STUDIES ON THE RAMAN EFFECT OF ORGANIC SUBSTANCES. VI. RAMAN EFFECT OF SESQUICHAMENE AND SOME OTHER TERPENES.

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Introduction. In the present paper, the Raman spectra of sesquichamene, $C_{15}H_{24}$, *d*-α-pinene, *d*-sabinene, *d*-verbenol, *d,l*-Δ^1-terpinenol-(4), menthyl acetate and isobornyl acetate are reported. The constitution of sesquichamene has not been thoroughly determined. Kafuku and Nozoe[1] suggested that sesquichamene is a sesquiterpene of tricyclic class like cedrene, the Raman spectrum of which has been studied by the present authors[2]. α-Pinene[8][9][10][11] and sabinene have been investigated by several authors, our results could be compared with theirs.

Experimental. Most of the substances used were kindly supplied by Ass. Prof. T. Nozoe and his co-workers.

Sesquichamene $C_{15}H_{24}$ was obtained from the essential oil of the leaves of "Arisan-hinoki" or *Chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata.[1] The physical properties of the sample used were as below: b. p. 120-123°/12 mm., d_4^{34} 0.92386, n_D^{34} 1.4883, $[\alpha]_D$ −86.31°.

d-Sabinene was obtained from the essential oil of the leaves of "Arisan-hinoki"[3] (b.p. 162° or 80–82°/50 mm., $d_4^{17.5}$ 0.8442, n_D^{20} 1.4681, $[\alpha]_D$ +72°).

d-α-Pinene was obtained from the oil of the roots of "hinoki" or *Chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata (b.p. 155–156°, n_D^{20} 1.4671, d_4^{20} 0.8585, $[\alpha]_D$ +45.25°).

d-Verbenol was obtained by the autoxidation of *d*-α-pinene.

d,l-Δ^1-Terpinenol-(4) was obtained from the leaves of *Liquidambar formosana*, Hance[4] (b.p. 123°/50 mm., n_D^{20} 1.4751, $[\alpha]_D$ −0.04°).

Menthyl acetate was obtained by heating *l*-menthol with acetic anhydride at 150° (b.p. 108°/15 mm., d_4^{20} 0.9185, n_D^{20} 1.4468).

Isobornyl acetate[5] was prepared by heating camphene[6] (m.p. 51–52°) with glacial acetic acid (b.p. 106.5–107.5°/15 mm., d_4^{15} 0.9866, n_D^{15} 1.4651).

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(1) K. Kafuku and T. Nozoe, this Bulletin, **6** (1931), 111.
(2) This Bulletin, **10** (1935), 220.
(3) K. Kafuku, T. Nozoe and C. Hata, this Bulletin, **6** (1931), 40.
(4) K. Kafuku, T. Nozoe and C. Hata, *J. Chem. Soc. Japan*, **55** (1934), 244.
(5) J. B. Cohen, "Practical Organic Chemistry," (1926), p. 293.
(6) Camphene was synthesized from pinene hydrochloride (m.p. 119–120°), J. B. Cohen, *ibid.*, p. 292.

All the substances were redistilled in vacuum before use. In the case of *d*-verbenol, about 3 c.c. of the sample was used. The observation of its Raman lines was difficult on account of the strong background. The Raman spectra were taken by means of spectrograph of three prisms[7]. The results are summarized in Table 1. The numbers of the Raman lines(n), the number of the plates and the conditions under which the spectra were taken, are summarized in Table 2. The results on α-pinene obtained by the authors are compared with those obtained by Bonino-Cella[8], Dupont-Daure-Allard[9], Venkateswaran-Bhagavantam[10], and Daure[11] in Table 3. Our results are in good agreement with those obtained by Daure.

Table 1. The Values of $\Delta\nu$ for Sesquichamene and Some Other Terpenes.

