

OXIDATIVE REACTIONS OF BIOGENETIC INTEREST

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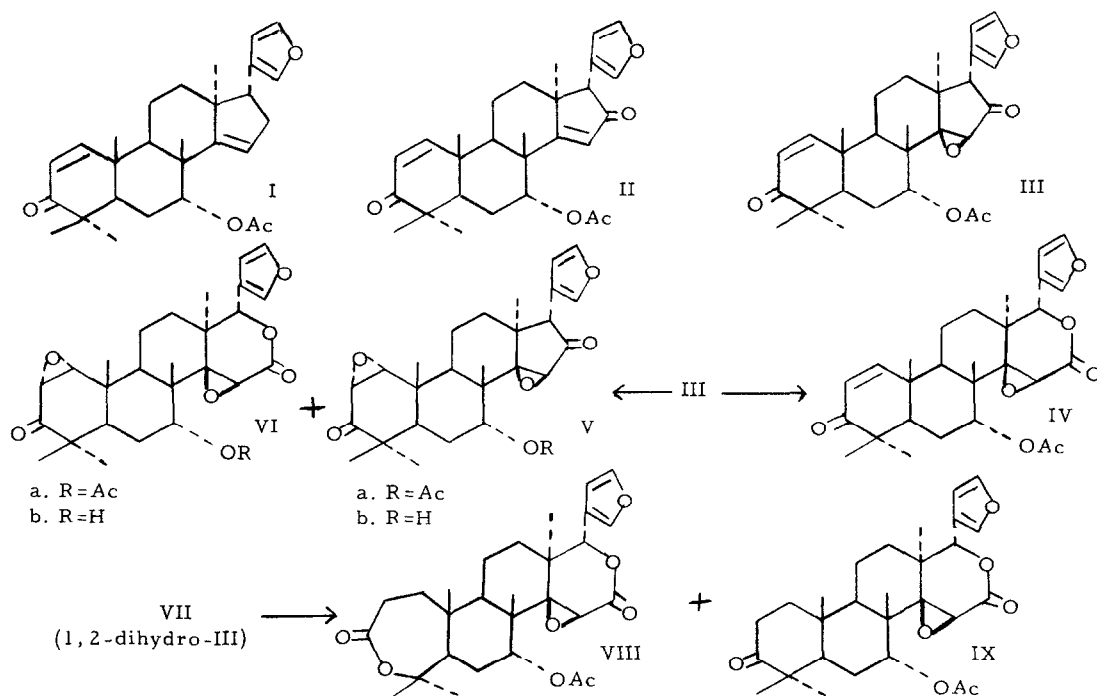
One of the outstanding processes of chemical degradation in nature is through stepwise oxidation. The isolation¹ from the seed oil of *Melia azadirachta* L. (Nim oil) of compounds in various oxidation stages such as azadirone (I), azadiradione (II), epoxyazadiradione (III) and gedunin (IV) supported the biogenetic pathway earlier proposed for limonin². These various steps of oxidation have been performed in the laboratory and lent support for the suggested natural sequence. The interconversion of I to II has been previously reported¹, while we now report the conversion of III to IV involving a Baeyer-Villiger oxidative cleavage of ring D. A recent publication³ along similar lines prompted us to report our results*.

Treatment of epoxyazadiradione (III) with perbenzoic acid at room temperature for 2 hrs gave gedunin⁴ (IV) (90% yield). However, upon treatment of III with 2N NaOH and H₂O₂ (30%) at 5° for 3 days, a mixture of four products was obtained. Chromatographic separation gave the following compounds identified as: 1 α ,2 α -epoxy-epoxyazadiradione (Va), m.p. 203-205°, C₂₈H₃₄O₇, [α]_D + 10° (c 0.1 CHCl₃), M⁺ 482, UV end absorption (at 217 nm ϵ 4500), ν_{\max}^{KBr} 1755 and 1700 cm⁻¹; 1 α ,2 α -epoxy-7 α -hydroxy-epoxyazadiradione (Vb), m.p. 284-286°, C₂₆H₃₂O₆, [α]_D + 15° (c 0.1 CHCl₃), M⁺ 440, UV end absorption (at 215 nm ϵ 5500); 1 α ,2 α -epoxy-gedunin⁴ (VIa) and 1 α ,2 α -epoxy-7 α -hydroxy-gedunin⁴ (VIb). These compounds were identified from their NMR, IR, UV spectra as well as by the fragmentation pattern of their mass spectra.

Oxidative degradation of ring A in the meliacin series leading to a seven membered ring lactone, as is the case in obacunone⁵ and nomilin⁶ type compounds, was observed on treatment of 1,2-dihydro-III (VII) with perbenzoic acid at room temperature for 9 hrs when two products were obtained; they were identified as 1,2-dihydro-7 α -obacunyl acetate (VIII), m.p. 197-199°, C₂₈H₃₆O₈, [α]_D + 2° (c 0.1 CHCl₃), UV end absorption (at 217 nm

* These results were reported in a series of lectures presented at the Institute Butantan, São Paulo, and the University of São Paulo, Brasil, in a National Symposium on Natural Products 10-28 June 1968.

ϵ 6000), $\nu_{\text{max}}^{\text{KBr}}$ 1770 cm^{-1} , and 1,2-dihydro-gedunin⁴ (IX). These two compounds were fully characterised from their NMR, IR, UV and mass spectral data.



We thereby present two oxidative degradation sequences involving both rings D and A. Such a process could also be applied for ring B cleavages leading to compounds such as andirobin⁷ and khayasin⁸.

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