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Mass Spectra and Organic Analysis. Part VII.¹ The Mass Spectra of the Menthols, Carvomenthols, their Acetates and related Alcohols

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The mass spectra of the saturated *p*-menthane alcohols are described. Fission occurs preferentially around the carbinol carbon and adjacent to the ring substituents. The tertiary alcohols lose water less readily than the secondary alcohols. Loss of methyl is appreciable in only one case (menth-1-ol). The stereochemical isomers of menthol and carvomenthol are readily distinguished by their mass spectra. The acetates of menthol and carvomenthol behave quite differently, resembling the menthenes formed from them by loss of acetic acid in a 1,2-elimination. Many of the hypothetical fragmentations were confirmed by deuteration studies.

SINCE a number of deuterated menthones were available,¹ we were able to examine some of the corresponding menthols obtainable by lithium aluminium hydride reduction.² The mass spectrum of menthol has been reported.³ Mass-spectral studies were mostly carried out on the mixture menthol-neoisomenthol obtained by gas chromatography ⁴ of the crude reduction product over a Carbowax column, but the unlabelled isomers were separated on a Hyprose column,⁵ a second passage over Carbowax being necessary to remove eluted Hyprose.

We have considered the mass spectra in terms of the least-strained conformer of the various menthols, which, in three cases [menthol (I), neomenthol (III), and isomenthol (IV)] will have the isopropyl group and at least one other ring substituent equatorial. Neoisomenthol (II) was once considered to have the isopropyl group equatorial,⁶ but later evidence suggests that this may not be so,⁷ and indeed, only one of the four, neomenthol (III), loses water distinctly more easily than the other three. Since we show below that the other hydrogen involved is mostly the one at C-8, the implication is that this is more favourably situated for water elimination in (III) than any of the others, a supposition that is supported by examination of models of structures (I)—(IV). Table 1 lists the figures for the intensities of the fragments as percentages of the most important fragment.* Apart from the loss of water, the mass spectra of the four isomers show fairly pronounced intensity differences, five of the most important fragments

⁴ Ref. 2, p. 40 gives a list of phases used in the gas chromatography of menthol stereoisomers, see also C. Baron and B. Maume, *Bull. Soc. chim. France*, 1962, 1113.

[•] Figures to the nearest 1% are listed, those under 1% are neglected, except for those of the molecular ion, which are given to two significant figures.

¹ Part VI, B. Willhalm and A. F. Thomas, J. Chem. Soc., 1965, 6478.

^a Leading references in, *e.g.*, "Die Aetherischen Oele," E. Gildemeister and F. Hoffmann, vol. IIIb, 4th edn., Akademie-Verlag, Berlin, 1963.

⁹ E. von Sydow, Acta Chem. Scand., 1963, 17, 2504.

⁵ D. R. Moore and A. D. Kossoy, *Analyt. Chem.*, 1961, **33**, 1437.

⁶ A. R. H. Cole and P. R. Jefferies, J. Chem. Soc., 1956, 4391; A. R. H. Cole, P. R. Jefferies, and G. T. A. Müller, *ibid.*, 1959, 1222.

^{1222.} ⁷ B. J. Armitage, G. W. Kenner, and M. J. T. Robinson, *Tetrahedron*, 1964, **20**, 747.

