

TERPENOID. XXVIII. ACORANE TYPE SESQUITERPENOID FROM JUNIPERUS RIGIDA AND  
HYPOTHESIS FOR THE FORMATION OF NEW TRICARBOCYCLIC SESQUITERPENOID

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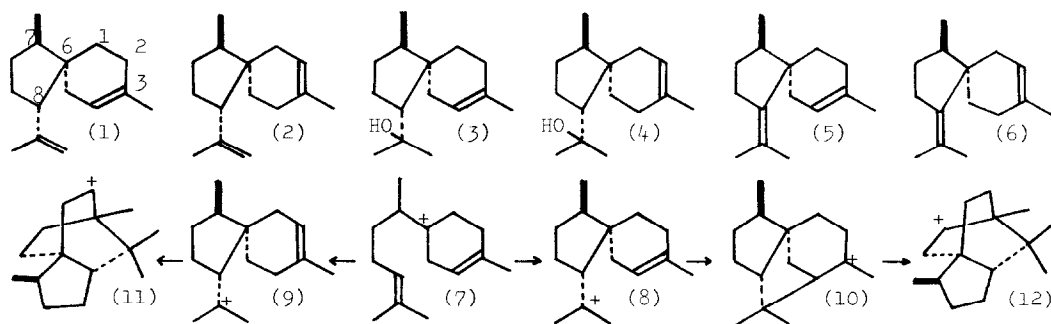
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In the preceding papers,<sup>1-2)</sup> we have reported on the stereostructures of acoradiene (1) and acorenol (3) isolated from the wood of Juniperus rigida and their transformation into (-)- $\alpha$ -cedrene. In this paper we wish to propose the revision of the name from acoradiene and acorenol to  $\alpha$ -acoradiene<sup>3)</sup> and  $\alpha$ -acorenol, respectively, and describe in continuation the structures of further isolated acorane-type sesquiterpenes;  $\beta$ -acoradiene,  $\beta$ -acorenol,  $\gamma$ -acoradiene, and  $\delta$ -acoradiene.

$\beta$ -Acoradiene(2) A new hydrocarbon,  $C_{15}H_{24}$ ,  $m/e$   $M^+$  204,  $[\alpha]_D +23^\circ$ , had a terminal double bond;  $\nu_{\max}^{liquid}$  1640 and 890  $cm^{-1}$ ;  $\delta$ (100 MC,  $CCl_4$ ) 4.60, 4.75(each 1H, br s), a tri-substituted double bond; 805  $cm^{-1}$ ;  $\delta$  5.25(1H, m), a secondary methyl group;  $\delta$  0.87(3H, d,  $J=7$  cps), and two allylic methyl groups;  $\delta$  1.60, 1.74(each 3H). On hydrogenation( $PtO_2/AcOH$ ) it gave a mixture of two tetrahydro derivatives,  $[\alpha]_D -58^\circ$ (mixture)<sup>4)</sup> both of which were identical with respective acoranes,  $[\alpha]_D -45^\circ$ (mixture)<sup>4)</sup> synthesized from  $\alpha$ -acoradiene by comparison of their IR spectra and Rts in GLC. From this result and its spectral similarity to  $\alpha$ -acoradiene the structure (2) is proposed for this hydrocarbon, named  $\beta$ -acoradiene in connection with formerly isolated  $\alpha$ -acoradiene.

$\beta$ -Acorenol(4) A new alcohol,  $C_{15}H_{26}O$ ,  $m/e$  ( $M-H_2O$ )<sup>+</sup> 204,  $[\alpha]_D \pm 0^\circ$ , shows the following spectral data;  $\nu_{\max}^{liquid}$  3400, 1130, 937 and 800  $cm^{-1}$ ;  $\delta$  0.86(3H, d,  $J=7$  cps), 1.24, 1.32(each 3H, s), 1.63(3H, br s), and 5.30(1H, m). Since dehydration of this alcohol with pyridine-modified alumina<sup>5)</sup> afforded a hydrocarbon identical with  $\beta$ -acoradiene in all respects, it must be represented by the structure (4) and named  $\beta$ -acorenol.

