

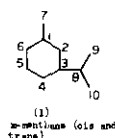
# An appraisal of the chemistry of m-menthane derivatives—virgin substrates for fragrance and flavor technology

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Natural members of the m-menthane family are scarce, but science is overcoming this scarcity by the ingenious tailoring of other monoterpenes to furnish a wide range of compounds belonging to this group. The p-menthane derivatives have been exhaustively exploited; their counterparts in the m-menthane series can be regarded as potential building blocks for terpene technology. There have been significant contributions to this rapidly expanding area.

## m-Menthadienes

Jettisoning of four atoms of hydrogen from m-menthane (1) theoretically generates not less than 25 m-menthadienes. Systematic naming of these compounds is based on m-menthane, which is numbered as in (1). Confusing generic names have been



used in some cases and so we have followed the recent recommendations of Bardyshev and Zen'ko.<sup>1</sup>

### Methods of production

*From isoprene.* For the construction of the m-menthane carbon framework from two isoprene units, tail-to-tail amalgamation is required as shown in (27)-(28). Such a process yields ( $\pm$ )-m-mentha-6,8-diene (2) (diprene).<sup>2-7</sup> Typical physical constants for diprene are first,<sup>2</sup> b.p. 68.5-69°(16 mm), 171.5-173°(752 mm),  $d_4^{20}$  0.8476,  $n_D^{20}$  1.4695; and, second,<sup>3</sup> b.p. 172-174.5°(752 mm),  $d_4^{19}$  0.8454,  $n_D^{17}$  1.4754.

However, these constants are not genuine since the samples are admixed with dipentene.<sup>5-7</sup> In contrast to dipentene (29), diprene on agitation with silver nitrate forms an adduct which is decomposed by water to give the pure parent hydrocarbon:  $d_4^{20}$  0.8451 and  $n_D^{20}$  1.4734.<sup>7,8</sup> More recently diprene has been identified as ( $\pm$ )-m-mentha-6,8-diene (2) (vide infra).<sup>55,56</sup> It is worthwhile to examine the dimerization of isoprene with a view to optimising the yield of diprene. This would open up an economical route to a member of the m-menthadiene family.

*By isomerization of carenes.* For entry into m-menthadienes, the most outstanding raw material is (+)-car-3-ene (30) and this is followed by (+)-car-2-ene (31). The 3-isomer is a constituent of numerous gum turpentine, <sup>9,10,13(a)</sup> particularly of *Pinus longifolia* (Roxb)<sup>11</sup> and also of sulphate turpentine.<sup>12(a),13(b)</sup> The (+)-2-isomer is found in a limited number of essential oils.<sup>14</sup> Synthetic (+)-car-2-ene is available; the most popular method to secure this hydrocarbon is by isomerization of (+)-car-3-ene.<sup>13-23,28</sup>

At first glance one would expect that the rearrangement of (+)-car-3-ene or (+)-car-2-ene with fission of the C<sub>6</sub>-C<sub>8</sub> bond would generate m-menthadienes. However, such a unilateral opening of the 3-numbered system seems impossible to realize experimentally.

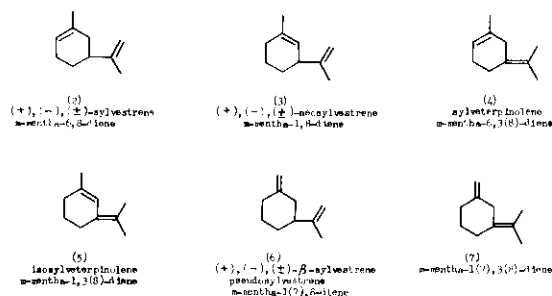
(+)-Car-3-ene is extraordinarily stable with respect to temperature.<sup>24-27(a)</sup> Thermal isomerization affords feeble amounts of (2),<sup>27(a)</sup> and (11).<sup>27(b)(c)</sup> This resistance to pyrolytic cleavage to give m-dienes is to be attributed to the absence in the initial free diradical (32) of a resonance-stabilized allylic system.<sup>25,26</sup> In striking contrast to this, (+)-car-2-ene collapses strictly sterically at elevated temperatures to give (+)-trans-isolimonene (33), with no trace of m-isomers.<sup>12,26,29</sup>

The conversion of (+)-car-3-ene to the conjugated

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dienes, *m*-mentha-1,3-diene (14), *m*-mentha-2,6-diene (22), and *m*-mentha-4,6-diene (20) with Pd-C,<sup>30</sup> MgO and CaO,<sup>19</sup> and diatomite<sup>31</sup> catalyst respectively is only of academic interest. H<sup>+</sup> induced isomerizations of (+)-car-3-ene,<sup>12(a),32-34</sup> and (+)-car-2-ene<sup>31,35</sup> do not provide *m*-menthadienes in quantity for proton attack generates complex mixtures which include, in addition to *m*-menthadienes, the sister *p*-isomers, and of the *m*-series only *m*-mentha-6,8-diene (2) and *m*-mentha-6,3(8)-diene (4) have been properly characterized. Furthermore, these hydrocarbons bluntly refuse to get resolved into pure components by precise fractionation. Out of the isomerizates, only *m*-mentha-6,8-diene is immediately extractable chemically by adduction with silver nitrate,<sup>36,73</sup> but this is a very expensive operation.

