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Synthesis of a Polycyclic π-Conjugated System Containing an Azulene Unit by the Flash Vacuum Pyrolytic Method. III.[1]
Synthesis and Properties of 4-Hydroxy-3*H*-cyclopent[*a*]azulen-3-one

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4-Hydroxy-3*H*-cyclopent[*a*]azulen-3-one, a new tricyclic π-conjugated system containing a hydroxyazulene unit and a cyclopentadienone moiety, was synthesized by the application of flash vacuum pyrolysis in the final step. All the proton magnetic resonances of the compound shifted up-field compared with those of the referenced 1,2-dihydro compound in terms of an induced paramagnetic ring current in the periphery of this molecule. The characteristic prototropic tautomerization of 4-hydroxyazulenes was not observed in this system.

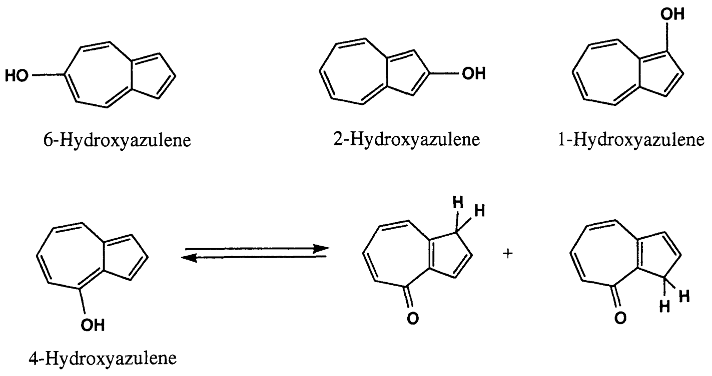
Prototropic tautomerization of hydroxyazulenes has been investigated in relation to the solvent used.[2–4] It has been shown that 2-hydroxyazulene exists in a tautomeric mixture of an enol form of 2-hydroxyazulene and a keto form of 2(1*H*)-azulenone in chloroform but only in the keto form in acetone. On the other hand, 1- and 6-hydroxyazulene exist in an enol form in both solvents. We have already investigated the tautomerization of 4-hydroxyazulene.[5] This hydroxyazulene exhibited an interesting prototropic tautomerization depending on the solvents (Scheme 1) and the substituents at the 1- and 3-positions.[6]

Recently, we reported the synthesis and properties of 3*H*-cyclopent[*a*]azulene-3-one (**2**)[7] which is formed by the condensation of antiaromatic cyclopentadienone with the five-membered ring of azulene. All the proton magnetic resonances of the azulene moiety shifted upfield indicating the contribution of a shielding effect due to an induced paramagnetic ring current in terms of a peripheral 12 π-electron framework (Scheme 2).

The title compound **1**, which has both the structures of 4-hydroxyazulene and 3*H*-cyclopent[*a*]azulen-3-one, is interesting with regard to the effect of the condensation of cyclopentadienone to the characteristic prototropic tautomerization of 4-hydroxyazulene. In this paper, the synthesis of 4-hydroxy-3*H*-cyclopent[*a*]azulen-3-one (**1**) is reported and the prototropic tautomerization and the tropicity of **1** is also be discussed.

Results and Discussion

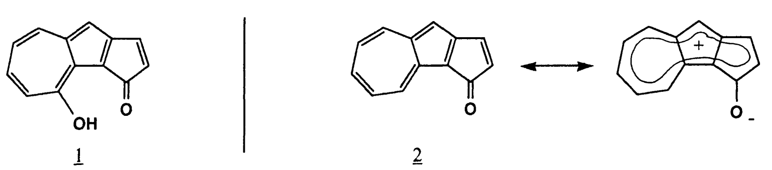
Synthesis of 4-Hydroxy-3*H*-cyclopent[*a*]azulen-3-one (1) by the FVP Method. We have already reported the effective application of Flash Vacuum Pyrolysis (FVP)



