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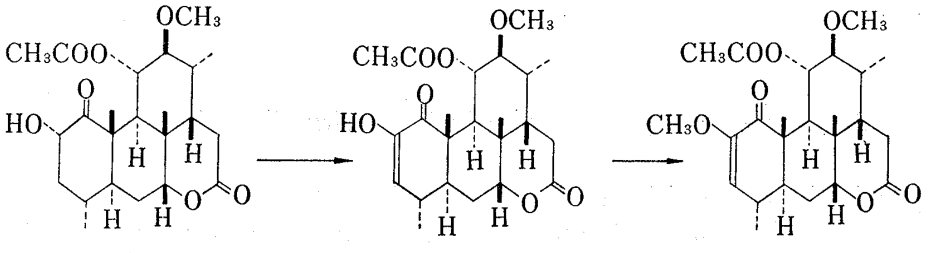
Stereostructure of Picrasin C, Simaroubolide of *Picrasma quassioides*

From the wood of the quassia tree, *Picrasma quassioides* Bennett (=*P. ailanthoides* Planchon) (Simaroubaceae), a number of bitter principles have recently been isolated, *i.e.* nigakilactone A, B, C,[1] E, F,[2] H, nigakihemiacetal A,[3] C,[4] quassin,[1] neoquassin[3] and picrasin A,[5] B,[6] D and E.[7] Further survey has led to the isolation of a new bitter for which the name picrasin C is given. In this communication, we wish to provide evidence that picrasin C is represented by formula I.



I II III

Picrasin C, mp 250—252°, has the composition $C_{23}H_{34}O_7$ (M^+ at m/e 422 in mass spectrum). Of the seven oxygen atoms, one is involved in a secondary hydroxyl next to a carbonyl (ν_{max} 3470 cm^{-1}, δ 4.68 ppm, formation of a monoacetate (mp 296—299°), consumption of periodate), two in an acetoxyl (ν_{max} 1720, 1247 cm^{-1}, δ 1.90, 5.22 ppm), two in a δ-lactone (ν_{max} 1727 cm^{-1}, δ 4.15 ppm, solution in aqueous alkali, no reaction with diazomethane), one in a saturated carbonyl in a six- or larger-membered ring (ν_{max} 1705 cm^{-1}, $[\theta]_{293}$ −2930) and one in a methoxyl (δ 3.40 ppm). Picrasin C contains two secondary methyls (δ 0.88, 1.03 ppm) and two tertiary methyls (δ 1.24, 1.27 ppm) other than the acetoxyl and methoxyl.

These functional groups along with the result of nuclear magnetic resonance (NMR) analysis have led us to conclude that picrasin C has the same structure as nigakilactone C (III)[1] except that the latter possesses the α-methoxy-α,β-unsaturated carbonyl and instead the former contains the α-hydroxy-saturated carbonyl. In confirmation, picrasin C was oxidized with bismuth trioxide to give the diosphenol (II) which on methylation with diazomethane afforded nigakilactone C (III).

These data established the structure of picrasin C together with the absolute configurations of all the asymmetric center except for C-2. The C-2 hydrogen signal occurring at 4.68 ppm in the NMR spectrum of picrasin C has the band width at half-height of 24 Hz demonstrating that it is axially situated (consequently α-oriented).

The stereostructure I is thus deduced for picrasin C.[8]

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[8] Immediately before the submission of this communication, there came to our attention that Prof. T. Takahashi and his co-workers, in their independent investigation, have also isolated the same substance and arrived at a similar conclusion about the structure as our own (T. Takahashi, private communication).

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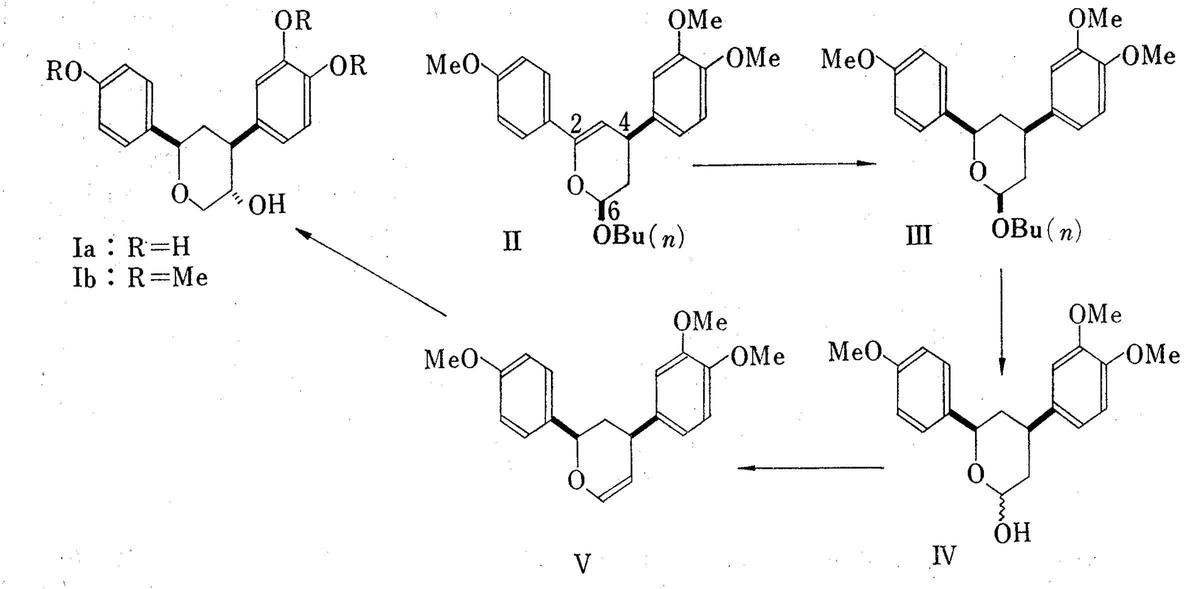
Synthesis of (±)-Hydroxysugiresinol (Sequirin B) Trimethyl Ether

Hydroxysugiresinol (Sequirin B) was isolated from the heart wood of *Cryptomeria japonica* D. Don[1] and *Sequoia sempervirens*.[2,3] Its structure was assigned as shown in Ia.[3,4] We report here the synthesis of (±)-hydroxysugiresionol (sequirin B) trimethyl ether (Ib), *via* a stereoselective route.

Diels–Alder reaction[5,6] of 3,4,4′-trimethoxychalcone with *n*-butoxyethylene at 180° gave the dihydropyran (II)[7] (83%), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1645. NMR (CCl_4) τ: 4.77 (1H, d, J=2.5 cps, C_3-H), 4.83 (1H, dd, J=2.5 and 7.5 cps, C_6-H), which was catalytically hydrogenated to the tetrahydropyran (III) (58%), NMR (CCl_4) τ: 5.46 (1H, dd, J=2.5 and 9 cps, C_2-H),



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