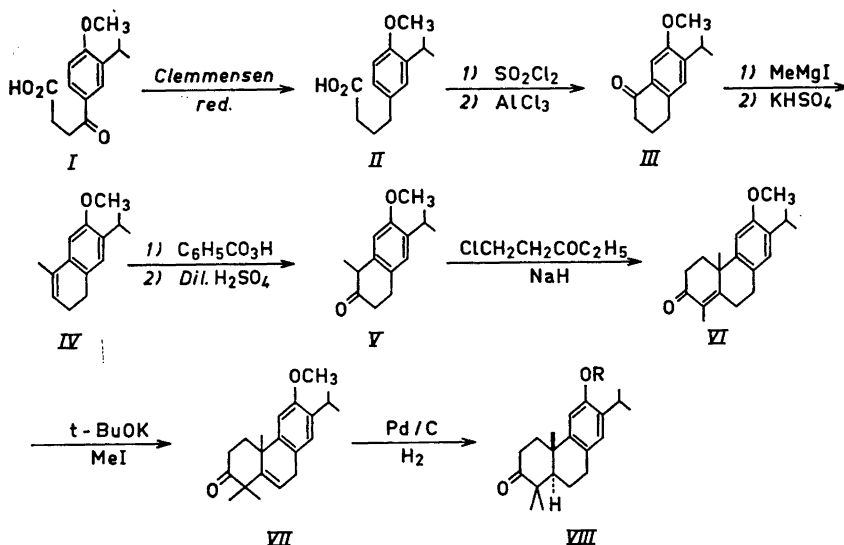


## The Synthesis of DL-Hinokione Methyl Ether

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Hinokione has been isolated from the heartwood of several conifers<sup>1</sup> and its structure has recently been shown to be VIII (R = H)<sup>1</sup>. A synthesis of the DL-form of hinokione methyl ether (R = CH<sub>3</sub>) has been carried out as indicated in the following scheme:



Succinoylation of 2-isopropylphenol methyl ether gave the keto-acid I, m.p. 133–135°, which furnished a deep red 2,4-dinitrophenylhydrazone, m.p. 85–88°. The keto-acid was reduced by Clemmensen's method to the acid II, m.p. 31–34°. The corresponding acid chloride when treated with aluminium chloride furnished the α-tetralone III, b.p. 136–138°/1 mm, λ<sub>max</sub> 263 mμ (ε, 12 700) and 225 (19 700), ν<sub>co</sub> 1 675 cm<sup>-1</sup> (film), further characterised as the deep red dinitrophenylhydrazone, m.p. 198–200°. The α-tetralone III reacted with methyl magnesium iodide giving a product that on treatment with potassium hydrogen sulphate underwent dehydration

to yield the dihydronaphthalene IV, b.p. 101–104°/0.3 mm. IV was epoxidised with perbenzoic acid and the product isomerised<sup>2</sup> with dilute sulphuric acid to the β-tetralone V, b.p. 111–116°/0.1 mm, ν<sub>co</sub> 1 715 cm<sup>-1</sup> (film) which gave a crystalline semicarbazone, m.p. 184–187°.

The β-tetralone V was condensed with β-chlorodiethyl ketone in the presence of sodium hydride<sup>2</sup> to give the α,β-unsaturated ketone VI, m.p. 92–94°, ν<sub>co</sub> 1 665 and ν<sub>c=c</sub> 1 623 cm<sup>-1</sup>, λ<sub>max</sub> 287 mμ (ε 4 160), 279 (4 720), 230 (16 000) and 247 (17 100), giving a red 2,4-dinitrophenylhydrazone, m.p. 225–228°. Methylation of VI with

methyl iodide and potassium *t*-butoxide led to the ketone VII, m.p. 92–94°, ν<sub>co</sub> 1 712 and ν<sub>c=c</sub> 1 668 cm<sup>-1</sup>, (2,4-dinitrophenylhydrazone, m.p. 212–214°), which was hydrogenated in ethanol in the presence of Pd/C to DL-hinokione methyl ether VIII (R = CH<sub>3</sub>), m.p. 119–121°, (2,4-dinitrophenylhydrazone, m.p. 215–218°). The I.R. spectra of the synthetic and the natural hinokione methyl ether (in carbon tetrachloride) were superimposable.

The U.V. spectra were taken in 95% ethanol solution and the I.R. spectra in carbon tetrachloride unless otherwise specified. Satisfactory analyses were obtained for all the compounds described.

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