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THE REVISED STRUCTURE FOR α-POMPENE AND THE ABSOLUTE CONFIGURATIONS OF (+)-α- AND (-)-β-POMPENE FROM *BAZZANIA POMPEANA*[1)]

A. Matsuo, H. Nozaki, M. Nakayama, Y. Kushi and S. Hayashi
Department of Chemistry, Faculty of Science,
Hiroshima University, Hiroshima 730, Japan
and
N. Kamijo
Government Industrial Research Institute, Osaka,
Midorigaoka, Ikeda 563, Japan

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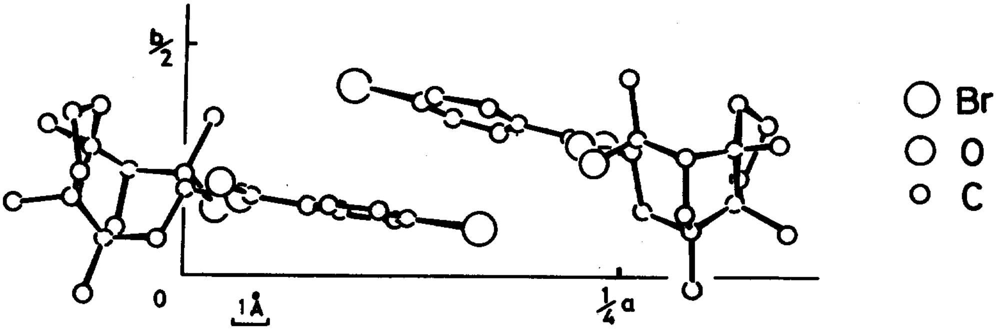
In our previous paper,[2)] two novel tricyclic sesquiterpene hydrocarbons named α- and β-pompene had been isolated from a liverwort, *Bazzania pompeana* (Lac.) Mitt., and a gross structure(I) had been proposed for α-pompene based on chemical and spectral evidences. In order to determine unequivocally the molecular structure of pompene, mono *p*-bromobenzoate(VI) of a diol derived from α-pompene was subjected to single crystal X-ray analysis. By measuring CD spectra of the derivatives the absolute configurations of (+)-α- and (-)-β-pompene were also determined.

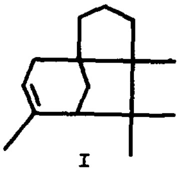
From α-pompene diol(V), $C_{15}H_{26}O_2$; mp 115-116^o; $[\alpha]_D$ -3.6^o; ν 3400 cm^{-1}; δ 0.82, 0.87, 1.02, 1.33(each 3H, s), 4.02(1H, q, J=10.5 and 6.5), which was obtained by OsO_4 oxidation of (+)-α-pompene(II), $C_{15}H_{24}$; $[\alpha]_D$ +48.3^o; ν 800 cm^{-1}; δ 0.85, 0.90, 1.00(each 3H, s), 1.67(3H, br.s), 5.24(1H, m), mono *p*-bromobenzoate (VI), $C_{22}H_{29}O_3Br$; mp 79-80^o, was prepared and recrystallized from a hexane-EtOAc mixture to afford colourless orthorhombic crystals elongated along the c-axis with the unit cell dimensions of $\underline{a}$ = 46.53(2), $\underline{b}$ = 12.20(2), $\underline{c}$ = 7.39(2) Å and the space group $P2_12_12_1$, D_x: 1.33 g/cm^3, D_m: 1.31 g/cm^3(in $ZnCl_4$) containing eight molecules in the unit cell. A total of 2840 independent reflexions was collected by visual estimation of equi-inclination Weissenberg photographs hk0-hk5 and h0l, obtained with Ni-Kα(λ = 1.6591 Å) radiation.

The position of bromine atoms was determined by the sharpened Patterson map, successive use of Fourier and difference Fourier techniques enabled us to assign the structure for this compound. Refinement of structural parameters was made by the block-diagonal matrix least squares calculations, and the anisotropic thermal parameters were used for the bromine atoms. The conventional R-value is 0.12 at this stage. The crystal structure of the *p*-bromobenzoate determined by the present X-ray analysis was shown in Figure(formula VI or its optical antipode). Because each position of two independent bromine atoms was co-related by pseudo symmetry, it was difficult to determine the absolute configuration using the effect of anomalous X-ray scattering by bromine atoms. Accordingly, the structure of (+)-α-pompene should be represented by formula II or its optical antipode.

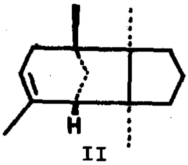


Figure

Both (+)-α-pompene(II) and (-)-β-pompene(III), $C_{15}H_{24}$, $[\alpha]_D$ -14.2°; ν 883 cm^{-1}; δ 0.87, 0.94, 1.07(each 3H, s), 4.64(2H, br.s),[3,4] had the same molecular formula and afforded respectively in catalytic hydrogenation over PtO_2 in AcOH dihydro compounds(IV), $C_{15}H_{26}$, which were confirmed to be identical each other in IR, NMR and MS spectroscopies. Furthermore, (-)-β-pompene containing an exo double bond was isomerized easily with formic acid to (+)-α-pompene($[\alpha]_D$ +47.7°) containing an endo double bond. Hence, the structure of (-)-β-pompene should be represented by formula III or its optical antipode.



