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Studies on the Constituents of Medicinal and Related Plants in Sri Lanka. IV.[1] Isolation and Structure Determination of Hyperenone-B, Mysorenone-B, and Mysorenone-C from *Hypericum mysorense* HEYNE and Synthesis of Hyperenone-A and -B

TOHRU KIKUCHI,* SHIGETOSHI KADOTA, SATOKO MATSUDA, and KEN TANAKA

Research Institute for Wakan-Yaku (Oriental Medicines), Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan

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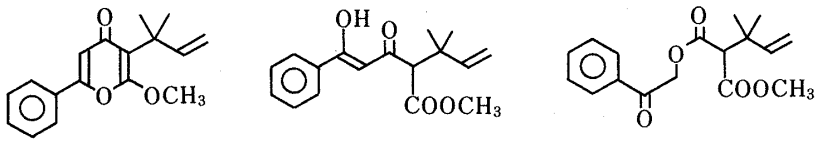
Three new compounds named hyperenone-B, mysorenone-B, and mysorenone-C were isolated from *Hypericum mysorense* HEYNE, collected in Sri Lanka, and their structures were determined. In addition, hyperenone-A and -B, novel γ-pyrone derivatives, were synthesized.

Keywords——*Hypericum mysorense*; Guttiferae; hyperenone-A; hyperenone-B; mysorenone-B; mysorenone-C; xanthone; γ-pyrone; synthesis

In a previous paper,[2] we reported the isolation and structure elucidation of several xanthone derivatives and three new compounds, hyperenone-A (**1**), mysorenone-A (**2**), and methyl phenacyl 1,1-dimethylprop-2-enylmalonate (**3**), from *Hypericum mysorense* HEYNE (Guttiferae) collected in Sri Lanka. In a continuation of that work, we recently obtained three new compounds named hyperenone-B (**4**), mysorenone-B (**12**), and mysorenone-C (**13**) from the leaves of this plant. This paper describes the isolation and structure determination of these compounds and also a synthesis of hyperenone-A (**1**) and -B (**4**).



1 **2** **3**

Chart 1

The ether extract of dried leaves of *H. mysorense* was roughly separated by silica gel column chromatography and the fractions were further purified by preparative thin layer chromatography (TLC) to give hyperenone-B (**4**), mysorenone-B (**12**), and mysorenone-C (**13**) along with hyperenone-A (**1**), mysorenone-A (**2**), and known xanthone derivatives.

Hyperenone-B (**4**), mp 170—172 °C, showed the molecular ion peak at *m/z* 256 in the mass spectrum (MS) and its molecular formula was determined to be $C_{16}H_{16}O_3$ by elementary analysis and high-resolution MS measurement. The ultraviolet (UV) spectrum of **4** exhibited maximum absorptions at 238 nm (log ε 4.19) and 329 nm (log ε 4.01), suggesting the presence of a conjugated aromatic chromophore. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum revealed signals due to an olefinic proton and two tertiary methyl groups, a vinyl moiety, and a mono-substituted phenyl group (see Experimental). This ^{1}H-NMR pattern closely resembled that of hyperenone-A (**1**) except for the appearance of a hydroxyl signal at

δ 7.88 (disappeared on addition of deuterium oxide) instead of the methoxyl methyl signal in **1**. In the MS, **4** showed strong fragment peaks at *m/z* 105 ($C_6H_5CO^+$) and *m/z* 77 ($C_6H_5^+$), indicating the presence of an oxygenic grouping at the benzylic position as in the case of **1**.

From the above spectral data and the molecular formula, the structure of hyperenone-B was deduced to be **4**. This was confirmed by the hydrolysis of hyperenone-A (**1**) under acidic conditions, giving a crystalline product (**4**), mp 169—171 °C, which was identical with natural hyperenone-B.

