(23)}$		1650$^{(23)}$		1672$^{(23)}$		
	1660$^{(23)}$		1675$^{(23)}$				1641$^{(26)}$
	1656$^{(24)}$		1675$^{(23)}$				
			1680$^{(23)}$				
			1677$^{(23)}$				

Table IX. The Raman Frequencies Associated with the $-\mathrm{C}=\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}-$ Linkage.

Butadiene$^{(28)}$	—	Geraniol$^{(29)}$	1388
1-Methyl-butadiene$^{(28)}$	1370	Linalool$^{(30)}$	1383
Isoprene$^{(28)}$	1380	Carvone$^{(31)}$	1378
2,3-Dimethyl-butadiene$^{(28)}$	1377	Pulegone$^{(32)}$	1379
Phenyl-ethylene$^{(28)}$	—	Cyclopentene$^{(22)}$	—
Phenyl-methyl-ethylene$^{(28)}$	1376	1-Methyl-cyclopentene-(1)$^{(23)}$	1385
Chloroprophylene$^{(28)}$	1375	Cyclohexene$^{(22)}$	—
Methyl crotonate$^{(28)}$	1375	1-Methyl-cyclohexene-(1)$^{(22)}$	1367
Methyl iso-crotonate$^{(29)}$	1367	Cycloheptene$^{(22)}$	—
Crotonic acid$^{(28)}$	1381	1-Methyl-heptene-(1)$^{(23)}$	1379
α-Pinene$^{(25)}$	1383	Octene$^{(22)}$	—
β-Pinene$^{(26)}$	—		

From these results, we may conclude that the most intense line corresponding to the frequency of $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is attributable to the C=C bond in the type of  $\mathrm{H_{20}C_{12}}\begin{cases}\mathrm{CH^{\cdot}} \\ \quad\| \\ \mathrm{C{-}CH_3}\end{cases}$, as described by the organic chemists. By comparing with the corresponding Raman

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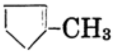
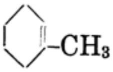
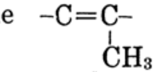
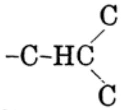
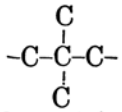
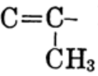
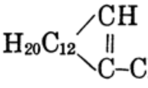
(22) M. Godchot, etc., *Compt. rend.*, **196** (1933), 780.
(23) M. Godchot, etc., *ibid.*, **197** (1933), 1407.
(24) L. Piaux, *ibid.*, **199** (1934), 67.
(25) Cf. (13).
(26) Cf. (12).
(27) G. B. Bonino, and P. Cella, *Mem. Accad. Italia*, **3** (1932), No. 4, 20.
(28) Kohlrausch, "Smekal-Raman-Effekt", (1931), p. 322–327.
(29) G. B. Bonino and P. Cella, *Mem. Accad. Italia*, **3** (1932), No. 4, 22.
(30) *Ibid.*, p. 21. (31) *Ibid.*, p. 8. (32) *Ibid.*, p. 6.

shift in 1-methyl-cyclopentene-(1) (Δν 1660 cm.$^{-1}$) and 1-methyl-cyclohexene-(1) (Δν 1675 cm.$^{-1}$), it seems that the frequency in question appears more likely in the case of 1-methyl-cyclopentene-(1) than in the case of 1-methyl-cyclohexene-(1). The difference is, however, too small to distinguish the latter from the former, as the frequency Δν 1666 cm.$^{-1}$ in cedrene is situated between the frequencies in 1-methyl-cyclopentene-(1) and 1-methyl-cyclohexene-(1). That is:  Δν 1660 cm.$^{-1}$; cedrene Δν 1666 cm.$^{-1}$;  Δν 1675 cm.$^{-1}$. This fact gives an evidence of the presence of a methyl group attached to the carbon atom of the double bond. The question whether the molecule of cedrene contains 1-methyl-cyclopentene-(1) ring or 1-methyl-cyclohexene-(1) ring is still unanswered from the study of the Raman effect.

Another possible evidence of the existence of the  $-C=\underset{\displaystyle CH_3}{\underset{|}{C}}-$ linkage in cedrene may be given by the occurrence of the Raman frequency of Δν 1375 cm.$^{-1}$. This frequency has been observed in the Raman spectra of such molecules as methyl-butadiene, isoprene, chloropropylene, geraniol, linalool, pulegone, 1-methyl-cyclopentene-(1), 1-methyl-cyclohexene-(1), 1,2-dimethyl-cyclohexene, and 1-methyl-cycloheptene-(1), etc., but not in butadiene, cyclopentene, cyclohexene, and cycloheptene, etc., as shown in Table IX.

Summary.

The Raman spectrum of cedrene has been studied. The frequencies of Δν 733, 780, 915 and 965 cm.$^{-1}$ are established to be attributable to the valency frequencies of the linkage,  $-C-HC\begin{smallmatrix}\diagup C\\ \diagdown C\end{smallmatrix}$ or  $-C-\overset{\displaystyle C}{\overset{|}{\underset{\displaystyle C}{\underset{|}{C}}}}-C-$ in the molecule of cedrene. The most intense line at Δν 1666 cm.$^{-1}$ is assigned to characterize the C=C bond. The occurrence of the Raman line at Δν 1375 cm.$^{-1}$ seems to give an evidence of the  $-C=\underset{\displaystyle CH_3}{\underset{|}{C}}-$ linkage in the cedrene molecule,  $H_{20}C_{12}\begin{matrix}\diagup CH\\ \quad\| \\ \diagdown C-CH_3\end{matrix}$.

In conclusion, the authors wish to express their thanks to Ass. Prof. T. Nozoe for his kind advices and supply of the sample. The authors express their indebtedness also to Dr. Ichikawa for his supply of cedrol.

Laboratory of Physical and Inorganic Chemistry,
Taihoku Imperial University, Taihoku, Japan.