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CRYSTAL STRUCTURE OF THE DIMER OF 1,2-DEHYDROISOPHOTOSANTONIC LACTONE

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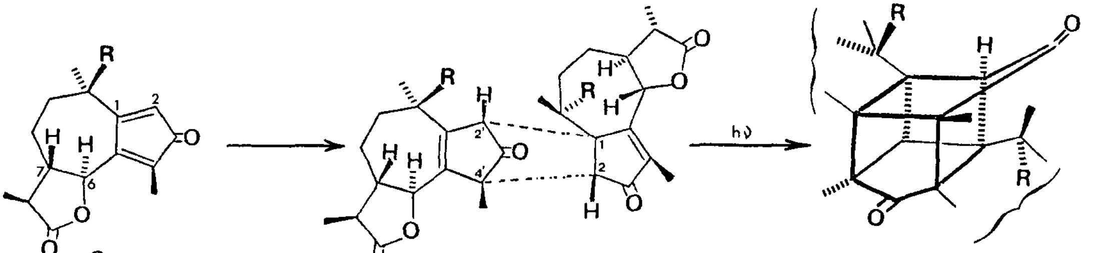
Summary : The structure of the dimer 3 of 1,3-dehydrophotosantonic lactone 2 was established by X-ray diffraction analysis.

During the course of our studies on the constituents of *Artemisia absinthium*[1] we have isolated in minute amounts a new guainolide dimer whose structural elucidation is in progress. It was evident from its spectral data that the new compound exhibited a dihydro cyclopentadienone dimer system.

In order to obtain a model compound which might facilitate our structural assignment we have studied the dimerization of the dienone 2 which was derived from acetyl isophotosantonic lactone 1[2].



2 3 4

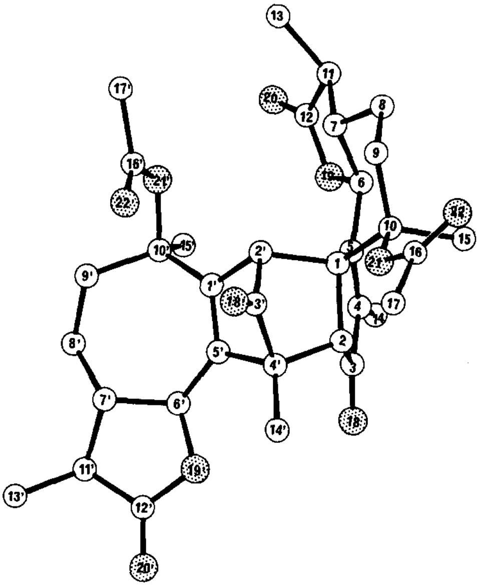
1 = 1,2-dihydro 2 R = OAc

Phenylselenylation of the latter (PhSeCl, AcOEt) followed by oxidative elimination of the selenide gave the dienone 2 which is relatively stable at room temperature in dilute solution . Its ^{1}H NMR spectrum showed H-2 and H-6 signals at 5.43 and 4.83 ppm, respectively. However , 2 could not be isolated from its solution. It dimerized spontaneously to give 3 , [$M^{\cdot +}$ 608 ($C_{34}H_{40}O_{10}$) mp 205-208°C; $[\alpha]_D$ + 40° (c 0.2, $CHCl_3$)] which was also obtained after phenyl selenic anhydride oxydation of 1. Its IR[ν_{max} 1790, 1780 and 1720 cm^{-1} (CO)] and UV [ν_{max} 240 nm, ε 8500] data suggested the presence of a dicyclopentadiene-1,8 dione. The ^{1}H and ^{13}C NMR spectra revealed informations consistent with structure 3 . In addition to the H-6 and H-6' doublets the ^{1}H NMR spectrum showed H-2 and H-2' , as two singlets favouring C-1/-C-2' and C-2 /C-4' bond formations . Irradiation of 3 (EtOH, HP lamp, Pyrex) provided the cage compound 4 which was devoid of UV absorption thus demonstrating that 3 was an endo-dimer.

For a complete structural determination, an X-ray analysis was carried out using crystals of 3 obtained from hexane/benzene:
Crystals are orthorhombic , space group $P2_12_12_1$ with Z=4 and 8 molecules of benzene in the unit cell : a= 9,I05 (2), b= 20.185 (4) , c =22.416 (5) Å . 4304 data were measured on a graphite-

monochromated diffractometer using CuKα radiation (λ = 1.5418 Å). Of these reflexions, 2001 having I >3 σ (I) were considered as observed. The structure was solved by direct methods using DEVIN (3) and refined by least-squares methods with SHELX 76 program (4). Two molecules of benzene were found in the difference map, one of them appeared to be disordered, with two positions of relative weights 0.72 and 0.18 (refined). They were considered as rigid groups with refined mean isotropic thermal parameters. Except those of the methyl groups, hydrogen atoms were located on successive difference maps. They were replaced geometrically (d_{C-H} = 1.0 Å) and assigned the equivalent isotropic thermal factor of the attached atoms. The final R and Rw were 0.080 and 0.082 (5). The absolute configuration has been deduced from that of isophotosantonic lactone 1 (6).

Finally , it is interesting to compare our results with those of Matsuura et al. [7] describing a santonin photoproduct which might have resulted from the dimerization of a photointermediate having the same cyclopentadienone functionality as 1, namely 1,2-dehydro-10-deoxyphotosantonic lactone 2 (R=H). The structure of the corresponding dimer was deduced from the CD data. It exhibited, as compound 3, a negative CD maximum which was associated with the 2-cyclopentenone chromophore . The above X-ray analysis suggests that the structure 2a depicted in reference (7) , but which was rejected by the Japanese authors, is in fact correct.



An ORTEP view of 3

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