ml of benzene; all solvents dried and distilled just before use) yielded, in addition to 334 mg of recovered lumisantonin, 172 mg of impure **11**. The identity of **11** with the product of lumisantonin formed in 10% yield by photolysis was established by the superimposability of their infrared, ultraviolet, and nmr spectra.

Graded sensitizer experiments are described in detail in a following paper of the series.

Low-Temperature Electron Spin Resonance Study. A 1-ml sample of lumisantonin in ethanol (approximately 2×10^{-2} *M*) was prepared in a quartz epr tube and degassed by three freeze–thaw cycles on a vacuum line. The tube was sealed, cooled to liquid nitrogen temperature, and irradiated with the 3130-Å mercury line in the phosphoroscope dewar apparatus. Within 15–20 min after the irradiation was begun, a rich blue color had been developed at the surface of the sample. The tube was then transferred to the precooled cavity of a Varian X-band spectrometer, Model 4500. The temperature was kept at $-190 \pm 2°$ by means of a variable-temperature controller, Model V-4540. A PRD Electronics Frequency meter, Type 535, was used for calibration. The region from 2000 to 4000 G was repeatedly scanned at settings of 6.3×100 (modulation amplitude) and 2×1000 (gain), but no signal was observed. No observable loss in the intensity of the sample color occurred during this time. Under identical conditions, but with a gain setting of 10, a strong pitch reference gave an easily discernible signal. We are grateful to Mr. Lahmer Lynds for help with this experiment.

Acknowledgments. We should like to thank Professor N. Lichtin for useful comments, the U. S. Public Health Service (Grant GM-10218) for generous financial support, and the National Science Foundation for a fellowship to M. H. F.

Photoproducts from Irradiation of Lumisantonin in Aprotic Medium

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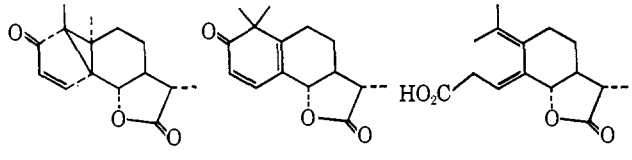
Received July 10, 1967

Abstract: Irradiation of lumisantonin in aprotic medium yields mazdasantonin, II, and double bond isomer of pyrolumisantonin, V. In addition, other monomeric photoproducts are isolated as well as a substance believed to be a dimer of mazdasantonin. Structural possibilities for these are discussed.

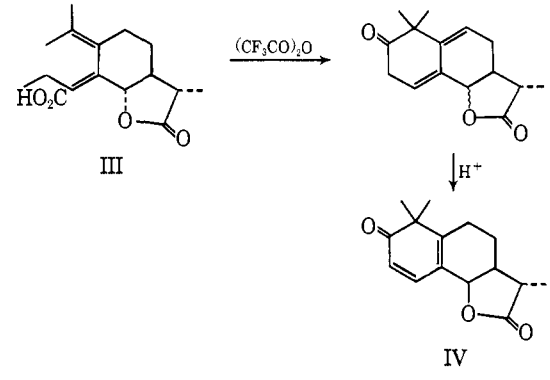
Irradiation of lumisantonin (I) in aprotic solvents such as benzene, with or without benzophenone as photosensitizer, leads to new photoproducts of which the major one is mazdasantonin[3] (structure II) and, together with another substance, probably a dimer of mazdasantonin, to be discussed subsequently, accounts for about 80% of the product mixture. A substance with this structure has previously been invoked as a transitory intermediate in the photoconversion of santonin to santonic acid (III).[4,5] In addition to mazdasantonin, other substances A, B, C, and F in addition to small amounts of photoproducts D and E which arise from B can be isolated from photolysis of lumisantonin in benzene by liquid–liquid partition chromatography.



I II III

No phenolic products are, however, formed.

