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# FULVENES DERIVED FROM ILLUDIN S

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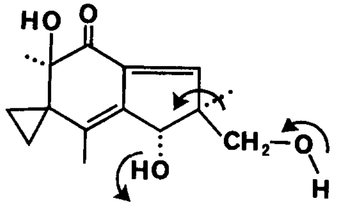
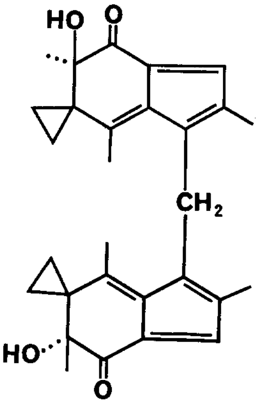
Illudin S (1) a metabolite of the Jack-o'-lantern mushroom *Clitocybe illudens*[1], is converted to fulvenes on brief treatment with ice-cold 40% sulfuric acid. The major product from this reaction is a bright-red crystalline solid, mp 196-8$^{\circ}$ (from 95% ethanol), having ultraviolet maxima (methanol) at 422 nm ($\epsilon$ 2640), 328 (7,400), 269 (10,500), 251 (11,700) and 237 (11,800).[2] It is optically active with $[\alpha]_D$ - 597 (c 0.23 in absolute ethanol). The mass spectrum[3] of this compound shows a molecular ion at m/e 444, indicating a dimeric structure. Analytical values[4] fit an empirical formula of $C_{29}H_{32}O_4$. The infrared spectrum in chloroform solution shows absorption at 3450, 1650 and 1575 cm$^{-1}$. The nmr spectrum in deuterochloroform clearly indicates a symmetrical dimer having structure 2: $\delta$ 7.07 (1H, s, vinyl); 4.10 (1H, s, methylene); 3.92 (1H, s, -OH); 1.90 (6H, s, allylic methyls); 1.35 (3H, s, acyloin methyl); 1.5 - 0.5 (4H, m, cyclopropyl).

Steam distillation of the reaction mixture afforded formaldehyde in about 40% yield as its dimedone derivative. Thus we believe that the acylfulvene 2 is derived from illudin S by a reverse Prins reaction (arrows in 1) to a monomeric acylfulvene 3, followed by electrophilic substitution of liberated formaldehyde on two molecules of acylfulvene 3.[5]



1



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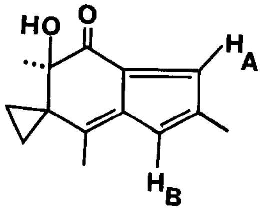

3

Examination of the recrystallization mother liquors in fact revealed a second pigment which could be purified by chromatography on silica gel, affording an unstable yellow oil. This compound has been assigned the acylfulvene structure 3 on the basis of the following spectral evidence: $\nu_{max}$ ($CHCl_3$) 3450, 1650 and 1600 $cm^{-1}$; $\lambda_{max}$ (methanol) 233 and 325 nm, with tailing to 450 nm; NMR ($CDCl_3$) $\delta$ 7.20 (1H, broad s, $H_A$), 6.46 (1H, q, J = 1.5 Hz, $H_B$), 3.97 (1H, s, -OH), 2.15 (3H, broad s. allylic methyl), 2.05 (3H, s, allylic methyl), 1.40 (3H, s, acyloin methyl), 1.6-0.6 (4H, m, cyclopropyl); mass spectrum ($M^+$): 216 m/e.

In order to test our mechanistic hypothesis, monomeric acylfulvene 3 was treated at 0° with 40% sulfuric acid containing a trace of formaldehyde. As anticipated, dimeric fulvene 2 was rapidly formed.

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   N. Harada and K. Nakanishi, Chem. Comm., 310 (1970) for the correct absolute configuration of the illudins.

2. For a recent review of the ultraviolet and NMR spectra of fulvenes see: P. Yates, "Advances in Alicyclic Chemistry", Academic Press, New York, N.Y., 1968, p. 59.

3. We are indebted to Mr. Dieter Klaubert, MIT, for mass spectra.

4. Analysis by Schwarzkopf Laboratories. Calculated for $C_{29}H_{32}O_4$: C, 78.35; H, 7.26. Found: C, 78.29; H, 7.29.

5. Simple fulvenes are reported to undergo acid catalyzed electrophilic substitution (nitrosation, Vilsmeier reaction) at the 1-position (see reference 2 and those below). However there do not appear to be any previous examples of such electrophilic substitution reactions on 1-acylfulvenes. E. D. Bergmann, Chem. Rev., 68, 41 (1968).
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