6-Hydroxyazulene 2-Hydroxyazulene 1-Hydroxyazulene

4-Hydroxyazulene

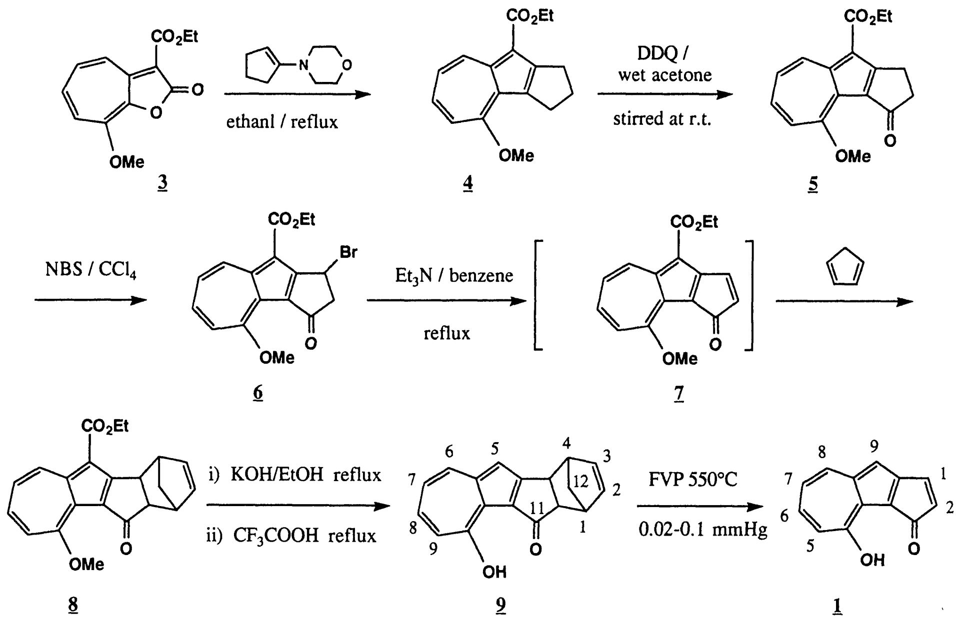
Scheme 1.



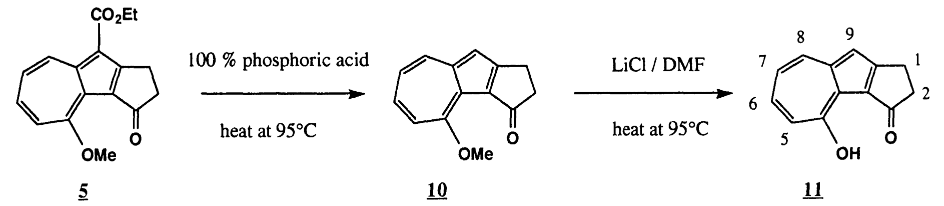
1

2

Scheme 2.



Scheme 3.



Scheme 4.

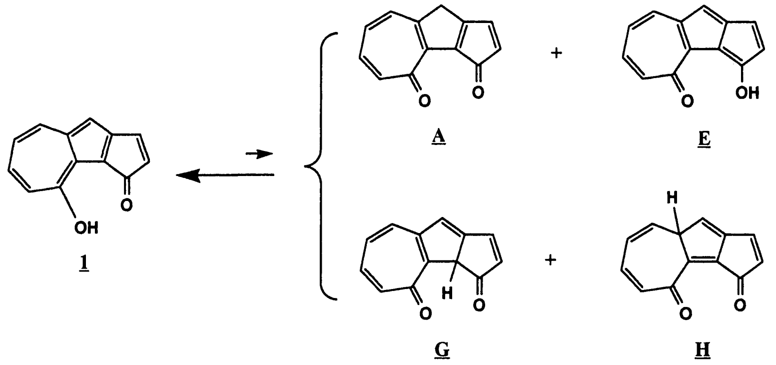
for the isolation of thermally unstable azulene derivatives such as 3*H*-cyclopent[*a*]azulen-3-one (**2**),[7] 1*H*-, and 3*H*-cyclopent[*a*]azulenes.[8] Since the target compound **1** seemed to be as unstable as 3*H*-cyclopent[*a*]-azulen-3-one (**2**), the FVP method was applied on the final step of the synthetic route of **1**. An appropriate precursor (**9**) of **1** for FVP was prepared starting from 3-ethoxycarbonyl-8-methoxycyclohepta[*b*]furan-2-one (**3**) (Scheme 3).

The reaction of **3**[9] with 1-morpholinocyclopentene gave ethyl 4-methoxy-2,3-dihydro-1*H*-cyclopent[*a*]azulene-9-carboxylate (**4**).[10] This azulene derivative (**4**) was oxidized with DDQ in aqueous acetone to give a ketone **5**.[11] Bromination of **5** with NBS gave a monobromide **6**, which was used for the next step without purification because of its instability. Dehydrobromination of **6** with triethylamine in the presence of cyclopentadiene gave a Diels–Alder adduct **8** by trapping of 4-methoxy-9-ethoxycarbonyl-3*H*-cyclopent[*a*]azulen-3-one (**7**) formed as a reactive intermediate. Hydrolysis of **8** with potassium hydroxide followed by decarboxylation with trifluoroacetic acid gave the appropriate precursor (**9**).

