

TWO NEW DITERPENOID OXIDES FROM  
THE LEAF OIL OF CHAMAECYPARIS NOOTKATENSIS\*

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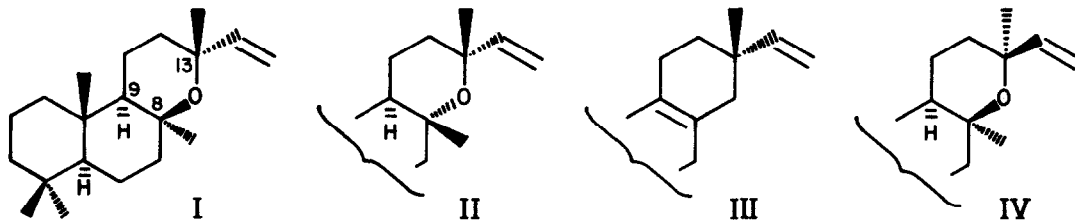
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8-Epimanoyl oxide (I),  $C_{20}H_{34}O$ , m.p. 44-5°,  $[\alpha]_D^{23} -9.5^\circ$  (c, 2.1;  $CHCl_3$ ), was obtained in 1% yield from the volatile leaf oil of Alaska (yellow) cedar (1). The ir and pmr ( $CCl_4$  solution, TMS reference) spectra showed a vinyl group ( $\nu_{Max}^{KBr}$  3080, 1825, 1625, 985, 905  $cm^{-1}$ ;  $\delta$  5.62, quartet, 1H,  $J=10.5, 17.5$  Hz;  $\delta$  4.75, 2H, two doublets,  $J=10.5, 17.5, 1.5$  Hz), confirmed by catalytic hydrogenation to the dihydroderivative, and five tertiary methyl groups, two of which are adjacent to an oxide function (2,3) ( $\delta$  1.25, 1.19, 0.97, singlets of 3H each;  $\delta$  0.86, singlet, 6H;  $\nu_{Max}^{KBr}$  1385, 1367  $cm^{-1}$  and 1150, 1130  $cm^{-1}$ ). The oxide ring was not opened by alkali metals (Li, Na) in liquid ammonia (4), lithium aluminum hydride, permanganate, or chromic acid; vigorous oxidation conditions gave intractable mixtures. Vioque (5) reported that Amberlyst XN-1005 resin (6) opens epoxides stereospecifically to give diols. When manoyl oxide (II) was treated with the freshly prepared resin (hexane solution, 1 hr, 25°) isopimara-8,15-diene (III) was the main product; no sclareol was detected. Thus, this reaction follows the typical acid-catalyzed pathway without affecting the configuration at  $C_{13}$  (7). 8-Epimanoyl oxide also gave isopimara-8,15-diene (75%), showing that it too has a labdane skeleton, an  $\alpha C_{13}$  vinyl group and that it can differ from manoyl oxide only in the configuration of the oxide ring. Of the four theoretically possible labdane isomers having the  $\alpha C_{13}$  vinyl configuration, only (I)

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is in agreement with the experimental data. The proximity of the oxide bridge and the C<sub>10</sub> methyl group results in the same chemical shift of the C<sub>10</sub> methyl signal ( $\delta$  0.97) as in 13(R)-8 $\beta$ ,13-oxido-20-hydroxy-labd-14-ene (8), the C<sub>8</sub> methyl group is in a favorable position for ring closure in the reaction with Amberlyst resin, and the C<sub>8</sub>, C<sub>10</sub> and C<sub>13</sub> methyl groups shield the oxide bridge against attack by ether cleaving reagents.



8,13-Diepimanoyl oxide (IV) was present in this leaf oil in trace amounts only: m.p. 79-84°,  $[\alpha]_D^{23} +23.4^\circ$  (c, 0.6; CHCl<sub>3</sub>). The spectral properties suggest it is the C<sub>13</sub> epimer of 8-epimanoyl oxide;  $\delta$  5.98, quartet, 1H, J=11, 18 Hz;  $\delta$  5.06, 2 doublets, 2H, J=11, 18, 1.5 Hz ( $\geq$ CH=CH<sub>2</sub>)  $\delta$  1.23 and 1.10, singlets, 3H each;  $\delta$  0.91, 0.89, 0.85, singlets, 3H each. Treatment of oxide IV and 13-epimanoyl oxide with Amberlyst XN 1005 resin gave pimara-8,15-diene in high yield. This confirms a labdane skeleton with the  $\beta$ C<sub>13</sub> vinyl group. Employing the same reasoning as above one arrives at structure IV.

#### References

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