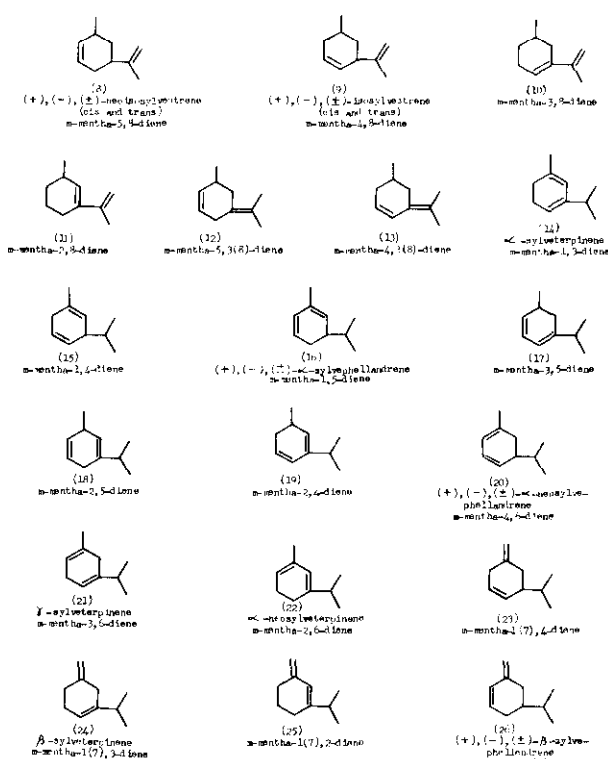
By dehydrohalogenation of *sylvestrene dihydrohalides*. We are therefore left with the classical route, discovered by Atterberg,<sup>37</sup> see also<sup>38</sup> and brilliantly illuminated by Simonsen and coworkers<sup>39-42</sup>, see also 2(c) 44-46 to the treasure caves of *m*-menthadienes. (+)-Car-3-ene adds the elements of hydrogen chloride to give a mixture of (+)-*sylvestrene dihydrochloride* (34) and (±)-dipentene dihydrochloride (36) from which the former can be isolated by fractional crystallization.<sup>39,42,50,51,60</sup> Analogous behaviour is displayed by the sparingly available (+)-car-2-ene.<sup>2(c),40,41</sup> Following the above discovery by the Simonsen school, (+)-car-3-ene has been firmly established as the most favoured source for *sylvestrene dihydrochloride*. Saturation of (+)-*sylve-α-terpineol m-menth-6-en-8-ol* (37) present in *Pinus sylvestris* turpentine with hydrogen chloride also affords (+)-*sylvestrene dihydrochloride* and it is claimed that its isolation is easier than from the post-reaction mixture resulting by the hydrochlorination of (+)-car-3-ene.<sup>53</sup> It may be added that (-)- and (±)-*sylvestrene dihydrochlorides* are also described in literature.<sup>54,63-65</sup> To sum up, (+)-carene ranks as the most convenient raw material for the preparation of (+)-*sylvestrene dihydrochloride* which is the precursor of *m*-menthadienes.



Depletion of the elements of hydrogen chloride from (+)-*sylvestrene dihydrochloride* theoretically yields 6 *m*-menthadienes (2-7). Reagents employed for this purpose include aniline,<sup>37(a),53,62,67</sup> diethylamine,<sup>57</sup> CH<sub>3</sub>COOH/CH<sub>3</sub>COONa,<sup>38(b),50,51,58</sup> NaCR (R = Me, Et, iso-pr, Bu, isoamyl),<sup>58-60</sup> and AgNO<sub>3</sub>/DMSO.<sup>61</sup> For example, with the exception of (7), all

the other expected *m*-menthadienes are released by cleavage of hydrogen chloride with CH<sub>3</sub>COOH/CH<sub>3</sub>COONa.<sup>60</sup> The *m*-menthadienes (8), (13), and (18) have also been detected<sup>58,60</sup> but these can only stem by isomerization of the initially formed *m*-menthadienes.

Like the optically active counterparts, six *m*-menthadienes (2-7) can originate from (±)-*sylvestrene dihydrochloride* (34) also. The investigations in this area with potassium/sodium acetate-acetic acid were only of a qualitative nature.<sup>2(c),3</sup> With aniline, the hydrocarbon mixture obtained contained (±)-*m*-mentha-6,8-diene (2), *m*-mentha-6,3(8)-diene (4) and *m*-mentha-1,3(8)-diene (5).<sup>55,56,78</sup> Most probably (±)-*m*-mentha-6,8-diene and diprene are one and the same hydrocarbon.<sup>78</sup>



For the reorganization of (+)-car-3-ene to *m*-compounds, there are references to the use of hydrogen bromide also.<sup>66,67</sup> Though not in appreciable quality, (+)-*sylvestrene dihydrobromide* (35) is obtained by the passage of hydrogen bromide into (+)-car-3-ene in acetic acid and this on warming with aniline gives *m*-menthadienes.<sup>66,67</sup>

We have projected the general methods available for the preparation of *m*-menthadienes. Specific methods—and also less known ones—will be taken up later.

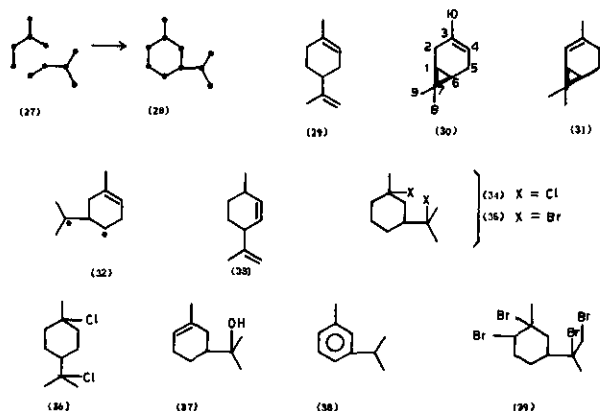
#### Chemistry of *m*-menthadienes

Before we consider the reactions of individual *m*-menthadienes, it may not be out of place to stress the fact that irrespective of the composition of the *m*-menthadienes that are obtained from (+)-*sylvestrene dihydrohalides*, the total dehydrohaloge-

nate is convertible to *m*-cymene (38), e.g., over Ni-Al<sub>2</sub>O<sub>3</sub>,<sup>68</sup>  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>,<sup>69</sup> or Pd-C.<sup>84</sup> Pure *m*-menthadienes are also amenable to such a transformation. Here we have a clean modification of (+)-car-3-ene and (+)-car-2-ene through (+)-sylvestrene dihydrohalides to *m*-cymene, free of its isomers. Availability of this aromatic in quantity is bound to stimulate interest in its exploitation.