(1) Sesquichamene

91 (3b, d); 132 (3b, d); 254 (3d); 280 (3); (302) (2d); (336) (2d); 360 (5d); 386 (5d); (407) (1); 434 (4); 496 (3); 539 (3); 572 (3); 590 (8); 604 (4); (684) (1/2); 770 (6); 814 (5); 843 (1d); 882 (4bb); 907 (4d); 926 (1d); 934 (2); 954 (4); 964 (4); 988 (1d); 1006 (4); 1022 (1d); (1042) (2); 1058 (2); 1100 (3b, d); 1119 (3b, d); 1155 (6b, d); (1186) (1); 1192 (4); 1208 (1); 1263 (4); 1296 (4); (1322) (2b); (1346) (2); 1375 (4); 1398 (4); 1434 (5); 1453 (4d); 1471 (4); 1647 (1); 1680 (10); 2844 (4b, d); 2869 (3bb, d); 2908 (6b, d); 2966 (2b, d); 3006 (5bb); 3084 (1); 3167 (4).

(2) *d*-Sabinene

(120) (3b, d); (169) (2b, d); (214) (1); 306 (3); 333 (1); 362 (3d); (373) (1/2); 441 (3); 491 (1d); 509 (3); 566 (2); 634 (3d); 655 (5); 785 (5); 808 (4d); 866 (4b, d); 882 (2d); 915 (6d); 930 (1); 954 (6bb); 989 (3); 1031 (5); 1067 (4); 1109 (6b, d); 1145 (4d); 1170 (3d); 1197 (6); 1214 (1d); 1270 (4b, d); 1308 (4bb); 1379 (3d); 1415 (8); 1438 (4d); 1447 (5d); 1468 (4d); 1656 (10b, d); 2830 (4); 2913 (2); 2940 (2); 2964 (6); 2996 (4b,d); 3070 (4b).

(3) *d*-α-Pinene

134 (3b,d); (208) (2b,d); 261 (3d); 306 (2d): (333) (0); 388 (3b,d); (426) (2); (465) (2); (488) (3); 564 (4); 620 (3); 667 (6); 774 (4); 822 (2); 844 (5); 885 (1); 905 (3); 930 (1); 953 (3b, d); (998) (0); 1015 (1d); 1042 (3d); 1085 (3); 1125 (2); 1163 (4); 1183 (3b, d); 1223 (3b, d); 1264 (4b, d); 1308 (2); 1328 (3b, d); 1374 (3d); 1433 (5d); 1444 (3b, d); 1468 (2); 1660 (6); 2833 (4d); 2874 (4b, d); 2912–2925 (5bb, d); 2951 (3b, d); 2988 (5d); 3031 (4b, d).

(7) This Bulletin, **9** (1934), 327.
(8) G. B. Bonino and P. Cella, *Mem. accad. Italia, Biol; Chim; Fis; Mat.*, **2** (1931), 5.
(9) G. Dupont, P. Daure and J. Allard, *Bull. soc. chim.*, **49** (1931), 1401.
(10) S. Venkateswaran and S. Bhagavantam, *Indian J. Physics*, **7** (1933), 585.
(11) P. Daure, *Compt. rend.*, **198** (1934), 725.

Table 1. (*Concluded*)

(4) *d*-Verbenol

141 (4); (204) (3); (313) (2); 402 (2); (470) (1); 517 (1); 577 (2); 614 (2); 651 (1); (689) (1/2); 730 (2); 777 (3); (799) (1); 843 (2d); (925) (3d); 946 (1b, d); 973 (2d); (1007) (1/2); (1037) (1b, d); 1092 (3d); 1150 (5bb, d); (1185) (3b); 1216 (3); 1258 (3); (1312) (1/2); (1338) (1); 1376 (3); (1395) (1d); 1446 (5d); 1593 (6); 1657 (5); 2860 (3); 2908 (3b, d); 2972 (3).