It should be noted here that the infrared (IR) spectrum of **4** in chloroform solution showed the carbonyl absorption at 1705 cm^{-1}, while in KBr disc the absorption appeared at 1650 cm^{-1}. The latter value is in accord with that of **1**. On the other hand, the UV absorption of hyperenone-B (**4**) showed a remarkable bathochromic shift (329 nm) compared with that of hyperenone-A (**1**) (276 nm). Similar behavior was previously observed in the IR and UV spectra of 6-phenyl-2,4-pyronone (**7**) by Djerassi *et al.*,[3] who reported that **7** appears to exist largely as the γ-pyrone tautomer (**8**) in the solid state, but predominantly as the α-pyrone tautomer (**6**) in ethanol solution. Likewise, hyperenone-B might be in the γ-pyrone form (**4**) in the crystalline state and in the α-pyrone form (**5a**) in solution.

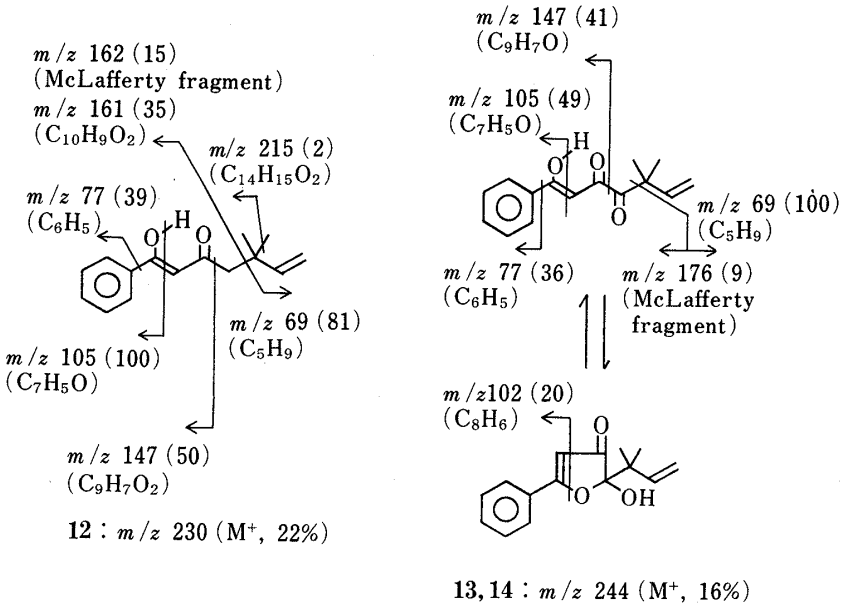


Fig. 1

Next, the synthesis of hyperenone-A (**1**) and -B (**4**) was undertaken for definite confirmation of their structures (Chart 2). The synthetic intermediate, 6-phenyl-2,4-pyronone (**7**), was prepared from ethyl benzoylacetate by way of **11** according to Djerassi's description.[3] This intermediate was converted to the sodium enolate and then treated with 3,3-dimethylallyl bromide in dimethylformamide to give the desired 4-*O*-dimethylallyl ether (**9a**) in 30—39% yield, along with *O*,*C*- and *C*,*C*-dialkylated products (**9b** and **10**). Claisen rearrangement of **9a** in dimethyl sulfoxide[4] proceeded smoothly to afford a crystalline product (**4**), mp 170—172 °C, $C_{16}H_{16}O_3$, which was shown to be identical with authentic hyperenone-B (**4**) by mixed fusion and MS, IR (KBr), and ^{1}H-NMR comparisons.

Reaction of **4** with diazomethane in ether gave two products in a ratio of 7 : 3, and these were separated by preparative TLC. The major product showed mp 85—87 °C and was concluded to be the 4-*O*-methyl ether (**5b**) on the basis of its spectral data, while the minor product was found to be identical with natural hyperenone-A (**1**).

Mysorenone-B (**12**) is a minor component obtained as an oil. It showed the molecular ion

peak at *m/z* 230 in the MS and its molecular formula $C_{15}H_{18}O_2$ was established by high-resolution MS measurement. The UV spectrum of **12** exhibited maximum absorptions at 209, 252, and 312 nm (log ε: 3.47, 3.41, and 3.61, respectively), corresponding to a conjugated aromatic chromophore. This UV pattern resembles that of mysorenone-A (**2**).[2] The ^{1}H-NMR spectrum was closely similar to that of mysorenone-A (**2**), but was characterized by the appearance of a singlet at δ 2.40 assignable to an active methylene group and the absence of the methine and ester methyl protons in **2**. In accordance with this finding, no ester carbonyl absorption was seen in the IR spectrum. Furthermore, the MS of **12** showed significant fragment peaks explainable as illustrated in Fig. 1.

