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FERN CONSTITUENTS: DRYOCRASSOL AND DRYOCRASSYL ACETATE ISOLATED FROM THE LEAVES OF ASPIDIACEOUS FERN

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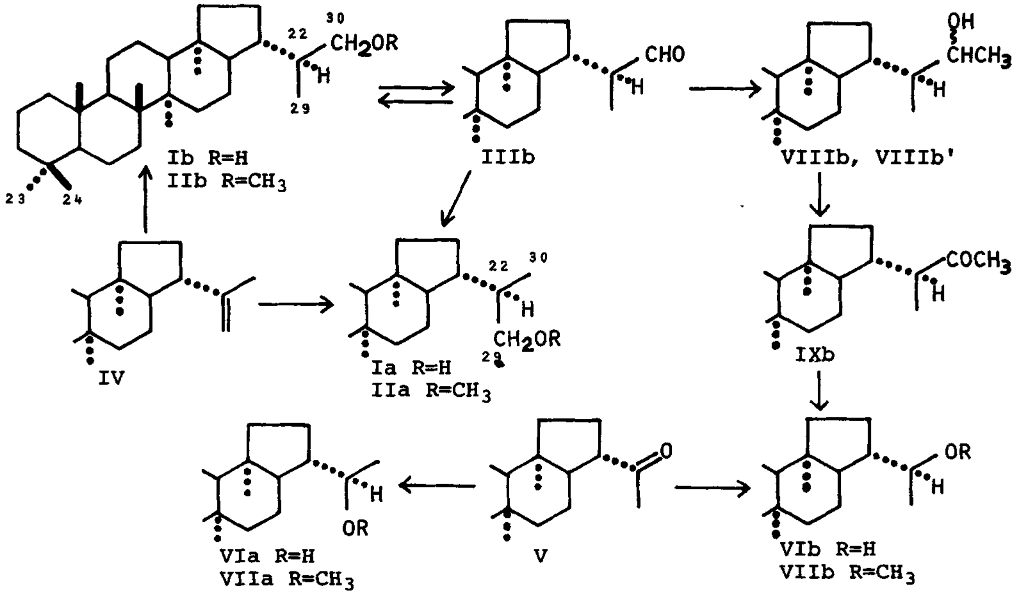
TWO hydrocarbons, hop-22(29)-ene and fern-9(11)-ene, have previously been reported from the leaves of *Dryopteris crassirhizoma* NAKAI (Oshida in Japanese) from our laboratory.[1] Further investigations on the triterpenoids from the same source afforded a new alcohol and its acetate, namely dryocrassol (Ib) and dryocrassyl acetate (IIb), along with 22-hydroxyhopane,[2] adiantone (V),[3] ferna-7,9(11)-diene, fern-9(11)-en-12-one,[1] and a β-sitosterol mixture. IIb has also been isolated from the leaves of *Arachniodes standisii* OHWI (Ryomenshida) and *Polystichum polyblepharum* PR. (Inode) as the main triterpenoid constituent.

Ib, $C_{30}H_{52}O$, m.p. 245-247°, $[\alpha]_D$ +68.0°, ν KBr cm^{-1} 3330, 1026, gave the acetate (IIb), m.p. 196-198°, $[\alpha]_D$ +58.0°, ν KBr cm^{-1} 1729, 1226. The PMR and MS of Ib [3H each at δ0.85(C-23), 0.79(24), 0.81(25), 0.96(26), 0.96(27), 0.73(28), 1.03d(J=6.5Hz. 29) and 2H at δ3.50m; m/e 428 (M^+ 5%), 413(2), 369(7), 207(100) and 191(64)] as well as of IIb strongly suggested Ib to be a triterpenoid of the hopane skeleton having a primary alcohol group on the side chain.

Chromic acid oxidation of Ib in pyridine gave an aldehyde (IIIb), m.p. 184-187°, $[\alpha]_D$ +60.0°, ν KBr cm^{-1} 2700, 1725, which was reduced into only Ib with $LiAlH_4$ and pure hopane,[4] m.p. 221-222°, by Wolff-Kishner method. Boiling of IIIb with 5%-KOH-methanol afforded unexpectedly a mixture of two alcohols, Ib and Ia, the latter of which, m.p. 242-244°, $[\alpha]_D$ +35.0° [acetate(IIa), m.p. 214-216°], was proved to be identical with neriifoliol[5] by comparison of m.p.s, IR and TLC characters with those of authentic sample. Hydroboration of hop-22(29)-ene (IV) gave also a mixture (1:1) of Ia and Ib. In consequence, either Ia or Ib should be hopane-29(or 30)-ol having a epimeric center at C-22.

By the way, $LiAlH_4$ reduction of adiantone (V) gave two isomeric alcohols, adiantol A (less polar)(VIa), m.p. 211-213°, $[\alpha]_D$ +40.0° [acetate (VIIa), m.p. 205-207°, $[\alpha]_D$ +35.0°] and adiantol B (more polar)(VIb), m.p. 252-256°, $[\alpha]_D$ +76.0° [acetate (VIIb), m.p. 222-224°, $[\alpha]_D$ +55.0°]. The absolute configuration at C-22 of the latter alcohol was proved to be 22*S* by X-ray analysis of the corresponding bromoacetate.[6] By Grignard reaction of IIIb with CH_3MgI there obtained a mixture (1:1) of two alcohols, VIIIb, m.p. 250-254°, ν KBr cm^{-1} 3430, 1127, and VIIIb', m.p. 255-258°, ν KBr cm^{-1} 3500, 1090. Chromic acid oxidation of VIIIb or VIIIb' in pyridine afforded the same methyl ketone (IXb), m.p. 239-242°, $[\alpha]_D$ +43.0°, ν KBr cm^{-1} 1713, which was oxidized with perbenzoic acid into an alcohol acetate as a sole product. The fact that the alcohol acetate was proved to be identical with adiantol B acetate (VIIb) established the configuration at C-22 of IXb, VIIIb, VIIIb', IIIb, Ib and IIb to be 22*S*, and of Ia and IIa to be 22*R* as shown as in



the chart. We would propose the numbering of side chain on the hopane skeleton so as neriifoliol (Ia) to be hopan-29-ol and dryocrassol (Ib) to be hopan-30-ol.

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