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α-POMPENE A NOVEL TRICYCLIC SESQUITERPENE HYDROCARBON FROM THE LIVERWORT, BAZZANIA POMPEANA[1)]

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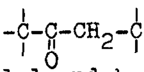
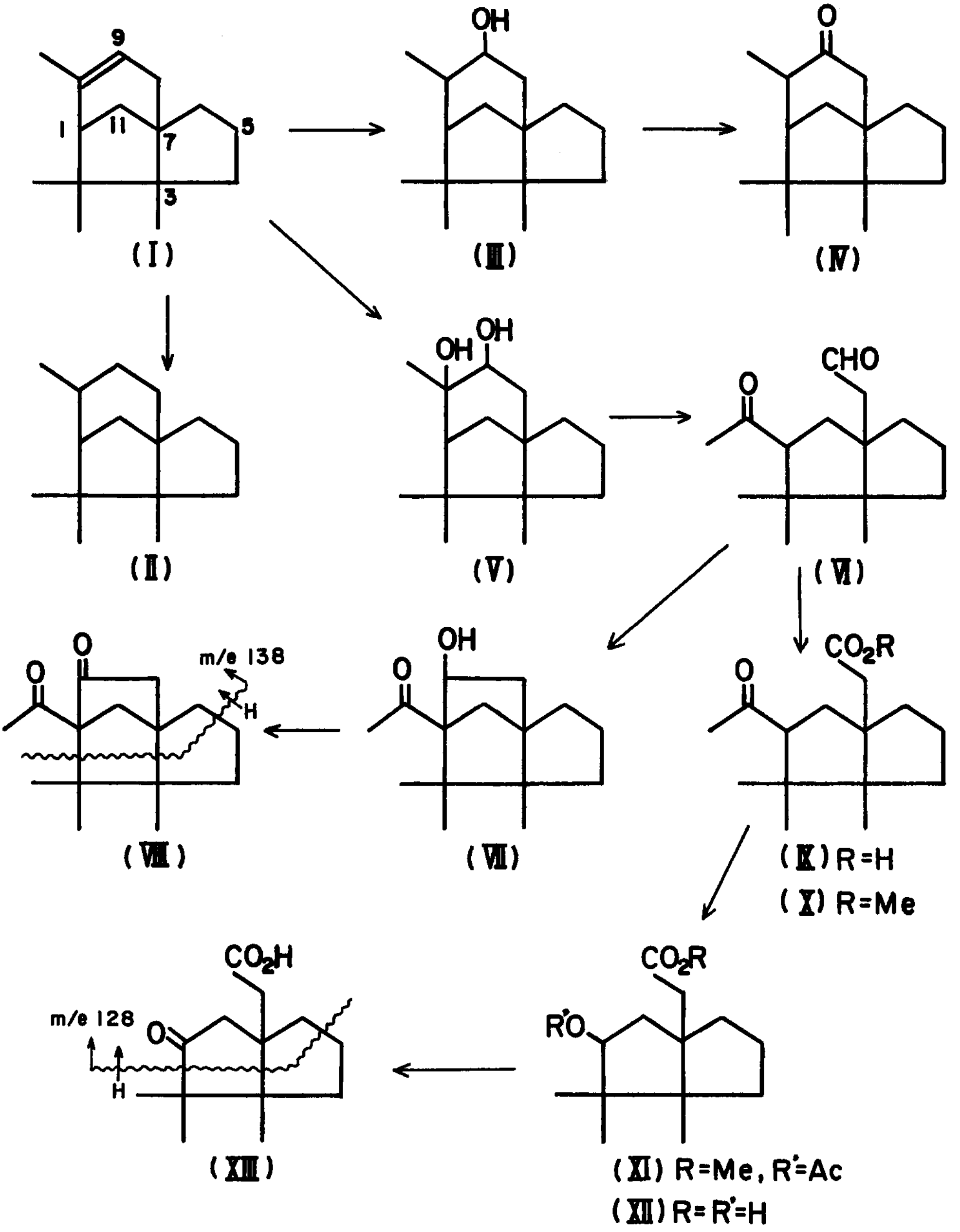
In previous papers[2-4)] three new sesquiterpenoids have been isolated from a leafy liverwort, Bazzania pompeana (Lac.) Mitt. (Hepaticae) to determine their structures. We have now isolated two additional novel sesquiterpene hydrocarbons named α- and β-pompene from the same liverwort. The present communication deals with the evidences of the proposed structure, 2,2,3,10-tetramethyl-tricyclo$[5.3.1.0^{3,7}]$undec-9-ene (I), for α-pompene.