The pyrolytic apparatus used is described in the experimental section. Pyrolysis of **9** at 550 °C under 0.02—0.1 mmHg (1 mm Hg=133.322 Pa) resulted in the complete [4+2] cycloreversion reaction of **9** to give **1** as dark red crystals on the cold finger. Immediate purification of these crystals gave 4-hydroxy-3*H*-cyclopent-[*a*]azulen-3-one (**1**) in an 81.5% yield.

Preparation of a Reference Compound, 4-Hydroxy-1,2-dihydro-3*H*-cyclopent[*a*]azulen-3-one (11). A reference compound (**11**) was prepared from ketone **5** (Scheme 4). Demethoxycarbonylation of **5** with 100% phosphoric acid gave 4-methoxy-1,2-dihydrocyclpent-[*a*]azulen-3-one (**10**). Hydrolysis of the methoxyl group of **10** with lithium chloride in DMF[12] gave the desired reference compound (**11**).

Characterization of 4-Hydroxy-3*H*-cyclopent[*a*]-azulen-1-one (1). The prototropic tautomerization and tropic properties of **1** were investigated. The prototropic tautomerization was investigated by NMR. Previously, we reported that 4-hydroxyazulene exists mainly in a keto form in chloroform, and in an enol form in acetone.[5] Possible prototropic tautomers of **1** are shown in Scheme 5. Among these, the tautomers **A** and **E** are extremely unacceptable owing to the isolated cyclopentadienone structure of **A** and the pentalene moiety of **E**, respectively. Tautomers **G** and **H** could be easily distinguished from the enol form of 4-hydoxy-3*H*-cyclopent[*a*]azulen-3-one (**1**) by the NMR spectra



Scheme 5.

because of the existence of an sp^3 carbon. The ^{1}H NMR spectra of **1** and the reference compound (**11**) in $CDCl_3$ and acetone-d_6 are shown in Fig 1. The spectrum of **1** observed in $CDCl_3$ was scarcely different from that in acetone-d_6. Furthermore, any signals owing to an sp^3 carbon were not observed in the ^{13}C NMR spectra of **1** in either solvents. These results make it clear that the hydroxy group of **1** exists only in the enol form in both solvents in contrast to 4-hydroxyazulene.

A similar discussion is applied to 4-hydroxy l-1,2-dihydro-3*H*-cyclopent[*a*]azulen-3-one (**11**) (Scheme 6). The ^{1}H NMR spectra of **11** and the methoxyl compound (**10**) (which has fundarmentally no tautomers) in $CDCl_3$ are shown in Fig 2. Differences between these spectra are significantly small, indicating the hydroxyl group of **11** also exits only in the enol form.

The tropicity of 4-hydroxy-3*H*-cyclopent[*a*]azulen-3-one (**1**) was investigated by means of chemical shifts in ^{1}H and ^{13}C NMR. We have already reported that the protons on the azulene part of **2** shifted to a higher field owing to the paramagnetic ring current induced by the peripheral 12 π-electron framework.$^{7)}$ Since the hydroxyl group of **1** and **11** exist only in the enol form as described above, the paratropic properties of **1** could be discussed by the use of its NMR data.

The ^{1}H and ^{13}C NMR spectral data of **1** and the reference compound **11** are summarized in Table 1. All the proton magnetic resonances on the azulene part of **1** shifted upfield by 0.17—0.27 ppm compared with those of **11**. On the other hand, there were no significant differences between the carbon magnetic resonances of **1** and **11** indicating a similarity of the electron density on the azulene part of these compounds. Therefore, the

