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1,3-Dipolar and Diels–Alder Cycloaddition Reactivity of Lumisantonin[1]

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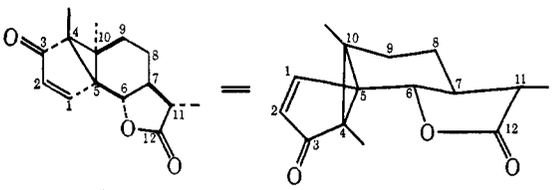
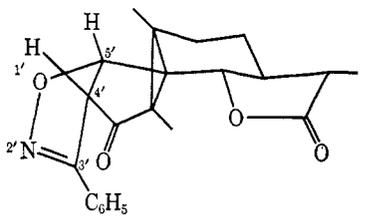
Some double-bond derivatives of lumisantonin (**1**) were prepared by its 1,3-dipolar and Diels–Alder cycloaddition reactions. Benzonitrile oxide, α,N-diphenylnitrone, and diazomethane afforded the corresponding 1:1 adducts **2**, **3a**, **3b**, and **4**, respectively, but diphenylnitrilimine, phenyl azide, and tosyl azide did not give any adduct. The pyrolysis and photolysis of **4** afforded 1-methyl lumisantonin (**5**) and 1,2-methylene lumisantonin (**6**), respectively; **6** was surprisingly stable on heating at 250°. The Diels–Alder reactions with cyclopentadiene, furan, isoprene, and myrcene were investigated, but only cyclopentadiene gave the corresponding 1:1 adduct **8a**. In the reactions with isoprene and myrcene, pyrolumisantonin was produced in very low yields as a by-product.

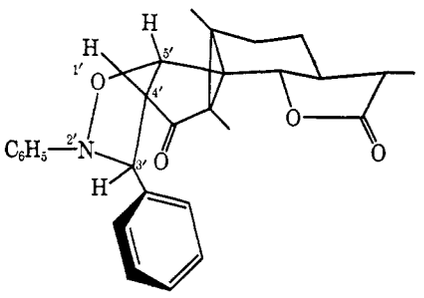
Although a number of double-bond derivatives of santonins and their derivatives have been reported,[2] only little about those of lumisantonin (**1**) has been known.[3] In aiming to prepare some double-bond derivatives of **1**, its 1,3-dipolar and Diels–Alder cycloaddition reactions were investigated. As the 1,3 dipoles were utilized, benzonitrile oxide, α,N-diphenylnitrone, diazomethane, diphenylnitrilimine, and phenyl and tosyl azide, the former three gave the corresponding adducts, **2**, **3a**, **3b**, and **4**, respectively, but the latter



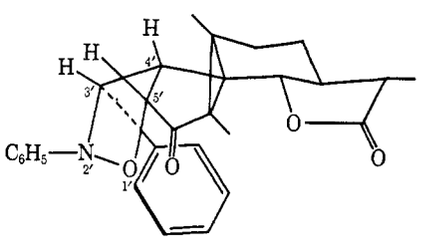
1



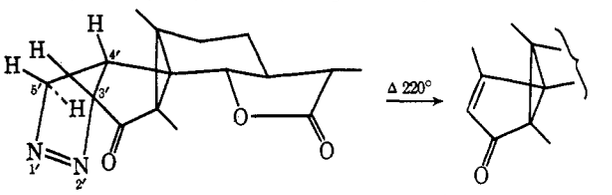
2



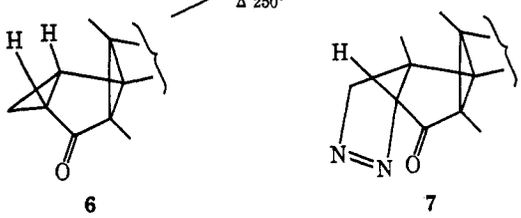
3a



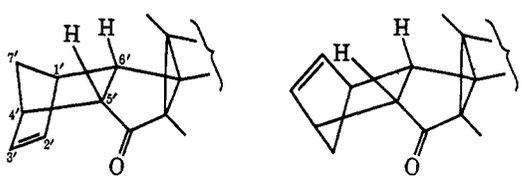
3b



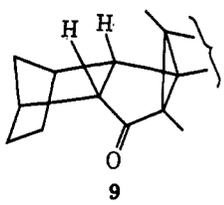
4 **5**



6 **7**



8a **8b**



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(1) Part III in the series of "Studies on the Reactions of Isoprenoids." Part II: T. Sasaki and S. Eguchi, *Bull. Chem. Soc. Jap.*, **41**, 2453 (1968).