In view of these spectral properties and the molecular formula, the structure of mysorenone-B was deduced to be **12**. This was confirmed by the following experiment. Alkaline hydrolysis of mysorenone-A (**2**) with sodium hydroxide in aqueous methanol, followed by decarboxylation under acidic conditions, afforded solely an oily compound (**12**), which was found to be identical with natural mysorenone-B. Thus the structure of mysorenone-B was established to be **12**.

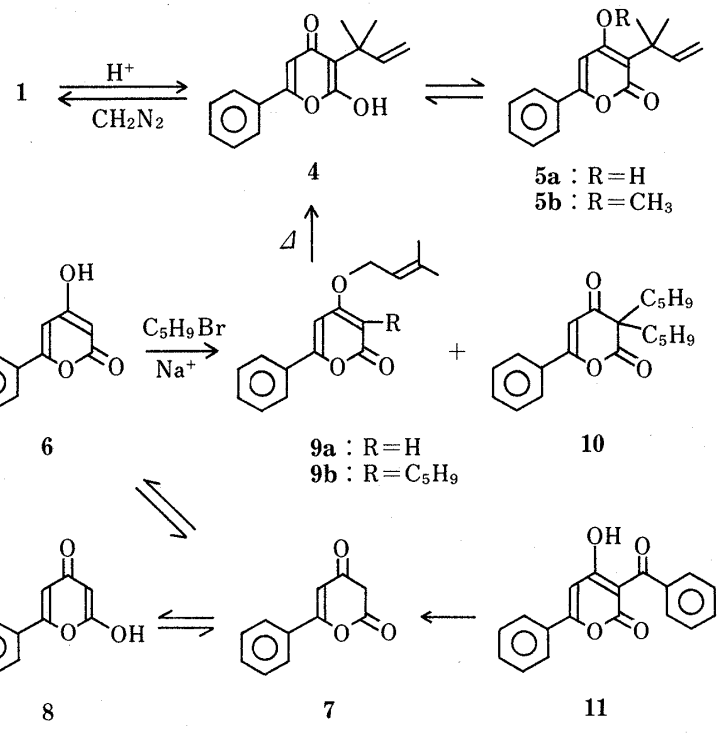


Chart 2

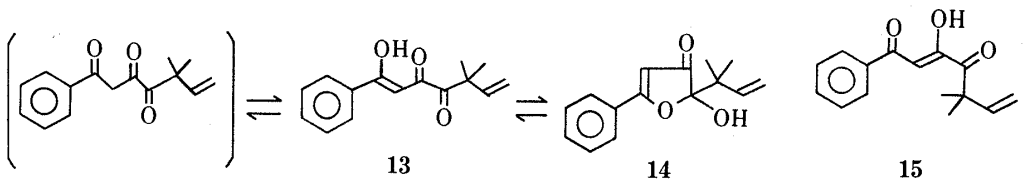


Chart 3

Mysorenone-C (**13**),[5] mp 117—119 °C, is also a minor component of *H. mysorense*. It showed the molecular ion peak at *m/z* 244 in the MS and its molecular formula was determined to be $C_{15}H_{16}O_3$ by high-resolution MS. The UV spectrum of **13** gave absorptions at 247 and 314 nm, similar to those of mysorenone-B (**12**), and the ^{1}H-NMR spectrum showed characteristic signals arising from an olefinic proton and a mono-substituted phenyl, a vinyl, and two tertiary methyl groups (see Experimental), suggesting that this compound (**13**) is closely related to mysorenone-B (**12**).

On the basis of the above spectral data and the biogenetic analogy, together with the MS fragmentation pattern, which could be interpreted as shown in Fig. 1, the structure of mysorenone-C should be represented by the formula **13**.

