

The Structure of Salviol, a New Phenolic Diterpene

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Summary Salviol, a new diterpenoid phenol, has been isolated from *Salvia miltiorrhiza* Bunge, and the structure determined on the basis of physical and chemical properties.

In previous communications^{1,2} we reported the structures of diterpenoid quinones, tanshinones, isolated from the roots of *Salvia miltiorrhiza* Bunge. In addition to these pigments, a colourless substance, salviol (I), C₂₀H₃₀O₂, m.p. 108° (benzene), M⁺ 302.227 (calc. 302.225), was isolated; we now report the structure of salviol.

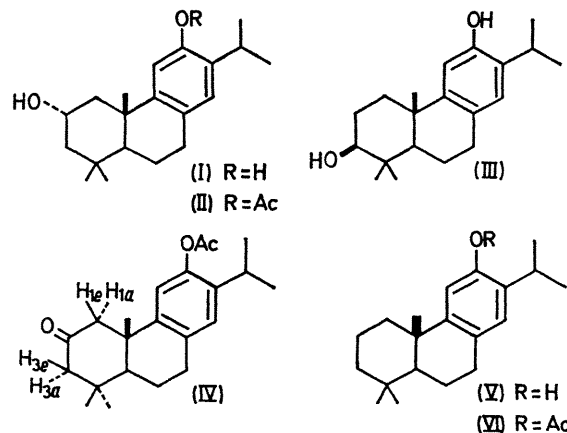
The i.r. spectrum (KBr) of (I), 3400br, 1620, and 1505 cm⁻¹, showed the presence of a phenol group, supported by the u.v. (EtOH) absorption maxima at 220sh (log ε 3.93) and 283 nm (3.62), as well as those shown at 213, 292, and 305sh nm in an EtOH-1N-KOH solution.

The n.m.r. spectrum (100 MHz) of salviol was similar to that of ferruginol derivatives³ and had signals at δ (CDCl₃)

0.95 and 0.99 (Me₂C<), 1.23 (Me-C-), 1.22 (d, J 7 Hz,

Me₂CH), 3.15 (sept., J 7 Hz, Me₂CH), 2.8 (br t, -CH₂-Ar), 6.78 (s, ArH), and 6.83 (s, ArH). The mass spectrum of (I) is very similar to that of hinokiol (III)⁴ except for the relative intensity, and shows the peaks at m/e 302 (M⁺), 287 (M⁺ - CH₃), and 269 (M⁺ - CH₃ - H₂O). The almost identical spectral pattern in the lower mass range of salviol and hinokiol suggests a close structural relationship between the two compounds. However, the i.r. spectrum and R_F value of salviol on t.l.c. were quite different from those of an authentic sample of hinokiol (III). The mass spectral analysis will be discussed in detail elsewhere.

One proton signal at δ 4.09 (d of t, J 3, 11 Hz, ω₁ 21 Hz) of salviol shows the presence of a secondary alcohol group bearing the two methylene groups in the structure, the coupling constant and half-width of which can be accounted for in terms of the axial proton at C-2. From these physical properties, the structure of salviol was deduced to be 2α-hydroxyferruginol (I). The position of the hydroxy-group and the carbon skeleton were confirmed by the conversion of salviol into ferruginol.



Salviol gave a monoacetate (II), ν_{max} (CHCl₃) 3450 and 1760 cm⁻¹, which afforded with CrO₃-C₅H₅N the keto-acetate (IV), ν_{max} (KBr) 1760 and 1710 cm⁻¹. The n.m.r.

spectrum (220 MHz) showed the presence of the $-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{H}}{\text{C}}-\text{CH}_2-$ group; δ 2.27 (dd, J 14, 2 Hz, H_{3e}), 2.33 (d, J 14 Hz, H_{3a}), 2.56 (d, J 12.5 Hz, H_{1a}), 2.84 (dd, J 12.5, 2 Hz, H_{1e}). Although an axial proton alpha to the carbonyl group in cyclohexanone is reported to be observed at lower field than its equatorial counterpart,⁵ the equatorial proton at C-1 of (IV) (H_{1e}) appears at lower field than the axial one (H_{1a}). This may be accounted for in terms of the deshielding effect of the aromatic ring.

Clemmensen reduction of (IV) afforded ferruginol. The positive c.d. sign, $[\theta]_{307} + 1760$, $[\theta]_{296} + 1990$ (c 0.001, dioxan), of the keto-acetate (IV) requires, by analogy with the c.d. of 5 α -cholestan-2-one,⁶ that salviol has the absolute configuration shown in (I).

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