TABLE 1

Mass spectra of menthols and deuterated menthols

		36	1 1_							
,	(T)	Ment	thois	(137)	1-[² H]	3-[² H]	5-[² H]	8-[² H]	2,2,4-[² H ₃]	
mje	(1)	(11)	(111)	(1V)	(82%) *	(98%) *	(80%)*	(70%) *	(91%) +	cis-mentil-1-or
29	17	16	18	10	20	15	13	13	11	8
30						7	4	4	10	
31	4	4	5	4	5	2	3	3	4	
32					17	5	10		3	
39 40	13	13		12	17	10 5	10	11	97	8
41	44	42	36	40	50	45	31	33	27	20
$\overline{42}$	7	6	6	7	20	16	15	17	25	2
43	33	32	30	32	41	33	29	27	31	62
45 16	3	3	3	3	3	0	2	3	11	
40 53	7	7	5	7	8	7	3	6	3	4
54	4	5	3	4	8	6	3	5	5	1
55	43	42	35	39	42	40	25	32	20	16
56 57	20 97	20	17	18	40	32	33	27	31	2
58	21	24	21	23	11	19	10	28 9	33 24	11
59	ĩ	1	ī	ĩ	$\tilde{2}$	4	2	ĩ	10	1
60						- فلسباني			4	
67 69	25	21	18	21	20 95	14	10	18	4	14
08 69	13	13 32	26	29	25 36	38	19 20	15 24	$\frac{12}{28}$	10
70	12	12	10	11	23	16	$\overline{20}$	18	33	4
71	100	100	100	100	45	15	100	100	25	100
72	5	5	5	5	100	100	10	17	100	13
73	2	1 2	$\frac{1}{2}$	23	2	3	1	1	12	1
78					-	.0 A	1		1	
79	3	4	3	4	3	3	2	2	1	2
80	8	5	5	6	6	9	4	6	2	
82	70 34	29	42 25	54 17	54 62	42	23 50	47	44	13
83	14	11	8	10	27	33	20	18	51	4
84	4	3	2	3	8	13	7	7	35	1
85	9	10	7	9	9	21	6	5	19	8
80 87	4		4	4	9 1	10	9 1	8	0 3	_
88			<u></u>						2	
91	2	2	1	1		2	-			
92						4				
93 Q4	3 4	3 · 4	2	3 3	2	16	2	23	1	
95	65	57	54	52	36	16	18	47	3	51
96	26	19	19	12	64	66	45	32	12	5
97	5	5	3	4	21	28	17	10	35	16
98	4	4		4	3 4	4		3 1	25	10
100		î		ī	ĩ	3	3	3	4	
109	10	11	8	8	7	6	5	5	2	3
110	5	5	5	4	10	10	7 9	7	4	
112	$\frac{2}{2}$	$\frac{2}{5}$	2	3	1	5 4	3 1	2	o 5	
113	ī	3	ĩ	ĭ	$\overline{2}$	$\bar{2}$	$\overline{2}$	3	2	29
114	<u> </u>						1		1	1
115	-								2	
123	28	20	17	20	15			12		11
124	-3	$\overline{2}$	2	$\tilde{2}$	28	30	18	11	_	
125				_	2	3	2	2	6	
126									30	
138	20	18	23	16	6		3	10		6
139	3	3	3	3	23	33	16	- 9		
140	_	<u> </u>			2	7	2	2	3	
141	1	1							23	9
156	0.19	0.76	0.35	0.26					4	4.8
			-							

* Isotopic purity.

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given as percentage total ionisation over m/e 27 being listed in Table 2. We shall return to these differences later. It will be immediately apparent that the customary stabilisation of the molecular ion that has been



observed in equatorially substituted compared with axially substituted cyclohexanes 1,8-10 does not hold in this series, a finding that was later made with the different carvomenthols (see below).

Table 1 also includes the figures for several of the deuterated menthols, and for menth-1-ol, which shows certain similarities with menthol in its mass spectrum.

TABLE 2 $\% \Sigma_{27}$ of certain fragments of menthol spectra

Loss of	f:	$H_0O +$	$H_{2}O +$	$H_{2}O +$	
	$H_{2}O$	ČH3	Ċ₃H,	C₄H,	C_6H_{13}
Compound m/	e: 138	123	95	81	71
(I)	$2 \cdot 6$	3.6	8.7	9.3	13.5
(ÌI)	2.7	2.8	8.1	7.4	14.5
(ÌII)	3.7	2.6	$8 \cdot 2$	6.3	15.3
(IV)	$2 \cdot 3$	3.0	7.9	$8 \cdot 2$	15.2

Location of most of the oxygen-containing fragments was effected by simultaneous introduction of menthol and deuterium oxide in the inlet system of the mass spectrometer. The only fragments where a significant intensity change occurred after this technique were the small fragments at m/e 141 and 99, about half the one at m/e 85, and about one quarter of the one at m/e 57, these proportions being in relation to an assumed displacement of almost all the main fragment at m/e 71. If we exclude simple 1,2-ketonisation, these shifts represent the only fragmentations occurring without loss of water. This conclusion is supported by the highresolution spectrum of menthol,* which indicates that the fragments at m/e 141 (trace only), 99, 86, 85, and 71 were almost entirely oxygen-containing, while m/e 57 was predominantly so. The lower proportion of some of the fragments containing oxygen found by the D₂O

* We are greatly indebted to Professor Klaus Biemann for this determination. For the "element map" method used, see ref. 11.