Interestingly, the hydroxyl proton signal in the ^{1}H-NMR spectrum of **13** was markedly shifted upfield (δ 3.79) compared with that of **12** (δ 16.15) and the IR spectrum in chloroform solution exhibited a hydroxyl band at 3300 cm^{-1} and a carbonyl absorption at 1700 cm^{-1} corresponding to a conjugated five-membered ketone. Therefore, mysorenone-C appears to exist predominantly as the cyclic hemiketal form (**14**) in chloroform solution, but as the tautomer **13** in ethanolic solution. Support for the possibility of the structure **14** was provided by the MS fragment peak observed at *m/z* 102 ($C_6H_5C{\equiv}CH^+$), which may be explained by the fragmentation at the dihydrofuranone ring (Fig. 1). Further, it is interesting to note that the IR spectrum of mysorenone-C in potassium bromide pellet showed the hydroxyl absorption at 3150 cm^{-1} (broad) and the carbonyl absorption at 1665 cm^{-1}. Thus, it is possible that the alternative tautomeric form **15** contributes to the structure of mysorenone-C in the solid state, although no definitive evidence is available.

Experimental

Melting points were determined on a Kofler-type apparatus and are uncorrected. UV spectra were taken in EtOH solutions and IR spectra in $CHCl_3$ solutions, unless otherwise noted. ^{1}H-NMR spectra were measured on a Varian XL-200 spectrometer in $CDCl_3$ solutions using tetramethylsilane as an internal standard and chemical shifts are recorded in δ values. MS and high-resolution MS were obtained with a JEOL JMS-D 300 spectrometer (ionization voltage, 70 eV; accelerating voltage, 30 eV) using a direct inlet system and relative intensities of peaks are given in parentheses. Gas chromatography (GC) was done on a Shimadzu GC-6AM instrument with a 2% OV-17 column (2 m × 3 mm i.d. glass tube; injection temp., 230—260 °C; column temp., 220—230 °C; carrier gas, nitrogen). Column chromatography was carried out with Mallinckrodt silica gel, and the eluted solutions were concentrated *in vacuo*. For TLC, Merck Kieselgel 60 F_{254} was used and spots were detected by coloration with $Ce(SO_4)_2$–H_2SO_4 reagent or under UV light. For preparative TLC, Merck Kieselgel PF_{254} or F_{254} (0.5 mm thickness) was employed and plates were examined under UV light. Extraction of substances from silica gel was done with MeOH–CH_2Cl_2 mixture (5 : 95 or 1 : 9) and solutions were concentrated *in vacuo*.

Extraction, Isolation, and Properties of New Compounds from *H. mysorense* ——Air-dried leaves (1 kg) of *H. mysorense*, collected at Horton Plains, Sri Lanka, in the flowering season (July, 1983), were extracted with ether (5 l × 3) for 7 d at room temperature and the combined solutions were concentrated to give an ether extract (34 g). The plant material was then extracted with boiling MeOH (5 l × 3) for 3 h to give a methanol extract (550 g).

The ether extract was subjected to silica gel (500 g) column chromatography, eluted successively with CH_2Cl_2 (F-1, 22.5 g), MeOH–CH_2Cl_2 (1 : 99) (F-2, 2.7 g), MeOH–CH_2Cl_2 (3 : 97) (F-3, 0.6 g), MeOH–CH_2Cl_2 (5 : 95) (F-4, 5.4 g), and MeOH–CH_2Cl_2 (15 : 85) (F-5, 0.5 g). F-2 was again chromatographed on silica gel (60 g) and the CH_2Cl_2 eluate (0.4 g) was further purified by preparative TLC using $CHCl_3$ as the eluent, whereupon mysorenone-A (**2**) (25 mg), an oil, was obtained from the less polar fraction and hyperenone-B (**4**) (200 mg) from the more polar fraction.

F-3 was also separated into two fractions by preparative TLC using MeOH–$CHCl_3$ (2 : 98) as the developing solvent. The less polar fraction, on trituration with ether–hexane, gave hyperenone-A (**1**) (135 mg), colorless prisms, mp 81—82 °C. The mother liquor (300 mg) was again separated by preparative TLC with $CHCl_3$ as the developing solvent, giving mysorenone-B (**12**) (8 mg) as the more mobile fraction and an additional crop of mysorenone-A (**2**) (9 mg) as the less mobile fraction.