Of the *m*-menthadienes we shall confine our discussion to *m*-mentha-6,8-diene (2)(sylvestrene), *m*-mentha-1,3(8)-diene (5)\* (isosylvesterpinolene), and *m*-mentha-6,3(8)-diene (4)\* (sylveterpinolene) since in the development of *m*-menthane chemistry these hydrocarbons have played a notable role.

*m*-Mentha-6,8-diene. Evidence available up to 1953 established that (+)-sylvestrene is not a naturally occurring hydrocarbon but rather an artifact originating from the carenes (30 and 31) and is an inseparable mixture of the hydrocarbons (2) and (3). The prophecy of Bardyshev<sup>47</sup> that (+)-sylvestrene is probably the hydrocarbon (2) gained confirmation from the PMR analysis of (+)-sylvestrene tetrabromide (39) and from the debromination of the latter to the parent hydrocarbon.<sup>36,49,73</sup> One is, however, puzzled by the recent announcement that sylvestrene is present to the extent of 20% in the  $\alpha$ -pinene-free residue of turpentine from *Pinus sylvestris* resin.<sup>72</sup> If sylvestrene really exists as an original constituent of the oil, then it demolishes the conclusion that it is not a plant product and demands revision of its genetic relationship to other terpenes.



From the dehydrohalogenate of (+)-sylvestrene dihydrochloride (34), (+)-sylvestrene, which constitutes the bulk, can be isolated in a fair degree of purity by precise fractionation.<sup>36,47,53</sup> Nevertheless, if perfectly homogeneous hydrocarbon is required, it is retrieved from the mixed *m*-menthadienes through costly aduction with silver nitrate.<sup>36,73</sup> However, the most outstanding method is the debromination of (+)-sylvestrene tetrabromide (39) with zinc dust in ethanol-ether medium; the required tetrabromide is prepared by bromination of crude sylvestrene.<sup>36</sup>

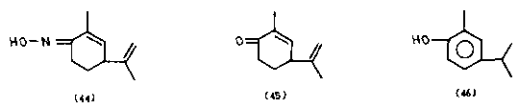
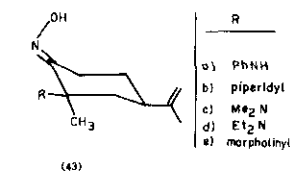
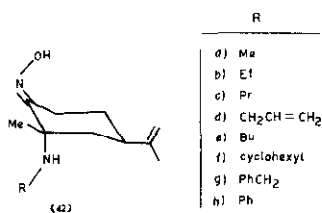
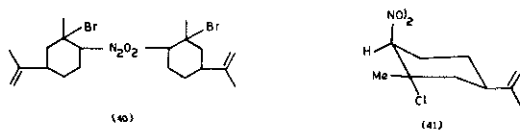
On the other hand, for ( $\pm$ )-sylvestrene, the starting

\*Previously (5) and (4) were respectively known by the generic names sylveterpinolene and isosylvesterpinolene.<sup>62,70</sup>

point is ( $\pm$ )-sylvestrene dihydrochloride (34) formed by hydrochlorinating either (4) or (5).<sup>62</sup> Dehydrochlorination of ( $\pm$ )-(34) gives optically inactive m-menthadienes. From the latter, ( $\pm$ )-sylvestrene is obtained by a process parallel to that applied for ( $\pm$ )-sylvestrene.<sup>55,56</sup>

The physical contents reported for pure (+)-sylvestrene and ( $\pm$ )-sylvestrene are respectively: (1)<sup>56</sup> b.p. 173-174° (742 mm),  $n_D^{20}$  1.4743,  $d_4^{24}$  0.8422,  $(\alpha)_D^{20} + 118.8^\circ$  (c 2.0, CHCl<sub>3</sub>); and (2)<sup>56</sup> b.p. 170-171° (736 mm),  $n_D^{20}$  1.4734,  $d_4^{22}$  0.8334,  $(\alpha)_D^{20} + 0^\circ$  (c 2.0, CHCl<sub>3</sub>).

Worthy of mention of the derivatives of (+)- and ( $\pm$ )-sylvestrene useful for characterization are the tetrabromides (39), (+)-, m.p. 137-138°<sup>70</sup> and ( $\pm$ )-, m.p. 123.5°,<sup>56</sup> the nitrosobromides (40) (+)-, m.p. 104-105°<sup>56</sup> and ( $\pm$ )-, m.p. 124° (dec.)<sup>56</sup> and the nitrosochlorides (41), (+)-, m.p. 110-111°<sup>70</sup> and ( $\pm$ )-, m.p. 125° (dec.)<sup>56</sup>



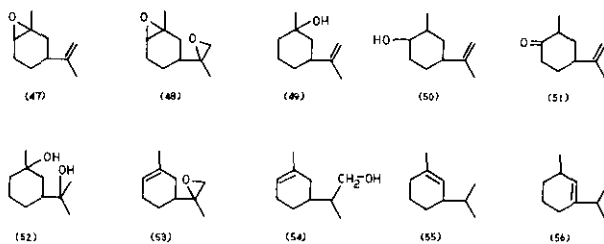
One interesting field in which considerable effort is presently being expended is the preparation of amino oximes of the types (42) and (43) through the intermediacy of (+)- and ( $\pm$ )-sylvestrene nitrosochlorides (41).<sup>76,77</sup> Whether these compounds have novel pharmacological activity deserves scrutiny.