Mazdasantonin ($C_{15}H_{18}O_3$) is isomeric with santonin and shows a single intense peak in the ultraviolet spectrum at 318 mμ (log ε 3.89). The 6-epi isomer of mazdasantonin is chemically accessible by treatment of photosantonic acid with trifluoroacetic anhydride followed by acid-catalyzed rearrangement of the double bonds (III → IV).[6] Chapman also obtained[7] the dinitrophenylhydrazone derivative of 6-epimazdasantonin by treatment of the products of irradiation of lumisantonin with dinitrophenylhydrazine under acidic conditions. In the ultraviolet spectrum, 6-epimazdasantonin has a maximum at 308 mμ which is far from the value of 338 mμ predicted for this system.[8] The hypsochromic shift of 10 mμ when mazdasantonin is isomerized at C-6 (to a *cis*-fused lactone) probably reflects differences in planarity of the dienone chromophore.



(1) NSF Predoctoral Fellow, 1960–1964.
(2) Author to whom inquiries should be addressed.
(3) Named after Ahura Mazda (also called Ormazd or Ormuzd), the "Good Spirit" and god of light of Zoroastrianism.
(4) K. Weinberg, E. C. Utzinger, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 236 (1960).
(5) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).
(6) E. E. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky, and P. E. Aldrich, *ibid.*, **81**, 1666 (1959).
(7) O. Chapman and L. F. Englert, *ibid.*, **85**, 3028 (1963).
(8) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 219.

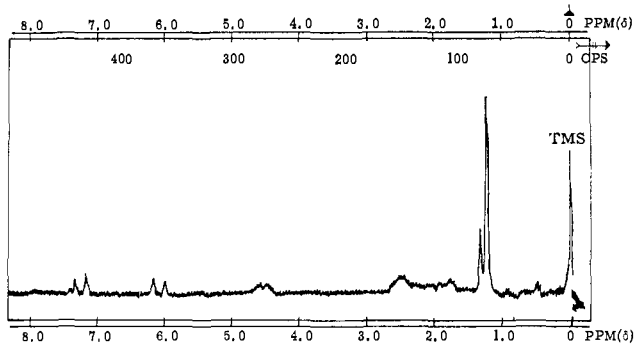


Figure 1. Mazdasantonin in $CDCl_3$.

When exposed to the acidic conditions of van Tamelen's synthesis of the C-6 epimer,[6] mazdasantonin is smoothly converted into 6-epimazdasantonin. The role of mazdasantonin itself as a true intermediate in the photoconversion of lumisantonin to photosantonic acid is strengthened by the observation that irradiation of mazdasantonin in moist ether rapidly and quantitatively produces photosantonic acid.

In addition to the ultraviolet spectrum and chemical evidence (photoconversion into photosantonic acid and acid-catalyzed isomerization to the known 6-epimazdasantonin), the structure assigned to mazdasantonin is confirmed by the infrared and nmr spectra. The infrared spectrum of mazdasantonin shows three peaks in the region 1800–1650 cm^{-1}. One of these at 1783 cm^{-1} is due to the *trans*-fused γ-lactone (in 6-epimazdasantonin, the *cis*-fused γ-lactone absorbs at 1777 cm^{-1}). Another carbonyl absorption of approximately equal intensity is observed at 1666 cm^{-1} due to the $\Delta^{1,3}$-dienone system; this absorption is displaced to 1670 cm^{-1} in the 6 epimer. The third band, at 1630 cm^{-1}, is attributable to the disubstituted double bond in conjugation with the ketone. The second, tetrasubstituted, double bond is not observed.[9]

The nmr spectrum of mazdasantonin (Figure 1) shows in the methyl region one singlet (six protons, δ 1.23 ppm) and a doublet (three protons, centered at δ 1.27 ppm, J = 6 cps). In Figure 1, the second peak is under the absorption at δ 1.23 ppm. This second peak can, however, be observed at lower concentration when the *gem*-dimethyl singlet shifts to lower fields (see below). The doublet arises from the methyl group α to the carbonyl of the lactone and the singlet is due to the two *gem*-dimethyl groups. In the olefinic region, there is an AB pattern (two protons) centered at δ 6.67 ppm (J = 10 cps) in which the absorption centered at higher field (6.1 ppm) is probably due to the proton at C-3.[10]

The nmr spectrum of mazdasantonin is extremely dependent on concentration and exhibits considerable shifts of the *gem*-dimethyl singlet as well as a general sharpening of all peaks on dilution. This spectral indication of intermolecular complex formation may be significant in the observed photodimerization of mazdasantonin to be discussed subsequently.