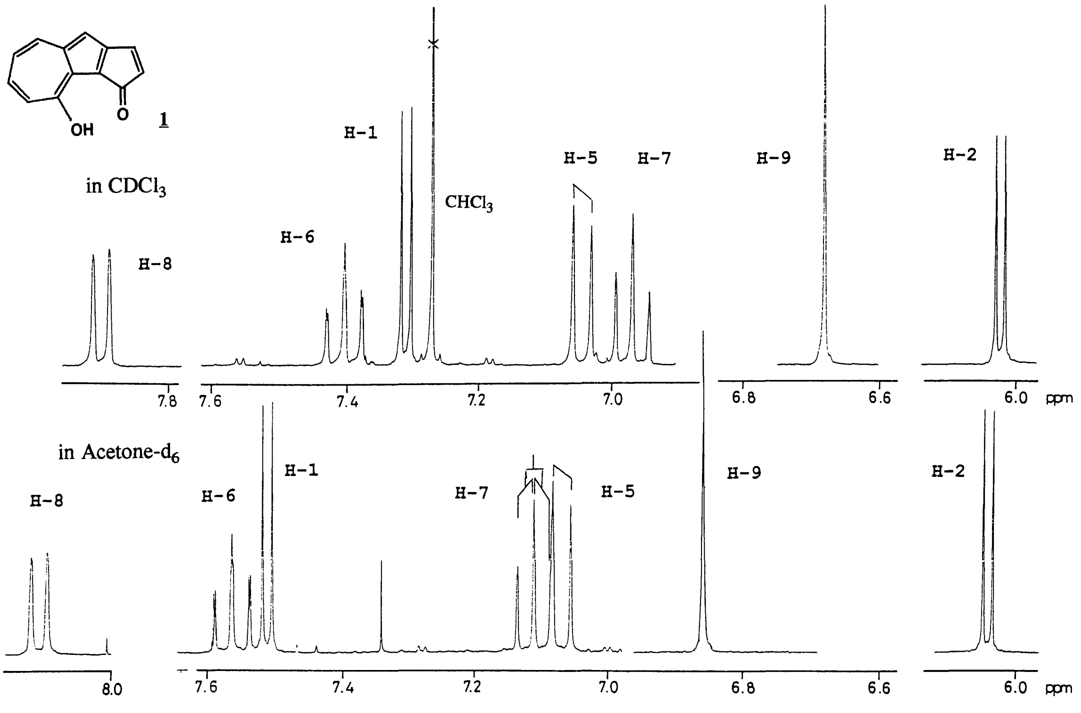


Fig. 1. ^{1}H NMR spectra of the 4-hydroxy-3*H*-cyclopent[*a*]azulen-3-one (**1**) in $CDCl_3$ and acetone-d_6 (200 MHz).

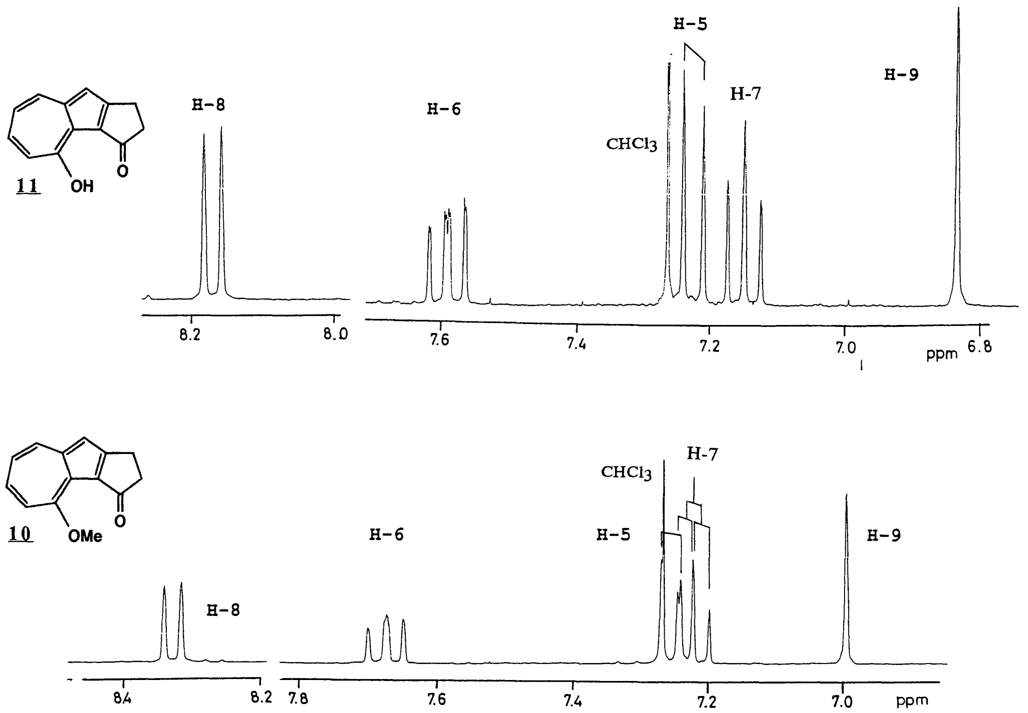
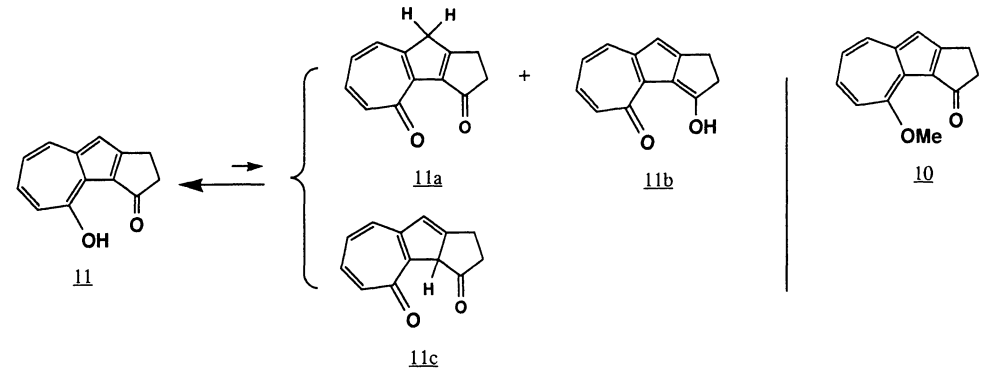