⁸ P. Natalis, Bull. Soc. chim. belges, 1960, 69, 519; 1964, 73, 961.

⁹ A. F. Thomas and B. Willhalm, Helv. Chim. Acta, 1964, 47, 475. Q

method suggests that some exchange between the hydroxyl hydrogen and other hydrogens must occur, a phenomenon known to happen in cyclohexanol.^{12,13} We were unable to observe metastable peaks associated with any of these transitions retaining oxygen (illustrated in Scheme 1) but in the deuterated compounds the fragments can often be located as the highest of the group; thus, the fragment at m/e 99 clearly shows the expected displacements on deuterating in the sidechain (see Figure 1 for the menthol hexadeuterated at C-9 and C-10). The fragment at m/e 85 must arise mostly by a route involving the side-chain (Figure 1, fragment at m/e 91). The main fragment at m/e 71 is clearly of the structure indicated, but sources other than the molecular ion cannot be excluded. Its formation involves the breaking of two ring bonds and one hydrogen transfer, and it is presumably favoured when the bond ruptures are required to relieve strain, as when either the hydroxyl or the methyl are axial (III) and (IV), less in menthol (I), and also in neoisomenthol (II) where, if the isopropyl is axial as we have written it, the hydrogen transfer from C-2 would be hindered.



All the remaining fragments, comprising the greater part of the ionisation, involve the loss of water. Figure 1 and the 8-deuterated compounds show that the hydrogen comes predominantly from the side-chain, about a

¹⁰ G. Ohloff, G. Uhde, A. F. Thomas, and E. sz. Kováts, Tetrahedron, 1966, 21, in the press

¹¹ K. Biemann, P. Bommer, and D. M. Desiderio, Tetrahedron Letters, 1964, 1725.

12 C. G. MacDonald, J. S. Shannon, and G. Sugowdz, Tetrahedron Letters, 1963, 807.

13 H. Budzikiewicz, Z. Pelah, and C. Djerassi, Monatsh., 1964, 95, 158.

quarter from the terminal carbon and about half from C-8, showing that menthol behaves more like an openchain alcohol¹⁴ than a cyclohexanol.¹³ A small amount of hydrogen does come from C-1 in this fission, but none comes from C-2, -3, -4, -5, or -6.* Subsequent loss of methyl occurs about 80% from the isopropyl group and 20% from C-1, as observed from Figure 1 and by comparing the distribution of the fragments at m/e 124–128



in Figure 2. The fragments at m/e 109 and 110 correspond to loss of water and a two-carbon fragment, but the similarity of the region in the menthols deuterated at C-1, -3, -5 or -8 implies that two paths leading either to loss of C-5 and C-6 or of C-2 and C-3 are available, though the former appears to be predominant.

Figure 1 shows that the fragments at m/e 95 and 96 have mostly lost the side-chain. Since these fragments arise from the radical-ion at m/e 138 (Scheme 2, m^* 65.4) and we know that at least 75% of these fragments have already lost a proton from the side-chain, it is clear that

the fragment at m/e 95 will mostly involve a hydrogen transfer from the ring, while that at m/e 96 will not. Significantly, the 2,2,4-[2H₃] compound shows an important fragment at m/e 97, implying that much of this



hydrogen comes from C-2 or C-4. This particular hydrogen transfer renders exceedingly difficult the explanation of all lower fragments except those retaining oxygen, since it must occur at the m/e 138 stage, and all the fragments without oxygen ultimately derive from this point.