The nmr spectrum of 6-epimazdasantonin showed small but significant differences from the nmr of mazdasantonin. For example, the lactonic proton of mazdasantonin is a broad, complex absorption at δ 4.55 ppm due to coupling with the adjacent proton and additional longer range coupling with the vinyl hydrogen. In 6-epimazdasantonin, the lactonic proton is shifted downfield and considerably sharpened into a broad doublet (δ 4.92 ppm, J = 6 cps). The AB pattern is also simpler in the 6 epimer; the higher field peaks are no longer further coupled to the lactonic proton and the lactonic methyl peak is shifted somewhat relative to the other methyl peak. Most of these changes are paralleled in model compounds used for comparison, for example, santonin and 6-episantonin (*cf.* Table I).[11,12]

Table I[a]

Solvent		Latonic proton	Lactonic methyl	Singlet methyl
$CDCl_3$	Santonin	4.88	1.27	1.37
$CDCl_3$	6-Episantonin	5.62	1.39	1.30
$CDCl_3$	Mazdasantonin	4.55	1.27	1.23
$CDCl_3$	6-Epimazdasantonin	5.00	1.30	1.25

[a] Using tetramethylsilane as internal reference.

Though both mazdasantonin and its 6-epimer are extremely difficult to obtain crystalline and when stored as an oil gradually oxidize to tarry products, mazdasantonin can be crystallized from acetone–hexane as yellow prisms which are stable indefinitely in the absence of air and light.

Another substance A accounts for about 10% of the photolysis product of lumisantonin and has been shown to be V, a double bond isomer of pyrolumisantonin (VI). In previous work, two types of perhydroazulenes have been obtained from lumisantonin. One type is exemplified by isophotosantonic acid lactone (VII) obtained by treatment of lumisantonin with strong acid.[13] Another structural type is exemplified by pyrolumisantonin (VI), obtained by Arigoni, *et al.*,[14] by the thermal rearrangement of lumisantonin or by treatment with hydrogen bromide followed by elimination of hydrogen bromide.

Compound A is also formed in greater than 90% yield when lumisantonin is pyrolyzed at 200° for 1 hr. Compound A is itself not pyrolumisantonin but can be converted into pyrolumisantonin by passage in benzene solution over neutral alumina, a method used in purification of pyrolumisantonin.[14] Passage of A over acid-washed alumina does not effect rearrangement to pyrolumisantonin. Thus the photoproduct A and the primary pyrolytic product are identical and a double bond isomer of pyrolumisantonin. As proof that the conversion of A or the primary pyrolytic product of lumisantonin involves only double bond isomerization, the infrared spectra of tetrahydro-A and tetrahydropyrolumisantonin were found to be superimposable.

With the establishment of the carbon skeleton of A as that of pyrolumisantonin, the location of the two

(9) J. P. Phillips, "Spectra Structure Correlation," Academic Press Inc., New York, N. Y., 1964, p 73.

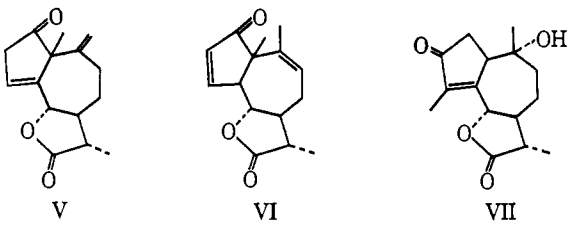
(10) N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 90.

