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# THE CHEMISTRY OF THE ORDER ARAUCARIALES 6[1]. ABSOLUTE CONFIGURATIONS OF AGATHARESINOL HINOKIRESINOL AND SUGIRESINOL

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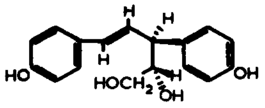
Agatharesinol (1), hinokiresinol (2) and sugiresinol (3) form a set of related compounds representing a new type of plant phenol. The present paper describes evidence showing that they have the absolute configurations given in formulae 1, 2 and 3.



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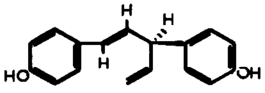

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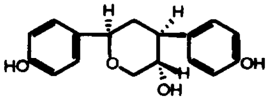

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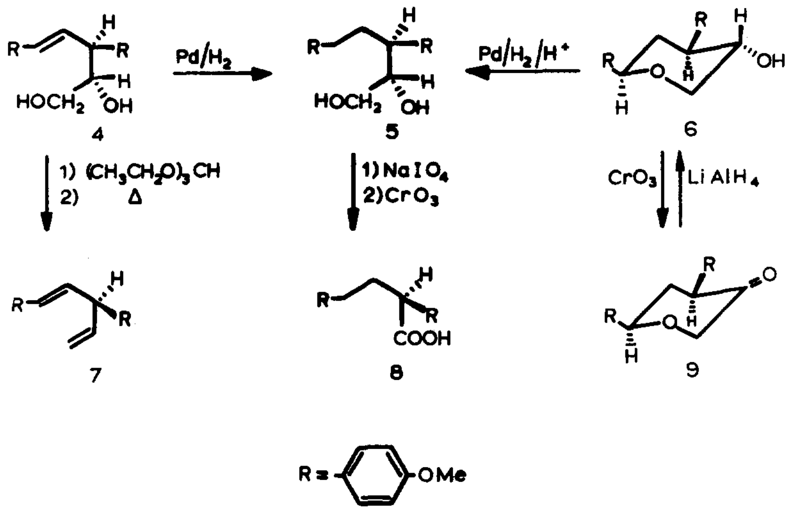
Although these diphenylpentane-type phenols were isolated only recently it already appears that this type of compound is of widespread occurrence in conifers. Agatharesinol[2] is present in relatively large amounts in the heartwood of Agathis australis. Hinokiresinol is found in the wood of Chamaecyparis obtusa (hinoki)[3] and in Agathis australis. Sugiresinol is present in the wood of Cryptomeria japonica (sugi)[4] and in Agathis australis and Sequoia sempervirens[5].

These compounds seem usually to be present in a mixture of similar compounds apparently produced along the same biogenetic route[2]. During the present investigation two of the minor components in Agathis australis were identified as sugiresinol (m.p. 250-251°; the m.p. previously recorded[4] appears to be low) and hinokiresinol. The nmr spectrum of the Agathis material (see below) showed unequivocally that the first of these must have the structure assigned to sugiresinol and its identity was confirmed by m.p.s of the acetate and the dimethyl ether. The second component was identified as hinokiresinol by its nmr spectrum and Rf on a thin layer plate.

The structures of the three phenols follow both from nmr and mass spectra and are supported by chemical evidence. The only points remaining unsettled were the stereochemistry of sugiresinol and the absolute configurations of the three compounds.

In the present investigation, chemical evidence on the stereostructure and on the relationships between the three compounds was obtained by the transformations shown below. Agatharesinol dimethyl ether and sugiresinol dimethyl ether both yield dihydroagatharesinol dimethyl ether (5; $[\alpha]_D^{CHCl_3}$ +35°) demonstrating that these compounds have the same configuration at C(3) and C(4).

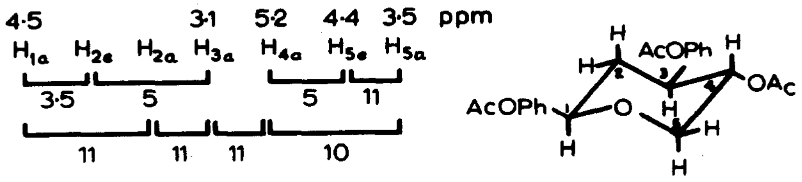
Hinokiresinol was shown to have the same configuration at C(3) as agatharesinol by conversion of the glycol grouping in agatharesinol to a double bond by the smooth and elegant procedure of Crank and Eastwood[6] using thermal decomposition of the acetal formed on heating with triethyl orthoformate. On the dimethyl ether this afforded hinokiresinol dimethyl ether (7) with the same rotatory dispersion curve as that of the natural compound. Conversion of hinokiresinol dimethyl ether to agatharesinol dimethyl ether was accomplished by formation of the dibromide, hydroxylation with performic acid and debromination, giving a dimethyl ether with infrared spectrum identical with that of agatharesinol dimethyl ether.



The pyran ring in sugiresinol has a chair conformation with both p-hydroxyphenyl substituents and the C(4) hydroxyl group in an equatorial configuration since sugiresinone dimethyl ether (9; m.p. 100-101°, $[\alpha]_D^{CHCl_3}$ +21°, prepared by oxidation with chromic acid in acetone) was recovered unchanged after treatment with base and was converted back to sugiresinol dimethyl ether (6; m.p. 104-105°, $[\alpha]_D^{CHCl_3}$ -4°) in 80 per cent yield on reduction with lithium hydridoaluminate. Equilibration at C(3) would allow the C(1) and C(3) substituents to take up a cis, diequatorial relationship on a chair form ring and thus the relative configuration of the three asymmetric centres is that shown in structure 3.

Analysis of the nmr spectrum of sugiresinol triacetate with the aid of double resonance scans gives the succession of couplings along the aliphatic chain of the molecule shown below (Fig. 1). Since sugiresinol is in the most stable configuration these coupling constants also show the relative configuration of the asymmetric centres.

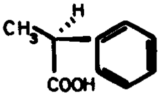
FIG. 1. Nmr spectrum of sugiresinol triacetate



The absolute configurations of the three naturally occurring compounds were shown to be those given in structures 1-3 by a positive difference between the molecular rotation of sugiresinol dimethyl ether (6) and that of the corresponding p-nitrobenzoate ($\Delta M = M_{CH} - M_{PNB} = +560°$) (cf. ref. 7) and by the rotatory dispersion curves of sugiresinone dimethyl ether (9) and of the nor-acid (8).

Sugiresinone dimethyl ether showed a positive lowamplitude Cotton effect for the carbonyl n-$\pi^*$ transition (330-300 nm, a = +8, MeOH), in accord with an equatorial phenyl group in the absolute configuration shown in structure 9 (*cf*. ref. 8). The Cotton effect at lower wavelengths (280-250 nm, a = -8, MeOH) associated with the aromatic rings gave no further useful information.

The acid 8 (m.p. 59-61°), obtained from dihydroagatharesinol dimethyl ether (5) by successive oxidation with periodate and chromic acid in acetone, showed a positive Cotton effect in the carboxylic acid region (235-218 nm, a = +250, MeOH), analogous to that of S-(+)-hydratropic acid[9] (10; 230-208 nm, a = +320 ! MeOH)[10]. This shows, in agreement with the



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other results, that the three naturally occurring diphenylpentane-type phenols isolated so far have the absolute stereostructures 1-3 with, as expected, the same configuration at C(3) in each case.

All new compounds gave satisfactory analyses or mass spectrometric molecular weights.

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