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Studies on the Constituents of Medicinal and Related Plants in Sri Lanka. II.[1] Isolation and Structures of New γ-Pyrone and Related Compounds from *Hypericum mysorense* HEYNE

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Neutral constituents of *Hypericum mysorense* HEYNE, collected in Sri Lanka, were examined. Hyperenone-A, mysorenone-A, and compound-C (methyl phenacyl 1,1-dimethylprop-2-enyl-malonate) were isolated and their structures were determined on the basis of chemical and spectroscopic evidence. Four known xanthones were also isolated and identified.

Keywords——*Hypericum mysorense*; Guttiferae; hyperenone-A; γ-pyrone; mysorenone-A; methyl phenacyl 1,1-dimethylprop-2-enylmalonate; xanthone; catalytic hydrogenation

Some plants of *Hypericum genus* (Guttiferae) are used as folk medicines in Sri Lanka and India.[2] For instance, *Hypericum perforatum* LINN. was used as an antiseptic or an antihelmintic[3] and *H. japonicum* THUNB. as an antidysenteric.[2] Chemical investigations of some *Hypericum* species have been done by several groups of workers, and flavonoids, xanthones, bis-anthraquinones, and other constituents were reported.[4] In 1979, a chemotaxonomic study on *Hypericum mysorense* HEYNE was carried out by Gunatilaka *et al.*,[5] who reported the isolation and identification of 2,3-dimethoxyxanthone (II) from the timber of this plant. Recently we also examined the constituents of this plant and isolated four known xanthones and three new compounds, named hyperenone-A, mysorenone-A, and compound-C. The present paper describes the structure elucidation of these new compounds.

Methanolic extract of dried leaves and twigs of *H. mysorense*, collected in Sri Lanka, was digested successively with ether and ethyl acetate. The ether-soluble portion was roughly separated by silica gel column chromatography and the fractions were further separated by preparative thin layer chromatography to give 2-methoxyxanthone (I),[6] 2,3-dimethoxyxanthone (II),[5] 1,7-dihydroxyxanthone (III),[7] 2-hydroxyxanthone (IV),[6] mysorenone-A (XI), compound-C (XV), and hyperenone-A (V). Of these, the four xanthones were identified by comparisons of their melting points (mp) and ultraviolet (UV), infrared (IR), and proton nuclear magnetic resonance (^{1}H-NMR) spectral data with those reported in the literature.[5-7]

Hyperenone-A (V), mp 81—82 °C, showed the molecular ion peak at *m/z* 270 in the mass spectrum (MS), and the microanalytical data were consistent with the molecular formula $C_{17}H_{18}O_3$, which was confirmed by the high-resolution MS. The UV spectrum of V showed maximum absorptions at 236 nm (log ε 4.12) and 276 nm (log ε 4.07), indicating the presence of a conjugated aromatic chromophore, and the IR spectrum gave a strong absorption corresponding to a conjugated carbonyl grouping. The ^{1}H-NMR spectrum exhibited signals due to two *tert*-methyl, a methoxyl, a vinyl, and a mono-substituted phenyl (5H, δ 7.5—7.8) groups and the MS of V showed significant fragment peaks at *m/z* 105 ($C_6H_5CO^+$) and 77 ($C_6H_5^+$), suggesting that an oxygenic group is located at the benzylic position.

