Constitution of Sequirin-D (*Sequoia sempervirens*), a Novel Dihydronaphthalene Norlignan

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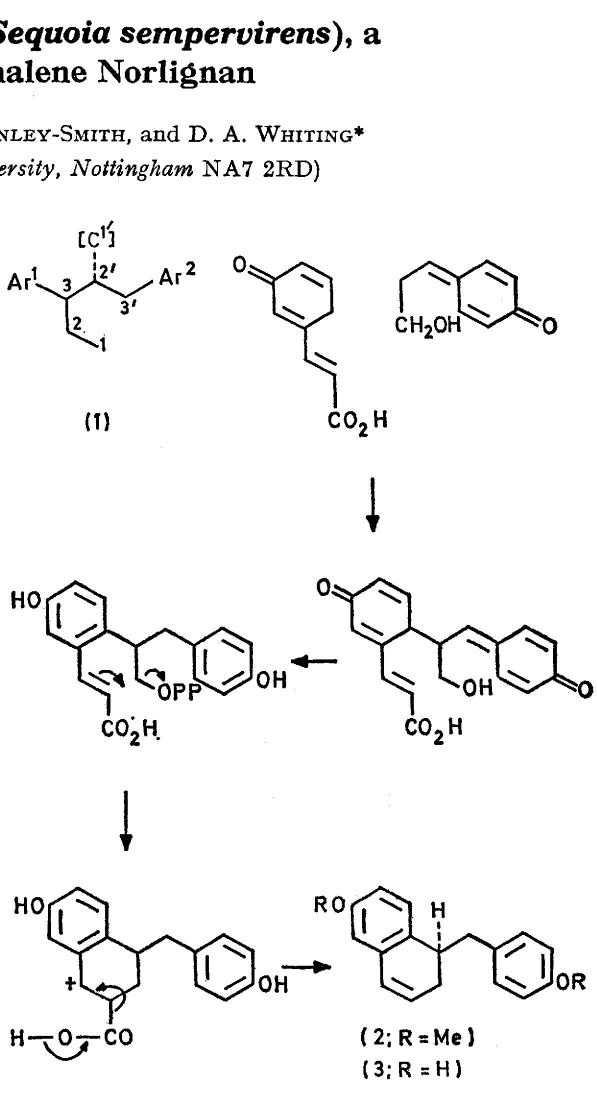
Summary *Sequoia sempervirens* contains a new norlignan with a novel skeleton; the constitution is demonstrated by *X*-ray analysis of its methyl ether (**2**) using direct methods, and the absolute configuration deduced from chiroptical data.

Natural lignans[1] are considered to arise through oxidative coupling of the 2- and 2′-carbons of phenolic cinnamate units. In contrast, the biosynthesis of known norlignans, with the basic structure (**1**) *e.g.* sequirins A—C[2] (*Sequoia sempervirens*) appears to involve 2′–3 linkage of cinnamates with one carbon loss. A different mode of formation now appears in a new norlignan metabolite (Sequirin-D) of *S. sempervirens*, whose novel (dihydronaphthalene) structure we now report.

The phenolic extractive gave a diethyl ether, and a dimethyl ether (**2**), m.p. 107·5—109°, $C_{19}H_{20}O_2$, crystallising in space group $P2_1$ with unit cell dimensions $a = 10{\cdot}43$, $b = 5{\cdot}44$, $c = 14{\cdot}05$ Å, and $\beta = 105{\cdot}64°$, and $Z = 2$. Intensity data were collected with Cu-K_α radiation using an automatic four-circle diffractometer, and 1622 reflections were considered observed. The structure was solved by direct methods using the Multan program[3] and refined by block-diagonal least-squares to a current R index 12·6%.

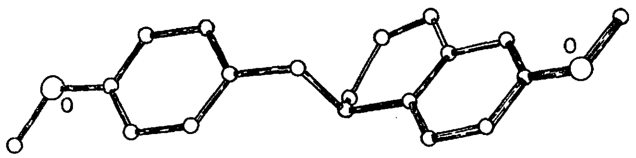
Sequirin-D methyl ether (**2**) displays a strong positive Cotton effect (246—266 nm, $a = +56$) which, on comparison with model skewed styrenes[4] indicates a chromophore twisted in the left hand sense. Since the *p*-methoxybenzyl substituent adopts the axial orientation (Figure) the absolute configuration shown (**2** and **3**) is inferred. The measured dihedral angle between the double bond and the ring, in the chromophore, is 13°.

Biosynthesis of sequirin-D (**3**) may, as illustrated, involve



(1)

(2; R = Me)
(3; R = H)



Figure

oxidative coupling of *m*-hydroxycinnamic acid with a *p*-hydroxycinnamyl alcohol. Ring closure ensues, by electrophilic addition to the α-unsaturated acid with subsequent decarboxylation; precedent[5] can be found for such addition.

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