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A PHOTO ARTEFACT FROM LINDERAZULENE

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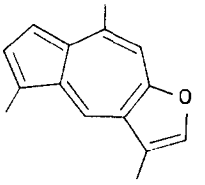
Abstract: Exposure of an ethanolic solution of linderazulene to direct sunlight yields the sesquiterpene keto-lactone 2.

During the isolation[1] of the violet pigment linderazulene 1 from the gorgonian *Paramuricea chamaeleon* we detected a yellow pigment in minute amount. We subsequently found this to be a photo-oxidation product, and it can be obtained by exposing an ethanol solution of linderazulene to direct sunlight for six days (5 mg from 100 mg linderazulene, after chromatographic purification).

The photo-product, $C_{15}H_{12}O_3$,[2] m.p. 107-110°C (from MeOH) shows $\lambda_{max.}$ (MeOH) 272, 285sh, 415sh, 430 nm; $\nu_{max.}$ (KBr) 1758, 1684, 1620, 1540 cm^{-1}; and a very simple ^{1}H NMR spectrum ($CDCl_3$) consisting of three 1H singlets at δ 6.82, 6.52 and 6.22, and three 3H singlets at δ 2.69, 2.32, and 2.12. These data are consistent with the keto-lactone structure 2 and the compound is generally similar to the isomer, malaphyllidin 3, isolated[3] from *Ferula malacophylla*. However, if the formation of the photo-product involves skeletal rearrangement as well as oxidation then isomeric structures must be considered, such as 4, which is also consistent with the spectroscopic data. To exclude this possibility the compound was subjected to X-ray crystallography which confirmed structure 2.



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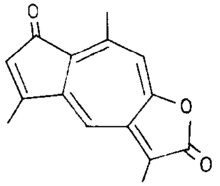

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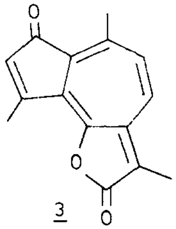

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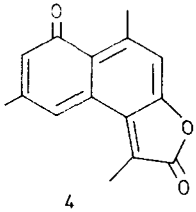

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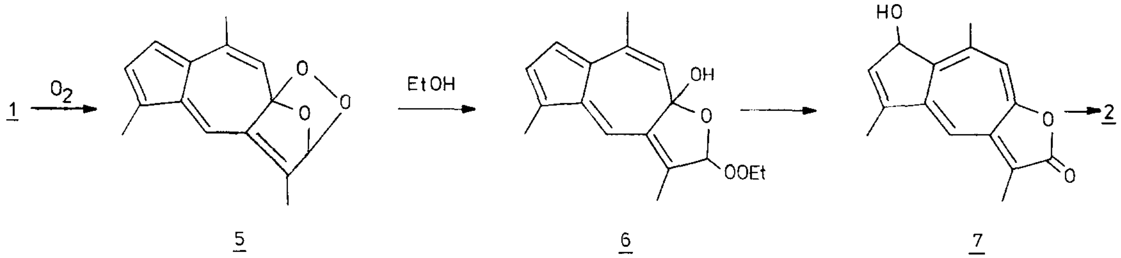
The molecules of the photo-product crystallise in the monoclinic space group *C*2/*c* with cell dimensions a = 11.677(8), b = 15.911(15), c = 13.898(6)Å, β = 116.31(4)° and Z = 8. X-ray intensity data were measured with Mo-K_α radiation on an automatic four-circle diffractometer adjusted by least-squares calculations that converged at R 5.5% over 904 independent reflexions.



Mechanistically it seems likely that the oxidation proceeds by attack on the furan ring to form the endoperoxide 5,[4] followed by solvolysis to 6, loss of ethanol and allylic migration to give the alcohol 7, and final oxidation. Endoperoxide formation requires singlet oxygen;[4] possibly linderazulene itself acts as a photosensitiser although azulene does not as its low energy triplet is very short-lived.[5]

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