(5) *d,l*-Δ^1-Terpinenol-(4)

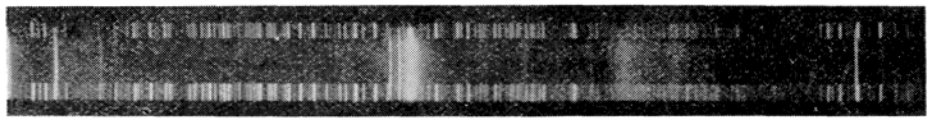
194 (1bb, d); 323 (3d); 434 (4); 455 (1/2d); 495 (1/2d); 518 (3); 546 (1/2); 568 (1/2d); 651 (3); 683 (3); 732 (8); 765 (4b,d); 802 (4b,d); 839 (1d); 864 (3d); 890 (5); 928 (2); 951 (5); 962 (1d); (996) (2); 1027 (2b); 1051 (2); 1073 (6); 1096 (1/2); 1131 (8b, d); 1163 (6d); 1250 (5d); 1312 (6bb, d); 1371 (6d); 1428 (6); 1449 (6); 1468 (4); 1682 (8); 2832 (2d); 2849 (6b); 2879 (6bb, d); 2910 (6bb, d); 2932 (6); 2966 (3); 3020 (1/2).

(6) Menthyl acetate

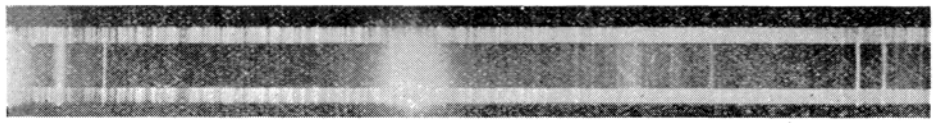
230 (1/2); 293 (3); 318 (3); (409) (3); (424) (0); 465 (2); 504 (3); 544 (4d); 596 (2); 651 (3); (717) (1/2)?; 768 (5); 776 (6); 809 (4); 846 (2); 875 (5); (905) (2); (924) (1); 930 (1); (954) (3); 975 (3); 1042 (4); (1062) (1/2); 1081 (6b, d); 1150 (6bb, d); 1163 (6bb, d); 1184 (6d); 1242 (5); 1271 (4); 1347 (3); 1381 (3d); 1443 (5); 1462 (6d); 1737 (2d); 2848 (6b, d); 2870 (6bb, d); 2930 (4d); 2966 (6d).

(7) Isobornyl acetate

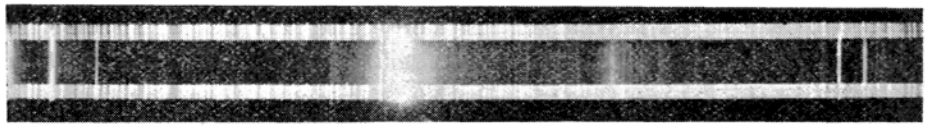
234 (1); 260 (1); 315 (1/2); 345 (1); 387 (2b); 526 (3); 586 (1/2); 621 (5); 655 (3); 747 (2d); 803 (1d); 859 (4); 897 (2); 942 (3); 987 (2); 1022 (3); 1077 (1); 1104 (4); 1131 (2); 1164 (8); 1246 (3); 1323 (2b); 1376 (3b); 1440 (4b, d); 1473 (1/2); 1735 (3); 2874 (2); 2932–2968 (8b).



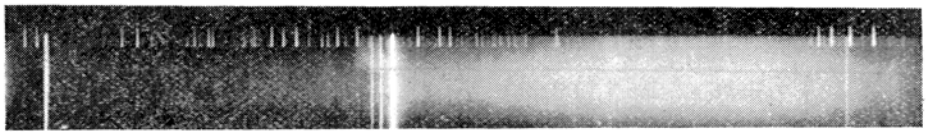
(1) Sesquichamene



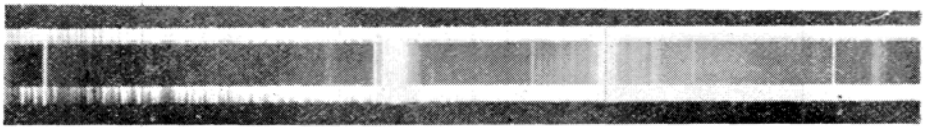
(2) *d*-Sabinene



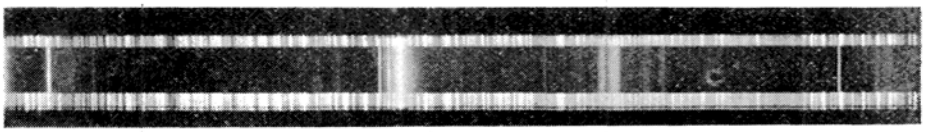
(3) *d*-α-Pinene



(4) *d*-Verbenol



(5) *d,l*-Δ^1-Terpinenol-(4)



(6) Menthyl acetate

(7) Isobornyl acetate

Table 2.