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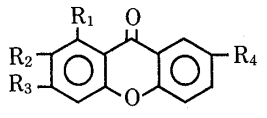
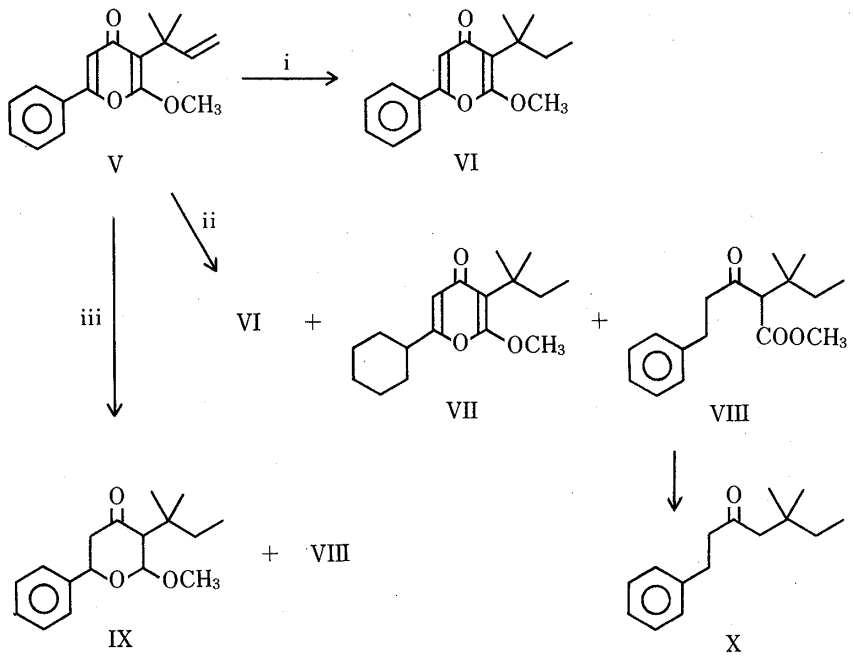


I : $R_2=OCH_3$, $R_1=R_3=R_4=H$
II : $R_2=R_3=OCH_3$, $R_1=R_4=H$
III : $R_1=R_4=OH$, $R_2=R_3=H$
IV : $R_2=OH$, $R_1=R_3=R_4=H$



reagents: i, H_2/Wilkinson's complex; ii, H_2/PtO_2; iii, H_2/10% Pd–C

Chart 1

Catalytic reduction of V on Wilkinson's complex afforded only a dihydro compound (VI), mp 125—127 °C, MS *m/z* 272 (M^+, $C_{17}H_{20}O_3$). The ^{1}H-NMR spectrum of this product (VI) showed characteristic signals at δ 0.76 (3H, t) and 1.84 (2H, q) due to a newly formed ethyl group instead of the vinyl group, while the UV spectrum gave a pattern practically identical with that of the parent compound (V), indicating that the vinyl group is not conjugated with other chromophores.

Similarly, hydrogenation of V on Adams catalyst afforded mainly the same dihydro compound (VI) as above, but in this case two other products were obtained in samll amounts. One was an octahydro compound (VII), MS *m/z* 278 (M^+, $C_{17}H_{26}O_3$), which was produced by hydrogenation at the vinyl and phenyl groups in V, as judged from the UV and ^{1}H-NMR spectral data, and the other was a hexahydro compound (VIII), oil, MS *m/z* 276 (M^+, $C_{17}H_{24}O_3$). On the other hand, catalytic hydrogenation of V using 10% palladium-carbon (Pd–C) afforded the above mentioned VIII and another hexahydro product (IX), MS *m/z* 276 (M^+, $C_{17}H_{24}O_3$).

Compound VIII exhibited IR absorptions at 1715 cm^{-1} (CO) and 1740 cm^{-1} (ester), and in the ^{1}H-NMR spectrum it showed partly overlapped multiplets at δ 2.75—3.00 due to two newly formed methylene groups and a one-proton singlet at δ 3.43 along with the signals arising from the ethyl, *tert*-methyl, methoxyl, and phenyl protons.

Treatment of VIII with potassium hydroxide in aqueous methanol, followed by refluxing in acidic medium, gave rise to an oily decarboxylated compound (X), MS *m/z* 218 (M^+, $C_{15}H_{22}O$), in the ^{1}H-NMR spectrum of which the methoxyl signal and the one-proton singlet had disappeared and, instead, a multiplet due to two protons newly appeared at δ 2.10. Thus,