The more polar fraction was a crystalline mass, which was recrystallized from ether–hexane to afford 1,7-dihydroxyxanthone (80 mg), yellow needles, mp 239—242 °C. The mother liquor (120 mg) was further purified by repeated preparative TLC to give mysorenone-C (**13**) (6 mg).

Hyperenone-B (**4**): Colorless prisms (from ether–hexane), mp 170—172 °C. UV λ_{max} nm (log ε): 205 (4.30), 238

(4.19), 329 (4.01). IR ν_{max} cm^{-1}: 3400, 1705, 1650, 1560 (in $CHCl_3$); 3400, 1650, 1620, 1560 (in KBr). ^{1}H-NMR δ: 1.56 (3H×2, s, *tert*-CH_3), 5.48, 5.58 (each 1H, dd, J=1, 11 and 1, 17 Hz, respectively; =CH_2), 6.32 (1H, s, =CH), 6.46 (1H, dd, J=11, 17 Hz; =CH), 7.48 (3H, m, aromatic protons), 7.80 (2H, m, aromatic protons), 7.88 (1H, s, OH; disappeared on addition of D_2O). MS *m/z* (rel. int.): 256 (M^+, 60), 241 (M^+-CH_3, 55), 201 (50), 188 (McLafferty fragment, 45), 105 (100), 77 (40), 69 (45). High-resolution MS: Found 256.1053, Calcd for $C_{16}H_{16}O_3$ (M^+) 256.1099; Found 241.0853, Calcd for $C_{15}H_{13}O_3$ 241.0864; Found 201.0509, Calcd for $C_{12}H_9O_3$ 201.0552; Found 188.0459, Calcd for $C_{11}H_8O_3$ 188.0473; Found 105.0339, Calcd for C_7H_5O 105.0340; Found 77.0375, Calcd for C_6H_5 77.0391; Found 69.0690, Calcd for C_5H_9 69.0704. *Anal.* Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.68; H, 6.24.

Mysorenone-B (**12**): Slightly colored oil. UV λ_{max} nm (log ε): 209 (3.47), 252 (3.41), 312 (3.61). IR ν_{max} cm^{-1}: 1605 (br), 1575, 1465. ^{1}H-NMR δ: 1.18, 1.27 (each 3H, s, *tert*-CH_3), 2.40 (2H, s, CO–CH_2–), 5.00, 5.015 (each 1H, d, J=11 and 17 Hz, respectively; =CH_2), 5.97 (1H, dd, J=11, 17 Hz, =CH), 6.14 (1H, s, =CH), 7.51 (3H, m, aromatic protons), 7.80 (2H, m, aromatic protons), 16.15 (1H, s, C=C–OH; disappeared on addition of D_2O). MS: see Fig. 1. High-resolution MS: Found 230.1312, Calcd for $C_{15}H_{18}O_2$ (M^+) 230.1307; Found 215.1072, Calcd for $C_{14}H_{15}O_2$ 215.1072; Found 162.0686, Calcd for $C_{10}H_{10}O_2$ 162.0681; Found 161.0555, Calcd for $C_{10}H_9O_2$ 161.0602; Found 147.0437, Calcd for $C_9H_7O_2$ 147.0446; Found 105.0342, Calcd for C_7H_5O 105.0340; Found 77.0389, Calcd for C_6H_5 77.0391; Found 69.0689, Calcd for C_5H_9 69.0704.

Mysorenone-C (**13**): Optically inactive, colorless prisms (from isopropyl ether–hexane), mp 117—119 °C. UV λ_{max} nm (log ε): 247 (3.94) and 314 (4.18). IR ν_{max} cm^{-1}: 3300, 1700, 1610, 1600, 1570 (in $CHCl_3$); 3150, 1665, 1600, 1590, 1555 (in KBr). ^{1}H-NMR δ: 1.20, 1.28 (each 3H, s, *tert*-CH_3), 3.79 (1H, br, OH; disappeared on addition of D_2O), 5.24, 5.25 (each 1H, d, J=11 and 18 Hz, respectively; =CH_2), 5.99 (1H, s, =CH), 6.12 (1H, dd, J=11, 18 Hz, =CH), 7.58 (3H, m, aromatic protons), 7.86 (2H, m, aromatic protons). MS: see Fig. 1. High-resolution MS: Found 244.1110, Calcd for $C_{15}H_{16}O_3$ (M^+) 244.1099; Found 176.0470, Calcd for $C_{10}H_8O_3$ 176.0473; Found 147.0453, Calcd for $C_9H_7O_2$ 147.0446; Found 105.0343, Calcd for C_7H_5O 105.0340; Found 102.0469, Calcd for C_8H_6 102.0469; Found 77.0434, Calcd for C_6H_5 77.0391; Found 69.0705, Calcd for C_5H_9 69.0704.