Again, sylvestrene nitrosochloride (41) has been transformed through its oxime (44) to the interesting ketone, isomeric with carvone viz. neosylvestrenone-6 (45) [m-mentha-1,8-dien-6-one, originally called sylvecarvone]<sup>77,79-81</sup> which may have perfumery and flavour properties. H<sup>+</sup> catalysed aromatization of the ketone affords the rare 2-methyl-4-isopropylphenol (46).<sup>77</sup>

Exoxidation is a powerful tool for the modification of (+)-sylvestrene.<sup>53,82</sup>

With peracetic acid, the hydrocarbon yields essentially 1,6-epoxy-m-menth-8-ene (47) accompanied by a small amount of diepoxide (48).<sup>53</sup>

When reduced with LiAlH<sub>4</sub>, (47) affords m-menth-8-en-1-ol [sylve- $\beta$ -terpineol] (49) and m-menth-8-en-6-ol (50) in 2:1 ratio.<sup>82</sup> Splitting of this mixture through either fractionation or derivatization seems to be not feasible. On the other hand, oxidation of the reduction products with Beckmann's chromic acid mixture leaves the alcohol (49) intact but converts the sister member to sylvedihydrocarvone [m-menth-8-en-2-one] (51), semicarbazone, m.p. 192°.<sup>82</sup>



Sylve- $\beta$ -terpineol, m.p. 37°,  $(\alpha)_D^{20} + 10.1^\circ$  (c 4.5, C<sub>2</sub>H<sub>5</sub>OH) affords phenylurethane, m.p. 110° (from CH<sub>3</sub>OH), m-menthan-1-ol, m.p. 35°,  $(\alpha)_D^{20} + 14.5^\circ$  (c 4.0, C<sub>2</sub>H<sub>5</sub>OH) on hydrogenation in presence of Raney nickel, (+)-sylvestrene dihydrochloride (34) on shaking with conc. HCl and trans-sylveterpin [m-menthane-1,8-diol; sylve-1,8-terpin] (52) on hydration with 10% H<sub>2</sub>SO<sub>4</sub> and displays tendency to dehydration to m-mentha-6,8-diene (2) and m-mentha-1,8-diene (3).<sup>82</sup>

It is to be noted, however, that the formation of 8,9-epoxy-m-menth-6-ene (53) cannot be excluded in this reaction and therefore the homogeneity of the "sylvestrene oxide" is questionable. As a matter of fact, in a test run of (+)-sylvestrene (1 mole) with m-chloro-perbenzoic acid (1 mole) in CH<sub>2</sub>Cl<sub>2</sub> solution, an epoxide mixture is obtained in which the monoepoxide—both (47) and (53) plus stereoisomers—predominated; some diepoxide appears to be present.<sup>83</sup>

Another mode of reorganization of (+)-sylvestrene is through hydroboration. Thus, the reaction between di-isosanyl borane and (+)-sylvestrene is selective in attacking C = CH<sub>2</sub> group to give after oxidation and work up as the main product m-menth-6-en-9-yl carbinol (54), presumably as a mixture of stereoisomers.<sup>83</sup> This area invites further study.

A study has been reported on the hydrogen transfer in sylvestrene (2), apparently formulated as m-mentha-1,8-diene (3), by heating with Pd-C (20% Pd) (5%) catalyst at 135° for 2.5 hr.<sup>87</sup> The intermediate postulated is m-mentha-1,3(8)-diene (5) which then adds hydrogen to give m-menth-1-ene (55), m-menth-2-ene (56), m-menth-3-ene (57), and m-menth-6-ene (58). Exhaustive disproportionation by heating with 5% catalyst for 10 hr gives mainly m-cymene (38) and m-menthane (cis and trans) (1).<sup>87</sup>

By reacting a genuine sample of (+)-sylvestrene (2) with Pd-C (10% Pd) (~ 10%) catalyst at 130  $\pm$  2° for 11 hr, the disproportionation essentially follows the equation: 3C<sub>10</sub>H<sub>16</sub> (sylvestrene)  $\rightarrow$  2C<sub>10</sub>H<sub>14</sub> (m-cymene) + C<sub>10</sub>H<sub>20</sub> (m-menthane, cis and trans).<sup>88</sup>

## M-menthane derivatives

Let us now consider the products of hydrogenation of (+)-sylvestrene (2).

With Pt black, addition of one mole of hydrogen to the hydrocarbon gives 88% *m*-menth-6-ene (58) and two moles of hydrogen, 56% *cis* and *trans* *m*-menthanes (1).<sup>85,86</sup>

Whereas complete hydrogenation of (+)-sylvestrene in ethyl acetate on PtO<sub>2</sub> gives 38% *cis* and 62% *trans* *m*-menthane (1), addition of one mole of hydrogen using Raney nickel leads to *m*-menth-6-ene (58).<sup>50,51</sup>

Contrary to the belief that sylvestrene is stable,<sup>89</sup> stirring of (+)-sylvestrene (2) with 20% phosphoric acid at 100° for 20 hr gives an isomerizate containing *m*-mentha-6,3(8)-diene (4) (56%) and *m*-mentha-1,3(8)-diene (5) (22%).<sup>36</sup>

Again, with trichloroacetic acid at 174 ± 2° for 4 hr, only 3% of the substrate survived reorganization. The oil received included the isomers (3) (15%), (4) (5.1%), (5) (36.2%), (6) (2.0%), *m*-menth-1-ene (55) (6.1%), and *m*-cymene (38) (23.9%).<sup>75</sup>

Two base catalysed transformations of (+)-sylvestrene have been reported.<sup>75,90; see also 91</sup>

In the presence of *N*-lithioethylenediamine at 50-80°, sylvestrene yields *m*-mentha-1,3(8)-diene (5) (≥ 76.2% yield) and lesser amounts of (3), (4), and (6) plus *m*-cymene (38). At 110°, aromatization is complete.<sup>90</sup>

A 3 hr processing of (+)-sylvestrene with *K*-tert-butoxide in DMSO at 82 ± 2° affords (3) (3.0%), (4) (5.5%), (5) (45.0%), and (6) (0.9%).<sup>75</sup>

Thus by the isomerization of (+)-sylvestrene we get the optically inactive hydrocarbons (4) and (5) and these are substrates for the hard-to-get (±)-sylvestrene dihydrochloride (34).<sup>62</sup>