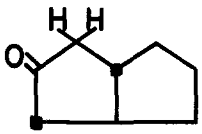
α-Pompene (I), $C_{15}H_{24}$(M^+ 204); $[\alpha]_D$ -26.0°, was isolated from an extract of the liverwort as a colorless oily substance by means of combination of fractional distillation and elution chromatography. The IR and NMR spectra revealed this hydrocarbon to have a trisubstituted double bond bearing a methyl group ($H\underset{|}{C}=\underset{|}{C}-CH_3$), ν 800; δ 1.67(3H, br. s), 5.24(1H, m), together with a geminal dimethyl and tertiary methyl group, ν 1385, 1380; δ 0.85, 0.90, 1.00 (each 3H, s). The hydrocarbon took up one molar equivalent of hydrogen in catalytic hydrogenation over Adams catalyst in acetic acid to give a saturated dihydro-compound (II), $C_{15}H_{26}$(M^+ 206), which contained each of secondary methyl, δ 1.14(3H, d, J=7.0), geminal dimethyl and tertiary methyl groups, ν 1385, 1380; δ 0.78, 0.87, 1.00(each 3H, s). When α-pompene was submitted to hydroboration, it was converted into a secondary alcohol (III), $C_{15}H_{26}O$(M^+ 222.199); mp 80-81°; ν 3300; δ 4.13(1H, six, J=10.0, 10.0, 6.5), which was then oxidized with Jones reagent to afford a 2-methylcyclohexanone derivative (IV), $C_{15}H_{24}O$(M^+ 220.182); ν 1710, 1390, 1380; δ 0.92, 0.93, 1.02(each 3H, s), 1.14(3H, d, J=7.0). These evidences indicate that α-pompene is a tricyclic compound containing a 1-methylcyclohexene system, a geminal dimethyl group and a tertiary methyl group.

Glycol (V), $C_{15}H_{26}O_2$(M^+ 238); mp 115-116°; $[\alpha]_D$ -3.6°; ν 3400, 1385, 1375; δ 0.82, 0.87, 1.05, 1.33(each 3H, s), 4.02(1H, q, J=10.5, 6.5), which was obtained by osmic acid oxidation of α-pompene, was submitted to glycol fission with periodic acid to give a keto-aldehyde (VI) possessing an acetyl group on a tertiary carbon atom, ν 1710; δ 2.16(3H, s), 2.78(1H, q, J=12.0, 6.0), and a formyl methyl group on a quarternary carbon atom (■-CH_2-CHO), ν 1720, 1415; δ 2.35(2H, d, J=3.0), 9.87(1H, t, J=3.0), together with the original geminal dimethyl and tertiary methyl groups, ν 1390, 1375; δ 0.88, 1.02, 1.32(each 3H, s). Since VI was very unstable in contact with air and the intramolecular aldol condensation was expected, it was treated with methanolic HCl to be transformed successfully into a tricyclic keto-alcohol (VII), $C_{15}H_{24}O_2$(M^+ 236); mp 63-64°; $[\alpha]_D$ -39.7°; ν 3450, 1695; δ 2.13(3H, s), 4.30(1H, q, J=6.5, 3.5). VII was then oxidized with Jones reagent to give a cyclopentanone derivative (VIII), $C_{15}H_{22}O_2$(M^+ 234.159); mp 53-54°; ν 1745, which contained only one AB-type methylene group, ν 1415; δ 2.17, 2.28(each 1H, d, J=13.0), as the active hydrogens adjacent to the carbonyl group. Thus, it is certain that the cyclopentanone ring in this derivative contains a  $-\overset{|}{\underset{|}{C}}-\underset{\underset{O}{\|}}{C}-CH_2-\overset{|}{\underset{|}{C}}-$ system, and that $C_{(1)}$ and $C_{(7)}$ in α-pompene, which correspond to allyl and homoallyl positions, should be tertiary and quarternary carbons.