Substance	n	No. of plates	Width of slit (10^{-2} mm.)	Temp. (C.)	Time of exposure (hours)
Sesquichamene	104	258	76	24°	6
		259	76	25	14
		260	64	24	8
		261	64	23	12
d-Sabinene	83	176	64	19	10
d-α-Pinene	85	174	70	19	10
		175	64	19	10
d-Verbenol	54	145	90	21	12
d,l-Δ^1-Terpinenol-(4)	70	172	70	19	6
		173	60	19	10
Menthyl acetate	64	266	70	23	6
		267	64	23	12
Isobornyl acetate	41	184	70	19	14

Table 3. Comparison of the Results on α-Pinene.

Bonino -Cella[8]	Venkateswaran -Bhagavantam[9]	Dupont etc.[10]	Daure[11]	Nevgi-Jatkar[12]	The authors
123	134		139	139	134
213	213	222	207	204	208
266	261	278	258	259	261
308	306	308	307	308	306
			335		333?
392	388	391	389	390	388
			394		
	428		424	421	426
478	476	477	467	474	465
			483		(488)
565	564	573	565	568	564
619		623	613	620	620
			623		
	647				
673	666	672	668	662	667
778	774	776	771	774	774
			789		
	816		820		822
847	844	840	845	840	844
	878		889		885
	904		908	901	905
	931		930		930
			940		
953	949	962	952	949	953
	994		1000		998
			1018		1015
1045	1042	1048	1047	1038	1042
			1070		
1086	1087	1091	1085	1081	1085
1127	1131	1134	1124	1121	1125
1174	1175	1177	1166	1167	1163
			1184		1183
			1205		
1218	1224	1234	1223	1217	1223
1268	1270	1271	1269	1262	1264
	1305	1299	1309		1308

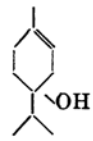
(12) G. V. Nevgi and S. K. Kulkarin Jatkar, *J. Indian Inst. Sci.*, **17A** (1934), 189.

Table 3. (*Concluded*)

Bonino -Cella	Venkateswarna -Bhagavantam	Dupont etc.	Daure	Nevgi-Jatkar	The authors
1328	1332	1332	1330	1324	1328
			1339		
1378	1375	1383	1377	1376	1374
	1436	1430	1437		1433
1449			1448	1445	1444
			1457		
		1490	1476		1468
1656	1661	1672	1659	1653	1660
	2833				2833
2863	2876			2876	2874
2923	2917			2914	2912
					2925
	2948				2951
2987	2989			2988	2988
3034	3029			3025	3031
3110					
3157					

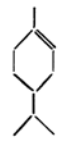
Discussion. From the point of view of organic chemists, sesquichamene as well as cedrene is a tricyclic sesquiterpene. As shown in Table 4, most of the Raman lines in sesquichamene agree well with those in cedrene. The remarkable difference is that the intense lines corresponding to $\Delta\nu$ 733, 656 and 630 cm.$^{-1}$ in cedrene, disappear in sesquichamene, and that the Raman frequency associated with the C:C linkage is found at $\Delta\nu$ 1682 cm.$^{-1}$ in sesquichamene, while at 1666 cm.$^{-1}$ in cedrene. This seems to lead to the consideration that sesquichamene may have the chemical constitution similar to that of cedrene, excepting the ring containing the C:C linkage. In the previous paper[2], we summarized the Raman frequencies associated with the C:C linkage, and concluded that  -CH_3 has the frequency of $\Delta\nu$ 1660 cm.$^{-1}$, while  -CH_3 has that of $\Delta\nu$ 1675 cm.$^{-1}$ In the case of sesquichamene, the fact that the corresponding frequency is found at $\Delta\nu$ 1682 cm.$^{-1}$, seems to suggest that sesquichamene may have a 1-methyl-cyclohexene-(1) ring if cedrene has a linkage of 1-methyl-cyclopentene-(1), as suggested by the