The fragments at m/e 81 and 82 stem from the hydrocarbon radical-ions at m/e 138 (metastable peaks at 47.5 and 48.7) and mass 81 also to some extent from the ions at m/e 123 and 96. The side-chain has been lost in nearly all the ions at m/e 81, but nearly half is retained in the ion at m/e 82 (Figure 1). This C₆ fragment is relatively rare in cyclic monoterpene hydrocarbons⁹ (though common in C₁₀ open-chain paraffins ¹⁶), menth-8-ene,¹⁷ with a weak C-3,4 bond, being one of the few menthenes to have a notable fragment at m/e 81.⁹ Menthol clearly forms this fragment from C-1, -2, -3, -5, -6, and -7, but the hydrogen exchange is complex. For example, from the spectra of the deuterated compounds it is seen that deuterium is lost from C-1, -2 or -4

Cf., e.g., A. Herlau, Brennstoff-Chem., 1964, 45, 244, 261.
A. F. Thomas and M. Stoll, Helv. Chim. Acta, 1964, 47, 413.

^{*} The percentage of deuterium in the deuterated menthols is calculated by assuming no isotope is lost during the LiAlH₄ reduction of the menthones, the isotopic distribution in which is accurately known.¹ For example, Figure 2 shows the same isotope distribution at m/e 139—143 as the menthone from which it is derived. The fact that only about 80% of the hydrogen in the water loss is accounted for is ascribed to isotopic variation.¹⁵

¹⁴ W. Benz and K. Biemann, J. Amer. Chem. Soc., 1964, 86,

^{2375;} S. Meyerson and L. C. Leitch, *ibid.*, p. 2555. ¹⁵ Cf. F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957, p. 204; E. Lund, H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 941.

and even to some extent from C-3, while a certain amount of deuterium at C-8 is retained. Deuterium is lost preferentially from C-1, in fact, and Scheme 2 shows some of the possibilities for the formation of this ion, and for the ions at m/e 82 and 69 retaining the side-chain. In view of the partial retention of the hydrogen at C-8, it seems likely that the m/e 81 fragment is formed more easily from the ion at m/e 138 that has lost hydrogen from the terminal atom of the side-chain. If this hypothesis is true, it would account for the fact that the fragment is most easily formed (Table 2) in the isomers (I) and (IV) where the hydroxyl is closest to the end of the chain when the molecule is in its least strained conformation.

The menthols represent an extreme in the complexity of the various available pathways, so it becomes progressively more difficult to unravel these as the fragments become lighter. The C_4 fragment at m/e 55, for instance, arises partly from the side-chain (the C-8 deuterated menthol has the ion partly shifted to m/e 56), probably a little from C-7, -1, -6, and -5 as in menthone,¹ but also to a considerable extent from C-7, -1, -2, and -3, since nearly half shifts to m/e 56 in the C-3 deuterated menthol.

Turning now to the carvomenthols, we see from Table 3 that their mass spectra differ considerably from the menthols, as was the case with the corresponding ketones.¹ They are somewhat more similar to one another than the menthols, as one might expect if the hydroxyl group now behaved independently of the side-chain, but there are still characteristic differences that enable them to be identified unambiguously. The five main heavy fragments are listed as percentage total ionisation in Table 4, and, in terms of conformations (V)-(VIII),^{17,18} it can be seen that loss of water again occurs most easily from the axially placed hydroxyl (VII), just as the isopropyl group is most easily lost when it is axial (VI). The most unusual feature of the group is again, however, the fact that it is not the molecular ion of the allequatorial compound (V) that is the most stable.8-10

Scheme 3, proposed for the main fragments, shows that two routes are used to give the base peak at m/e 95. We suppose the small loss of methyl occurring from the fragment at m/e 138 to involve C-1, since it is slightly favoured when the latter is axial (Table 4), and leads to an ion where the charge is stabilised by being distributed over three carbon toms, and is furthermore subsequently cleaved to a fragment at m/e 67 by losing a C₄ radical. The fragment at m/e 95 also forms a fragment at m/e67 (possibly preceded by a double hydrogen transfer), but this is not the same as the one just mentioned.