Fig. 2. ^{1}H NMR spectla of the 4-methoxy- (**10**) and 4-hydroxy-1,2-dihydro-3*H*-cyclopent[*a*]azulen-3-one (**11**) in CDCl$_3$ (200 MHz).

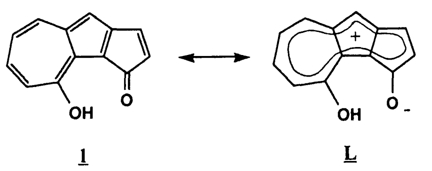


Scheme 6.

Table 1. ^{1}H and ^{13}C NMR Spectra of **1** and **11** (400 MHz, CDCl$_3$, δ/ppm)

Position		5	6	7	8	9	av
	1	7.05	7.40	6.96	7.90	6.68	7.20
^{1}H	**11**	7.23	7.59	7.15	8.17	6.85	7.40
	$\Delta\delta$(**1**−**11**)	−0.18	−0.19	−0.19	−0.27	−0.17	−0.20
	1	119.36	137.32	124.30	137.57	115.62	126.83
^{13}C	**11**	123.09	137.45	124.82	138.45	112.60	127.28
	$\Delta\delta$(**1**−**11**)	−3.73	−0.13	−0.52	−0.88	+3.02	−0.45

upfield shifts of the proton magnetic resonances of **1** should reflect the contribution of a shielding effect by an induced paramagnetic ring current originating from a peripheral 12 π-electron framework such as **L** (Scheme 7).



Scheme 7.

Experimental

General. Melting points were determined with a Yamato Model-MP21 melting point apparatus. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. NMR spectra were recorded on an R-24B, an EM-390, a JEOL-90Q (^1H) or Varian XL-200 (^1H & ^{13}C), and chemical shift values are given in δ ppm relative to internal tetramethylsilane. Infrared, ultraviolet, and mass spectra were recorded on Hitachi Model 260-30, Hitachi Model 323, and Hitachi M-50 spectrometers, respectively.

Pyrolytic Apparatus and Procedure. The apparatus used in the pyrolytic synthesis consisted of an empty horizontal tube (30 by 1.5 cm o.d.) with small protrusions in the middle of the tube. The tube was heated with an external electric furnace at 550 °C, measured with a thermocouple, over 25 cm. The precursor was sublimed into the heated tube from the sample tube heated at 190 °C with an air bath. The pyrolytic products were collected on the cold finger attached to the outlet of the pyrolytic tube cooled by dry ice–methanol. After completion of sublimation of the precursor, the refrigerant was removed and the cold finger was warmed to room temperature. The products on the surface of the cold finger were dissolved with a small amount of chloroform and the solution was chromatographed on a silica gel short column with chloroform. Further details are described below.

Preparation of Ethyl 4-Methoxy-2,3-dihydro-1*H*-cyclopent[*a*]azulene-9-carboxylate (4). 1-Morpholinocyclopentene (3.83 g, 25 mol) was added to a solution of **3** (1.24 g, 5 mmol) in anhydrous EtOH (50 ml), and the mixture was refluxed for 45 min. After being cooled to room temperature, the reaction mixture was poured into water (200 ml) and extracted with chloroform. The organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was chromatographed with a silica-gel column eluted with benzene to give **4** (1.32 g, 98%). Recrystallization from EtOH gave violet plates.

