# An Accidental Synthesis of (±)-Herbertene

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(±)-Herbertene (**1**) was synthesized by acid-catalysed rearrangement of the alcohol (**3**) with a drimane skeleton.

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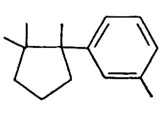
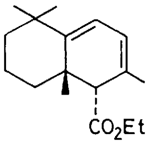
(−)-Herbertene, a new aromatic sesquiterpene from the liverwort *Herberta aduna*, was recently described by Matsuo *et al.*[1] It has the 1,2,2-trimethyl-1-*m*-tolylcyclopentane structure while the well known cuparene-type sesquiterpenes contain a *p*-tolyl-residue (*e.g.* ref. 2).

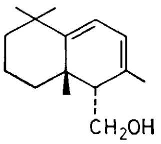
This communication describes a serendipitious synthesis of (**1**). Some years ago we reported[3] the preparation of the



(1)



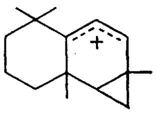
(2)

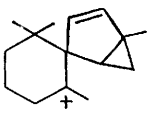


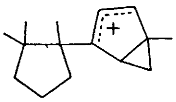
(3)

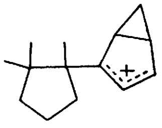
bicyclic ester (**2**) with a drimane skeleton, reduction of which with $LiAlH_4$ in ether yielded (**3**) (80% yield). We wanted to transform (**3**) into a bicyclo[5.4.0]-framework by ring-enlargement. Treatment of (**3**) with acid (0.02 M perchloric acid in formic acid, 10 min at reflux) gave rise to a mixture of volatile hydrocarbons (43% yield; the residue of the distillation was a hard, resinous material). About 95% of this mixture consisted of only two components in a 3:1 ratio;† they were isolated by preparative g.l.c. and the main product turned out to be identical in every respect (g.l.c. i.r., and $^1H$ n.m.r.) with herbertene.‡

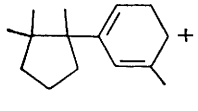
The mechanistic interpretation of the unexpectedly specific rearrangement of (**3**) to (**1**) is uncertain. Especially remarkable is the lack of formation of cuparene.† The following explanation is suggested. After formation of (**4**), two successive 1,2-migrations lead to (**5**) and (**6**), respectively. Intermediate (**6**) is in equilibrium with four other cyclopropylcarbinyl ions resulting from cyclopropane migrations.[4] Three of these can open to give a cyclohexadienyl ion with the required *meta*-substitution, and two a cyclohexadienyl ion with *para*-substitution. The $\Delta\Delta G^{\ddagger}$ value for the cyclopropane rearrangement and the formation of the cyclohexadienyl ions is probably small[4] ($\leqslant$4 kcal/mol) compared with the overall $\Delta G^{\ddagger}$ for these reactions. Therefore the relative stability of (**6**) and its four isomers could be of importance in the outcome of the reaction. *E.g.* collapse of (**7**) which we suppose to be the most stable among these isomers, would lead to (**8**) and thus to (**1**).[5] There are other possible formal ways to convert (**3**) into (**1**).


(**4**)


(**5**)


(**6**)


(**7**)


(**8**)

I thank Professor A. Matsuo for comparing our spectra (i.r., $^1H$ n.m.r.) with those of herbertene and for g.l.c. co-injection of our sample with an authentic material. I also thank Professor D. Arigoni for discussion and Dr. J. Schmid for the mass spectra.

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## References

1 A. Matsuo, S. Yuki, and M. Nakayama, *J. Chem. Soc., Chem. Commun.*, 1981, 864.
2 A. Matsuo, M. Nakayama, T. Maeda, Y. Noda, and S. Hayashi, *Phytochemistry*, 1975, **14**, 1037.
3 G. Fráter, *Helv. Chim. Acta*, 1974, **57**, 2446.
4 R. F. Childs, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, 1968, **90**, 7144; R. F. Childs and S. Winstein, *ibid.*, p. 7146.
5 For similar homoallyl–cyclopropylcarbinyl cation rearrangements see *e.g.* Y. Hikino and P. de Mayo, *Chem. Commun.*, 1965, 550; S. W. Pelletier, S. Nakamura, and Y. Shimizu, *ibid.*, 1966, 727.

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† There is less than 0.5% of cuparene, if any, in the reaction-mixture (g.l.c.–mass spectrometry). Cuparene is stable under the reaction conditions.

‡ The mass spectra of cuparene and herbertene are nearly identical with one small but reproducible difference: the ratio of the intensities of the peaks at *m/z* 119 and 120 is *ca.* 2 in cuparene and *ca.* 0.5 in herbertene.