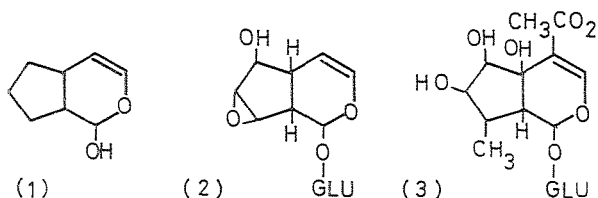


09.2-16 STEREOCHEMICAL ASPECTS AND CRYSTAL STRUCTURE OF TWO NATURALLY OCCURRING IRIDOID COMPOUNDS: M.K. Strumpel and G. Ruban, Free University of Berlin, Institut für Kristallographie, Takustraße 6, D-1000 Berlin 33, West-Germany

Iridoid compounds are substances that contain the bicyclic hemiacetal (1). Two naturally occurring iridoids are Unedoside (2) and Pulchelloside (3), named after their flowering plant sources. Geisman et al. (Tetrahedron Letters 1966, p. 1245), and Rimpler and Timm (Z. Naturforsch. 29c, 1974, p. 368) suggested different stereochemistries for (2). A structure determination on 3,4-Dihydro-unedoside-pentaacetate, a derivative of (2), was undertaken to determine the correct configuration.

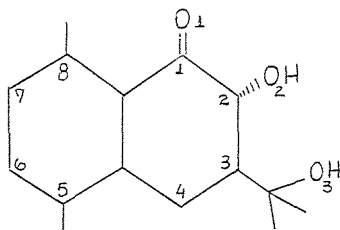
Two stereoisomers, Pulchelloside I and II (3), were isolated and characterised by Milz and Rimpler (Tetrahedron Letters 1978, p. 895). The structure of Pulchelloside II was determined by X-Ray analysis.

Both substances crystallize in space group $P2_12_12_1$ with $Z = 4$ and cell dimensions of $a = 34.217$, $b = 10.822$, $c = 7.572$ Å for (2)-acetate and $a = 26.943$, $b = 9.235$, $c = 7.902$ Å for (3). The structures were solved by direct methods. The stereochemistry of these compounds is discussed.



09.2-17 THE CRYSTAL STRUCTURE OF (2R,3S)-2-HYDROXY-3-HYDROXYISOPROPYL-5,8-DIMETHYL-1-KETO-1,2,3,4-TETRAHYDRONAPHTHALENE, A NATURAL PRODUCT PRESENT IN ENMOTUM NITENS (ICACINACEAE). By M.T.P. Gambardella, J.Z. Schpector, Y.P. Mascarenhas and A.B. de Oliveira, Instituto de Física e Química de São Carlos, 13560 São Carlos, S.P., Brazil.

The crystal data are: cryst. sys. = orthorhombic; sp. g. = $P2_12_12_1$; cell dim. $a = 9.417$ Å, $b = 16.037$ Å, $c = 17.952$ Å; cell vol. = 2711.1 Å³; $Z = 8$ (2 independent molecules per asymmetric unit) dens. = 1.23 g.cm⁻³; calc. dens. = 1.21 g.cm⁻³. The intensities of 1929 independent reflexions were measured using a Nonius CAD-4 diffractometer, with graphite-monochromated MoK α radiation. The structure was determined by direct methods using MULTAN programmes and successive difference Fourier syntheses. Both independent molecules are practically identical. Intramolecular hydrogen bonds are present between O1 and O2 and between O2 and O3 with distances O...O, respectively, 2.691 Å and 2.674 Å in molecule A and 2.649 and 2.673 in molecule B. There are two intermolecular hydrogen bonds between the two independent molecules linking O2 of molecule A to O3 of molecule B with distance O...O equal to 2.731 Å and a longer one linking O3 of molecule A to O2 of molecule B equal to 2.901 Å. The structure was refined to final R of 13.6% using only 942 reflection with $F > 3\sigma(F)$.

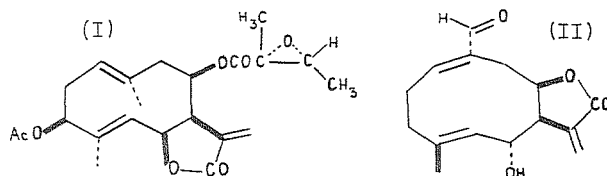


Work supported by FAPESP, CNPq and BID-FINEM

09.2-18 NATURALLY OCCURRING SESQUITERPENE LACTONES. EXAMPLES OF THE STRUCTURALLY UNUSUAL GERMACROLIDES. By U. Rychlewska, Institute of Chemistry UAM, Poznań, Poland.

Two structures presented here have been solved by X-ray diffraction method. Ursiniolide A (I) is a representative of the trans, trans-germacradiene class of sesquiterpenes, sub-group germacrolides. The crystals are tetragonal space group $P4_1$, with $a = b = 13.921$ (2), $c = 11.187$ (1), $z = 4$. The ten-membered ring adopts a chair-boat conformation with methyl groups oriented syn on the α -face of the molecule. (I) belongs to the group of ursiniolides, the first germacrolides described with a lactone ring closed to C(6) and cis-annulated to the homocycle.

Schkuhriolid (II) is a representative of the cis-1(10),trans-4,5-germacradiene class of sesquiterpenes, sub-group melampolides. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 6.968$ (1), $b = 9.603$ (1), $c = 22.478$ (3), $z = 4$. Cis, trans configuration of the double bonds and the anti-arrangement of the substituents at C(4) and C(10) observed in this structure is common for all melampolides. However, the orientation of the lactone ring in schkuhriolid is exceptional; the γ -lactone is closed to C(8) and cis-annulated to the homocycle.



09.2-19 CRYSTAL AND MOLECULAR STRUCTURE OF DL-1 β -METHYL-7-METHOXY-1,2,3,4,4a,9 α -HEXAHYDRO-1 α ,9 α -ETHANOFLUORENE-11-ONE (C₁₇O₂H₂₀). S.G. Biswas, A. Kabiraj, Physics Department, Visva-Bharati University, Santiniketan 731235, W. Bengal, India.

A novel stereospecific intramolecular rearrangement of some angularly fused cyclobutanones has been developed and utilised (Ghatak U.R. et al, J. Chem. Soc. Trans 1, 1980, 2881) as the key step in the synthesis of appropriately angularly functionalised hydrophenanthrene and hydrofluorene derivatives of complex diterpenoids. The X-ray analysis of a strained cyclobutane fused hydrofluorene was undertaken to establish its molecular architecture.

The X-ray data of the title compound were collected by photographic methods and 612 unique reflexions were observed. The compound crystallizes in the space group $Pbca$ with $a = 7.75$, $b = 17.05$, $c = 21.32$ Å, $\mu(\text{CuK}\alpha) = 0.617$ mm⁻¹, $Z = 8$. The structure was solved by MULTAN. The geometry of a planar fragment was used to modify the Wilson plot by applying spherically averaged molecular scattering factor. 200 reflexions with $E > 1.25$ were used to solve the structure. An E-map computed from the phase set with the highest figure of merit revealed the positions of all the non-hydrogen atoms. The structure was initially refined by the full-matrix least-squares method with isotropic temperature factors, and then finally by the block-diagonal least-squares method with anisotropic temperature factors. A final difference synthesis revealed no significant residual electron density. However, all the positions of the hydrogen atoms were generated and included in the computation of the R-value. The final R-value was 0.141. The bond lengths and angles are approximately within expected values and the non-bonded contacts are always greater than the sum of the van der Waals radii.