4: Violet plates, mp 112.5—114.5 °C; UV (MeOH) 218 (log ε 4.36), 243.5 (4.26), 262 (4.27), 303.5 (4.63), 328 (4.28), 360 (3.87), 380.5 (3.65), 522 (3.26), and 550 (3.03) nm; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.36 (3H, t, *J*=7.0 Hz, $OCH_2C\underline{H}_3$), 2.2—2.6 (2H, m, H-2), 3.26 (4H, m, H-1,3), 3.90 (s, OMe), 4.33 (2H, q, *J*=7.0 Hz, $OC\underline{H}_2CH_3$). 6.6—7.6 (3H, m, H-5,6,7), and 9.30 (1H, dm, *J*=9.0 Hz, H-8). Found: C, 75.53; H, 6.71%. Calcd for $C_{17}H_{18}O_3$: C, 75.56; H, 6.69%.

Preparation of Ketone 5 by DDQ Oxidation of 4. DDQ (4.3 g, 18.7 mmol) was added to a solution of **4** (2.3 g, 8.5 mmol) in aqueous acetone (acetone 135 ml, H_2O 15 ml) at 0 °C with stirring. After being stirred at room temperature for 30 min, the solvent was removed under reduced pressure, and dioxane was added to the residual oil. Precipitated DDQH was removed by filtration and the filtrate was evaporated to dryness under reduced pressure. Chromatography of the resulting oil on an alumina column eluted with benzene gave the ketone (**5**) (2.1 g, 86.8%).

5: Light orange needles (from ethyl acetate); mp 186.5—187.5 °C; UV (MeOH) 237 (sh, log ε 4.42), 253.5 (4.76), 312.5 (4.47), 327 (sh, 4.01), 362 (sh, 4.01), and 468 (3.12) nm; IR (KBr) 1688 and 1672 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.43 (t, *J*=7.0 Hz, $-OCH_2C\underline{H}_3$), 2.93 (m, H-2), 3.39 (m, H-1), 4.21 (s, -OMe), 4.40 (q, *J*=7.0 Hz, $-OC\underline{H}_2CH_3$), 7.13—8.6 (m, H-5, 6, and 7), and 9.70 (d, *J*=10.0 Hz, H-8); MS *m*/*z* 285 ($M^+ +1$, 19.1%) and 284 (M^+, 100.0%). Found: C, 71.92; H, 5.62%. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%.

Preparation of 8 via Mono-Bromide 6. NBS (1.5 g, 8.7 mmol) was added to a solution of **5** (2.2 g, 7.9 mmol) in chloroform (150 ml) and the mixture was stirred at room temperature for 87 h. Chromatography of the reaction mixture on a short silica-gel column eluted with ethyl acetate gave a crude mono-bromide (**6**) which was used for the succeeding reaction without further purification.

Triethylamine (8.0 g, 79.2 mmol) and a large excess of freshly distilled cyclopentadiene (35 ml) as a trapping reagent were added to a solution of the mono-bromide (**6**) in benzene (200 ml) and the mixture was refluxed for 3.5 h. After being cooled to room temperature, the reaction mixture was chromatographed on a silica short column eluted with ethyl acetate. Chromatography on a prepacked column (Merck, Si60, gross C) eluted with chloroform gave two products which were not identifiable. Further elution with ethyl acetate gave **8** (1.4 g, 51.0% from **5**).

8: Orange plates (from ethanol); mp 144.0—144.5 °C; UV (MeOH) 242.5 (sh, log ε 4.44), 256 (4.60), 314 (4.43), 328 (4.51), 365 (sh, 3.98), and 470 (3.16) nm; IR (KBr) 1672 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.52 (t, *J*=6.8 Hz, $-OCH_2C\underline{H}_3$), 1.77 (m, H-12), 3.33—3.57 (m, H-1, 4, and 11a), 4.10 (dd, *J*=6.0 and 3.8 Hz, H-4a), 4.20 (s, -OMe), 4.45 (2H, q, *J*=6.8 Hz, $-OC\underline{H}_2CH_3$), 5.48 (dd, *J*=5.7 and 3.0 Hz, H-2), 5.96 (dd, *J*=5.7 and 3.0 Hz, H-3), 7.50 (d, *J*=10.8 Hz, H-9), 7.59 (dd, *J*=10.8 and 10.8 Hz, H-7), 8.79 (dd, *J*=10.8 and 10.8 Hz, H-8), and 9.47 (d, *J*=10.8 Hz, H-6); MS *m*/*z* 349 (M^++1, 3.4%), 348 (M^+, 15.9%), and 320 (100.0%). Found: C, 75.79; H, 5.82%. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79%.