Acid Hydrolysis of Hyperenone-A (1)——Ten percent HCl (0.5 ml) was added to a solution of hyperenone-A (**1**) (5 mg) in acetone (0.5 ml) and the mixture was stirred at room temperature overnight. The mixture was then subjected to preparative TLC with acetone–$CHCl_3$ (2:98) as the eluent to give a crystalline product (**4**) (2 mg), which on recrystallization from ether–hexane gave colorless prisms, mp 169—171 °C. This product was found to be identical with authentic hyperenone-B (**4**) by GC, MS, IR, and ^{1}H-NMR comparisons. A small amount of the starting material (**1**) (1.3 mg) was recovered from the more polar fraction.

Synthesis of Hyperenone-A (1) and -B (4)——1) 3,3-Dimethylallylation of 6-Phenyl-2,4-pyronone (**7**): A solution of **7**[3] (200 mg) in MeOH (10 ml) was mixed with 0.1 N NaOH–MeOH (10 ml), and the solution was concentrated to dryness *in vacuo*. The residue was dissolved in *N,N*-dimethylformamide (DMF) (10 ml) and then a solution of 3,3-dimethylallyl bromide[6] (206 mg) in DMF (10 ml) was added dropwise with vigorous stirring at room temperature. Stirring was continued for 3 h, then the reaction mixture was diluted with ether (50 ml) and washed with water (30 ml×7), and the water layer was extracted with ether (30 ml×2). The combined ether solutions were dried (anhyd. $MgSO_4$) and concentrated to give a crystalline residue, which was subjected to preparative TLC with $CHCl_3$ as the developing solvent. The least polar fraction (58 mg) gave the *C,C*-dialkyl product (**10**), oil. UV λ_{max} nm (log ε): 223 (4.03), 228 (4.02), 303 (4.23). IR ν_{max} cm^{-1}: 1780, 1665, 1630. ^{1}H-NMR δ: 1.63 (3H×4, br s, vinyl CH_3), 2.75 (2H×2, d, J=7.5 Hz, C–CH_2–CH=), 5.05 (1H×2, t, J=7.5 Hz, C–CH_2–CH=), 6.33 (1H, s, C=CH), 7.4—8.2 (5H, aromatic protons). The next fraction (25 mg) afforded the *O,C*-dialkylated product (**9b**), colorless prisms (from ether–hexane), mp 91—92 °C. UV λ_{max} nm (log ε): 241 (4.28), 337 (4.16). IR ν_{max} cm^{-1}: 1700, 1640, 1560. ^{1}H-NMR δ: 1.78 (3H×4, s, vinyl CH_3), 3.20 (2H, d, J=7 Hz, =C–CH_2–CH=), 4.72 (2H, d, J=6 Hz, O–CH_2–CH=), 5.26 (1H, t, J=7 Hz, =C–CH_2–CH=), 5.37 (1H, t, J=6 Hz, O–CH_2–CH=), 6.63 (1H, s, =CH), 7.47 (3H, m, aromatic protons), 7.83 (2H, m, aromatic protons). *Anal.* Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 78.25; H, 7.43. The third fraction (75 mg) gave 4-(3,3-dimethylallyl)oxy-6-phenyl-α-pyrone (**9a**), colorless needles (from ether–hexane), mp 65—69 °C. UV λ_{max} nm (log ε): 221 (4.09), 255 (4.10), 317 (3.99). IR ν_{max} cm^{-1}: 1720, 1640, 1560. ^{1}H-NMR δ: 1.76, 1.83 (each 3H, s, vinyl CH_3), 4.56 (2H, d, J=6 Hz, O–CH_2–CH=), 5.46 (1H, t, J=6 Hz, O–CH_2–CH=), 5.54, 6.46 (each 1H, d, J=2 Hz, =CH), 7.50 (3H, m, aromatic protons), 7.83 (2H, m, aromatic protons). MS *m/z* (rel. int.): 256 (M^+, 61), 241 (100), 213 (27), 105 (56), 77 (32). *Anal.* Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.74; H, 6.39. From the starting line zone, the unchanged starting material (**7**) (45 mg) was recovered.