*m*-Mentha-1,3(8)-diene. By precise fractionation of *m*-menthadienes, it is possible to isolate homogeneous (GLC) title compound.<sup>62</sup> The required *m*-menthadiene pool is released either from (+)-sylvestrene dihydrochloride (34) by dehydrohalogenation<sup>62</sup> or from (+)-sylvestrene by isomerization.<sup>36</sup>

From isomeric *m*-menthadienes or their mixtures, (5) has been prepared by heating with lithioethylenediamine.<sup>91</sup>

*m*-Mentha-1,3(8)-diene gives an adduct with thiourea, m.p. 171-172°, from which steam distillation regenerates the parent hydrocarbon, thus constituting a unique technique to suck out the hydrocarbon from mixed *m*-menthadienes.<sup>61</sup>

Though the structural pattern forbids 1:4-linking with maleic anhydride, this conjugated diene affords an adduct, m.p. 304-308°,<sup>36,57,62</sup> 308-309 (decomp).<sup>60</sup> How this takes place is not clear but the wandering of the exo double bond into the ring prior to adduction is not excluded.<sup>60</sup> This reaction has been utilized to strip off the hydrocarbon from *m*-menthadiene mixtures.<sup>62</sup>

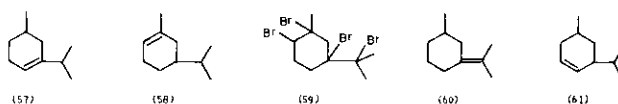
Perhaps of industrial value is the adduct, average molecular weight ~750, derived from the hydrocarbon by reaction with fumaric acid in the presence of glycerin oligoesters.<sup>94</sup>

Considerable resistance is displayed by *m*-mentha-1,3(8)-diene to isomerization with either 20% H<sub>3</sub>PO<sub>4</sub><sup>62</sup> or *K*-tert-butoxide in DMSO.<sup>75</sup> On the other

hand, reaction with trichloroacetic acid leaves ~ 45% of the starting material unmoled; conversion to *m*-cymene (38) (~ 30%) is encouraged via disproportionation.<sup>73</sup>

Hydrogenation of *m*-mentha-1,3(8)-diene on Pt black gives the *m*-menthenes (55), (58), and (60); *m*-cymene (38), and *m*-menthanes (*cis* and *trans*) (1).<sup>85,86</sup>

A fascinating study relates to the action of calcium hexammoniate on *m*-menth-1,3(8)-diene.<sup>92</sup> The hydrocarbon is reduced to the menthenes (55) (38%), (56) (6%), (57) (19%), and (60) (8%).



Disproportionation of *m*-mentha-1,3(8)-diene to *m*-cymene (38) (63.4%) and *m*-menthanes (1) (33.7%) takes place by a 10 hr refluxing at 140 ± 2° with Pd-C catalyst (10%).<sup>62</sup>

At 130-135°, in presence of Pd-C (20% Pd) (5%) catalyst, *m*-mentha-1,3(8)-diene undergoes hydrogen transfer at a faster rate than sylvestrene (2) to give a catalysate similar to that derived from the latter.<sup>87</sup> By contact with the catalyst for 8 hr, the hydrocarbon affords *m*-cymene (38) and *m*-menthanes (*cis* and *trans*) (1).<sup>87</sup>

As expected, dehydrogenation of *m*-mentha-1,3(8)-diene affords *m*-cymene (38).<sup>31</sup>

Finally, an outstanding reaction of *m*-mentha-1,3(8)-diene is its conversion with hydrogen halides to (±)-sylvestrene dihalides (34 and 35).<sup>62</sup> See below.

*m*-Mentha-6,3(8)-diene. Our knowledge of *m*-mentha-6,3(8)-diene (4) is very meagre. The isolation of this hydrocarbon in ~ 93% purity from the dehydrohalogenate of (+)-sylvestrene dihydrochloride involves the following steps.<sup>62,74</sup>

(+)-sylvestrene dihydrochloride  $\xrightarrow{a}$  *m*-menthadienes (b.p. 69-88°/20 mm)  $\xrightarrow{b}$  *m*-menthadienes (b.p. 85-88°/20 mm)  $\xrightarrow{c}$  *m*-mentha-6,3(8)-diene + *m*-mentha-1,3(8)-diene  $\xrightarrow{d}$  *m*-mentha-1,3(8)-diene

a—aniline; b and c—fractional distillation; and d—maleic anhydride/acetone

If pure (GLC) *m*-menthadiene is required, then the crude sample is converted to the tetrabromide (59), m.p. 128° and then debrominated with Zn.<sup>62</sup>

Isomerization of the hydrocarbon with trichloroacetic acid and *K*-tert-butoxide leads to shifting of the endocyclic double bond to give predominantly *m*-mentha-1,3(8)-diene.<sup>75</sup> The tetrabromide mentioned above is the only known authentic derivative of the hydrocarbon.

Like *m*-mentha-1,3(8)-diene, this sister isomer yields (±)-sylvestrene dihydrohalides (34 and 35).<sup>62</sup>

Thus *m*-mentha-1,3(8)-diene and *m*-mentha-6,3(8)-diene or mixtures of these which yield

## M-menthane derivatives

(±)-sylvestrene dihalides are the rare and precious substrates for entry into (±)-sylvestrene series.<sup>54,55,56,62,77,93</sup>

### m-Menthenes

Unlike p-menthenes, the chemistry of m-menthenes is very imperfectly understood.

#### Routes to m-menthenes

Excluding the specialized procedures developed by Gollnick and Schade,<sup>50,51</sup> there are five types of reactions leading to m-menthenes: catalytic hydrogenation of m-menthadienes; hydrogen transfer of m-menthadienes; dehydration of m-menthanols; isomerization of car-3-ene (30) and car-2-ene (31); and decyclization of carane.