(11) H. Ishikawa, *Bull. Pharm. Soc. Japan*, 76, 504, 507 (1956); *Chem. Abstr.*, 51, 303*d* (1957).

(12) D. H. R. Barton, J. E. D. Levisalles, and J. T. Pinhey, *J. Chem. Soc.*, 3472 (1962).

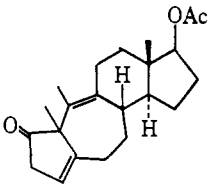
(13) D. H. R. Barton, P. de Mayo, and M. Shafiq, *Proc. Chem. Soc.*, 345 (1957); *J. Chem. Soc.*, 929 (1957).

(14) D. Arigoni, H. Bosshard, H. Bruderes, B. Buchi, O. Jeger, and L. J. Krebaum, *Helv. Chim. Acta*, 40, 1732 (1957).



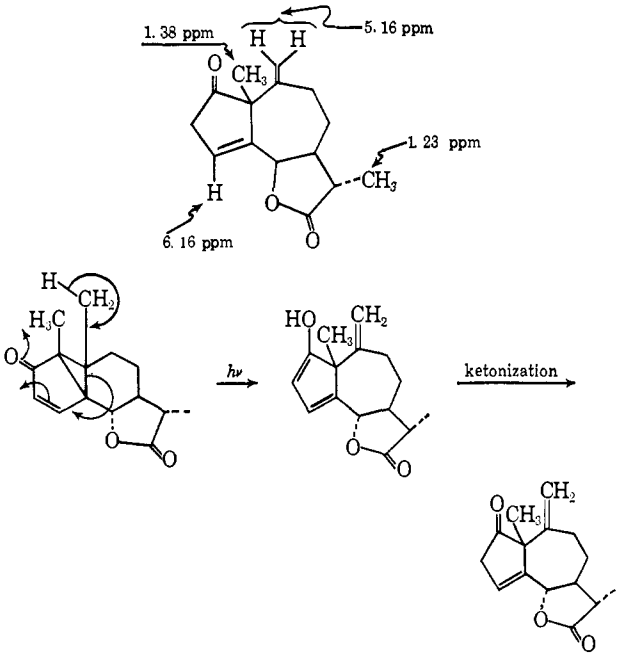
V VI VII

double bonds remains. The ultraviolet spectrum of A does not exhibit absorption characteristic of a conjugated unsaturated ketone and the infrared absorption at 1755 cm^{-1} in chloroform is characteristic of an unconjugated cyclopentenone, and is the basis for the assignment of the cyclopentenone double bond as in V. This assignment is also consonant with the product VIII obtained directly from the pyrolysis of lumi-4-methyldehydrotestosterone acetate.[15]



VIII

The remaining double bond is assigned to an exocyclic methylene group on the basis of the nmr spectrum shown in Figure 2. In the methyl region there are absorptions from two methyl groups: a singlet from the quaternary methyl group (three protons, δ 1.38 ppm) and the doublet of the lactonic substituent (three protons, δ 1.23 ppm, J = 6.5 cps). In the double bond region there is a doublet (two protons, δ 5.1, 5.2 ppm) due to the two protons of the exocyclic methylene group and at lower field a broad absorption (one proton, δ 6.16 ppm) attributable to the proton on the double bond of the cyclopentenone ring. The structure of A also accords with mechanistic considerations in which the excited chromophore of lumisantonin undergoes an intramolecular hydrogen abstraction leading to the enol of H which ketonizes to the unconjugated β,γ-unsaturated ketone.