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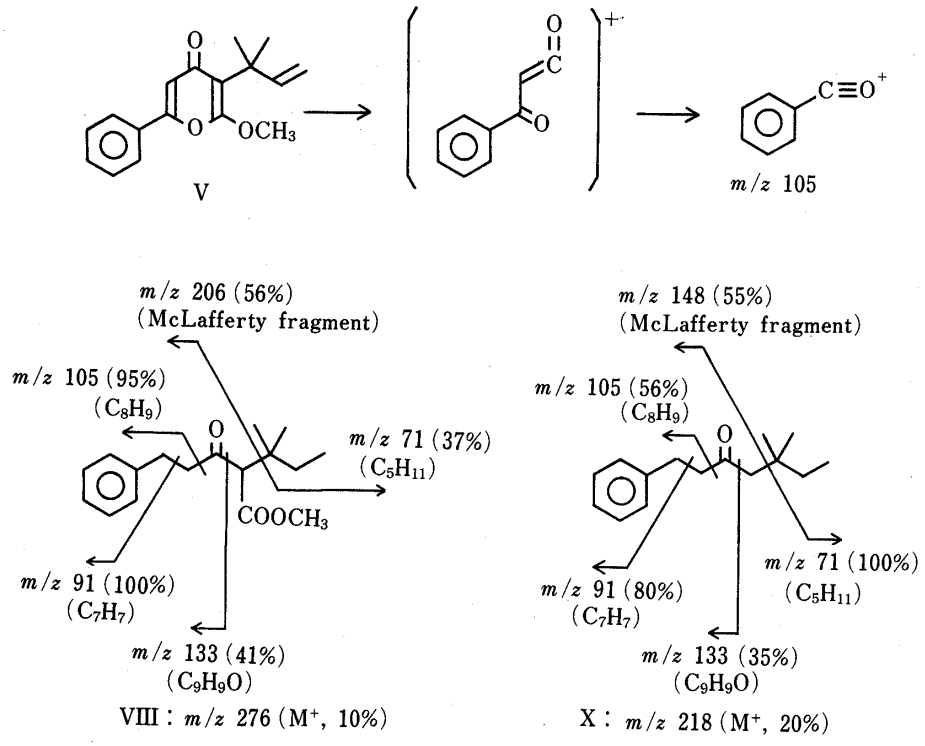

Fig. 1

compound VIII should be a β-keto ester.

From these findings, coupled with the fact that the mass spectra of VIII and X could be interpreted as shown in Fig. 1, this hexahydro compound was deduced to have the structure VIII.

The other hexahydro product (IX) exhibited a carbonyl absorption at 1715 cm^{-1} in the IR spectrum. In the ^{1}H-NMR spectrum, it showed three characteristic double doublets at δ2.54 (J=3, 17 Hz), 3.01 (J=13, 17 Hz), and 5.18 (J=3, 13 Hz) and a pair of doublets at δ2.74 and 5.16 (J=3 Hz), which could be reasonably ascribed to the partial structure –O–CH–CH_2–CO–CH–CH(OCH_3)–O–, besides the signals due to the ethyl, two *tert*-methyl, methoxyl, and phenyl groups. The mutual coupling relations among these signals were fully analyzed by detailed decoupling experiments.

Thus, the structure of the above product should be IX, and accordingly the structure of hyperenone-A should be represented by the formula V. Formation of the fragment ion at m/z 105 in the MS of V can be explained reasonably on the basis of retro-Diels–Alder fragmentation (Fig. 1).[8]

Mysorenone-A (XI), oil, showed the M^+ peak at m/z 288 in the MS and its molecular formula was determined to be $C_{17}H_{20}O_4$ by the high-resolution MS. The IR spectrum of XI revealed absorptions at 3100 (OH), 1740 (ester), and 1605 cm^{-1} (conjugated CO) and the UV spectrum showed a strong absorption at 321 nm (log ε 4.04). The ^{1}H-NMR spectrum of XI was characterized by the appearance of three singlets at δ3.38 (methine proton flanked by two carbonyl groups), 6.42 (olefinic proton), and 16.17 (hydroxyl proton) in addition to diagnostic signals due to a phenyl, a vinyl, a methoxyl, and two *tert*-methyl groups. The MS showed significant fragment peaks at m/z 105 ($C_6H_5CO^+$), 147 ($C_6H_5COCH_2CO^+$), and 220 ($M^+ - C_5H_8$, McLafferty fragment) (Fig. 2), suggesting the presence of an oxygenic function at the benzylic position and a *tert*-pentenyl group in XI.