$\gamma$ -Acoradiene(5) and  $\delta$ -Acoradiene(6) Besides  $\alpha$ - and  $\beta$ -acoradiene two new acorane type hydrocarbons were also isolated: A)  $M^+$  204,  $[\alpha]_D -66^\circ$ ,  $\delta$  0.90(3H, d,  $J=7$  cps), 1.62(3H, s), 1.67(6H, br s), 5.27(1H, m); B)  $M^+$  204,  $[\alpha]_D +15.5^\circ$ ,  $\delta$  0.86(3H, d,  $J=7$  cps), 1.62(6H, br s), 1.72(3H, br s), 5.35(1H, m). On catalytic hydrogenation( $PtO_2/AcOH$ ) both A and B were stereo-selectively reduced to give the same tetrahydro derivative which was identified as one of acoranes from  $\alpha$ -acoradiene(IR, GLC). Thus above spectral data led



to the alternative structure (5) or (6) for A and B. Acid treatment of  $\alpha$ -acoradiene in EtOH-HCl(0.03N) at 90° for 2 hrs produced A (yield 3%) as one of by-products. On the other hand  $\beta$ -acoradiene afforded B (yield 36%) besides many other products on the same acid treatment. Therefore the trisubstituted double bond of A(named  $\gamma$ -acoradiene) is located at  $\Delta^3$  like  $\alpha$ -acoradiene and that of B( $\delta$ -acoradiene) at  $\Delta^2$  like  $\beta$ -acoradiene.

Probable biogenetic pathway Two kinds of tertiary cations, (8) and (9), can be formally derived from  $\gamma$ -bisabolene by protonation. Recently a biogenetic derivation of the cedrane cation (10) from cation (8) has been confirmed by the synthetic methods.<sup>2,6,7)</sup> Though it has been reported<sup>8)</sup> that the cation (12) can be formally derived by a Wagner-Meerwein rearrangement<sup>9)</sup> of the cedrane cation (10), our attempts to synthesize the cation (12) from the cedrane cation resulted in a failure. Now we wish to propose the formation of the cation (11) of the same tricyclic skeleton<sup>10)</sup> as (12) from the cation (9) produced from  $\beta$ -acoradiene and  $\beta$ -acorenol. As the cyclization of the tertiary cation to C<sub>2</sub> in (9) is sterically hindered, the cyclization to C<sub>3</sub> seems to be favorable and give the cation (11). The alcohol corresponding to the hydroxylation product of (11) has been already isolated from Juniperus rigida and Biota orientalis, and synthesized by acid catalyzed cyclization of  $\beta$ -acoradiene. These will be reported in forth-coming papers.

#### REFERENCES AND FOOTNOTES

- 1) B. Tomita, Y. Hirose and T. Nakatsuka, Mokuzai Gakkaishi **15**, 48(1969)
- 2) B. Tomita and Y. Hirose, Tetrahedron Letters **143**(1970)
- 3) Recent investigation has been revealed that initially isolated acoradiene,  $[\alpha]_D^{20}$ , involved  $\beta$ -acoradiene(30%) and pure  $\alpha$ -acoradiene has a higher value of  $[\alpha]_D^{20}$  -36.7°
- 4) The ratio (3:7) of mixture determined by GLC was similar to that (4:6) of two kinds of acoranes synthesized from  $\alpha$ -acoradiene.
- 5) E. Von Rudloff, Can. J. Chem. **39**, 1860(1961)
- 6) E. J. Corey, N. N. Girotra and C. T. Mathew, J. Am. Chem. Soc. **91**, 1557(1969)
- 7) T. G. Crandall and R. G. Lawton, J. Am. Chem. Soc. **91**, 2127(1969)
- 8) W. Parker, J. S. Roberts and R. Ramage, Quart. Rev. **21**, 331(1967)
- 9) Though this derivation was not sterically considered by Parker et al., such rearrangement from (10) would produce the cation (12) as postulated sterically.
- 10) We wish to propose the name "allo-cedrane" and widespread co-existences of this type sesquiterpenoids with cedrane type ones in nature are to be anticipated.