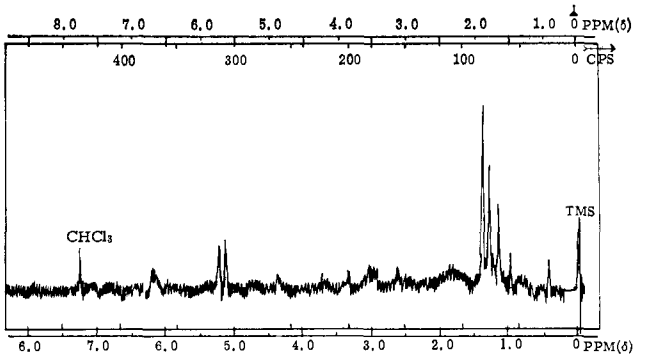
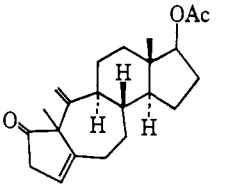


Figure 2. Photoproduct A in $CDCl_3$.

The cycloheptene unsaturation in pyrolumi-4-methyldehydrotestosterone acetate (VIII) was assigned by analogy to pyrolumisantonin. Based on the structure of the first pyrolytic intermediate of lumisantonin, the double bond in the steroid analog may well also have an exocyclic location and IX be, then, the true structure for pyrolumi-4-methyldehydrotestosterone acetate.



IX

Mazdasantonin and its dimer account for 80% of the mixture obtained on photolysis of lumisantonin in aprotic solvents; A accounts for about 10%. The remaining material (10%) consists of two compounds, B and C, in roughly equal yield plus traces of D and E, tertiary photoproducts arising from further reaction of B. Photoproducts B and C were isolated in approximately 3% yield after almost any time of irradiation except after very long photolyses (5 days) when neither was present.

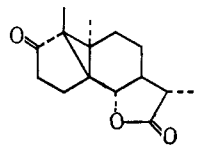
Table II

	Infrared, λ_{max}^{KBr}, cm^{-1}	Ultraviolet, λ_{max}^{EtOH} mμ (log ϵ)
Lumisantonin	1703, 1576	239 (3.70)
Compound B	1695	244 (3.67)
		338 (2.02)
Compound C	1700	237

The spectra of B and C show many similarities to those of lumisantonin (see Table II). Hydrogenation of lumisantonin yields the known substance X. Hydrogenation of B or C under identical conditions using Adams catalyst led to homogeneous compounds the infrared spectra of which were identical with that of dihydrolumisantonin except for small differences in the fingerprint region. The structural similarity of B and C to lumisantonin is also supported, albeit in a negative way, by the observation that neither lumisantonin, B,

(15) D. H. R. Barton, P. de Mayo, and M. Shafiq, *Proc. Chem. Soc.*, 205 (1957); *J. Chem. Soc.*, 140 (1958); D. H. R. Barton, P. de Mayo, and M. Shafiq, *ibid.*, 3314 (1958).

nor C forms a dinitrobenzylhydrazone derivative in contrast to santonin, mazdasantonin, their 6 epimers and a substance, to be discussed subsequently, believed

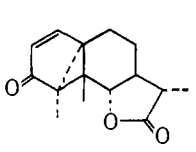


X

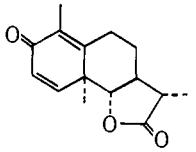
to be a dimer of mazdasantonin.

The nmr spectra also suggest that B, C, and lumisantonin have very similar structures. Each has an AB doublet of doublets, two singlets corresponding to two quaternary methyl groups, and a doublet due to the lactonic methyl group. The C-6 (lactonic) proton is also similar for lumisantonin, B, and C but quite unlike the absorption pattern for this proton in other isomers (Table III). In lumisantonin, B, and C, this proton gives rise to a doublet that is shifted to considerably higher fields than in the precursor santonin, or in subsequent photoproducts such as mazdasantonin.

A possible structure for B is XI formed *via* XII, the formation of which has precedence in the work of Arigoni, *et al.*,[14] in the photolysis of a number of steroid systems.



