BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 51 (2), 653—654 (1978)

# The Derivation of a Brominated Algal Component from Myrcene

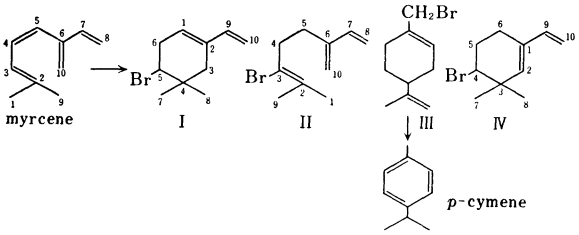
Kazuo Yoshihara and Yoshio Hirose

*The Institute of Food Chemistry, Wakayamadai 1-chome, Shimamotocho, Mishima-gun, Osaka 618*

(Received June 24, 1977)

**Synopsis.** The supposed structure, 5-bromo-4,4-dimethyl-2-vinyl-1-cyclohexene, for a brominated monoterpene from *Desmia* (*Chondrococuus*) *hornemanni* was derived from myrcene through a one-step reaction, and the structure was confirmed.

Many halogenated monoterpenes have been isolated from *D. hornemanni* and characterized.[1-4] Most of them are acyclic myrcene derivatives, and one cyclic compound from Japanese *hornemanni* has been supposed to have the structure of 5-bromo-4,4-dimethyl-2-vinyl-1-cyclohexene (I).[2] We presumed that those halogenated monoterpenes were the products of a halogenium-ion attack on the double bond of myrcene, and tried to derive I by the cyclization of myrcene with the bromonium ion.



Several cyclizations were carried out. Among the reagents tested, 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one (TBCO)[5] was the most desirable for our purposes. The reaction of myrcene with TBCO in nitromethane at 0 °C afforded a mixture containing five monobromides and the starting hydrocarbon. The mixture was run out through $SiO_2$-column and gas chromatography (GC), thus isolating three monobromides. One of them was identified with the natural cyclic monobromide mentioned above in its IR and NMR spectra, except for one singlet signal at $\delta$ 1.21. This signal is found in the NMR spectrum of the natural compound, but not in the synthetic one, therefore, we may conclude that this signal is due to contamination. The NMR spectrum (including the irradiation technique), the IR and the mass spectra of the synthetic compound were satisfied with the supposed structure (I). Two other bromides were also isolated, their structures were assigned as 3-bromomyrcene (II) and 7-bromolimonene (III) from a comparison of the NMR spectra with those of 3-bromo-7-chloromyrcene[1] and limonene respectively. The double bond isomer of I, 4-bromo-3,3-dimethyl-1-vinyl-1-cyclohexene (IV), was not separated from I, but from the NMR and GC-mass spectra of the mixture the existence of compound (IV) was sopposed. In our experiment, the isolation using preparative GC was often accompanied with decomposition, and especially, the allyl bromide (III) was coverted to *p*-cymene. I, as well as II, were unstable for long storage, even in an ice stocker. We think that II can be used for the synthesis of 3-bromo-7-chloromyrcene, *etc.* Other attempts at cyclization, such as HOBr attack by NBS–$H_2O$ or NBA–$H_2O$ in acetone and the acid-catalyzed cyclization of myrcene-2,3-epoxide, followed by bromination, could not afford our expected compounds.

## Experimental

An analytical GC was performed with a Hitachi 063-type apparatus equipped with a HB-2000 capillary column, and preparative GC with Varian's model 90 fitted OV-17 on Chromosorb-W, operated at 100 °C with a detection filament current of 70 mA. In the operation of the latter apparatus over a filament current of 100 mA, allyl bromide (III) was dehydrobrominated in a detector, as was shown by the unusual base-line dropping. For the measurement of the physical data, Hitachi RM-50GC-type GC-mass (fitted with a OV-17 glass capillary column and operated at an ionization voltage of 70 eV) spectrometer were used.

*The Reaction of Myrcene with TBCO.* To a solution of $CH_3NO_2$ (500 ml) containing myrcene (20 g), TBCO (40 g) was added, after which the mixture was stirred for 30 min at 0 °C. The resulting mixture was extracted with pentane. The extract (18.4 g) was chromatographed through a $SiO_2$ column several times, using pentane as the carrier, the process was monitored by means of analytical GC. First myrcene (10.3 g) was extracted, then a mixture of I, II, and IV (3.3 g), and at last a mixture of I and III (2.8 g). The ratio of the products, I: II: III: IV, was 3: 1: 2: 1.

