

THE STRUCTURE OF RADERMACHOL, AN UNUSUAL PIGMENT FROM *RADERMACHERA XYLOCARPA* K. SCHUM.

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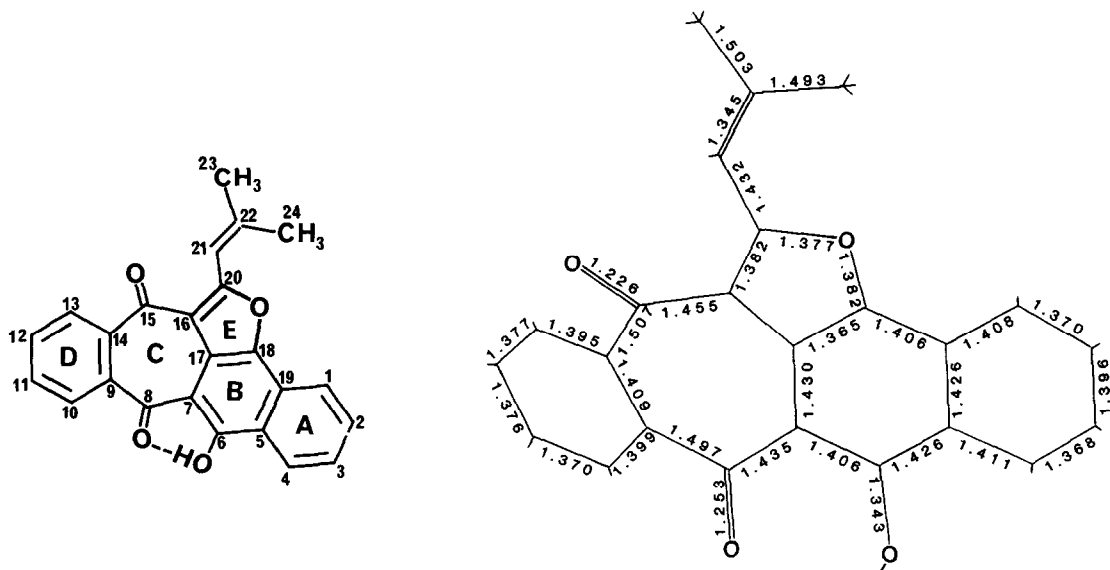
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Summary: The structure of radermachol 1, isolated from the roots of Radermachera xylocarpa K. Schum., has been determined by spectral and X-ray analysis. The fused aromatic ring system of this compound appears to be unique.

Radermachera xylocarpa K. Schum. (family: Bignoniaceae) is a species which is indigenous to the Western Ghats of India.¹ In a previous communication we have reported the isolation of *o*-acetyl oleanolic acid from this plant.² By chromatographic separation of the hexane extract of the roots on silica gel, we have isolated stigmasterol³ and a crystalline red pigment (0.004%; tlc, silica gel, hexane: benzene, 1:1, R_f 0.7), m.p. 217-218°, designated as *radermachol*. Its molecular formula C₂₄H₁₆O₄ was derived from the elemental analysis (Found: C, 78.0; H, 4.8; C₂₄H₁₆O₄ requires: C, 78.2; H, 4.4%) and mass-spectrum (M⁺, m/z 368). The mass spectrum exhibited a base peak at m/z 353 indicating the loss of a methyl group and showed only little fragmentation. Other minor fragments appearing at m/z 339 and m/z 336 are due to the loss of methylene and hydroxyl ions from the base peak. *Radermachol* was insoluble in aq. NaOH and gave a deep brown coloration with ethanolic ferric chloride, indicating a chelated hydroxyl group; ν_{\max} (nujol) 1630 cm⁻¹. The IR spectrum does not show any hydroxyl bands in the 3500 cm⁻¹ region and the other bands observed appear at 1730 cm⁻¹ (weak, carbonyl) 1600, 1578 cm⁻¹ (aromatic). Although *radermachol* appeared to contain two carbonyl groups, unlike the naphtha- and anthraquinones, it failed to give a leuco compound on reduction with neutral or alkaline sodium hydrosulfite.⁴ The ¹H-nmr spectrum (60 MHz; CDCl₃) displayed 16 protons: δ 2.1 (3H, br s, vinylic CH₃), 2.3 (3H, br s, vinylic CH₃), 7.1 (1H, br s, vinylic-H), 7.2-8.0 (5H, m, aromatic-H), 8.3- 8.7 (3H, m, aromatic-H), 15.4 (1H, s, chelated OH; exchanged with D₂O). The noise decoupled ¹³C-nmr spectrum of *radermachol* showed twenty-four lines due to 24 carbon atoms of the

