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Lead Tetraacetate Oxidation of Cedrol. Syntheses of 8,14-Cedranoxide and 14,8-Cedranolide

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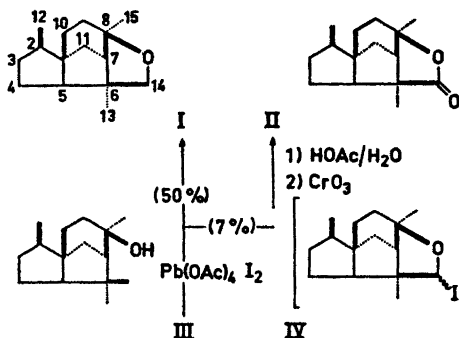
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Recently a sesquiterpene oxide¹ and a lactone,² from *Juniperus foetidissima* Willd.¹ were characterised and shown to be the cedrane derivatives, 8,14-cedranoxide *I* and 14,8-cedranolide *II*.² We now report the syntheses of these constituents *via* transannular lead tetraacetate oxidations of cedrol *III*,* the structure of which has been previously ascertained by a total synthesis.³

Transannular oxygenations of saturated carbon atoms with oxygen species generated by lead tetraacetate are well known, particularly for the syntheses of various steroid oxides.⁴ The C(14)-methyl group in cedrol *III* is suitably orientated for an attack by a similar 8 S oxygen species. Preliminary oxidation experiments on cedrol *III* in benzene confirmed that upon

* A compound which must be identical to 8,14-cedranoxide has recently been prepared from cedrol *via* similar transannular oxygenations (Blumenthal, J. H., Stork, G. and Theimer, E. T. *U.S. patent* 3,281,432/1966).

prolonged treatment traces of the oxide *I* were formed. The reaction rate was very low and side reactions were observed. However, using the method of Heusler *et al.*,⁵ in which the oxidation is carried out in the presence of iodine, the oxide *I* was formed in high yield (50%). Treatment of the crude lead tetraacetate oxidation product with aqueous acetic acid followed



by a chromic acid oxidation yielded, apart from the oxide *I* (50% yield), small amounts of 14,8-cedranolide *II* (7% yield), probably formed *via* an intermediate iodoether *IV*, since the oxide *I* was found to be stable under these reaction conditions.

Experimental. Lead tetraacetate (4 g) and calcium carbonate (2 g) were heated under reflux in cyclohexane (125 ml) for 10 min. Iodine (1 g) and cedrol (300 mg; m.p. 86–87°; $[\alpha]_D +10.1^\circ$) were added and the mixture was refluxed for 2.5 h. After cooling, the precipitate was filtered off and washed with ether. The combined organic solutions were washed consecutively with 5% aqueous potassium iodide, 5% aqueous sodium thiosulphate, and water. The organic phase was dried (Na_2SO_4) and the solvents evaporated. The residue was adsorbed from light petroleum (b.p. 40–60°) on to a silica gel column (30 g). Ether (4%) in light petroleum eluted 8,14-cedranoxide (150 mg, yield 50%). Rechromatography on silica gel (15 g) with ether (4%) in light petroleum followed by distillation (bath temp. 100°; 0.1 mm Hg) yielded a pure product identical in all respects ($[\alpha]_D$, IR, NMR, mass spectrum, TLC, and GLC) to those of natural 8,14-cedranoxide.^{1,2} The rotations of our synthetic and natural 8,14-cedranoxide samples were considerably higher ($[\alpha]_D -96^\circ$, c 1.91 in CHCl_3) than the value previously reported¹ ($[\alpha]_D -69^\circ$, misprint?) for the natural product.

In a separate experiment cedrol (0.6 g) was oxidised with lead tetraacetate according to the procedure described above. The reaction mixture was hydrolysed in a mixture of acetic acid and water followed by a further oxidation in acetone solution with 8 N chromic acid in sulphuric acid (Jones reagent) as described for similar oxidations by Heusler *et al.*⁵ The product thus obtained was adsorbed from light petroleum on to a silica gel column (40 g). Ether (4 %) in light petroleum eluted 8,14-cedranoxide (0.3 g). Further elution with increasing concentrations of ether gave more polar fractions of which one (0.05 g, eluted by 15 % ether in light petroleum) was identified as 14,8-cedranolide III (TLC, IR, and GLC). This oily compound was further characterised by a lithium aluminium hydride reduction which yielded the crystalline 8S, 14-cedrandiol.³

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Crystal Structure of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$

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In connection with the problem of bonding of the nitrate group in copper(II) complexes, the structure of one of the hydrates, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ has been established. Some preliminary structural data

for this material have been published¹ and now the results of a complete X-ray analysis are reported briefly.

Crystals from two different sources were used for the X-ray studies: a) commercially available copper(II) nitrate with the formula $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, pro analysi (product of Lachema, Czechoslovakia), b) material obtained by crystallisation from nitric acid solution according to the reported preparation of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$.² (Found for a: Cu 27.10, 27.14; N 11.32, 11.47; H 2.28, 2.36. Calc. for $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: Cu 26.30; N 11.60; H 2.50. Found for b: Cu 27.46, 27.56; N 11.09, 11.38; H 2.30, 2.30. Calc. for $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$: Cu 27.32; N 12.04; H 2.50).

Both kinds of crystals are hygroscopic or efflorescent, depending on the temperature and humidity of the air. Single crystals were coated with nitrocellulose to prevent decomposition during the X-ray investigation.

Crystal data for $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$: The crystals are monoclinic, with $a = 16.455 \pm 0.003$; $b = 4.941 \pm 0.001$; $c = 15.962 \pm 0.003$ Å, $\beta = 93.75 \pm 0.01^\circ$. The measured density at 23°C (by flotation) is 2.28 g/cm³. The calculated density, corresponding to 8 formula units per cell, is 2.37 g/cm³. Weissenberg photographs showed the following reflection conditions:

$$F_{hkl} \text{ were present only for } h+k+l=2n,$$

$$F_{hol} \text{ were present only for } h=2n, l=2n.$$

This leads to the space groups $I2/c$ or Ic . A transformation of the axes: $X=x$, $Y=y$, $Z=x-z$, leads to the International Tables space groups No. 15, $C2/c$ and No. 9, Cc , respectively.³ The solution of the structure of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was based on the centrosymmetric $I2/c$ space group symmetry.

The three-dimensional intensities were recorded by equi-inclination Weissenberg photography with $\text{CuK}\alpha$ radiation and estimated photometrically. The hnl ($n=0-4$) data were collected. The structure has been solved by the heavy atom method on the basis of a three dimensional Patterson synthesis. The atomic positions, isotropic temperature parameters, and scale factors have been refined by the least squares full matrix method using the programs of Gantzel *et al.*⁴ The weighting scheme of Cruickshank⁵ was used. The R value, based on observed structure factors only, is 0.109. Differential Fourier synthesis did not show larger maxima of electron