*5-Bromo-4,4-dimethyl-2-vinyl-1-cyclohexene (I).* NMR ($CCl_4$) $\delta$ 1.03 and 1.07 (each s, 3H, assigned to C-7 and C-8 dimethyl respectively), 2.02—2.40 (m, 2H, C-3 methylene), 2.69—2.90 (m, centered at 2.75, 2H, C-6 methylene), 4.03 (dd, 1H, $J=7.5$ and 6.0 Hz, C-5 methylene which changed into a singlet signal upon irradiation with C-6 methylene), 4.88 and 5.00 (each d, 1H, $J=11$ and 17 Hz, *cis*- and *trans*-olefin protons on C-10, respectively; irradiation with the C-9 olefin proton changed those signals into two broad s, signals), 5.49 (m, 1H, C-1 olefin, which changed into a broad s, upon irradiation with C-6 methylene), and 6.73 (dd, 1H, $J=11$ and 17 Hz); IR $\nu$ 3080, 1660, 1600, 1370, 1350, and 890 $cm^{-1}$; MS *m/e* 216 and 214 ($M^+$, $C_{10}H_{16}Br$, 9.7%), 201 and 199 (−Me, $C_9H_{13}Br$, 1%), 135 (−Br, $C_{10}H_{15}$, base peak), 119 ($C_9H_{11}$, 32%), 107 (30%), 93 (50%), and 79 (36%).

*3-Bromomyrcene (II).* NMR $\delta$ 1.73 and 1.83 (allyl-coupled broad s, each 3H, C-1 and C-9 vinyl methyl), a signal centered at 2.25 (m, 4H, C-4 and C-5 methylenes), 4.98 and 5.20 (each d, 1H, $J=12$ and 18 Hz, *cis*- and *trans*-olefin protons on C-8), 5.00 (broad s, 2H, C-10 olefin), and 6.22 (dd, 1H, $J=12$ and 18 Hz, C-7 olefin proton); IR $\nu$ 3070, 1640, 1375, 1200, 990, 895, and 660 $cm^{-1}$; MS *m/e* 216 and 214 ($M^+$, $C_{10}H_{15}Br$, 3%), 173 and 171 (7%), 135 (−Br, $C_{10}H_{15}$, base peak), 119 (34%), 107 (27%), and 79 (49%).

*7-Bromolimonene (III).* NMR $\delta$ 1.73 (s, 3H, C-9 methyl), 3.83 (s, 2H, C-7 methylene), 4.68 (s, 2H, C-10 olefin protons), and 5.38 (m, 1H, C-2 olefin proton); IR $\nu$ 3060, 1640, 1200, 885, 810, and 600 cm$^{-1}$; MS *m/e* 216 and 214 (M$^+$, $C_{10}H_{15}Br$, 7%), 171 and 173 ($-C_3H_7$, $C_7H_8Br$, 15%), 135 ($-Br$, $C_{10}H_{15}$, base peak), 119 (37%), 93 (72%), and 68 ($C_6H_6$, 67%). The decomposed product in a GC detector with a filament current of 150 mA, *p*-cymene, was identified by a comparison of its IR and mass spectra with those of an authentic sample.

*4-Bromo-3,3-dimethyl-1-vinyl-1-cyclohexene (IV).* This compound was not purified, but some NMR signals in a mixture with I and the mass spectrum were obtained. NMR 1.15 (s, C-7 and C-8 *gem.* dimethyl), 1.60—2.00 (complex), 5.43 (broad s, C-4 methylene), and 6.25 (dd, $J$=12 and 18 Hz, C-9 vinyl methyl); MS *m/e* 216 and 214 (7%), 201 and 199 (3%), 135 (base peak), 119 (38%), 109 (27%), 93 (52%), and 79 (23%).

We wish to thank Professor Toshio Miwa of Osaka City Univ. for the measurement of 100 MHz NMR, to Mr Hiroshi Nii of the Nagaoka Perfumery Co., Ltd., for providing the myrcene, to Dr. Kiichi Nishimura of the Suntory Co., Ltd., for the measurements using the GC-mass spectrometer, and to Dr. Yoko Naya for providing the spectral data on haloterpenes and useful suggestions.

## References

1) N. Ichikawa, Y. Naya, and S. Enomoto, *Chem. Lett.*, **1974**, 1333.

2) N. Ichikawa, Y. Naya, and S. Enomoto, The Abstract of the 18th Symposium of Terpene, Essential Oils, and Aromatic Chemistry, 67 (1974).

3) B. J. Burreson, F. X. Woolard, and R. E. Moore, *Tetrahedron Lett.*, **1975**, 2155.

4) B. J. Burreson, F. X. Woolard, and R. E. Moore, *Chem. Lett.*, **1975**, 1111.

5) T. Kato, I. Ichinose, A. Kamoshita, and Y. Kitahara, *J. Chem. Soc., Chem. Commun.*, **1976**, 516.