(2) See, for example, J. B. Hendrickson and T. L. Bogard, *J. Chem. Soc.*, *B*, 1678 (1962).

(3) For pioneering works on lumisantonin and its stereochemistry, see (a) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger, and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957); (b) W. Cocker, K. Crowley, J. Edwards, T. B. H. McMurry, and E. R. Stuart, *J. Chem. Soc.*, 3416 (1957); (c) D. H. R. Barton, P. de Mayo, and M. Shafiq, *ibid.*, 140 (1958); (d) D. H. R. Barton, and P. T. Gilham, *ibid.*, 4596 (1960); (e) D. H. R. Barton, J. T. Pinhey, and R. J. Wells, *ibid.*, 2518 (1964).

three did not. The pyrolysis and photolysis of **4** afforded 1-methyl lumisantonin (**5**) and 1,2-methylene lumisantonin (**6**), respectively.

In the Diels–Alder reactions, cyclopentadiene, furan, isoprene, and myrcene were applied as the diene, in which only cyclopentadiene gave the corresponding Diels–Alder adduct **8a** in a low yield.

Results and Discussion

The reaction of lumisantonin (**1**) with benzonitrile oxide was carried out by refluxing an ethereal solution of **1** and benzohydroxamoyl chloride[4] in the presence of triethylamine. Purification of the reaction products afforded a 1:1 adduct in a 51% yield as colorless needles which exhibited infrared absorption bands at 1770 (γ-lactone), 1710 (cyclopentanone conjugated with a cyclopropane), 1602 and 710 (phenyl) cm^{-1}. Assuming principally the occurrence of a β side addition of benzonitrile oxide to **1** because of the presence of C-10 α-methyl group in **1**, the structure was assigned as **2** based on the nmr data which had signals at τ 4.41 and 5.71 (a pair of d, J = 6.5 Hz, assignable to protons at 4′ and 5′ positions of a oxazoline ring), and those at τ 2.07–2.70 (5 H, m, phenyl protons), 6.14 (1 H, d, J = 8.2 Hz, C-6 H), 8.65 (3 H, d, J = 6.5 Hz, C-11 methyl protons), 8.73 and 8.78 (each 3 H, s, C-4 and C-10 methyl protons).

Reaction of **1** with α,N-diphenylnitrone in refluxing benzene afforded two kinds of 1:1 adducts, **3a** and **3b**, in 24 and 8% yields, respectively. The nmr spectrum of the main product **3a** had two doublets at τ 4.83 (J = 9.0 Hz) and 4.92 (J = 6.0 Hz), assignable to 3′ and/or 5′ protons, and a quartet at τ 6.52 (J = 9.0 and 6.0 Hz) assignable to 4′ proton besides signals due to two phenyl protons at τ 2.40–2.81 (10 H, m) and three methyl protons at τ 8.72 (3 H, d, J = 6.5 Hz, C-11 methyl protons), 8.99 and 9.33 (each 3 H, s, C-10 and C-4 methyl protons). The fact that the chemical shift of C-4 methyl protons was considerably higher than those of **2** and **1**[5] may be explained by a diamagnetic anisotropy of 3′-phenyl ring[6] supporting the structure **3a**. The structure of the minor product, therefore, could be assumed reasonably to be **3b** which was supported by the nmr signals at τ 2.30–2.88 (10 H, m, two phenyl ring protons), 3.61 (1 H, slightly broad s, C-5′ H of a oxazolidine ring), 5.63 (1 H, d, J = 5.8 Hz, C-3′ H of a oxazolidine ring), 6.47 (1 H, d, J = 8.5 Hz, C-6 H), 6.57 (1 H, d, J = 5.8 Hz, C-4′ H of a oxazolidine ring), 8.72 (3 H, d, J = 5.5 Hz. C-11 methyl protons), 9.00 and 9.42 (each 3 H, s, C-10 and C-4 methyl protons).[7]