Catalytic hydrogenation of mysorenone-A (XI) on Adams catalyst yielded a dihydro compound (XII), MS m/z 290 (M^+), and an octahydro compound (XIII), MS m/z 296 (M^+),

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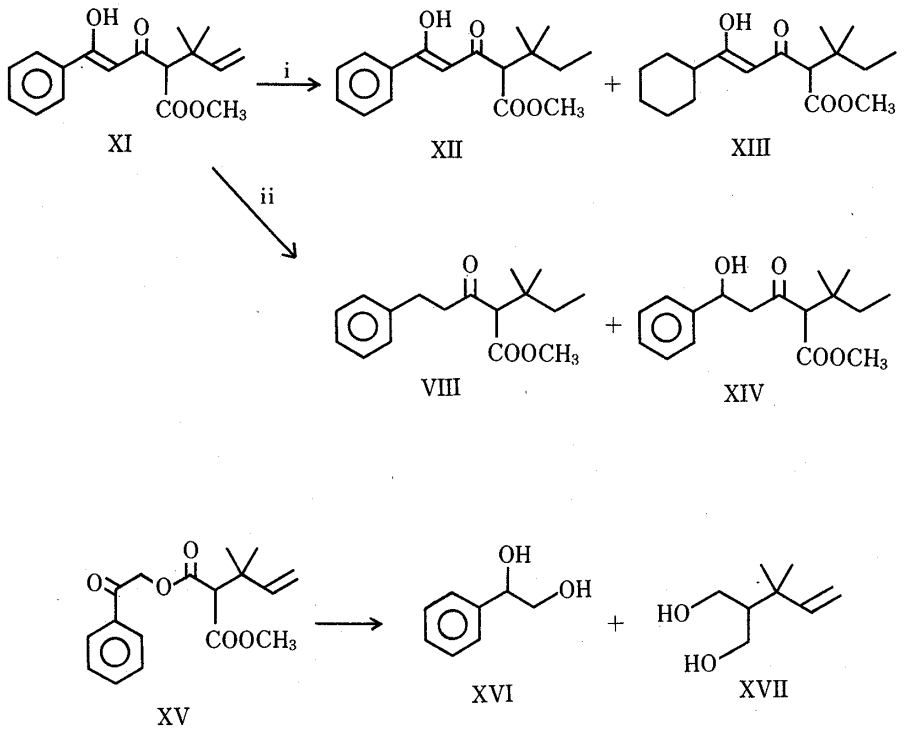

reagents: i, H_2/PtO_2; ii, H_2/10% Pd–C

Chart 2

as in the case of hyperenone-A (V). The UV spectrum of XII was practically the same as that of the parent compound (XI) and the ^{1}H-NMR spectrum exhibited new signals assignable to an ethyl group instead of the vinyl group, whereas the ^{1}H-NMR spectrum of XIII showed signals ascribable to an ethyl and a cyclohexyl group instead of the vinyl and the phenyl group. It is now evident that the vinyl group is not conjugated with other unsaturated groups.

On the other hand, hydrogenation of XI on Pd–C gave a tetrahydro compound (XIV) and a deoxo compound (VIII), which was proved to be identical with VIII obtained by hydrogenation of hyperenone-A (V). The MS of the former product (XIV) failed to give the molecular ion peak, but it showed the dehydrated ion peak at *m/z* 274 along with other significant peaks at *m/z* 204 ($M^+ - H_2O - C_5H_{10}$, McLafferty fragment), 131 ($C_6H_5CH=CHCO^+$, base peak), and 103 ($C_6H_5CH=CH^+$), and the ^{1}H-NMR spectrum showed signals at δ 5.19 (1H, dt, $J=3$, 6 Hz), 3.22 (1H, d, $J=3$ Hz), and 2.93 (2H, d, $J=6$ Hz), corresponding to the partial structure –CH(OH)–CH_2–CO–. Compound VIII is presumably produced by hydrogenolysis of XIV.

Based on the above results, the structure of mysorenone-A should be represented by the formula XI.

It is particularly interesting that the catalytic hydrogenation of both V and XI with Adams catalyst proceeded preferentially at the phenyl group rather than the γ-pyrone or enolic double bond in sharp contrast to the result observed with Pd–C.