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molecule and the SFORD spectrum showed the presence of 13 singlets, 9 doublets and 2 quartets, δ (ppm, from TMS): 191.9 (s, $>C=O$), 185.0 (s, $>C=O$), 164.1 (s), 160.7 (s), 148.1 (s), 141.1 (s), 138.3 (s), 135.6 (s), 133.2 (d), 132.4 (d), 132.0 (d), 131.2 (d), 130.9 (d), 125.7 (s), 125.3 (s), 124.4 (s), 123.1 (s), 119.4 (d), 117.3 (d), 117.1 (d), 114.2 (d), 107.4 (s), 28.7 (q, CH_3), 21.8 (q, CH_3). The off-resonance ^{13}C -nmr spectrum excluded the presence of methylene carbons in the molecule. The UV-visible spectrum ($CHCl_3$) λ_{max} 252, 276, 305, 330, 363 and 460 nm (log ϵ , 4.59, 4.4, 4.34, 4.21, 4.31 and 3.59 respectively); (CH_3OH) λ_{max} 250, 275, 300, 330, 360 and 455 nm; ($CH_3OH + NaOH$) 240, 265, 330 (infl.), 350 and 470 nm, is complex and novel, bearing no similarity to any known chromophore. Structure 1 has been assigned for radermachol by a single crystal X-ray diffraction study.



1, Radermachol

Crystals suitable for X-ray studies were grown by diffusion of hexane into a solution of methanol. A crystal of dimensions 0.175 x 0.30 x .50 mm was used for crystallographic study. Crystals were triclinic, space group PT, with $a = 8.179(1)\text{\AA}$, $b = 10.115(1)\text{\AA}$, $c = 11.563(2)$, $\alpha = 110.65(1)\text{\AA}$, $\beta = 90.06(1)$, $\gamma = 95.84(1)$, $V = 890.0(4)\text{\AA}^3$, $D_c = 1.375 \text{ g cm}^{-3}$ and $Z = 2$. 3774 unique reflections were collected up to $\theta = 77^\circ$ using Ni filtered CuK (1.5418\AA) radiation. 2585 reflections were considered observed ($I > 2(I)$) and were used in the refinement. The structure was solved using the program MULTAN⁵ and was refined by full matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atom positions were located using the difference fourier map. The final refinement of all the atoms gave an R-factor = 0.04 for 2585 observed reflections.

Figure 1 shows an ORTEP⁶ drawing of the molecule with the numbering of the atoms. The bond lengths and angles agree well with the expected values. However, bond C(8) = O(3) has a value of $1.253(1)\text{\AA}$ which is significantly longer than that observed for C(15) = O(4) which has a value of $1.226(1)\text{\AA}$. The hydroxyl at C(6) is involved in a very short intramolecular hydrogen

bond with O(3), the O(2)-H---O(3) distance being 1.50Å. The O(2)-H---O(3) angle is 153° which seems to be unusual since it has been documented⁷ that shorter hydrogen bonds tend to be more linear.

The fused ring system of radermachol contains three six-membered, one five-membered and one seven-membered rings. The two six-membered rings (B and D) fused to the seven-membered ring C can be considered to be slightly non-planar with a maximum deviation of 0.020(2)Å from the best plane through the rings. The five membered ring (E) and the six membered ring (A) are perfectly planar. The conformation of the fused ring system can be described by the dihedral angles formed by planes through the different rings (A-B = 0.6°, B-C = 10.0°, B-E = 5.6°, C-D = 17.6°, C-E = 9.7°). The seven membered ring can be described as having a boat conformation, the atoms C(9), C(14), C(16) and C(17) forming the basal plane with the atom C(15) at the prow and C(7) and C(8) forming the stern. The basal plane of the boat shows a zigzag shape with deviations of $\pm 0.038\text{Å}$ for the four atoms with the bow atom C(15) and the stern atoms C(7) and C(8) removed from the base by 0.273, 0.207 and 0.41Å respectively. Although radermachol is non-planar, the molecule is probably not rigid. Flipping of the carbonyls would make it achiral and hence no optical activity is observed. A number of furano- and dihydrofurano-naphthaquinones have been isolated from *Radermachera sinica* Hems⁸. However, the fused aromatic ring system of radermachol is unique and has not been encountered so far in any other natural product; it is biogenetically interesting.

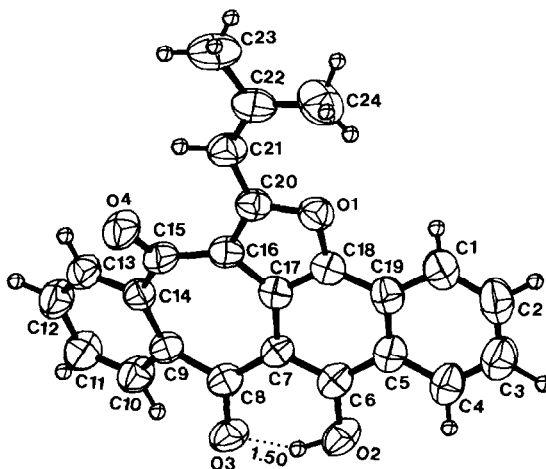


Figure 1. ORTEP drawing of radermachol (1).

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