Contrary to benzonitrile oxide and α,N-diphenylnitrone, diazomethane reacted very smoothly with **1** even at room temperature to give a 1:1 adduct (**4**) almost quantitatively, the structure of which was assigned from the following spectral evidence: 1-pyrazoline structure has been shown by the infrared absorption band of N=N stretching frequency at 1560 cm^{-1} and by the lack of NH band, and a typical azoalkane n–π^* ultraviolet absorption at 322 mμ (ϵ 535).[8] In the nmr spectrum of **4**, the signal due to 3′ proton appeared at τ 4.60 in a doublet (J = 8.0 Hz) which was further split into a quartet (J = 2.5 and 1.5 Hz) by the long-range coupling with 5′-methylene protons, those of 5′ protons at τ 4.92 and 5.14 as AB portions of an ABX pattern, in which a X portion due to 4′ proton appeared at τ 7.18 in a broad quartet.[8] The signals due to C-6 H and three methyl protons appeared at τ 6.30 (1 H, d, J = 10.3 Hz), 8.61, 8.64, and 8.74 (9 H, s), respectively, at the similar positions to those of **1** and **2**. This structure was also supported by its pyrolytic decomposition to 1-methyl lumisantonin (**5**); **4** on heating at 210–220° for several minutes yielded a brownish mass which was purified on a silica gel column to give needles with a melting point of 155–157° in a 54% yield. This compound was characterized as 1-methyl lumisantonin (**5**) by the analytical and the spectral data. The infrared absorption bands at 1768, 1688, and 1595 cm^{-1} and the ultraviolet absorption maxima at 215.5 mμ (ϵ 6182) and 257 (3448) were compatible with the structure **5**. The nmr spectrum had signals at τ 4.27 (1 H, q, J = 1.5 Hz) assignable to C-2 H, and 7.81 (3 H, d, J = 1.5 Hz) assignable to C-1 methyl protons, besides those due to C-6 H at τ 6.12 (d, J = 10.0 Hz) and three methyl groups at C-4, C-10, and C-11 at τ 8.77 (s), 8.83 (s), and 8.72 (d, J = 6.0 Hz), respectively. In the above pyrolysis, no trace of a cyclopropane derivative **6** could be isolated, and the minor possibility that **6** had been produced at first as an intermediate in the decomposition, followed by its rearrangement to **5**, was excluded by the fact that **6** was stable in the pyrolytic conditions.[9] This compound **6**, on the other hand, was obtainable in a 50% yield on the photolytic decompositions of **4** at 20°. The presence of a cyclopropane structure in **6** was indicated by its nmr spectrum, which had the signals at τ 8.34–9.20 in a complex multiplet for four protons.

It should be mentioned here that the formation of **5** on pyrolysis and **6** on photolysis both from **4** might supply an example of decomposition of 1-pyrazoline that might proceed *via* a dipolar intermediate on pyrolysis and *via* a diradical intermediate on photolysis.[10]

1-Methyl lumisantonin (**5**) had been treated also with diazomethane to examine its reactivity in the cycloadditions. However, an adduct **7** melting at 229–232° dec was produced in a very low yield, suggesting considerable steric hinderance of C-1 methyl

(4) M. H. Benn, *Can. J. Chem.*, **42**, 2313 (1964), and references cited therein.

(5) The chemical shifts of C-4 and/or C-10 methyl protons have been reported as τ 8.77 and/or 8.88: J. T. Pinhey and S. Sternhell, *Aust. J. Chem.*, **18**, 543 (1965).