Compound-C (XV) was isolated as a colorless oil in small amount and its molecular formula was determined to be $C_{17}H_{20}O_5$ by the MS and high-resolution MS. The ^{1}H-NMR spectrum of XV closely resembled that of mysorenone-A (XI) except for the appearance of a pair of doublets due to methylene protons at δ 5.35 and 5.50 (each 1H, $J=16$ Hz) and its MS gave peaks at *m/z* 136 ($C_8H_8O_2^+$) and 168 ($C_9H_{12}O_3^+$), together with peaks at *m/z* 105, 141, and 236 (Fig. 2), suggesting that it might be an ester-type compound having the formula XV. Furthermore, the IR spectrum showed carbonyl absorptions at 1760 and 1740 cm^{-1} in

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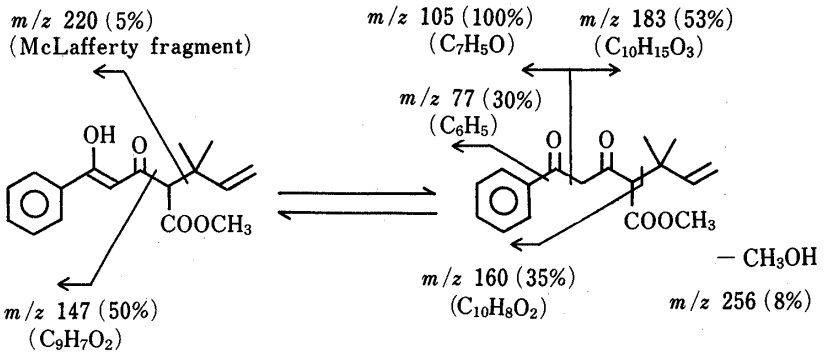
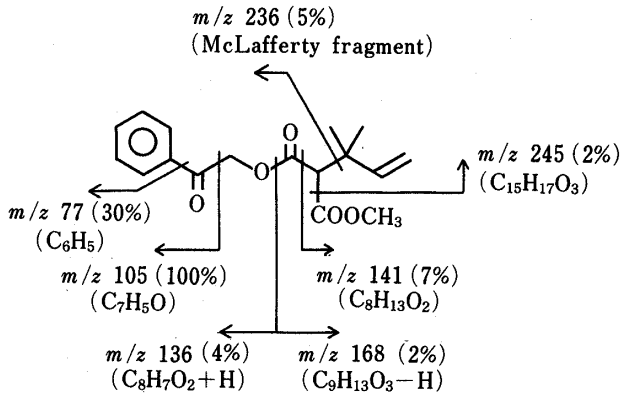


XI: m/z 288 (M^+, 8%)



XV: m/z 304 (M^+, 2%)

Fig. 2

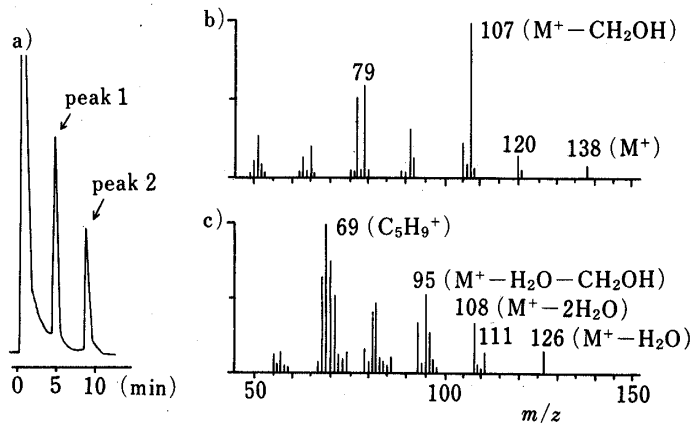


Fig. 3. Gas Chromatogram and GC-MS of the Reduction Product of Compound-C (XV)

a) Gas chromatogram. b) Mass spectrum of peak 2. c) Mass spectrum of peak 1.

accordance with the presumed malonate ester structure.[9]

As expected, lithium aluminum hydride reduction of XV afforded a mixture of diols (XVI and XVII), which gave two peaks on gas chromatography (GC) (Fig. 3). The GC-MS of the later peak (Fig. 3) showed the molecular ion peak at m/z 138 ($C_8H_{10}O_2$), and this product was found to be identical with authentic α,β-dihydroxyethylbenzene (XVI).[10] The MS corresponding to the earlier GC peak showed a peak at m/z 126 assignable to the ($M^+ - H_2O$) ion, although the molecular ion peak was not observed. The other fragment ion peaks given in Fig.

