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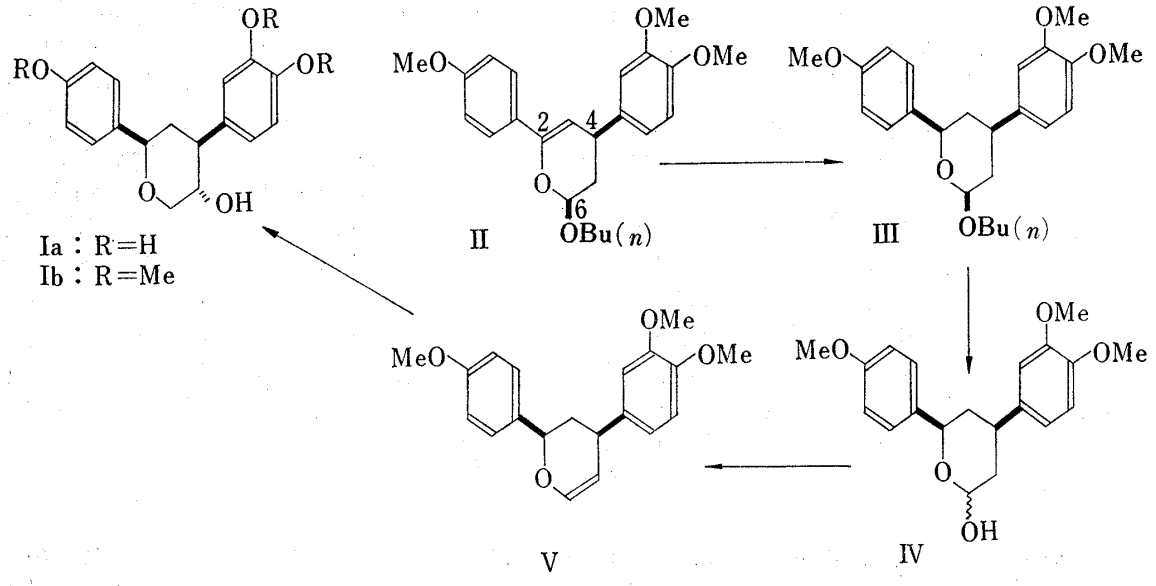
Synthesis of (±)-Hydroxysugiresinol (Sequirin B) Trimethyl Ether

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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5.62 (1H, dd, J=2.5 and 11 cps, C_6-H). Hydrolysis of III with 5% hydrochloric acid-acetone at room temperature gave the hemiacetal (IV) (60%), which was dehydrated by means of acetic anhydride in β-picoline at 170°, to give the dihydropyran (V) (46%), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1640, NMR ($CDCl_3$) τ: 3.33 (1H, dd, J=2.5 and 6 cps, C_6-H), 5.03 (1H, dd, J=3 and 11.5 cps, C_2-H). Hydroboration[6] of V in tetrahydrofuran at 0°, followed by oxidation with 30% hydrogen peroxide in alkaline solution gave (±)-Ib (38%), mp 137.5—139°, which was identical with an authentic sample, prepared from natural product.

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