(6) An inspection of the Drieding stereomodel indicated obviously that the carbonyl group hindered sterically a free rotation of 3′-phenyl ring.

(7) A larger steric hindrance for a free rotation of 3′-phenyl ring with a lactone ring in **3b** was suggested by the Dreiding model inspection, and this steric hindrance may cause to lower **3b**'s yield more than **3a**'s. The higher chemical-shift values of C-4 methyl protons might be ascribable to a diamagnetic anisotropy of the 3′-phenyl ring.

(8) For spectral properties of 1-pyrazolines, see R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Amer. Chem. Soc.*, **88**, 3959 (1966), and references cited therein. The observed geminal coupling constant of 5′-methylene protons in **4** was *ca.* 16 Hz.

(9) Compound **6** was stable and unchanged on heating *in vacuo* even at 250° for 2 hr, though **1** has been known to decompose on heating at 200°; see ref 3a.

(10) In extrusion reactions of nitrogen from 1-pyrazoline, two different intermediates (nitrogen-free diradical and dipolar or ionic) have been postulated depending on reaction conditions and on the substituents: (a) B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press Ltd., Oxford, 1967, pp 116–134; (b) D. E. McGreer and W-S. Wu, *Can. J. Chem.*, **45**, 461 (1967); (c) R. J. Crawford and L. H. Ali, *J. Amer. Chem. Soc.*, **89**, 3909 (1967); and references cited in 10a–c.

group for cycloadditions.[11] 1-Pyrazoline structure of **7** was evidenced by its spectral data (see Experimental Section). The stability of 1-pyrazoline structure in **4** and **7** might come from their characteristic ring system, even though they have an enolizable hydrogen at the 3′ position.[12]

Diphenyl nitrilimine, known as a 1,3 dipole of nucleophilic character,[13] did not react with **1** at all. This lower reactivity might come from the steric hindrance of bulky phenyl group as observed in the reaction of α,N-diphenylnitrone with **1**. Since organic azides are known to be 1,3 dipoles of rather electrophilic character and their reactivity toward some strained olefins are relatively higher,[13] **1** was treated with phenyl azide and tosyl azide, but no addition had occurred.

The Diels–Alder reaction of **1** with cyclopentadiene was carried out by heating a mixture of **1** and dicyclopentadiene in a sealed tube at 180–185° for 24 hr. The product was purified on a silica gel column to afford a 1:1 adduct in a 28% yield. The structure was assigned as the *endo* isomer **8a** rather than the *exo* isomer **8b** from its nmr spectrum; a comparison of the chemical shifts due to two methyl groups at C-4 and C-10 (τ 9.05 and 8.86) of this adduct with those (τ 8.85 and/or 8.90) of a dihydro derivative **9**, indicated the presence of a diamagnetic shift due to a double bond for one of the two methyl groups. In **8a**, C-4 methyl protons are held in the shielding cone of the double bond, whereas in **8b**, both methyl protons at C-4 and C-10 are remote from the double bond and thus the signal at τ 9.05 could be assignable to C-4 methyl protons, supporting the assigned *endo* structure **8a**.[14]

Diels–Alder reactions of **1** with furan (at 100° for 3 days), isoprene (at 145° for 40 hr), and myrcene (at 150° for 64 hr) were all unsuccessful, recovering the starting **1**. In the latter two reactions, however, a compound with a melting point of 126–128° was isolated in low yields in addition to the recovered **1** by chromatography. This product was identical with the known pyrolumisantonin[3a] by the mixture melting point determination and the perfect superimposition of the infrared spectrum with an authentic sample's.

As a conclusion, it can be stated that lumisantonin is a good 1,3 dipolarophile with nucleophilic 1,3 dipoles involving no bulky substituents, but its dienophilic reactivity seems to be considerably low.