The ion at m/e 113 gives rise to the fragment at m/e 57. Since this is displaced to both m/e 58 and 59 in 1,3,3-trideuterated carvomenthol, it probably consists of the two ions formed, as shown in Scheme 3, by fission on either side of the hydroxyl group. The

¹⁸ S. H. Schroeter and E. L. Eliel, J. Org. Chem., 1965, **30**, 1, includes an excellent review of earlier literature on the preparation, conformations, and spectral data (not including mass spectra) of the carvomenthols.

TABLE 3

Mass spectra of carvomenthols and deuterated carvomenthols Deuterated carvomenthols

					Doubor	133-	0111011010
		Carvor	nentho	ls	2-[2H]	[² H ₃]	cis-Menth-
m e	(V)	(VI)	(VII)	(VIII)	(98%)*	(82%) *	4-ol
27	14	15	15	16	13	13	97
29 30		17	11	<u>12</u>	6	13	
31	4	4	3	3	1	5	
32 39	11	12	11	12	3 10	1 9	
4 0	2	$\tilde{2}$	2	$\frac{1}{2}$	3	ő	
41	38	38	32	41	33	28	19
42 43	46	45	6 43	46	12 38	22 49	3 65
$\overline{45}$	9	10	8	9	6	17	
46 52	 6		 		5	7	
53 54	3	$\frac{1}{2}$	2	2	4	3 4	
55	48	47	44	51	36	22	15
56 57	9 55	9 57	9 55	10 56	21 13	32 35	$\frac{2}{7}$
58	8	8	7	8	46	55	
59 60	1	1	1	1	8	23	
67	14	14	14	14	7	3	10
68	10	9	9	11	11	9	2
69 70	27	27	26	28	28	27 91	9
71	14	13	13	14	8	24	* 6
72	1	2	1	1	10	14	
73	-1	1		2	$\frac{z}{1}$	4	
79	2	3	$\overline{2}$	$\overline{2}$	1	—	$\hat{2}$
80 81	4 91	3 10	2 91	3 91	3 10		2
82	23	13	14	20	26	17	2
83	24	21	20	23	17	21	3
84 85	0 1	5 1	5	4	19	19 24	
86					ĩ	4	4
93 04	1 5	2 5	2	1			1
95	100	100	100	100	17	3	78
96	17	15	15	17	100	14	7
97 98	3	3	2	3	$\frac{16}{2}$	47 100	2
99	3	4	4	2	ī	14	27
100	1	2	2	1	6	5	1
109	-8	6	6	6	3		
110	5	4	4	4	8	3	
111	1	4	1	12	2	92	4
113	45	$\overline{56}$	53	36	3	3	100
114	4	4	4	2	50	4	8
115						12 55	
117						4	
123	12	10	11	13	12		3
125			·		ĩ	3	_
126	10			17		13	
139	2	$\frac{20}{2}$	$\frac{27}{2}$	1	24^{1}		Z
140					2	6	
141 142						30 3	
156	1.8	$5 \cdot 2$	$2 \cdot 8$	1.6			0.65
157					2		
109			* I	sotopic ·	purity.	ა	

 C_4 fragment at m/e 55 arises to the extent of about 30% from C-7, C-1, C-2, and C-3, being displaced by this extent to m/e 56, but in view of the likelihood of the ions at m/e 138 and 95 being symmetric, fragments of

these ions (such as mass 55 may well be) will come equally from both sides of the ring.

The mass spectra of *cis*-menth-1-ol (IX) and *cis*menth-4-ol (X) have been included for comparison, in Tables 1 and 3, respectively. It is well known ¹⁹ that tertiary alcohols have a greater tendency to form cleavage in menth-4-ol leading to a corresponding fragment at m/e 99.