I



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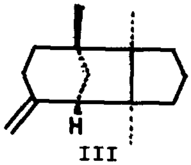

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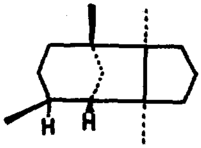

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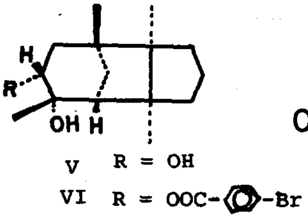
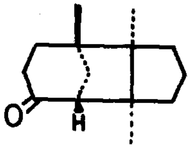
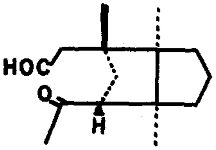


V R = OH

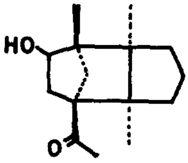
VI R = OOC-⟨⟩-Br



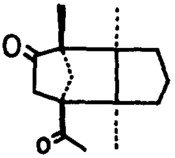
VII



VIII



IX

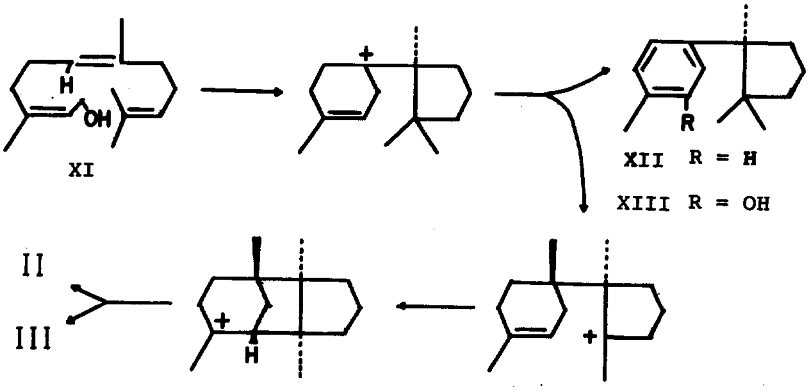


X

The absolute configurations of (+)-α- and (-)-β-pompene were determined as follows. In ozonolysis of (-)-β-pompene, nor-ketone(VII), $C_{14}H_{22}O$; $[\alpha]_D$ -50.1°; ν 1710 cm^{-1}; δ 0.97, 1.01, 1.09(each 3H, s), was prepared. Furthermore, the diol(V) was subjected to glycol fission with periodic acid to convert into an unstable keto-aldehyde(VIII), ν 1720, 1710 cm^{-1}; δ 0.88, 1.02, 1.32, 2.16(each 3H, s), 2.35(2H, d, J=3.0), 2.78(1H, q, J=12.0 and 6.0), 9.87(1H, t, J=3.0). The keto-aldehyde(VIII) was then treated with methanolic HCl to give a tricyclic keto-alcohol(IX), $C_{15}H_{24}O_2$; mp 63-64°; $[\alpha]_D$ -39.7°; ν 3450, 1695 cm^{-1}, which was oxidized with Jones reagent into a cyclopentanone derivative(X), $C_{15}H_{22}O_2$; mp 53-54°; ν 1745, 1700 cm^{-1}; δ 0.93, 0.99, 1.07, 2.29(each 3H, s), 2.17, 2.28(each 1H, d, J=13.0). CD spectra of the nor-ketone(VII) and the cyclopentanone derivative(X) thus obtained were measured to show commonly a negative Cotton effect; for the former, $[\theta]_{292}$ = -4050 in MeOH and for the latter, $[\theta]_{278}$ = -1700 in MeOH. The evidence revealed that the absolute configurations of the nor-ketone and cyclopentanone⁵⁾ were represented by stereostructures VII and X.

Accordingly, the absolute configurations of (+)-α- and (-)-β-pompene should have stereostructures II and III, respectively.

When it is considered that (-)-cuparene(XII) and (-)-δ-cuparenol(XIII) were co-occurrence in the same liverwort,[6] two novel sesquiterpene hydrocarbons may be biosynthesized from *cis*-farnesol(XI) through a stereospecific pathway shown below.[7]



References

1) Chemical Constituents from *Hepaticae*, Part XXIII.

2) A. Matsuo, T. Maeda, M. Nakayama and S. Hayashi, Tetrahedron Lett., 1973, 4131.

3) In this investigation IR and NMR spectra were measured in CCl_4 solutions and optical rotations were determined in $CHCl_3$ solutions at room temperature.

4) The spectral data of a hydrocarbon isolated from another liverwort, *Gymnomitrion obtusum*, together with gymnomitrol were identical with those of α-pompene. We acknowledge to Prof. J.D. Connolly for sending the spectral data(J. Chem. Soc. Chem. Commun., 1972, 1320).

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6) A. Matsuo, M. Nakayama, T. Maeda, Y. Noda and S. Hayashi, Phytochemistry, in press.

7) S. Iwasaki and S. Nozoe, "Natural Products Chemistry, Vol. 1", Ed. by K. Nakanishi *et al*, Kodansha(Tokyo) and Academic Press(New York and London), p 159 (1973).