Experimental Section[15]

Reaction of 1 with Benzonitrile Oxide.—To a refluxing mixture of 248 mg (1.00 mmol) of lumisantonin (prepared from α-santonin by the method of Arigoni, *et al.*[3a]) and 187 mg (1.20 mmol) of benzhydroxyamoyl chloride[4] in 20 ml of ether was added slowly a solution of triethylamine (140 mg) in 10 ml of ether in *ca.* 0.5 hr. Refluxing was continued for further 2 hr, and the reaction mixture was washed with water, dried over anhydrous sodium sulfate, and dried up to give a white solid which was purified on a silica gel (Mallinckrodt, 100 mesh) column. The first fractions eluted with chloroform gave 100 mg of diphenylfuroxan, mp 115–117° (from ethanol, lit.[16] mp 115°), and the second fractions gave 50 mg of the recovered **1**. The third fractions afforded 185 mg (51%) of **2**, mp 263–265° (from chloroform–*n*-hexane).

Anal. Calcd for $C_{22}H_{23}O_4N$: C, 72.31; H, 6.34; N, 3.83. Found: C, 71.92; H, 6.22; N, 3.58.

Reaction of 1 with α,N-Diphenylnitrone.—A mixture of 248 mg (1.00 mmol) of **1** and 197 mg (1.00 mmol) of α,N-diphenylnitrone[17] in 10 ml of benzene was refluxed for 15 hr, and the crude products were chromatographed on a silica gel column. From the fractions eluted with chloroform, 34 mg (8%) of **3b** was obtained as needles (from chloroform–*n*-hexane): mp 201–203°; ir (KBr), 1763 (γ-lactone), 1725 (cyclopentanone), 1601, 1590, 765, and 700 (phenyl) cm^{-1}.

Anal. Calcd for $C_{28}H_{29}O_4N$: C, 75.82; H, 6.59; N, 3.16. Found: C, 75.52; H, 6.55; N, 3.07.

From the fractions eluted with chloroform–methanol (2% methanol v/v), 105 mg (24% yield) of **3a** was obtained as needles (chloroform–*n*-hexane): mp 210–212°; ir (KBr), 1770 (γ-lactone), 1725 (cyclopentanone), 1600, 760, and 700 (phenyl) cm^{-1}.

Anal. Calcd for $C_{28}H_{29}O_4N$: C, 75.82; H, 6.59; N, 3.16. Found: C, 75.53; H, 6.66; N, 2.97.

Reaction of 1 with Diazomethane.—To a solution of **1** (496 mg, 2.0 mmol) and a few drops of triethylamine in a minimum amount of chloroform (*ca.* 3 ml) was added an ethereal solution of diazomethane (prepared from 2.0 g of nitrosomethylurea in 100 ml of ether). The mixture was kept standing in a dark place at room temperature for 24 hr. Large needle crystals were separated which was almost pure **4**, melting at 203–207° dec, and amounted to 560 mg (97%). An analytical sample was recrystallized from chloroform–ether: mp 207–208° dec; ir (KBr), 1770 (γ-lactone), 1728 (cyclopentanone), and 1560 (N=N) cm^{-1}.

Anal. Calcd for $C_{16}H_{20}O_3N_2$: C, 66.64; H, 6.99; N, 9.72. Found: C, 67.04; H, 7.02; N, 10.06.

Pyrolysis of 4.—Heating of 300 mg of **4** in a longer test tube (25-cm length and 1.5-cm diameter) at 210–220° completed nitrogen extrusion in a few minutes, and the resulting dark brown mass was purified on a silica gel column. From the fraction eluted with chloroform, 140 mg (54% yield) of 1-methyl luminsantonin **5** was obtained as needles (from methanol), mp 155–157°.

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.59; H, 7.97.