XI



XII

Lumiproducts such as XI are stable compounds and should undergo further photoreactions characteristic of lumisantonin. Accordingly B was irradiated and found to produce two new products D and E in the ratio 4:1 (by vpc); the infrared spectra of these substances showed them to be similar to the analogous A and mazdasantonin, respectively, obtained by irradiation of lumisantonin. Inspection of models shows D to be free of strain (like A in this regard) whereas E should be considerably destabilized by steric interaction of the *gem*-dimethyl group with the lactonic oxygen on the same end of the double bond. This may account for the reversal in relative yields in products with azulenic and naphthalenic structures from lumisantonin or its "upside-down" isomer. Such interaction may also explain the hyposchromic shift of the carbonyl absorption of E to 1685 cm^{-1} in chloroform (mazdasantonin absorbs at 1665 cm^{-1}). Structures such as XVIII and XVII can therefore be suggested for D and E, respectively.

Another major photolytic process occurs when mazdasantonin is irradiated in aprotic solvent to give F which may be a dimer of mazdasantonin and which is much more polar and far less soluble than any other photoproduct. Formation of F is very markedly a function of the concentration of mazdasantonin and an obvious trend to lower relative yields of F is seen as the concentration of mazdasantonin is reduced. The formation of such a possibly dimeric product from mazdasantonin may be related to the observation, mentioned earlier, that the nmr spectrum of mazdasantonin is very susceptible to concentration. Another interesting aspect of the formation of F is the observation that, of all the photoreactions discussed hitherto, this is the only one to be quenched by azulene or oxygen.

Experimental Section

Melting points are corrected.

Liquid–Liquid Chromatography. Celite (Johns-Manville 535) was allowed to stand in warm dilute hydrochloric acid overnight. The Celite was collected by suction filtration and washed twice with water, and the acid treatment repeated. After three washings with distilled water, the Celite was washed with a 1:1 mixture of methanol–ethyl acetate, twice with water, once with 1:1 methanol–ethyl acetate, and finally five additional times with distilled water. The Celite was then dried in an oven for 2 days.

Phases were prepared by combining 500 ml of nitromethane (dried over anhydrous calcium sulfate and distilled, bp 100°), 1 l. of decanted hexane (dried 1 day each over two successive portions of anhydrous calcium chloride, then refluxed at least 4 hr over calcium hydride, then distilled, bp 68°), and 200 ml of benzene (purified in the same fashion as the hexane, bp 79°) in a 3-l. erlenmeyer flask and agitating on a shaking machine for at least 4 hr. The phases were separated and the volume of the lower phase brought to 500 ml before the next equilibration by addition of fresh nitromethane. Owing to slow decomposition of the lower phase on standing in glass containers, it was usually redistilled before each run.

Chromatography was performed at 30.0° (Brinkmann constant-temperature bath) in a 2 in. × 1 m thermal-jacketed column. To 320 g of Celite, prepared as described above, was added 150 ml of the lower phase and the resulting mixture was stirred until a consistent, essentially dry, texture was obtained. This Celite was then packed in the column in heaping tablespoonsful and tamped down. The charge (usually 2 g), dissolved in 6 ml of the lower phase, was mixed with 20 g of Celite. Residual charge was rinsed into the 20-g portion of Celite in two 2-ml portions of lower phase. The total mixture (charge + Celite) was stirred until a consistent, essentially dry, texture was obtained and packed into the column.

Before chromatography was begun, the column reservoir (2 l.) and equilibration chamber (2 l.) were equilibrated at 30.0° for at least 1 hr. The eventual flow rate was approximately 7 ml/min and cuts of 140 ml were taken. Ultimate consumption of upper phase was 10–12 l./run.

Mazdasantonin was prepared by irradiation of lumisantonin (1.34 g) for varying lengths of time in 750 ml of anhydrous benzene under nitrogen. The light source was a Hanovia 200-W lamp (s-654 A) whose output was filtered through a uranium glass sleeve filter (cutoff ~3200 Å).