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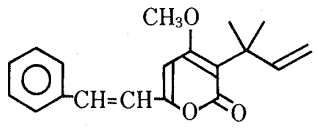
3, c) could be rationalized in terms of the presumed formula XVII. Thus, compound-C is concluded to be methyl phenacyl 1,1-dimethylprop-2-enylmalonate (XV).



XVIII

Chart 3

It is worth noting here that mundulea lactone (XVIII), which is closely related to hyperenone-A, was reported to be a constituent of *Mundulea suberosa* BENTH. (Leguminosae).[11]

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. 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 or a GC injection system (2% OV-17 2 m × 2 mm i.d. glass column at column temperature 120—200 °C, carrier gas He) and the relative intensities (%) of peaks are give in parentheses. GC was done on a Shimadzu GC-6AM instrument with a 2% OV-17 column (2 m × 3 mm i.d. glass tube; injection temperature, 220 °C; column temperature, 200 °C; carrier gas, N_2). Column chromatography was carried out using Mallinckrodt silica gel and the eluates were concentrated *in vacuo*. For thin layer chromatography (TLC), Merck Kieselgel 60 F_{254} was used and spots were detected under UV light or by coloration with $Ce(SO_4)_2$–H_2SO_4 reagent. For preparative TLC, Merck Kieselgel PF_{254} or F_{254} (0.5 mm) 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 extracts were concentrated *in vacuo*.

Extraction, Isolation and Properties of Xanthones and New Compounds from *H. mysorense*——Air-dried leaves and twigs (120 g), collected at Horton Plains, Sri Lanka in the flowering season (January, 1982), were extracted with refluxing MeOH (500 ml × 3) for 3 h and the combined extract was concentrated *in vacuo*. The residue (20 g) was digested successively with ether and ethyl acetate to give the ether-soluble fraction (1.9 g) and the ethyl acetate-soluble fraction (2 g).

The ether-soluble fraction was chromatographed on silica gel (60 g) and eluted successively with CH_2Cl_2 (F-1 and F-2), 2% MeOH–CH_2Cl_2 (F-3), and 3% MeOH–CH_2Cl_2 (F-4).

F-2 (0.4 g) was then separated by preparative TLC with $CHCl_3$, and the less polar fraction was recrystallized from ether–hexane to give 2-methoxyxanthone (I) (3 mg), colorless needles, mp 133—134 °C. The more polar fraction (mixture) was further separated by preparative TLC with benzene as the eluent, giving mysorenone-A (XI) (35 mg), slightly colored oil, from the upper zone and compound-C (XV) (4 mg), colorless oil, from the lower zone.

F-3 (0.17 g) was further separated by preparative TLC with MeOH–$CHCl_3$ (2 : 98) as the eluent to give 2,3-dimethoxyxanthone (II) (7 mg), colorless needles from isopropyl ether –hexane, mp 163—166 °C.

F-4 (0.38 g) was also separated by preparative TLC with MeOH–$CHCl_3$ (2 : 98). The least polar fraction gave hyperenone-A (V) (120 mg) after recrystallization from isopropyl ether–hexane and the next most polar fraction gave 1,7-dihydroxyxanthone (III) (5 mg), yellow needles from $CHCl_3$, mp 239—242 °C. The most polar fraction gave 2-hydroxyxanthone (IV) (4 mg), yellowish needles from $CHCl_3$, mp 240—242 °C.