2) Claisen Rearrangement of 4-(3,3-Dimethylallyl)oxy-6-phenyl-α-pyrone (**9a**): A solution of **9a** (50 mg) in DMSO (10 ml) was heated for 3 h at 130 °C in an oil bath. After evaporation of DMSO *in vacuo*, the residue was purified by preparative TLC (developed with $CHCl_3$) and then recrystallized from ether–hexane to give colorless prisms (**4**) (45 mg), mp 170—172 °C. *Anal.* Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.22; H, 6.22. This product was shown to be identical with hyperenone-B (**4**) by mixed fusion and GC, MS, IR, and ^{1}H-NMR comparisons.

3) Methylation of **4** with Diazomethane: Crystals of **4** (20 mg) were added to a solution of excess CH_2N_2 in ether (8 ml) and the mixture was left at room temperature overnight. The reaction mixture showed two peaks on GC in a ratio of 7:3. After evaporation of the solvent, the residue was separated by preparative TLC with MeOH–$CHCl_3$

(1 : 99) as the eluent. The more mobile fraction gave the 4-methyl ether (**5b**) (14 mg), colorless prisms (from ether–hexane), mp 85—87 °C. IR ν_{max} cm^{-1}: 1700, 1640, 1530. ^{1}H-NMR δ: 1.50 (3H × 2, s, *tert*-CH_3), 3.90 (3H, s, OCH_3), 4.89, 4.96 (each 1H, dd, J=1, 11 Hz and 1, 18 Hz, respectively; CH=C$\underline{H}_2$), 6.22 (1H, dd, J=11, 18 Hz, C$\underline{H}$=CH_2), 6.55 (1H, s, =CH), 7.47 (3H, m, aromatic protons), 7.84 (2H, m, aromatic protons). MS *m/z*: 270 (M^+, 45), 255 (60), 227 (80), 215 (70), 125 (10), 105 (10), 77 (45). *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.85. Found: C, 75.60; H, 6.70. The less mobile fraction gave the 2-methyl ether (**1**) (6 mg), colorless prisms (from ether–hexane), mp 81—82 °C. *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.85. Found: C, 75.81; H, 6.70. This product was shown to be identical with hyperenone-A (**1**) by mixed fusion and GC, IR, MS, and ^{1}H-NMR comparisons.

Hydrolysis and Decarboxylation of Mysorenone-A (2)——A mixture of mysorenone-A (**2**) (4 mg), 2% aq. NaOH (0.6 ml), and MeOH (2.2 ml) was heated for 1 h in a water bath (bath temperature, 80 °C), then the mixture was acidified by addition of 10% HCl (0.8 ml) and heated for 1.5 h at 80 °C. After evaporation of the solvent *in vacuo*, the residue was taken in ether, and the ether solution was washed with brine, dried (anhyd. $MgSO_4$), and concentrated. The residue was purified by preparative TLC with $CHCl_3$ as the eluent to give an oily product (**12**) (3.5 mg). This was shown to be identical with mysorenone-B (**12**) by GC, GC-MS, and ^{1}H-NMR comparisons.

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References and Notes

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5) Mysorenone-C (**13**) is rather unstable and it decomposes to a complex mixture on standing in solution in EtOH or $CDCl_3$ for 3—7 d.
6) 3,3-Dimethylallyl bromide was prepared according to the method of Staudinger *et al.* See H. Staudinger, W. Kreis, and W. Schilt, *Helv. Chim. Acta*, **5**, 743 (1922).