organic chemist.[13] The fact that the corresponding frequencies are found at $\Delta\nu$ 1682 cm.$^{-1}$ in *d,l*-Δ^1-terpinenol-(4) (I), 1681 cm.$^{-1}$ in carvomenthene (II)[10] 1677 and 1638.5 cm.$^{-1}$ in sylvestrene (III)[14], 1675.5 cm.$^{-1}$ in Δ^1-*m*-menthene (IV)[14], 1681 and 1668 cm.$^{-1}$ in terpinolene (V)[14], 1636 and 1678 cm.$^{-1}$ in Δ^3-carene (VI)[15], 1660 cm.$^{-1}$ in α-pinene (VII), 1657 cm.$^{-1}$ in *d*-verbenol (VIII), 1675 cm.$^{-1}$ in 1-methyl-cyclohexene (IX)[16] and 1680 cm.$^{-1}$ in 1,4-dimethyl-cyclohexene-(1)[16], as shown below seems to give a confirmation for it.



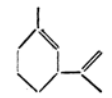
(I)

$\Delta\nu$ 1682



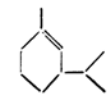
(II)

1681



(III)

1677
1638.5

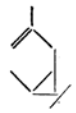


(IV)

1676

(V)

1678
1636

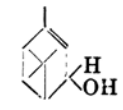


(VI)

$\Delta\nu$ 1678

(VII)

1660



(VIII)

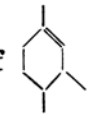
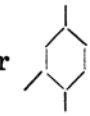
1657

(IX)

1675

(X)

1680

When we take the frequencies of 1638.5 and 1636 cm.$^{-1}$ as due to the ethylene linkage of the side chain, in the case of III and V respectively, we may conclude that the frequency associated with the ethylene linkage in the ring, is found at $\Delta\nu$ 1680 cm.$^{-1}$ in the case of  or  type, and $\Delta\nu$ 1660 cm.$^{-1}$ in the case of  . It is possible to consider that sesquichamene has a 1-methyl-cyclohexene ring in its molecule if there is not any remarkable spanning effect due to the tricyclic bond upon the C:C linkage.

(13) K. Kafuku, *J. Chem. Soc. Japan*, **55** (1934), 1235.
(14) G. Dupont, P. Daure and J. Lévy, *Bull. Soc. Chim.*, **51** (1932), 921.
(15) G. Dupont and R. Gachard, *ibid.*, **51** (1932), 1579.
(16) M. Godchot, E. Canales and G. Cauquil, *Compt. rend.*, **197** (1933), 1407.

Table 4.

Sesqui-chamene	Cedrene	Sabinene	α-Pinene	*d*-Verbenol	*dl*-Δ^1-terpinenol-(4)	Menthyl acetate	Isobornyl acetate
91	(87)						
132	(124)	(120)?	134	141			
	144						
	189	(169)			194		
		(214)	(208)	(204)			
	237					230	
254	260		261				260
280	(288)					293	
(302)	308	306	306	(313)	329	318	315
	317						
336	340	333	(333)?				345
360	(364)	362					
386	389	(373)	388	402		(409)	387
(407)	410		426			(424)	
434	437	441			434		
	454		465	(470)?	455	465	
496	491	491	488		495		
		509		517	518	504	526
539	532				546	544	
572	571	566	564	577	568		
590	587					596	586
604	611			614			
	630	634	620				621
	656	655	667	651	651	651	655
(684)	698			(689)	683		
	733			730	732	(717)?	747
770	780	785	774	777	765	768	
						776	
	802	808		(799)	802	809	803
814	819		822				
843	(833)		844	843	839	846	859
	850	866			864	875	
882	(873)	882	885		890		897
907	915	915	905			(905)	
926							
934	938	930	930	(925)	928	(924)?	
						930	942
954	965	954	953	946	951	(954)	