Photolysis of 4.—Irradiation of a suspension of 320 mg (1.11 mmol) of **4** in 200 ml of ether at room temperature (*ca.* 20°) through a quartz cooling jacket with a 100-W high-pressure mercury lamp (UM-102, Ushio Denki Co., Tokyo) caused an evolution of nitrogen. It was completed in *ca.* 3 hr; at the end of this period the suspension became to a clear solution which was dried up to give a yellowish residue. Purification on a silica gel column using chloroform as an eluent afforded 143 mg (50% yield) of **6** as plates (from chloroform–*n*-hexane): mp 253–256° (the crystal form changed at *ca.* 200°); uv max (EtOH) 273 mμ (ε 126); ir (KBr) 3055 (cyclopropane C–H), 1770 (γ-lactone), and 1710 (cyclopentanone conjugated with cyclopropanes) cm^{-1}; nmr τ 6.44 (1 H, d, J = 9.0 Hz, C-6 H), 8.34–9.20 (complex m, superimposed with the signals of three methyl groups but total area for this region corresponded to 9 H + 4 H = 13 H; this indicated the presence of 4 H attached to a cyclopropane), 8.72 (d, J = 7.5 Hz), 8.76 (s) (each *ca.* 3 H and assignable the former to C-11 methyl protons and the latter to C-10 methyl protons), and 8.92 (*ca.* 3 H, s, C-4 methyl protons).

(11) A nonbonded interaction of C-1 methyl with C-10 methyl in the product as well as C-1 methyl's steric hindrance for the approach of a attacking molecule may cause lower the yield.

(12) A facile isomerization of 1-pyrazolines to 2-pyrazolines is known as a general trend of 1-pyrazolines with an active hydrogen at the 3 position; see also ref 13a.

(13) (a) For a recent review, see R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, pp 806–878; (b) R. Huisgen, H. Knupfer, R. Sustman, G. Wallbillich, and V. Weberndörfer, *Ber.*, **100**, 1580 (1967).

(14) In the Diels–Alder reactions of a cyclic dienophile with cyclic dienes, the *endo*-addition rule is well established; see ref 13a, pp 910–912.

(15) All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were carried out on a Yanagimoto C. H. N. Corder Model MT-1. Infrared spectra were recorded on a Jasco Model IR-S infrared spectrophotometer and ultraviolet spectra, on a Jasco Model ORD/UV-5 spectrophotometer. Nmr spectra were obtained in $CDCl_3$ with a Varian A-60 or a Hitachi H-6013 spectrometer and are reported in τ values relative to tetramethylsilane as an internal standard and singlet peaks are designated as s, doublet as d, triplet as t, quartet as q, and multiplet as m.

(16) H. Reinbolt, *Ann.*, **451**, 164 (1927).

(17) A. H. Wragg and T. S. Stevens, *J. Chem. Soc.*, 461 (1959).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.86; H, 8.10.

Reaction of 5 with Diazomethane.—A mixture of 290 mg (1.11 mmol) of **5** and a few drops of triethylamine in 3 ml of chloroform was treated with an excess of diazomethane in ether, and the mixture was kept standing in a dark place for 1 week at room temperature. After removal of the excess diazomethane and the solvent, the residue was chromatographed on a silica gel column. Fractions eluted with chloroform afforded 190 mg of the starting **5**, and the fractions eluted with ethyl acetate gave 65 mg (21.5% yield) of the adduct **7** as fine needles from chloroform–*n*-hexane: mp 229–232° dec; ir (KBr) 1780 (γ-lactone), 1710 (cyclopentanone), and 1557 (N=N) cm^{-1}; nmr τ 4.60–5.50 (3 H, these signals were very weak because of low solubility in $CDCl_3$, 1-pyrazoline ring protons), 6.45 (1 H, d, J = 10.0 Hz, C-6 H), 8.69, 8.76, and 8.93 (each 3 H, s, three methyl protons at C-1, C-4, and/or C-10), and 8.80 (3 H, d, J = 7.0 Hz, C-11 methyl protons).

Anal. Calcd for $C_{17}H_{22}O_3N_2$: C, 67.52; H, 7.33; N, 9.27. Found: C, 67.95; H, 7.73; N, 9.41.

