Absolute Configuration of Neolinderane, Pseudoneolinderane, and Linderadine

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IN a previous communication,[1] it was reported that neolinderane[2] (I) and two new ten-membered furan sesquiterpenes, pseudoneolinderane (II) and linderadine (III), were isolated from *Neolitsea aciculata* Koidz. We report here the absolute configuration of neolinderane (I), and the structures and absolute configurations of pseudoneolinderane (II) and linderadine (III).

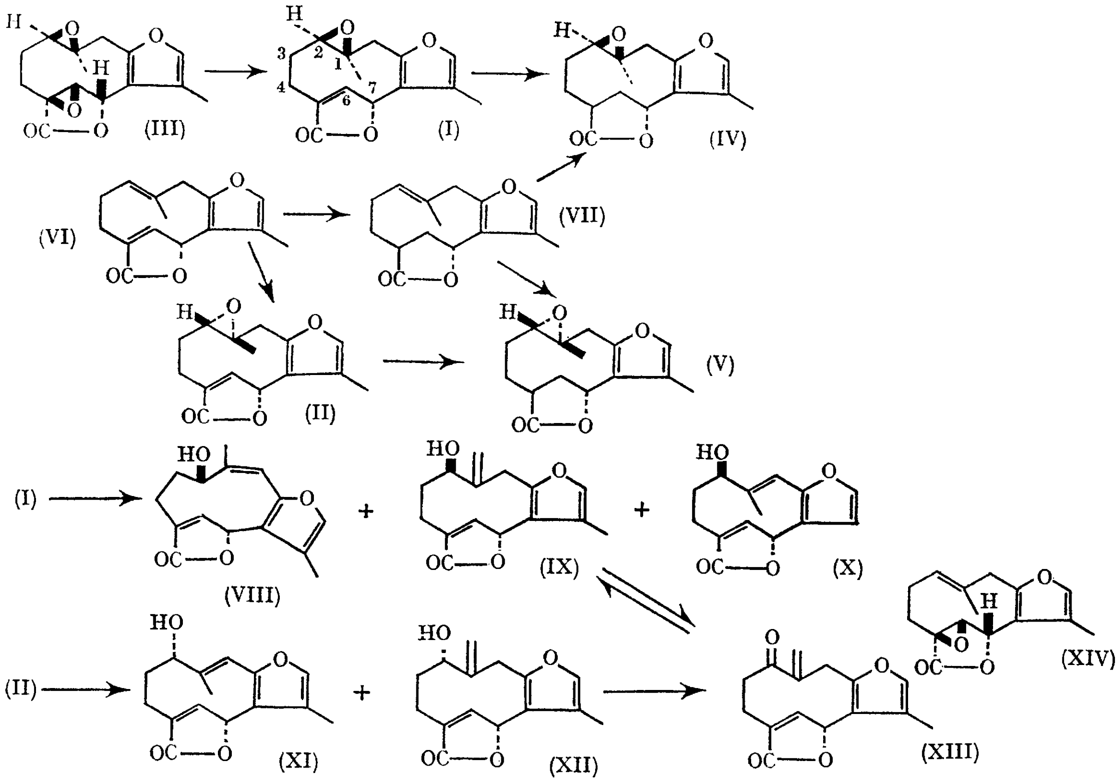
On hydrogenation with 10% palladised charcoal in ethanol and ethyl acetate, neolinderane, $C_{15}H_{16}O_4$, m.p. 182—183°, $[\alpha]_D$ $+32{\cdot}2°$, and pseudoneolinderane, $C_{15}H_{16}O_4$, m.p. 200—202°, $[\alpha]_D$ $+90{\cdot}3°$, gave the corresponding dihydro-derivatives, (IV), m.p. 225—227° and (V), m.p. 192—194°.

These compounds, (IV) and (V), were also obtained in a ratio of about 1 : 1·5 by treatment of dihydrolinderalactone[3] (VII) with *m*-chloroperbenzoic acid. Dihydrolinderalactone was obtained from linderalactone[3] (VI) and its absolute configuration has already been confirmed.[4] Treatment of linderalactone (VI) with the same reagent gave only pseudoneolinderane (II) in 65% yield.

From these results, neolinderane and pseudoneolinderane have the same absolute configuration as linderalactone, and are epoxides derived from the addition of oxygen to the ethylenic double bond at C-1–C-2 in linderalactone (VI); (VI) possesses a methyl at C-1 *trans* to a hydrogen at C-2.[4] However, (I) and (II) differ in the stereochemistry of the epoxy-ring.

In order to determine the stereochemistry of these epoxy-rings, neolinderane (I) and pseudoneolinderane (II) were treated with boron trifluoride in absolute methanol at room temperature. The former gave desacetylzeylanine[1,2] (VIII), (m.p. 230—231·5°) and its isomers (IX) (m.p. 156—157·5°, ν_{max} 3574, 1753, and 889 cm.$^{-1}$) and (X) [m.p. 178—179°, ν_{max} 3590, 1749, and 1660 cm.$^{-1}$,

λ_{sh} (EtOH) 240 mμ (ϵ 4600)] while the latter gave (XI) [m.p. 218—219°, ν_{max} 3581, 1753, and 1661 cm.$^{-1}$, λ_{sh} (EtOH) 239 mμ (ϵ 4500)] and (XII) (m.p. 182—183°, ν_{max} 3563, 1754, and 880 cm.$^{-1}$).



As the hydroxy-group of desacetylzeylanine (VIII) was found to be β-oriented,[1] compounds (IX) and (X) must also have a β-hydroxy-group: thus the epoxy-ring of neolinderane (I) should possess the β-configuration.

Hence the epoxy-ring of pseudoneolinderane has the opposite configuration. On oxidation with chromium trioxide in pyridine, compound (XII) gave an $\alpha\beta$-unsaturated ketone (XIII) [m.p. 178—180°, ν_{max} 1755 and 1683 cm.$^{-1}$, λ_{sh} (EtOH) 228 mμ (ϵ 10,000)] which was also obtained from compound (IX) in the same way: when this ketone (XIII) was reduced with sodium borohydride, it was converted into the alcohol (IX).

Therefore, compound (XII) has an α-hydroxy-group and the epoxy-ring of pseudoneolinderane (II) should possess the α-configuration.

Linderadine (III) ($C_{15}H_{16}O_5$, m.p. 130—132°, $[\alpha]_D$ $-68{\cdot}7°$) was converted into neolinderane (I) by the action of chromous acetate in acetic acid, and its n.m.r. in chloroform shows signals of the C-6 and C-7 protons at τ 6·00 and 4·60 as singlets. As these values are in good agreement with those of linderane[4] (XIV), the epoxy-ring between C-5 and C-6 is also assigned to the β-orientation and linderadine is represented by the formula (III).

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