Formation of m-menthenes through the first two reactions mentioned above has been covered earlier. It may be stressed that for such processings, 1,3(8)-, 6,3(8)-, and 6,8-m-menthadienes have been used and these are available only in restricted quantities. It is almost certain that the mixed m-menthadienes originating from (+)-sylvestrene dihydrochloride are equally acceptable for this purpose. According to the data of Deshechits and Bardyshev, dehydration of trans-m-menthan-8-ol (68, X = OH) gives m-menthenes as summarized in Table I.<sup>126</sup> Whereas p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl and KHSO<sub>4</sub> cause excellent dehydration to trans-m-menth-8-ene (65), SiO<sub>2</sub> and p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H encourage conversion to m-menth-3-ene (57).

**Table I. Dehydration of trans-m-menthan-8-ol**

| Reagent   | Temp. | Time | % m-Menthenes |      |      |      |
|---|-------|------|---------------|------|------|------|
|   |       |      | (60)          | (65) | (56) | (57) |
| p-MeC <sub>6</sub> H <sub>4</sub> SCl <sub>2</sub>  | 100°  | 2    | 30.2          | 58.0 | 4.6  | 7.2  |
| KHSO <sub>4</sub>                                   | 130°  | 2    | 34.8          | 41.1 | 8.7  | 15.4 |
| SiO <sub>2</sub>                                    | 215°  | 3    | 11.2          | 5.7  | 32.8 | 50.3 |
| p-MeC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H | 145°  | 5    | 8.2           | 3.6  | 34.1 | 54.1 |

The m-menthenes derived by routes (1), (2), and (3) are meritorious in being free from the p-isomers. However, as it stands now, the isolation of the m-menthenes from reaction mixtures and further splitting of the m-menthenes to homogenous components is extremely difficult and demands gas-liquid chromatographic techniques.

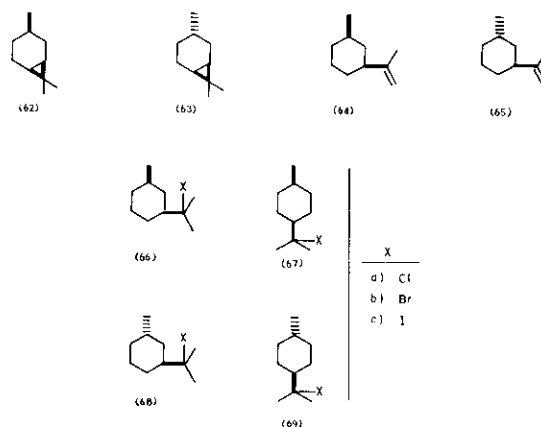
Concerning the formation of m-menthenes from either (+)-car-3-ene (30) or (+)-car-2-ene (31) by reaction with acid catalysts, this is as a consequence of hydrogen transfer involving the initially released m-menthadienes. For instance, m-menth-4-ene (61) is obtained from (30) and (31) by reaction with activated clay<sup>95</sup> and abiectic acid<sup>35</sup> respectively; m-menth-1-ene (55) originates from car-3-ene by contact with diatomite.<sup>31</sup> Again, from the complex mixture, it is not worthwhile to retrieve the m-menthenes.

Finally let us look at carane as the precursor of m-menthenes. This hydrocarbon exists in the cis and trans modifications (62) and (63). Its synthesis and

formation by catalytic hydrogenation of (+)-carene are well documented.<sup>96</sup>

Thermal isomerization of cis-carane (62) gives m-menth-3-ene (57), cis and trans-m-menth-8-ene (64), and (65) in conjunction with p-isomers.<sup>97</sup> Also, the same trend is displayed by (+)-trans-carane (63).<sup>97</sup>

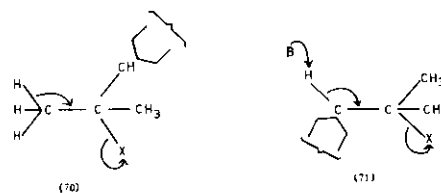
On heating in a sealed tube with p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H at 80° for 10 hr, both the caranes afford the menthenes (54), (57) and (60) with p-isomers.<sup>98</sup>



In analogy to the carenes, the dimethylcyclopropane system in caranes must also decapitulate two-directionally with acceptance of hydrogen halides to give derivatives of the m- and p-series. Contradictory findings are reported with respect to this, the reaction yielding either m- or p- halogen members.<sup>99</sup> However, the above prediction that halogen derivatives of both the series must stem from caranes has been fulfilled by recent investigations.<sup>99</sup>

It is found that addition of HX (X = Cl, Br, I) to cis-carane (62) affords cis-8-halo-m-menthane (66) and cis-8-halo-p-menthane (67); corresponding trans pairs (68) and (69) are obtained from trans-carane (63).<sup>99,100</sup>

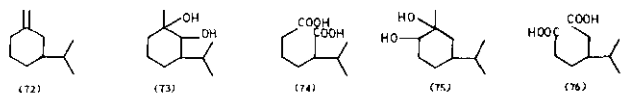
This discussion is confined to the m-series. Splitting off of hydrogen halides from the halogen compounds derived from a mixture of cis- and trans-caranes has been affected with sodium isoamylate, sodium isopropylate, CH<sub>3</sub>COOH/CH<sub>3</sub>COONa, KOH/C<sub>2</sub>H<sub>5</sub>OH, aniline, pyridine, and quinoline.<sup>99</sup> Except with the last two reagents, dehydrohalogenation takes place essentially through the sterically difficult transition state (70) giving cis/trans-m-menth-8-ene (64/65) according to the Hofmann rule. Increase in volume of ion pair of base augments the liberation of this hydrocarbon. Saytzeff's rule is operative when pyridine or quinoline is used, the elimination occurring through the transition state (71) to provide hydrocarbon (60) with lateral double bond, probably due to lack of solvation of base.