Reaction of 1 with Diphenylnitrilimine.—To a solution of 496 mg (2.00 mmol) of **1** and 450 mg (2.00 mmol) of benzphenylhydrazidoyl chloride[18] in 25 ml of benzene was added 0.5 ml of triethylamine, and the mixture was stirred for 15 hr at 40°. After being washed with water and dried over sodium sulfate, the mixture was evaporated to dryness, which, on purification by chromatography, gave 300 mg of the starting **1** (mp 155–157°) but no other crystalline products.

Reactions of 1 with Phenyl and Tosyl Azides.—**1** was treated with an equimolar amount of phenyl[19] and tosyl azide[20] in benzene solution at 40° for 2 weeks, and the product was examined on tlc, only a spot corresponding to the starting **1** being observed, which was recovered in 80–90% yield.

Reaction of 1 with Cyclopentadiene.—A mixture of 496 mg (2.00 mmol) of **1**, 200 mg (1.5 mmol) of dicyclopentadiene, and 10 mg of hydroquinone was heated at 180–185° for 24 hr in a sealed tube (under reduced pressure of 30 mm). The product was purified on a silica gel column, using chloroform as an eluent. The first fractions gave the excessd icyclopentadiene, and the second fractions afforded 175 mg (28% yield) of **8a** as needles from chloroform–*n*-hexane: mp 198–200°; ir (KBr) 1770 (γ-lactone), 1713 (cyclopentanone), and 1640 (as shoulder, double bond) cm^{-1}; uv max (MeOH) 283 mμ (ε 72); nmr τ 3.81 and 4.01 (each 1 H, AB q, J = 5.5 Hz, each peak was further split into doublet, J = 3.0 Hz) assignable to C-2′ and C-3′ H, 6.40 (1 H, broad s, C-4′ H, superimposed with the signal due to C-6 H), 6.50 (1 H, d, J = 10 Hz, C-6 H), 6.84 (1 H, broad s, C-1′ H), 7.18 and 7.28 (2 H, AB q, J = 5.0 Hz, C-1 and C-2 H = C-5′ and C-6′ H), 8.76 (3 H, d, J = 7.0 Hz, C-11 methyl protons), 8.86 and 9.05 (each 3 H, s, C-10 and C-4 methyl protons).

Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.88; H, 8.25.

Hydrogenation of 8a.—A mixture of 94 mg (0.30 mmol) of **8a** and 300 mg of prereduced Pd–C (10%) in 20 ml of ethyl acetate was hydrogenated at 21° for 5 hr. After work-up product was recrystallized from dichloromethane–*n*-hexane to afford 74 mg (79% yield) of **9** as prisms: mp 208–210°; ir (KBr) 1770 (γ-lactone) and 1720 (cyclopentanone) cm^{-1}; nmr τ 6.30 (1 H, d, J = 9.6 Hz, C-6 H), 7.05 (1 H, broad s, C-4′ H), 7.47 (3 H, broad unsymmetrical s, C-1′, C-1, and C-2 H), 8.75 (3 H, d, J = 6.0 Hz, C-11 methyl protons), 8.85 and 8.90 (each 3 H, s, C-4 and/or C-10 methyl protons).

Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.36; H, 8.88.

Reactions of 1 with Furan, Isoprene, and Myrcene.—An equimolar amount of **1** and furan, isoprene, and myrcene was heated in the presence of a catalytic amount of hydroquinone in a sealed tube at 100° for 3 days, 145° for 40 hr, and 150° for 64 hr, respectively. After work-up and chromatography on a silica gel column the product was only the starting **1**, respectively, but in the reactions with isoprene and myrcene, pyrolumisantonin was also obtained in 3–13% yields as needles (from *n*-hexane), mp 126–128° (lit.[3a] mp 126–127°), which was identified with an authentic sample by no depression of a mixture melting point and a superimposition of the infrared spectra.

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 72.69; H, 7.30.

Registry No.—**1**, 467-41-4; **2**, 17668-46-1; **3a**, 17603-79-1; **3b**, 17658-99-0; **4**, 17603-80-4; **5**, 17668-48-3; **6**, 17668-47-2; **7**, 17668-49-4; **8a**, 17668-50-7; **9**, 17668-51-8.

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