Separation by liquid–liquid partition chromatography and two recrystallizations from acetone–hexane yielded yellow prisms: mp 118.2–119°; λ_{max} 318 mμ (log ε 3.89); $\nu_{max}^{KBr\ pellet}$ 1781, 1661, and 1629 cm^{-1}; $\nu_{max}^{CHCl_3}$ 1783, 1666, 1632 cm^{-1}.

The nmr spectrum in deuteriochloroform is shown in Figure 1.

Anal. Calcd for $C_{13}H_{13}O_3$: C, 73.17; H, 7.14. Found: C, 72.99; H, 7.32.

The dinitrophenylhydrazone was prepared by reaction of mazdasantonin with an ethanolic solution of dinitrophenylhydrazine and phosphoric acid.[16] The same derivative was obtained upon reaction of mazdasantonin with an ethanolic solution of dinitrophenylhydrazine and sulfuric acid.[17] Three recrystallizations from chloroform–ethanol gave red-orange plates: mp 240.8–241.0° dec; $\lambda_{max}^{CHCl_3}$ 403 mμ (log ε 4.18).

Anal. Calcd for $C_{21}H_{22}O_6N_4$: C, 59.15; H, 5.16; N, 13.14. Found: C, 58.76; H, 5.30; N, 13.06.

Note: Mazdasantonin and the other photoproducts described can all be obtained more conveniently (in that the isolation and purification of lumisantonin is not required) by irradiation of santonin itself under conditions identical with those reported herein using lumisantonin.

6-Epimazdasantonin.[6] Mazdasantonin (10 mg) was treated for 2 hr at room temperature with a mixture of 1 ml of concentrated hydrochloric acid and 2 ml of glacial acetic acid. The solution was then diluted with water, neutralized with saturated sodium carbonate solution, and extracted two times with chloroform. The chloroform solution was dried over anhydrous magnesium sulfate

(16) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 344.

(17) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 219.

and the chloroform was removed to give an oil which had single absorption at 307 mμ (lit.[6] 308 mμ). The carbonyl absorption at 1666 cm^{-1} in mazdasantonin had been shifted to 1670 cm^{-1} in chloroform.

The dinitrophenylhydrazone prepared as above was recrystallized from chloroform–ethanol to give plates, mp 255°. A mixture melting point with a sample provided by Professor Chapman was not depressed and the infrared spectra of the two derivatives were superimposable.[7]

Compound A. Lumisantonin (502 mg) was heated in a sealed degassed ampoule at 200° (Wood's metal bath) for 1 hr. Liquid–liquid partition chromatography of the resulting oil led to recovery of 334 mg (67%) of lumisantonin and yielded 172 mg (33%) of impure A.

Compound A was also obtained directly from photolysis mixtures of santonin or lumisantonin after irradiations for 6–20 hr by liquid–liquid partition chromatography generally in 5–10% yield based on the amount of santonin or lumisantonin which had reacted. The product is a colorless oil which could be induced to crystallize: $\lambda_{max}^{C_2H_5OH}$ 299 mμ; $\nu_{max}^{liq\ film}$ 1783 and 1753 cm^{-1}; $\nu_{max}^{CHCl_3}$ 1781 and 1755 (strong), 1638 cm^{-1} (weak). An analysis of A was not obtained.

When A was passed through alumina (Woelm, neutral grade II), it was converted to pyrolumisantonin which showed absorptions at 1779 and 1716 cm^{-1} in a potassium bromide pellet (lit.[14] 1770 and 1705 cm^{-1} in KBr). Catalytic hydrogenation over platinum of either A or pyrolumisantonin gave the same products with superimposable infrared spectra and major peaks at 1770 and 1735 cm^{-1} in potassium bromide (lit.[14] 1770 and 1730 cm^{-1}).