Utilizing genuine samples of *cis*- and *trans*-carane, hydrochlorination is found to furnish, as in the previous case, *m*-derivatives (66) and (68) in addition to the *p*-derivatives (67) and (69) respectively.<sup>100</sup> Dehydrochlorination of the *m*-derivatives with sodium isoamylate has been investigated. The *cis* derivative (66) yields essentially *cis*-*m*-menth-8-ene (64) with a small quantity of the *trans*-isomer (65) and the *trans* derivative (68), *trans*-*m*-menth-8-ene (65) with a small quantity of the *cis*-isomer (64). Formation of the *trans*-*m*-menth-8-ene (65) from the *cis* derivative (66) and of *cis*-*m*-menth-8-ene (64) from the isomer (68) is attributed to *cis*-*trans*-isomerization process.<sup>100</sup>

Thanks to Bardyshev and co-workers,<sup>31,87,92,98</sup> the IR characteristics of all the *m*-menthenes isolated by them have been documented, but apparently the PMR data of only the *m*-menthenes (55), (58), and (72) are available.<sup>51</sup>

Only the fringes of the chemical properties of the *m*-menthenes are known. *m*-Menth-1-ene (55) affords a nitrosochloride for which divergent melting points have been recorded: 136-137°,<sup>86</sup> 128.5°,<sup>92</sup> 128-128.5°,<sup>31</sup> and 124°.<sup>87</sup> Nitrolaniline, m.p. 155-157°,<sup>86</sup> and nitropiperidine, m.p. 233-235°.<sup>86</sup> Moreover, with 1%  $\text{KMnO}_4$ , the hydrocarbon furnishes *m*-menthane-1,2-diol (73), m.p. 86-88° which with 3%  $\text{KMnO}_4$  gets degraded to  $\alpha$ -isopropyladipic acid (74), m.p. 63-66°.<sup>86</sup>



Apparently, *m*-menth-2-ene has not been chemically characterized.

The isomeric 3-, 3(8)-, and 4-*m*-menthenes (57, 60, and 61) furnish nitrosochlorides m.p. 149.5°,<sup>87</sup> 150-151°,<sup>92</sup> 148.5°,<sup>92</sup> and 126-127°<sup>95</sup> respectively.

With regards to *m*-menth-6-ene (58), it yields a nitrosochloride for which m.p.s 109-110.2°<sup>87</sup> and 60-61°<sup>86</sup> have been reported. On oxidation with 1%  $\text{KMnO}_4$ , the hydrocarbon affords *m*-menthane-1,6-diol (75), m.p. 73-75°;<sup>86</sup> further oxidation with 3%  $\text{KMnO}_4$  yields  $\beta$ -isopropyladipic acid, (76) m.p. 82-85°.<sup>86</sup>

Only a blurred picture has emerged from the work on the chemical characterization of the *m*-menthenes. This aspect of the problem calls for further investigation.

### ***m*-Cymene and *m*-Menthanes**

*m*-Cymene, the only aromatic of the *m*-series which is rare but now potentially available (see below), holds the key to a wide spectrum of novel chemicals. In all probability at least some of them will be recognized as important aroma-contributors.

(+)-Car-3-ene is the most attractive source for *m*-cymene. However, since the terpene succumbs to two-way cleavage of the 3-membered ring furnishing *m*- and *p*-derivatives, its dehydrogenation either in the liquid or vapour phase gives a mixture of *m*- and *p*-cymenes.

In this context, the comprehensive investigation on

the vapour phase aromatization of (+)-carene over chromia-alumina catalysts is a major contribution.<sup>101</sup> The catalysts practically consists of a mixture of m- and p-cymenes. Since it is feasible to resolve the cymenes through clathration with inorganic complexes,<sup>102</sup> this reaction may prove to be an economical route to m-cymene.

On the other hand, we can funnel the reorganization of (+)-car-3-ene to m-cymene through the dehydrogenation of the m-menthadienes derived from (+)-sylvestrene dihydrochloride (see below).

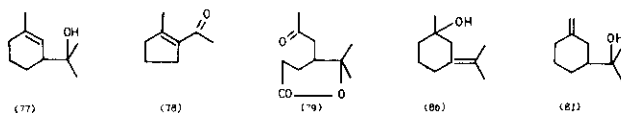
Catalytic hydrogenation of m-cymene (also of m-menthadienes and m-menthenes) affords cis- and trans-m-menthanes (1). As expected, hydrogenolysis of cis- and trans-caranes (62 and 63) over Pt/C catalyst at 180-300° gives m-menthanes, but admixed with p-isomers.<sup>103</sup> Technically, m-menthanes are likely to match p-menthanes in their utility.

### m-Menthenols and m-Menthols

*m-Menthenols.* On the alcohols derived from (+)- and (±)-sylvestrene dihydrochloride revolve notable contributions of great academic and practical value.

Classical work unfolded the fact that hydroxylation of (+)-sylvestrene dihydrochloride with 2% KOH furnishes an unsaturated, optically active tertiary alcohol, C<sub>10</sub>H<sub>17</sub>OH, designated as sylveterpineol.<sup>104</sup> This consists of m-menth-1-en-8-ol (Neosylve- $\alpha$ -terpineol<sup>1</sup>) (77) and m-menth-6-en-8-ol (sylve- $\alpha$ -

terpineol<sup>1</sup>) (37) as evidenced by oxidation with dilute aq. KMnO<sub>4</sub> to: 1) 2-acetyl-1-methyl- $\Delta^1$ -cyclopentene (78) and 2) the  $\delta$ -lactone of  $\epsilon$ -keto-8-hydroxy-isopropylheptonic acid (79) respectively;<sup>105</sup> these alcohols have been synthesized.<sup>65,106,107</sup>



Soviet investigators have hydroxylated (+)-sylvestrene dihydrochloride according to the method of Wallach and also by the action of 5-10% aq. solution of Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and CaCO<sub>3</sub> suspension at 60-100° and different ratio of reacting substances.<sup>108,109</sup> Terpene alcohols have also been obtained by treating (+)-sylvestrene dihydrochloride with NaOAc-CH<sub>3</sub>COOH followed by boiling with KOH-EtOH.<sup>110</sup> An exceptionally high yield (65-70%) of alcohols is obtained when (+)-sylvestrene dihydrochloride (1 part) mixed with soap powder (VTU No 18/36-44) (2-2.5 parts) and water (15 parts) are stirred together at 70-80° for 2-2.5 hr. These processings afford m-menthane-1,8-diol (52) and the monohydric alcohols (77), (37), m-menth-3(8)-en-1-ol (80), m-menth-1(7)-en-8-ol (81), and m-menth-8-en-1-ol (82). Of these, (77) and (37) have been obtained in quantity and their structures have been confirmed by oxidative degradation. Through gas-liquid chromatography, others (80), (81), and (82) have been redeemed from the reaction mixture.

