09.2-16  
STEREOCHEMICAL ASPECTS AND CRYSTAL STRUCTURE OF TWO NATURALLY OCCURRING IRIDIUM COMPOUNDS: 
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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. 1285), and Rimpling and Timm (Z. Naturforsch. 29c, 1974, p. 388) 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. 896). The structure of Pulchelloside II was determined by X-Ray analysis.

Both substances crystallize in space group P2₁2₁2₁ with Z = 4 and cell dimensions of a = 34.217, b = 10.822, c = 7.902 Å. The structure was refined to final R of 0.200. The geometry was determined by direct methods. The stereochemistry of these compounds is discussed.

09.2-18  
NATURALLY OCCURING SESQUITERPENE LACTONES. EXAMPLES OF THE STRUCTURALLY UNUSUAL GERMACRANOLIDES. By U. Rychlewski, Institute of Chemistry UAN, Poznan, Poland.

Two structures presented here have been solved by X-ray diffraction method. Ursinolide A (1) is a representative of the trans, trans-germacradiene class of sesquiterpenes, sub-group germacrolides. The crystals are tetragonal space group P4₁, with a = 13.92 Å, c = 11.187 Å. The ten-membered ring adopts a chair-boat conformation with methyl groups oriented syn on the a-zase of the molecule. (1) belongs to the group of urainolides, the first germacranolides described with a lactone ring closed to C(6) and cis-annelated to the homocycle.

Schiukhirolid (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 P2₁2₁2₁, with a = 22.478 Å, b = 6.509 Å, c = 22.478 Å. Cis, trans configuration of the double bonds and the anti-arrangement of the substituants at C(4) and C(10) observed in this structure is common for all melampolides. However, the orientation of the lactone ring in schiukhirolid is exceptional; the y-lactone is closed to O(2) and cis-annelated to the homocycle.

The crystal data are: cryst.sys.=orthorhombic; sp.g. = P2₁2₁2₁; cell dim. a=22.478 Å, b=6.509 Å, c=22.478 Å; cell vol. = 1711 Å³; Z=2 (2 independent molecules per asymmetric unit) dens.=1.23 g.cm⁻³; calc.dens.=1.21 g.cm⁻³. The intensities of 1399 independent reflections were measured using a Nonius CAD-4 diffractometer, with graphite-monochromated MoKα radiation. The structure was determined by direct methods using SHELXL 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 equal respectively, 2.601 Å and 2.674 Å in molecule A and 2.649 Å and 2.673 Å 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 2.713 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 > 3σ(F).

The crystal data are: cryst.sys.=orthorhombic; sp.g. = P2₁2₁2₁; cell dim. a=7.75 Å, b=17.05 Å, c=21.32 Å; cell vol. = 1711 Å³; Z=4. The ten-membered ring adopts a chair-boat conformation with methyl groups oriented syn on the a-zase of the molecule. The structure was refined to final R of 0.200. The geometry of a planar fragment was used to modify the Wilson plot by applying spherically averaged molecular scattering factor. 200 reflections 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 experimental error, and the bonded contacts are always greater than the sum of the van der Waals radii.