The Pyrolytic Precursor 9 of 4-Hydroxy-3*H*-cyclopent[*a*]azulen-3-one (1). A solution of the ester (**8**) (1.4 g, 4.0 mmol) in 10% KOH-aqueous EtOH (EtOH 55 ml, H_2O 45 ml, KOH 10 g) was refluxed for 19 h. After being cooled to room temperature, the reaction mixture was poured into water and acidified with 6 M HCl (1 M=1 mol dm^{-3}) to pH 3. Precipitates of the carboxylic acid formed were collected by filtration and dried under reduced pressure. The carboxylic acid was dissolved in trifluoroacetic acid (20 ml) and the solution was refluxed for 1.5 h. After being cooled to room temperature, the reaction mixture was diluted with water, extracted with chloroform and the organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated to dryness under reduced pressure and the resulting oil was chromatographed on a silica-gel column eluted with chloroform to give a crude product. Further re-chromatography on an ODS column (Merck, RP-18, Gross B) eluted with acetonitrile–water (7:3) gave **9** (425.0 mg, 40.5% from **8**).

9: Light orange microprisms (from cyclohexane); mp 127.5—128.5 °C; UV (MeOH) 217.5 (log ε 4.40), 240 (sh, 4.29), 313 (sh, 4.25), 334 (4.48), 367 (4.04), 387 (3.88), and 445 (2.86) nm; IR (KBr) 1599 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ=1.75 (broad d, *J*=8.5 Hz, H-12), 1.87 (ddd, *J*=8.5, 1.5, and 1.5 Hz, H-12), 3.23 (m, H-1), 3.35 (m, H-4), 3.60 (dd, *J*=6.0 and 4.5 Hz, H-4a), 3.99 (m, H-11a), 5.53 (dd, *J*=5.5 and 3.0 Hz, H-2), 5.95 (dd, *J*=5.5 and 3.0 Hz, H-3), 6.75 (s, H-5), 7.10 (dd, *J*=10.5 and 10.0 Hz, H-8), 7.18 (d, *J*=11.5, H-9), 7.54 (ddd, *J*=11.5, 10.5, and 1.0 Hz, H-7), 8.11 (broad d, *J*=10.0 Hz, H-6), and 13.08 (s, OH); MS *m*/*z* 262 (M^+, 13.4%) and 196 ($M^+ - C_5H_6$, 100.0%). Found: C, 82.32; H, 5.44%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

Preparation of 4-Hydroxy-3*H*-cyclopent[*a*]azulen-3-one (1)

by Flash Vacuum Pyrolysis of Cycloadduct 9. Flash vacuum pyrolysis of precursor **9** was carried out by the apparatus as described above. The cycloadduct (**9**) (40.0 mg, 0.15 mmol) was pyrolysed at 550 °C (0.02—0.10 mmHg, 190 °C preheat) and the products were collected on the cold finger (−78 °C, dry ice–methanol) as brown crystals. The cold finger was warmed to room temperature and the crystals were swept with a small amount of chloroform. Immediate chromatography of the resulting solution on a silica-gel column eluted with chloroform gave 4-hydroxy-3*H*-cyclopent[*a*]azulen-3-one (**1**) (24.0 mg, 81.5%).

1: Dark brown crystals, mp 96.0 °C (decomp); UV (MeOH) 220 (sh, log ε 4.21), 238 (4.30), 259 (4.27), 278 (4.10), 334 (4.14), 370 (4.07), and 467 (3.35) nm; IR (KBr) 1628 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.03 (d, J=5.5 Hz, H-2), 6.68 (s, H-9), 6.96 (dd, J=10.0 and 9.5 Hz, H-7), 7.05 (d, J=11.0 Hz, H-5), 7.31 (d, J=5.5 Hz, H-1), 7.40 (ddd, J=11.0 10.0, and 1.0 Hz, H-6), 7.90 (broad d, J=9.5 Hz, H-8), and 11.8 (s, -OH); ^{13}C NMR (CDCl$_3$, 50 MHz) δ=115.62 (d, C-9), 119.36 (s, C-5), 121.43 (s), 124.30 (d, C-7), 128.73 (s), 135.82 (d, C-2), 137.32 (d, C-6), 137.57 (d, C-8), 143.67 (d, C-1), 148.06 (s), 152.59 (s), 162.90 (s), and 192.73 (s); MS m/z 197 (M$^+$ +1, 19.8%) and 196 (M$^+$, 100%). Found: C, 78.63; H, 4.34%. Calcd for $C_{13}H_8O_2$: C, 79.58; H, 4.11%.