Finally, we have examined the mass spectra of menthyl and carvomenthyl acetates (Table 5). Owing to the powerful tendency of secondary acetates to lose acetic acid by 1,2-elimination,²⁰ the mass spectra of these



Scheme 3

oxonium ions than secondary; thus, menth-1-ol is the only alcohol mentioned here with a significant fragment at m/e 141 $(M - 15)^+$, and in menth-4-ol, the increase in ease of loss of isopropyl results in the fragment at m/e 113 being the most important, loss of water being slight

TABLE 4

 $\% \Sigma_{27}$ of certain fragments of carvomenthol spectra

			$H_{0}O +$		$C_{H_7} +$
Loss of:		H_2O	СН3	$C_{3}H_{7}$	H_2O
Compound m/e :	156	138	123	113	95
(V)	0.2	2.9	1.8	6.6	15
(ŇI)	0.7	$3 \cdot 0$	1.5	8.3	15
(VII)	0.4	4.1	1.7	8.0	15
(VIII)	0.12	$2 \cdot 6$	$2 \cdot 0$	5.5	15

in both cases. The menthol-type cleavage (Scheme 1) between carbons C-3,4 and C-6,1 with hydrogen transfer is again possible in menth-1-ol (Scheme 4), a similar $(1 + 1)^{-1}$

* The figures we quote for the menthenes in this Paper should replace those of ref. 16 which contain two misprints.

 K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill, New York, 1962, p. 92.
Ref. 14, and ref. 19, p. 110.



compounds resemble those of the corresponding menthenes,⁹ which are included in Table 5,* but with an addi-

tional strong peak at m/e 43. In the case of carvo-

menthyl acetate, the mass spectrum is nearest to menth-2-ene (but not menth-1-ene, which contains an additional "retro-Diels" fragment at m/e 68⁹), and $1,3,3[^{2}H_{3}]$ -

TABLE 5

Mass spectra of menthyl acetate and related compounds. Menthyl acetate is given with fragments relative to m/e95 = 100, all other substances (as usual) as % most important fragment. In this Table, for isotopic content see Experimental section for menthenes; acetates are the same as the corresponding alcohols

		Terpene *													
m e	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(Ĥ)	(I)	(J)	(K)	(L)	(M)	(N)	(O)
27	11	10	13	9	8	4	7	6	10	7	9	5	6	12	7
29	11	6	11	5	5	6	6	3	6	8	8	4	4	8	6
30							4	2	3	2	3	3	2	3	3
39		11	18	10	- 9	4	4	5	9	6	7	3	5	11	6
40		î	3	2	ĭ		3	· 4	ő	2	3	2	4	7	2
41	30	23	46	22	13	16	15	10	18	21	23	13	12	24	21
42	3	1	4	2	1	_3	14	7	11	10	10	10	8	13	8
43	106	11	10	6	6	71	100	7	12	100	100	100	9	13	95
53	7	-9	12	-9		3	1	3	-5	3	23	3 8	3		3
54	3	3	6	ĭ	2	ĭ	2	4	6	4	3	12	4	8	2
55	28	20	39	20	17	17	10	6	14	19	21	10	8	18	17
56	5	1	5	1	1	2	14	9	13	11	14	7	9	13	10
57	12	2	5	1	1	7	13	5	8	10	7	3	5	10	5
59							2			*	1				2
67	19	6	55	36	26	8	$\overline{2}$	4	9	13	$\tilde{9}$	2	5	11	7
68	10	11	14	47	11	10	7	15	17	11	14	10	16	31	11
69 70	19	9	22	14	6	14	18	18	24	14	20	17	18	57	30
70	3 16		3	3		32	8	3 1	10	18	4	12	8	08 14	3
72						$\overline{2}$	18	_	_	4	19	3		2	4
73		—					2				1	4			
77	2	6	6	6	6	1		1	2	1	1			2	1
70		10	10			3		3 2	4 5		1 2		3 3	4 5	2
80	6	2	4	3	3	$\frac{3}{2}$	i	4	5	3 4	$\tilde{5}$	2	5	6	4
81	61	66	74	27	32	20	7	9	21	39	28	6	11	13	11
82	28	17	27	15	11	14	25	13	34	31	45	16	18	24	25
83 84	13	3	0	4	3	11	33	15	51 10	16	19	17	15	20	14
85	3						23		2	2	2	8		4	1
86	_				-		5			$\overline{3}$	3	3			
91		4	3	4	3									2	
93	1	4 12	4 7	5	4	1		1	2	1 77			2 2		3
95	100	100	100	100	100	100	3	$\overline{5}$	7	73	27^{-1}	6	8	12	27
96	24	22	17	17	17	18	17	16	23	40	88	24	21	28	100
97	4	2	3	1	1	3	57	100	100	14	21	79	100	100	18
98							45	13	23	2	3	33	14	39	3
109	9	4	7	4	3	5	ĩ		$\frac{2}{2}$	4	4		_	ī	3
110	5		1	1	ĩ	2	3	1	$\overline{2}$	$\overline{5}$	8	3	1	2	6
111	2						7	1	3	4	3	6	1	3	2
112						11	3		1		1	2		1	
113							2				4				12
115							ī			_		3	_		1
116							4					10		<u> </u>	
123	34 1	23	24	14	13	15	_	_		14	5 90	 Q		1 2	2 17
125		<u>د</u>					11	.9	25^{2}	3	25	13	10	14	2
126		_					$\overline{22}$		3	_		4	ì	4	
137	1					1	<u></u>								
138	48 5	27	20	28	18	42				81 22	4 53	5			3 42
140	_	4	4	J	4		32	14	$2\hat{8}$	33 4	7	37	16	29^{-1}	5
141	1						16	ĩ	4			5	2	11	<u></u>
142											2			1	
155 156						1									
158						_				_		1			