Recovery of the m-menthenols (37) and (79) by hydrolysis of their respective p-nitrobenzoates affords only the former in a pure state<sup>111-113</sup> but the isomeric alcohol from the sister ester needs further GLC purification.<sup>114</sup> PMR data confirm the structure of these alcohols.<sup>113,114</sup>

A refreshing approach to m-menthenols (37) and (77) from the m-menthadienes (2) and (3) (?) exploits Sucharda's method<sup>115</sup> in which the substrate is treated with 33% KNO<sub>3</sub> in conc. HNO<sub>3</sub> and then decomposing the esters with Zn powder in aq. ammonia.<sup>116</sup> By similar processing, (+)-car-3-ene yields alcohols but evidences presented point that these belong to the m- and p- series.<sup>116</sup>

Straightforward hydrochlorination of (+)-car-3-ene and then hydrolysis of the generated hydrochlorides yield m- and p-menthenols but it is extremely difficult to split the pair of alcohols.<sup>117-118</sup>

Biogenetically the occurrence of m-menth-6-en-8-ol (37) in turpentines from *Pinus Sylvestris* is of tremendous significance since it appears to be the only alcohol of the m-menthane series that occurs in nature.<sup>119-122</sup>

The chemistry of the alcohols (37) and (77) has received more attention than the sister isomers. In early literature, we have seen that alcohol (37) and (77) are discriminated through oxidative degradation to the lactone (79) and acetyl derivative (78) respectively. For the alcohol (37), the PMR data of the intermediate m-mentha-1,6,8-triol (83) strongly con-

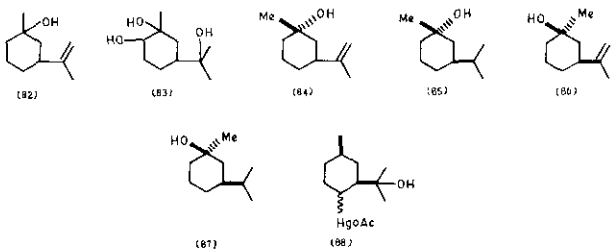


firm its utility as a useful derivative.<sup>113</sup>

*p*-Nitrobenzoates,<sup>111-114</sup> phenylurethanes,<sup>108,111</sup> and nitrosochlorides<sup>108</sup> are recommended as derivatives for these alcohols. Strangely, the melting points of the nitrosochlorides are identical<sup>108</sup> and no mixed melting point has been recorded. Of these derivatives, only the *p*-nitrobenzoate of (37) has withstood PMR scrutiny.<sup>113</sup> Other derivatives have to be examined further before declaring them genuine for identification purposes.

*m*-Menthanol. These compounds constitute an interesting group in the *m*-menthane series.

The classical route to these alcohols is by catalytic hydrogenation of *m*-menthenols.<sup>105,123</sup> More recently there has been renewed interest in these compounds.<sup>110</sup> Hydrogenation of *m*-menthenols (37), (77), and (81) gives isomeric menthanols (66, X = OH) and (68, X = OH); the *m*-menthenols (80) and (84) are transformed to (85) and (86) with (87).



Starting from *cis*- and *trans*-caranes (62 and 63), there are two routes to *m*-menthanols.

In one synthesis, the mixture of *cis*-8-chloro-menthanes (66 and 67, X = Cl) derived from (62) is saponified to yield *cis*-*m*-menthan-8-ol (66, X = OH) (21%) plus *cis*-*p*-menthan-8-ol (67, X = OH) (42%).<sup>124</sup> Similar processing of (68) and (69) affords *trans*-*m*-menthan-8-ol (68, X = OH) (41%) in conjunction with the *trans*-isomer (69, X = OH) (23%).

The other preparation is through hydroxymercuration of the caranes (62) and (63) and again leads to *m*- and *p*-menthanols.<sup>125</sup> Thus, the intermediate acetoxymercury derivative originating from (62) by treatment with mercuric acetate on decomposition with base gives the alcohol (88); reduction of the latter with sodium borohydride results in *cis*-*m*-menthan-8-ol (66, X = OH). The total yield of the mixed alcohols in the first case amounts to 65% containing 10% (66, X = OH) and in the other 60% containing 95% (68, X = OH).

One of the valuable properties of *m*-menthanol is its facile dehydration to *m*-menthenes. Deshechits and Bardyshev have demonstrated this transformation using *trans*-*m*-menthan-8-ol (68, X = OH) as the substrate.<sup>126</sup> See above.

## Conclusion

For over a century, the *p*-menthane, pinane, and bornane derivatives have been exploited for the naval stores industry. Tremendous advances in the syntheses of flavors and fragrances from sesquiterpenes have been made in the last two decades. Now, through the modification of (+)-*car*-3-ene [and to a

lesser extent (+)-*car*-2-ene] to (+)-sylvestrene dihydrochloride and caranes, we have *m*-menthadienes, *m*-menthenes, *m*-cymene, *m*-menthanes, *m*-menthenols, and *m*-menthanols. We should be on the lookout for novel substrates to expand the frontiers of the aroma industry. Perhaps the versatile *m*-menthane derivatives will meet this challenge. This is particularly likely because these chemicals are now in easy economic reach for the organic chemist devoted to producing novel and useful perfume and flavor materials.

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