Preparation of the Reference Compound, 4-Methoxy-1,2-dihydro-3*H*-cyclopent[*a*]azulen-3-one (10). Ketone **5** (281.0 mg, 1.0 mmol) was dissolved in 100% phosphoric acid (5 ml) and the mixture was heated at 95 °C for 14 h. After being cooled to room temperature, the reaction mixture was poured into water, extracted with benzene and the organic layer was dried over anhydrous MgSO$_4$. Evaporation of the solvent to dryness under reduced pressure gave **10** (201 mg, 95.8%).

10: Red crystals (from ethyl acetate); mp 148.0—149.5 °C; UV (MeOH) 244 (log ε 4.35), 245 (sh, 4.15), 260 (4.34), 308 (4.41), 331 (4.57), 373 (3.83), and 480 (2.75) nm; IR (KBr) 1664 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz), δ=3.04 (2H, m, H-2), 3.22 (2H, m, H-1), 4.05 (s, -OMe), 6.99 (s, H-9), 7.22 (dd, J=10.0 and 9.5 Hz, H-7), 7.25 (d, J=11.5 Hz, H-5), 7.68 (dd, J=11.5 and 9.5 Hz, H-6), and 8.33 (d, J=10.0 Hz, H-8); ^{13}C NMR (CDCl$_3$, 50 MHz) δ=22.93 (t, C-1), 43.05 (t, C-2), 56.94 (q, -OMe), 112.82 (d, C-9), 114.29 (d, C-5), 122.33 (s), 123.27 (d, C-7), 129.13 (s), 136.74 (d, C-6), 139.38 (d, C-8), 147.82 (s), 164.44 (s), 168.32 (s), and 198.61 (s); MS m/z 213 (M$^+$ +1, 14.1%) and 212 (M$^+$, 100%). Found: C, 78.96; H, 5.87%. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

Preparation of 4-Hydroxy-1,2-dihvdro-3*H*-cyclopent[*a*]-azulen-3-one (11). Lithium chloride (319.0 mg, 7.5 mmol) was added to a solution of **10** (200 mg, 0.9 mmol) in *N*,*N*-dimethylformamide (9.5 ml) and the mixture was heated at 95 °C for 22 h. After being cooled to room temperature, the reaction mixture was poured into water and the solution was acidified with 6 M HCl, then extracted with benzene. The organic layer was dried over anhydrous MgSO$_4$ and evaporated to dryness under reduced pressure. Chromatography of the resulting oil by a silica-gel column eluted with benzene gave **11** (162 mg, 86.7%).

11: Light orange needles (from benzene); mp 151.0—152.5 °C; UV (MeOH) 225 (log ε 4.45), 237 (sh, 4.33), 255 (sh, 4.19), 309 (4.25), 331 (4.50), 364 (4.00), 384 (3.85), and 444 (2.86) nm; IR (KBr) 1608 cm^{-1}; ^{1}H NMR (CDCl$_3$, 90 MHz) δ=3.10 (m, H-2), 3.31 (m, H-1), 6.85 (s, H-9), 7.15 (dd, J=10.0 and 9.5 Hz, H-7), 7.23 (d, J=11.5 Hz, H-5), 7.59 (ddd, J=11.5, 9.5, and 1.0 Hz, H-6), 8.17 (broad d, J=10.0 Hz, H-8), and 13.00 (s, -OH); ^{13}C NMR (CDCl$_3$, 50 MHz) δ=24.76 (t, C-1), 40.87 (t, C-2), 112.60 (d, C-9), 121.79 (s), 123.09 (d, C-5), 124.82 (d, C-7), 129.74 (s), 137.45 (d, C-6), 138.45 (d, C-8), 147.87 (s), 165.3 (s), 166.51 (s), and 201.8 (s); MS m/z 199 (M$^+$+1, 14.1%) and 198 (M$^+$, 100.0%). Found: C, 78.53; H, 5.02%. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09%.

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