Table 4. (*Concluded*)

Sesqui-chamene	Cedrene	Sabinene	α-Pinene	*d*-Verbenol	*dl*-Δ^1-Terpinenol-(4)	Menthyl acetate	Isobornyl acetate
964					962	975	
988	986	989	998	973	(996)		987
1000	1001		1015	(1007)	1027		
1022	1024						1022
(1042)	1038	1031	1042	(1037)		1042	
1058	1066	1067			1051	(1062)	
					1073	1081	1077
	(1087)		1085	1092	1096		
1100	1105	1109					1104
1119	1127		1125		1131		1131
	1143	1145		1150		1150	
1155	1167	1170	1163		1163	1163	1164
(1186)		1183	1183	(1185)		1184	
1192	1201	1197					
1208	1219			1216			
	1237	1214	1223			1242	1246
1263	1275	1270	1264	1258	1250	1271	
1296	1297	1308	1308	(1312)	1312		1323
(1322)	1325		1328	(1338)			
(1346)	1350					1347	
1375	1375	1379	1374	1376	1371	1381	1376
1398		1415		1395			
1443	1434	1438	1433		1428		
1453	1452	1447	1444	1446	1449	1443	1440
1471	1475	1468	1468	(1469)	1468	1462	1473
(1595)							
1647	(1646)?			1593			
1680	1666	1656	1660	1657	1682	1737	1735
2844	2830	2830	2833		2832		
					2849		
2869	2875		2874	2860	2879	2848	2874
2908	2916	2913	2912	2908	2910	2870	
	2937	2940	2925		2932	2930	(2932
2966	2967	2964	2951	2972	2966	2966	2968
3006		2996	2988				
3084	3030	3070	3031		3020		
3167							

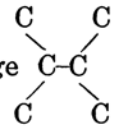
The Raman frequencies of sesquichamene, cedrene, *d*-sabinene, *d*-α-pinene, *d*-verbenol, *d,l*-Δ^1-terpinenol-(4), menthyl acetate and isobornyl acetate are tabulated in Table 4 for comparison. A glance at Table 4 enables us to notice that cedrene and sesquichamene have the most complicated Raman spectra. The frequencies of ca. $\Delta\nu$ 496–532 and 572 cm.$^{-1}$ are found in all the substances in the present investigation. These may correspond to 491–514 and 590 cm.$^{-1}$ in the condensed ring compounds which have the linkage  , as shown in one of our previous papers.[17] The Raman lines in the region of $\Delta\nu$ 1453 cm.$^{-1}$, which are associated with the CH_2 group, are observed in the following six substances at the nearly equal intervals, as shown in Table 5.

Table 5.

Sesquichamene	Cedrene	Sabinene	α-Pinene	*d*-Verbenol	*d,l*-Δ^1-Terpinenol-(4)
1398 (4)		1415 (8)		1395 (1d)	
1434 (5)	1434 (8)	1438 (4d)	1433 (5d)		1428 (6)
1453 (4d)	1452 (8)	1447 (5d)	1444 (3b, d)	1446 (5d)	1449 (6)
1471 (4)	1475 (6b, d)	1468 (4d)	1468 (2)	1469 (6)	1468 (4)

The frequency of $\Delta\nu$ 1464 cm.$^{-1}$ is found also in naphthalene, which has not any CH_2 group. The further discussion will be reported after studying the Raman spectra of other terpenes, which are in the course of experiments.

Summary.

(1) The Raman spectra of the following substances have been measured: Sesquichamene. *d*-sabinene, *d*-α-pinene, *d*-verbenol, *d,l*-Δ^1-terpinenol-(4), menthyl acetate, and isobornyl acetate.

(2) The occurrence of the intense line at $\Delta\nu$ 1682 cm.$^{-1}$ seems to suggest that sesquichamene may have a linkage of 1-methyl-cyclohexene-(1) if cedrene has a linkage of 1-methyl-cyclopentene-(1).

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