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STUDIES ON THE ALKALOIDS OF PACHYSANDRA TERMINALIS SIEB. ET ZUCC. (7)(1). : STRUCTURE OF PACHYSANTERMINE-A, A NOVEL INTRAMOLECULAR ESTER ALKALOID.

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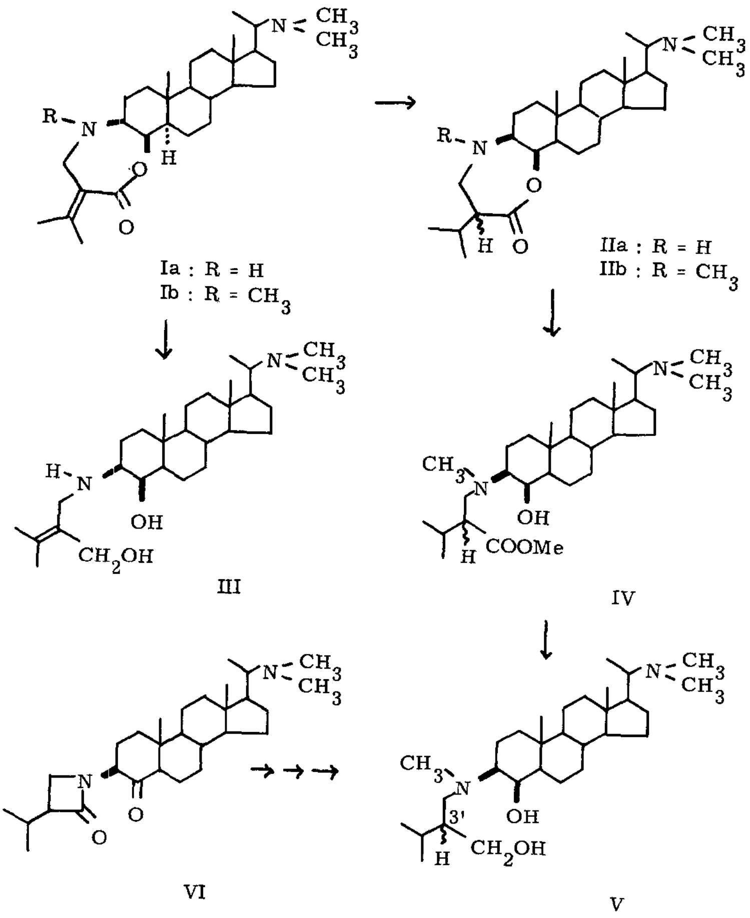
Pachysantermine - A, a minor alkaloid from the strong base fraction of Pachysandra terminalis SIEB. et ZUCC., was first reported as base XV in Part (3) of this series(2). As will be clear in the sequel, it represents a novel type of pregnane alkaloid carrying a seven-membered ring ester.

Pachysantermine - A (Ia), $C_{29}H_{48}O_2N_2$(3) (molecular ion peak at m/e 456 in the mass spectrum(4)), m.p. 260 - 263°(5), $[\alpha]_D + 43°$(6), showed IR $\nu_{max}^{CHCl_3}$ 1710 cm^{-1} (conjugated ester) and UV λ_{max}^{EtOH} ca. 210 mμ (ε 10,000) and NMR signals at 5.70 (1H, t., J 3 c.p.s., -C$\underline{H}$OCOR-), 6.48 (2H, m., NH-C$\underline{H}_2$-C=C-), 7.85 (6H, $N(CH_3)_2$, 8.18, 8.31 (6H, $(CH_3)_2C=C$), 8.96, 9.35 (6H, two tert. CH_3), and 9.15 τ (3H, d., J 6 c.p.s.; sec. CH_3).(7). Its ORD in methanol demonstrated a positive plane curve in the range of 300 - 700 mμ , suggesting that no carbonyl group is contained in the skeletal ring system.

Treatment of pachysantermine - A (Ia) with HCHO - HCOOH gave an N-methyl compound (Ib),$C_{30}H_{50}O_2N_2$, m.p. 258 - 261°, NMR signals: 7.62 (3H, NCH_3) and 7.85 τ(6H, $N(CH_3)_2$).



Ia : R = H
Ib : R = CH_3

IIa : R = H
IIb : R = CH_3

III

IV

VI

V

Upon hydrogenation of Ia over PtO_2 in AcOH - MeOH, there was obtained a dihydro compound (IIa), $C_{29}H_{50}O_2N_2$, m.p. 225 - 260°, $[\alpha]_D$ + 30° (in methanol), IR $\nu_{max}^{CHCl_3}$ 1720 cm^{-1} (saturated ester), which on N-methylation gave rise to an N-methyl-dihydro compound (IIb), m.p. 230 - 235°. Their NMR spectra were characterized by the disappearance of two allylic hydrogens (N-CH_2-$C{=}C$) and two allylic methyl signals and the appearance of new signals attributable to $(CH_3)_2CH$- grouping (6H, 9.03τ, d., J 7 c.p.s.).

Although Ia was not affected with $NaBH_4$, it was reduced with $LiAlH_4$ to give a diol (III), $C_{29}H_{52}O_2N_2$, m.p. 222 - 223°, $[\alpha]_D$ + 11°, whose NMR spectrum revealed the presence of a sec. alkohol (-C$\underline{H}$OH-, 6.27τ) and a prim. alkohol group ($C{=}C$-$C\underline{H}_2OH$, s., 5.73τ) in the molecule.

From these observations stated above, pachysantermine - A was believed to have a conjugated intramolecular ester grouping.

Base treatment of IIb led to an amino-acid, IR $\nu_{max}^{CHCl_3}$ 1590 cm^{-1}, which on subsequent methylation with diazomethane afforded a methyl ester (IV). This compound demonstrated ester bands at 1730 and 1165 cm^{-1} in its IR spectrum ($CHCl_3$), which is almost superimposable with that of IV obtained from pachystermine - A (VI).(1)

Upon reduction with $LiAlH_4$, the above methyl ester (IV) gave a diol (V), m.p. 170 - 172°, $[\alpha]_D$+ 36°. This was found to be identical by direct comparison (IR in KBr and mixed melting point) with the 3' -isodiol compound V derived from pachystermine - A (VI).(1)

On the basis of chemical evidences so far presented, the structure of pachysantermine - A could be represented by the formula Ia.

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REFERENCES

1. Part (6), T. Kikuchi and S. Uyeo, Tetrahedron Letters, in press.
2. T. Kikuchi, S. Uyeo, M. Ando, and A. Yamamoto, Tetrahedron Letters, 1817 (1964).
3. All the compounds with cited empirical formulas gave satisfactory elemental analyses.
4. Mass spectra were taken on a Hitachi Mass Spectrometer Model RMU-6D, using an all-glass inlet system.
5. All the melting points are uncorrected.
6. Optical rotations reported in this communication were measured in chloroform solutions at 10 - 30°C, unless otherwise specified.
7. All NMR spectra were taken in deuterated chloroform and chemical shifts are reported in τ values, using tetramethylsilane as the internal reference.