

TERPENOID. XXVI

ACORADIENE AND ACORENOL, KEY INTERMEDIATES OF CEDRANE GROUP SESQUITERPENOID,  
AND THEIR TRANSFORMATION INTO (-)- $\alpha$ -CEDRENE

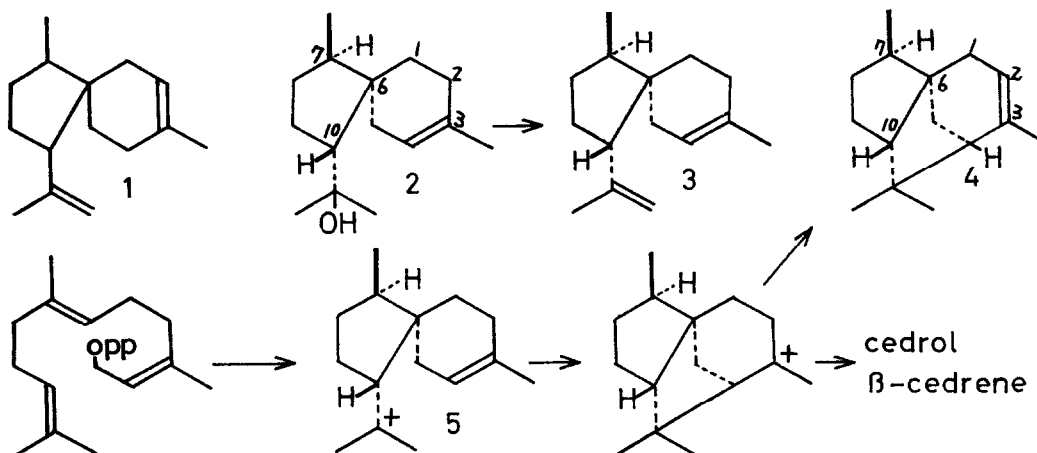
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In the preceeding papers, we have reported on the structure of acoradiene<sup>1)</sup>(1), as well as the analyses of sesquiterpenic constituents<sup>2)</sup> of the wood of Juniperus rigida, and described that the coexistence of acoradiene with cedrane-type sesquiterpenes in this wood is of importance from a biogenetic aspect. Acoradiene is considered to be produced from an ionic intermediate (5), which has been also considered as the precursor of cedrane-type sesquiterpenes.<sup>3)</sup> So the stereochemical relationship between these natural sesquiterpenes is a fascinating problem. Recently Corey and his co-workers<sup>4)</sup> and Crandall and Lawton<sup>5)</sup> have succeeded in synthesis of dl- $\alpha$ -cedrene from synthetic acorane-type alcohols by acid treatment. In this paper we wish to propose the name of acorenol for a new acorane-type alcohol<sup>6)</sup> isolated from the essential oil of this wood in our further investigation, and describe the transformation of these two acorane-type compounds into (-)- $\alpha$ -cedrene by acid treatment, that has spontaneously elucidated their absolute stereostructures.

Acoradiene The structure (1) was proposed for acoradiene excluding the stereochemistry by our preliminary investigation,<sup>1)</sup> and its identity with acorene<sup>7)</sup> from Juniperus virginiana was strongly suggested, since it has been reported that the IR spectrum of the catalytic reduction product of acorene was in agreement with the published spectrum<sup>8)</sup> for acorane like that of tetrahydro-acoradiene.<sup>1)</sup> Acid treatment of acoradiene in ethanolic hydrochloric acid (pH 1.2) at 50-60° for 2 hrs produced a new hydrocarbon,  $[\alpha]_D - 80^\circ$ , in a yield of above 80 %, which was identified as  $\alpha$ -cedrene (4) by comparison of its IR, NMR spectra and Rt in GLC with those of the authentic sample. The  $[\alpha]_D$  value of this hydrocarbon was in good accordance with that of natural  $\alpha$ -cedrene,  $[\alpha]_D - 91^\circ$ , of known absolute configuration, thus confirming that acoradiene has the same configuration at C-7 and C-10 as that of  $\alpha$ -cedrene. As to the configuration of spirane skeleton at C-6 it is matter whether the double bond in a six membered ring is located



at  $\Delta^2$  or  $\Delta^3$ . Ignoring the cationic attack at the allylic position in (5) as a matter of course, the double bond  $\Delta^2$  would give a diastereomer of  $\alpha$ -cedrene on acid treatment, that was not the case. Therefore the double bond in question and an isopropenyl group are situated face to face with each other to bring about the acid-catalyzed cyclization, and the absolute stereostructure (3) is proposed for acoradiene.

**Acorenol** A new alcohol, named acorenol,  $C_{15}H_{26}O$ ,  $[\alpha]_D - 36.1^\circ$ , shows the following spectral data; MS  $(M-H_2O)^+$  204, IR(liquid) 3400, 1155, 935 and  $800\text{ cm}^{-1}$ , NMR(100 MC,  $CCl_4$ )  $\delta$  0.87(3H, d,  $J=7$  cps), 1.17, 1.19(each 3H, s), 1.66(3H, br s) and 5.35(1H, br s). Dehydration of acorenol with pyridine-modified alumina<sup>9)</sup> gave a hydrocarbon, which was in all respects identical with acoradiene. This dehydration experiment and spectral data led to the structure (2) for this new alcohol exclusively. On treatment with formic acid acorenol did not produce acoradiene but (-)- $\alpha$ -cedrene in a above 90 % yield like the isomerization of acoradiene to (-)- $\alpha$ -cedrene.

#### REFERENCES AND FOOTNOTES

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