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THE PHOTOCHEMISTRY OF PARTHENIN AND CORONOPILIN

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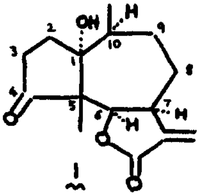
A note on the photochemistry of coronopilin (1)[1] prompts us to record our results on this and on the related sesquiterpene lactone parthenin (5).

As described by Yoshioka *et al.*, 1 at 253.7 nm in C_6H_6 under N_2 yielded 2, m.p. 95-98°, which we also obtained as the major photoproduct in $CHCl_3$, EtOAc or MeOH at 253.7, 300 or 350 nm. Anhydropsilostachyin (3) was the only product when either 1 or 2 was irradiated in EtOAc at 350 nm under oxygen.[2]

Partitioning of the biradical formed by α-fission of 1 must yield an unsaturated aldehyde (here as the hemiacetal 2) and a ketene. The latter was detected by irradiating a film of 1 at -190°. Two new ir peaks at 2110 and 2130 cm^{-1} disappeared on warm-up, and are ascribed to the isomeric ketenes resulting from hydrogen abstraction from C-3 by the planar radical at C-5. In solution, the ketenes were trapped as lactone 4, an oily mixture of C-5 isomers characterized by ir (no OH, broad carbonyl at 1770 cm^{-1}), mass spec (M.W. 264) and nmr ($CDCl_3$), which showed for the major isomer $C=CH_2$ at 6.38 and 5.60 (each a d, J=3 Hz), H-6 at 4.07 (d of d, J_1=7, J_2=3 Hz), H-7 at 3.4 (c), H-10 and CH_2's at 2.85-1.40 (c, 10 H's), C-5 CH_3 at 1.20 (d, J=7 Hz) and C-10 CH_3 at 1.03 ppm (d, J=7 Hz). The minor isomer (ca. 25%) was recognized by its CH_3 at 0.98 (d, J=7 Hz) and the $C=CH_2$ doublets at 6.34 and 5.65 ppm.



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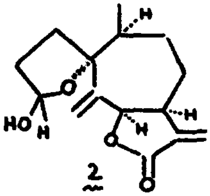

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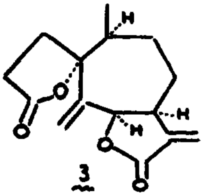

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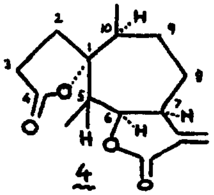

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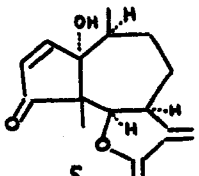
Another product usually obtained in small yield in the photolysis of 1 was finally traced to the presence of parthenin (5) impurity.[3] Photolysis of pure

5[4] took place readily, especially in EtOAc under N_2 at 350 nm, and gave **7** in 70% yield as an oil which could not be crystallized. It had M.W. 262 (mass spec.), contained no OH (ir and nmr in DMSO), and had carbonyls at 1779 (γ-lactone) and 1760 cm^{-1} ($\alpha\beta$-unsatd-γ-lactone). At 60 MHz in $CDCl_3$, the nmr showed $C{=}CH_2$ as two doublets (J=4 Hz) at 5.60 and 6.33, H-6 at 4.45 (d, J=9 Hz), H-7 at 3.5 (c), H-3 and H-10 at 2.92-3.05 (c, 3H's), H-8 and H-9 at 1.8-2.25 (c, 4H's), CH_3's at 1.27 (s, C-5) and 1.03 (d, J=7 Hz, C-10), masking H-2. In C_6H_6 at 90 MHz, the CH_3's were at 0.52 (d) and 0.80 (s), revealing H-2 at 1.08 (t, 4 Hz).[6] Irradiation at H-2 collapsed H-3 (d, 4 Hz, 2 H's) into a singlet at 2.15. Irradiation at H-7 (ca. 2.95) converted H-6 into a singlet at 4.07 and simplified C-8 at 1.22-1.50, which remained complex from coupling with CH_2 at C-9. Irradiation at 0.52 resolved H-10 into a triplet at 2.27 ppm (J=5 Hz), confirming a CH_2 at C-9.[7]



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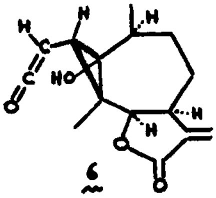

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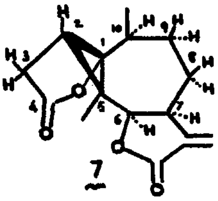

7

The newly discovered cyclopentenone-cyclopropyl ketene rearrangement[8] accounts for the conversion **5**→**6**→**7**. It must be stereospecific since **7** was obtained in MeOH with no decrease in yield, and there was no methyl ester from trapping the non-lactonizable ketene isomeric with **6**. Acidic treatment of **7** (CF_3COOH) yielded at least ten products, but the scarcity of **5** at our disposal prevented further structural studies. Further work on this new cyclopropanol synthesis is in progress.

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References

1. H. Yoshioka, T. H. Porter, A. Higo and T. J. Mabry, *J. Org. Chem.*, **36**, 229 (1971).

2. **3** was the only product (65% yield) in the $SOCl_2$-pyridine dehydration of psilostachyin, a marked improvement over the procedure published by T. J. Mabry, H. E. Miller, H. B. Kagan and W. Renold, *Tetrahedron*, **22**, 1139 (1966).

3. H. E. Miller, T. J. Mabry, B. L. Turner and W. W. Payne, *Amer. J. Bot.*, **55**, 316 (1968) reported on the occurence of both **1** and **5** in *A. psilostachyia*.

4. W. Herz, H. Watanabe, M. Miyazaki and Y. Kishida, *J. Amer. Chem. Soc.*, **84**, 2601 (1962).

5. We are grateful to Dr. P. J. Green for these determinations.

6. The spectrum in C_6H_6 shows accidental equivalence of the C-3 protons. The observed spacing of 4 Hz is $1/2(J_{AX} + J_{BX})$ in this ABX system, fitting reasonable conformations deduced from a Dreiding model. Addition of $Eu(DPM)_3$ to a $CDCl_3$ solution of **7** affected mostly the protons on the unsaturated lactone and did not allow a detailed analysis of the above ABX spectrum. Another example of accidental equivalence of CH_2's in a γ-lactone will be detailed shortly.

7. Attempted photochemical oxidation of **1** in presence of either O_2 or a carbonyl compound (CH_3COCH_3 or $CH_3COC_6H_5$) yielded neither **5** nor **7**.

8. W. C. Agosta, A. B. Smith, A. S. Kende, R. G. Eilerman and J. Benham, *Tetrahedron Letters*, 4517 (1969).