* (A), Menthyl acetate; (B) menth-3-ene; (C), carane; (D), menth-1-ene; (E), menth-2-ene; (F), carvomenthyl acetate; (G) $2,2,4-[^{2}H_{3}]$ menthyl acetate; (H) $2,4-[^{2}H_{2}]$ menth-2-ene; (I), $2,2-[^{2}H_{2}]$ menth-2-ene; (J) $8-[^{2}H]$ menthyl acetate; (K), $3-[^{2}H]$ menthyl acetate; (L), $1,3,3-[^{2}H_{3}]$ carvomenthyl acetate; (M), $1,3-[^{2}H_{3}]$ menth-2-ene; (N), $3,3-[^{2}H_{2}]$ menth-1-ene; (O) $2-[^{2}H]$ carvomenthyl acetate.

carvomenthyl acetate resembles the mass spectrum of 1,3[²H₂]menth-2-ene (but not 3,3[²H₂]menth-1-ene.)* Menthyl acetate, on the other hand, is much less specific, and only about two thirds of the acetic acid is lost by 1,2-elimination, the remainder being lost with a hydrogen from the side-chain, mostly from C-8. The 2,2,4-trideuterated acetate does not resemble 2,2-[2H2]menth-3-ene very closely, and a further point of interest is that 83% of the fragment at m/e 123 (of the undeuterated acetate) is displaced to m/e 126 in the deuterated acetate. It is clear that methyl is lost more easily from a $C_{10}H_{18}^+$ ion not derived from menth-3-ene (which would contain only two deuteriums), and since we know from the terminally hexadeuterated menthol acetate (Figure 3) that



this methyl is over 80% lost from the isopropyl group (like the corresponding fragment in menthol), a possible

* We found that pyrolysis of the trideuterated carvomenthyl acetate (mixture of isomers) led to menth-2-ene of good isotopic purity, $[{}^{2}H_{2}]$, but that the menth-1-ene in the mixture contained a small amount of $[{}^{2}H_{3}]$ product (~20%), implying a small loss of acetic acid other than by 1,2-elimination, followed by rearrangement

It is of interest to note that we found that palladised chart coal (10%)-catalysed reduction of car-3-ene gave a mixture of carane and 1,1,4-trimethylcycloheptane (see Experimental section). It has been reported ²¹ that a platinum catalyst gives only carane. Similar results have recently been obtained elsewhere, but were not available until this manuscript was completed.22

explanation is via an ion derived from carane, as shown in Scheme 5. The carane † mass spectrum is included in Table 5.

