SYLVESTRENE DIHYDROCHLORIDE AND CARVESTRENE DIHYDROCHLORIDE*

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An intriguing problem in the *m*-menthadiene field, already studied in great detail,[1–5] is the relationship of carvestrene to sylvestrene. One way this problem has been approached is through the dihydrochlorides of these hydrocarbons. Optically inactive carvestrene dihydrochloride, to which has been attributed the *trans* structure for reasons that are not now valid,[3,6] displays the same melting point as (±)-sylvestrene dihydrochloride prepared by mixing equal quantities of (+)- and (−)-sylvestrene dihydrochlorides.[7] Carvestrene dihydrochloride may therefore be the racemate of sylvestrene dihydrochloride, but this information does not provide direct evidence concerning the relationship[5] between carvestrene and (±)-sylvestrene as a common hydrochloride may be derived from various double bond isomers. Both (±)-sylvestrene[8] and (±)-carvestrene[9] (I) have very recently been synthesized by unambiguous routes. This paper discusses the structures of (+)-sylvestrene dihydrochloride and carvestrene dihydrochloride.

Carvestrene dihydrochloride and sylvestrene dihydrochloride are available by the hydrochlorination of many terpenoids.[5,10–12] For the present study, carvestrene and (+)-sylvestrene dihydrochlorides were prepared by hydrochlorination of pure (g.l.c.) sylveterpinolene and (+)-car-3-ene respectively. The dihydrochlorides in KBr disks showed infrared spectra that were superimposable except for minor differences around the 1400 cm^{-1} region. The two compounds in chloroform solution

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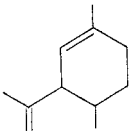
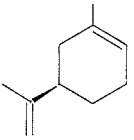
gave superimposable infrared spectra with complete correspondence of all bands (21 bands between 620 and 1050 cm^{-1}). The p.m.r. spectra of the two dichlorides were also identical, with a six-proton singlet at 8·45 τ due to the 2-chloroisopropyl group and a three-proton singlet at 8·37 τ due to a tertiary methyl group geminal to a chlorine. No resonance occurred below 7·7 τ and so both chlorines are tertiary. The complete correspondence of the infrared and p.m.r. solution spectra of the two compounds provides proof that carvestrene dihydrochloride is (±)-sylvestrene dihydrochloride.

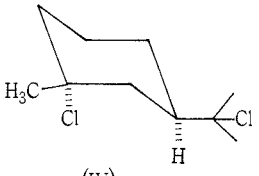


(I)

(II)



(III)



(IV)

The structure of (+)-sylvestrene dihydrochloride follows from the ensuing evidence. The (+)-isomer is related to (+)-car-3-ene (II) and to (+)-sylvestrene (III).[13,14] The bulky chloroisopropyl group will adopt an equatorial environment and the thermodynamically more stable arrangement for the remaining chlorine atom will be such that the chlorine is axial with the methyl group equatorial. This view is in accord with findings[15–17] that the more stable arrangement for 1-chloro-1-methyl cyclohexanes, obtained by either addition or substitution reactions in polar or semipolar solvents, has the "larger" methyl group equatorial. Therefore (+)-sylvestrene dihydrochloride has structure (IV). This formulation is confirmed by elimination reactions. Mild elimination of hydrogen chloride to give more than 70% of endocyclic double bond isomers[13,14] provides additional evidence of the axial nature of the chlorine atom.

Experimental

Carvestrene Dihydrochloride

Sylveterpinolene (10 g) $[\alpha]_D^{27}$ ±0° (*c*, 8·5 in $CHCl_3$) was dissolved in ether (36 ml) and treated exhaustively with a stream of hydrogen chloride, the temperature being kept at −10 to −5°. The reaction mixture was taken up in ether (60 ml), washed repeatedly with water, then with 10% sodium carbonate solution (50 ml), again with water, and dried ($MgSO_4$). After expulsion of ether, the resulting dark coloured liquid on distillation afforded a clear oil (b.p. 136–140°/20 mm). On cooling in a freezing mixture, the oil solidified to a white mass (5·6 g). This after two recrystallizations from methanol gave carvestrene dihydrochloride (1·45 g), m.p. 53° (lit.[5] 52·5°) $[\alpha]_D^{27}$ ±0° (*c*. 4·0 in $CHCl_3$) (Found: C, 57·3; H, 8·4; Cl, 33·6. Calc. for $C_{10}H_{18}Cl_2$: C, 57·4; H, 8·7; Cl, 33·9%). $\bar{\nu}$ ($CHCl_3$): 1052, 1030, 956, 937, 856 cm^{-1}. P.m.r. spectrum (CCl_4): 8·45 (6 proton singlet), 8·37 (3 proton singlet) τ.

(+)-*Sylvestrene Dihydrochloride*

A solution of (+)-car-3-ene (8 g) (b.p. 170°) $[\alpha]_D^{27}$ +11·8° (*c*, 6·78 in $CHCl_3$) in ether (5 ml) was hydrochlorinated at −10 to −5° for 4–5 hr. The crystals obtained were filtered under suction

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and dried on filter paper (2·3 g, m.p. 70°). Recrystallization from methanol (8 ml) afforded (+)-sylvestrene dihydrochloride (1·84 g), m.p. 72° (lit.[5] 72–73°) $[\alpha]_D^{27}$ +19·0° (*c*, 1·18 in $CHCl_3$) (Found: C, 57·3; H, 8·3; Cl, 33·8. Calc. for $C_{10}H_{18}Cl_2$: C, 57·4; H, 8·7; Cl, 33·9%). $\bar{\nu}$ ($CHCl_3$): as described above for carvestrene dihydrochloride. P.m.r. spectrum (CCl_4): as described above.

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