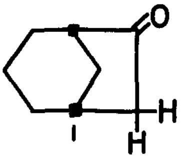
VI was also treated in turn with Jones reagent, diazomethane, trifluoro peracetic acid, potassium hydroxyde and again Jones reagent to be converted into keto-acid (IX), $C_{15}H_{24}O_3$(M^+ 252.170); mp 110-111°; ν 3500-2500, 1715; δ 2.15(3H, s), 2.31(2H, s), 2.70(1H, q, J=12.0, 6.5), 8.57(1H, br. s), keto-ester (X), $C_{16}H_{26}O_3$(M^+ 266); ν 1740, 1705; δ 2.09(3H, s), 2.22(2H, s), 2.63(1H, q, J=12.0, 6.0), 3.60(3H, s), diester (XI), $C_{16}H_{26}O_4$(M^+ 282); $[\alpha]_D$ +5.5°; ν 1740; δ 2.00(3H, s), 2.25(2H, s), 3.61(3H, s), 4.90(1H, q, J=11.0, 7.0), hydroxy-acid (XII), $C_{13}H_{22}O_3$(M^+ 226); mp 124-125°; ν 3500-2500, 3400, 1710; δ 2.25(2H, s), 3.92(1H, q, J=11.0, 7.0), 5.77(1H, s), 6.93(1H, s), and last bisnor-keto-acid (XIII), $C_{13}H_{20}O_3$(M^+ 224.144); mp 109-110°; $[\alpha]_D$ -10.3°; ν 1745.

XIII thus obtained had three substituents, a geminal dimethyl and tertiary methyl group, ν 1395, 1385, 1375; δ 1.00, 1.06, 1.10(each 3H, s) and a tertiary carboxy methyl group (■-CH_2-CO_2H), ν 3500-2500, 1715, 1420; δ 2.48(2H, s), 8.40 (1H, br. s), and contained only one methylene group adjacent to a quarternary carbon atom, ν 1420, δ 2.25, 2.78(each 1H, AB type q, J=18.0), as the active hydrogens.

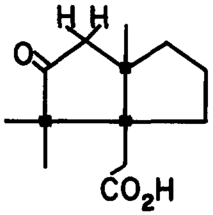




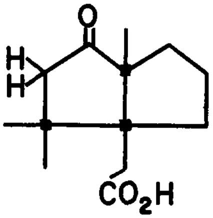
(A)



(B)



(XIII')



(XIII")

On the basis of the molecular formula and the spectroscopic evidences the gross structure of bisnor-keto-acid should be represented as substituted bicyclo[3.3.0]octanone (A) or bicyclo[3.2.1]octanone (B). However, the bicyclo[3.2.1]octanone system (B) was excluded from the following reason: if it has the formyl methyl group on $C_{(1)}$ as the indication of the above evidences, the formation of the tricyclic keto-alcohol (VII) which was obtained in the intramolecular aldol condensation of keto-aldehyde (VI) may be sterically impossible, because the position is a bridge head. Thus, it was certain that the bisnor-keto-acid has the bicyclo[3.3.0]octanone system (A). For the system, three isomers, (XIII), (XIII') and (XIII") are possible depending upon relative positions of the three substituents.

Now, the mass spectrum of keto-acid (XIII) showed characteristic ions at m/e 128.049(23 %: $C_6H_8O_3$) and m/e 96.095(base: C_7H_{12}), and that of diketone (VIII) the base ion at m/e 138.068($C_8H_{10}O_2$). The formation of these ions are explained only by structure (XIII) and its corresponding one (VIII).

Accordingly, the structure of α-pompene, isolated from <u>Bazzania pompeana</u>, was elucidated as 2,2,3,10-tetramethyl-tricyclo$[5.3.1.0^{3,7}]$undec-9-ene (I).

References

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