Compound B was isolated in yields of 1–3% from irradiations of 3–20-hr duration of santonin or lumisantonin as described above for mazdasantonin. After isolation by liquid–liquid partition chromatography, B was recrystallized from acetone–hexane to give colorless prisms: mp 174.4–175.0°; $\lambda_{max}^{C_2H_5OH}$ 244 mμ (log ε 3.67) and 338 (2.01); $\nu_{max}^{KBr\ pellet}$ 1791 and 1697 cm^{-1}. The mass spectrum showed a parent peak at *m/e* 246 ± 1, but the substance did not give an analysis for $C_{15}H_{18}O_3$, but repeated analyses (of the same material which gave a parent peak at *m/e* 246 ± 1) were more in accord with $C_{15}H_{18}O_4$ or $C_{15}H_{20}O_4$.

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.77; H, 7.32. Calcd for $C_{15}H_{18}O_4$: C, 68.70; H, 6.87. Calcd for $C_{15}H_{20}O_4$: C, 68.18; H, 7.58. Found: C, 68.83; H, 6.95.

Hydrogenation of B over platinum yielded a derivative which had $\nu_{max}^{CHCl_3}$ 1776 and 1715 cm^{-1}.

Compound C. Another substance, C, was also isolated in 1–3% yield by liquid–liquid partition chromatography of the products from irradiation of santonin or lumisantonin as described above. Compound C was a colorless oil which was easily oxidized by air to a yellow-green viscous material; C was also unstable even in the dark under nitrogen. The shape of the ultraviolet spectrum was very like the spectrum of B and lumisantonin and showed a maximum at 237 mμ in ethanol: $\nu_{max}^{CCl_4}$ 1803 and 1700 cm^{-1}; $\nu_{max}^{CHCl_3}$ 1777 and 1715 cm^{-1}. Catalytic hydrogenation over platinum produced a product which had $\nu_{max}^{CHCl_3}$ 1773 and 1714 cm^{-1}. The instability of C and the small amounts available precluded further, more definitive characterization of the substance.

Irradiation of Compound B. Fractions D and E. Irradiation of compound B in benzene solution under conditions used previously until the starting material is completely gone yields a mixture which can be separated by vpc into two fractions, D and E, in the ratio 4:1. Both D and E are oils. The infrared spectra of these are analogous to those of compound A and mazdasantonin, respectively. The ketonic carbonyl absorption of E however falls at 1685 cm^{-1} in chloroform.

Fraction F. The last material to be obtained from partition chromatography of mixtures from irradiation of santonin, lumisantonin, or mazdasantonin was F, the amount of which is a function of the concentration of the precursor. For example, at a concentration of about 10^{-2} *M* mazdasantonin, fraction F accounted for almost 25% of the photoproducts, whereas at a concentration of about 10^{-3} *M* mazdasantonin, fraction F was 6% of the products. Further purification was unsuccessful, the material could not be eluted from alumina (even the least active), and sublimation at 10^{-4} mm at 200° led only to decomposition. Fraction F has $\nu_{max}^{CHCl_3}$ 1778 and 1718 cm^{-1}; after hydrogenation in ethyl acetate over platinum (Parr apparatus) the product has $\nu_{max}^{CHCl_3}$ 1781 (broad), 1730, and 1720 cm^{-1}.

A Cyclobutadiene Cation Radical in the Mass Spectrometer. The *p*-Fluoro Substituent as a Label for the Study of Mass Spectral Reactions

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Abstract: The $(M - CO)\cdot^+$ ion in the spectrum of a tetracyclone is shown to have a closed structure, and therefore is a rectangular cyclobutadiene radical cation or possibly its tetrahedrane counterpart. A new general labeling technique is employed to obtain this result.

Several papers have now examined the effects of substituents on mass spectral reactions.[1-4] Some substituents rearrange after electron impact, as, for example, the nitro group,[1c,5] or promote ring expansion, as does the methyl group.[6] Most substituents cause appreciable variation in the intensities of product ions; if the product does not retain the substituent, it is often true that electronic effects similar to those observed in solution regulate intensities.[1a] So, for example, strongly electron-withdrawing substituents greatly decrease product intensities, while electron-releasing substituents enhance them; a product competing with a dimethylamino-substituted ring for the charge will almost never be a major

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