EXPERIMENTAL

Details of the mass-spectral determinations were given in part VI,¹ as were the preparations of the various deuterated menthones and carvomenthones. The corresponding menthols and carvomenthols were prepared by lithium aluminium hydride reduction in dry ether 2 and purified by gas chromatography using the same apparatus as described in Part VI¹ and Carbowax or Hyprose columns 4,5 (see beginning of theoretical part). All four isomeric menthols were isolated from the reduction mixture, but in the carvomenthol series, isocarvomenthol (VI) had to be made by catalytic reduction of (-)-trans-carveol.¹⁸ Menth-l-ol and menth-4-ol were isolated from the products of the catalytic reduction of ascaridole (ref. 9, footnote 3), and were accordingly ascribed the cis-structure. Acetates were made with acetic anhydride in dry pyridine, then purified by pentane extraction followed by gas chromatography.

N.m.r. and i.r. spectra were determined as previously described.1

Pyrolysis of 2,2,4-[²H₂]Menthyl Acetate (Isomer Mixture).²⁸ -This was effected at 400° on glass helices in a current of nitrogen, by introducing a benzene solution of the acetates (100 mg. in 3 ml. solvent) dropwise, washing the pyrolysis column afterwards with benzene (2 ml.), drying the combined organic phase over potassium carbonate, and allowing most of the benzene to evaporate at room temperature. The menthenes were finally purified by gas chromatography. This gave 2,4-[2H2]menth-2-ene (52% of mixture), isotopic purity 92%; n.m.r. showed only one vinyl hydrogen signal, at 5.47 p.p.m.; and 2,2-[2H3]menth-3-ene (47% of mixture), isotopic purity 90%.

Pyrolysis of 1,3,3-[²H₃]Carvomenthyl Acetate (Isomer Mixture).-This was effected in the same way, yielding 3,3-[²H₂]menth-1-ene (47%), isotopic purity 19.5% [²H₃], 71% [²H₂], 9.5% [²H₁]; and 1,3-[²H₂]menth-2-ene (53%), isotopic purity 91%; n.m.r. showed the presence of only one vinyl hydrogen, at 5.43 p.p.m.

Reduction of Car-3-ene.-The carene used was distilled from Indian turpentine (from Pinus longifolia) 24 and was gas chromatographically pure, b. p. $78^{\circ}/30$ mm., $n_{\rm D}^{20}$ 1.4720, d_4^{20} 0.8626, α_D^{20} +17.5. This material (50 g.) in ethanol (500 ml.) was hydrogenated in the presence of (10%) palladium-charcoal (0.5 g.). After 24 hr., 9.0 l. hydrogen were absorbed (at 0° and 760 mm., calc. for 1 mol., 8.25 1.). Working up by pouring into water and extracting with pentane gave 44.2 g. (88%) of a hydrocarbon, b. p. $46-50^{\circ}/$ 12 mm., that consisted, by gas-chromatographic analysis (100° on Carbowax), mainly of two peaks (cf. ref. 26).

Peak 1 (42%), identified as 1,1,4-trimethylcycloheptane by means of the spectra: i.r.²⁵ v_{max} (liquid) 810, 950,

t We thank M. Winter and P. Enggist for the preparation of a sample of carvomenthyl acetate.

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1178, 1361, 1373, 1382, 1458, ca. 2900 cm.⁻¹. N.m.r., CH₃-C- 0.87 p.p.m. (singlet), CH₃-C(H)- 0.87 p.p.m. (doublet, *J ca.* 5 c./sec.). There are 9 protons in this region, but the proximity of the signals does not allow a clear attribution); mass spectrum: molecular ion 6.8% base peak, m/e 55 (100%), 69 (99%), 70 and 41 (51%), 56 (44%), 97 (41%), 125 (37%), 43 (42%), 84 (41%), 83 and 56 (27%).

Peak 2 (46.5%), n_D^{20} 1.4540; identified as carane; i.r., identical with that given in ref. 21; n.m.r. $CH_3 - C = 0.94$ and 0.97 p.p.m. (singlets), $CH_3 - C(H) = 0.81$ p.p.m. (doublet, J = 5 c.se/c.); mass spectrum, see theoretical part.

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