Hyperenone-A (V): Colorless prisms, mp 81—82 °C. UV λ_{max} nm (log ε): 236 (4.12), 276 (4.07); IR ν_{max} cm^{-1}: 1650, 1605, 1560 (γ-pyrone). ^{1}H-NMR δ: 1.51 (3H × 2, s, *tert*-CH_3), 4.10 (3H, s, OCH_3), 4.92, 4.98 (each 1H, dd, J = 2, 11 Hz, and J = 2, 17 Hz, respectively; =CH_2), 6.23 (1H, dd, J = 12, 17 Hz, =CH), 6.65 (1H, s, =CH), 7.52 (3H, m, aromatic protons), 7.74 (2H, m, aromatic protons). MS *m/z* (rel. int. %): 270 (M^+, 25), 255 ($M^+ - CH_3$, 100), 241 (30), 239 ($M^+ - OCH_3$, 22), 227 (25), 105 (98), 77 (76). High-resolution MS: Found 270.1226, Calcd for $C_{17}H_{18}O_3$ (M^+) 270.1255; Found 255.1008, Calcd for $C_{16}H_{15}O_3$ 255.1020; Found 241.0878, Calcd for $C_{15}H_{13}O_3$ 241.0864; Found 239.1001, Calcd for $C_{16}H_{15}O_2$ 239.1071; Found 227.0799, Calcd for $C_{14}H_{11}O_3$ 227.0708; Found 105.0375, Calcd for C_7H_5O 105.0340; Found 77.0401, Calcd for C_6H_5 77.0391. *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.85. Found: C, 75.49; H, 6.85.

Mysorenone-A (XI): Slightly colored oil, UV λ_{max} nm (log ε): 220 (3.63), 250 (3.57), 321 (4.04); IR ν_{max} cm^{-1}: 3100, 1740, 1605, 1580. ^{1}H-NMR δ: 1.23, 1.24 (each 3H, s, *tert*-CH_3), 3.38 (1H, s, CO–CH–CO), 3.71 (3H, s, OCH_3),

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5.05 (2H, m, $=CH_2$), 6.09 (1H, dd, $J=12$, 17 Hz, $=CH$), 6.42 (1H, s, HO–C$=$C$\underline{H}$), 7.50 (3H, m, aromatic protons), 7.91 (2H, m, aromatic protons), and 16.17 (1H, s, $\underline{H}$O–C$=$CH; disappeared on addition of D_2O). MS: see Fig. 2. High-resolution MS: Found 288.1363, Calcd for $C_{17}H_{20}O_4$ 288.1361; Found 256.1131, Calcd for $C_{16}H_{16}O_3$ 256.1099; Found 183.1009, Calcd for $C_{10}H_{15}O_3$ 183.1021; Found 160.0529, Calcd for $C_{10}H_8O_2$ 160.0524; Found 147.0398, Calcd for $C_9H_7O_2$ 147.0446; Found 105.0348, Calcd for C_7H_5O 105.0340; Found 77.0366, Calcd for C_6H_5 77.0391.

Compound-C (XV): Colorless oil, UV λ_{max} nm (log ε): 243 (3.99) 282 (3.15); IR ν_{max} cm^{-1}: 1760, 1740, 1710. ^{1}H-NMR δ: 1.35, 1.36 (each 3H, s, *tert*-CH_3), 3.62 (1H, s, CO–C$\underline{H}$–CO), 3.78 (3H, s, OCH_3), 5.13 (2H, m, $=CH_2$), 5.35, 5.50 (each 1H, d, $J=16$ Hz, CO–C$\underline{H}_2$–O), 6.16 (1H, dd, $J=11$, 17 Hz, $=CH$), 7.62 (3H, m, aromatic protons), and 7.98 (2H, m, aromatic protons). MS: see Fig. 2. High-resolution MS: Found 304.1282, Calcd for $C_{17}H_{20}O_5$ 304.1311; Found 245.1174, Calcd for $C_{15}H_{17}O_3$ 245.1177; Found 236.0665, Calcd for $C_{12}H_{12}O_5$ 236.0684; Found 168.0817, Calcd for $C_9H_{12}O_3$ 168.0786; Found 141.0896, Calcd for $C_8H_{13}O_2$141.0915; Found 136.0548, Calcd for $C_8H_8O_2$ 136.0524; Found 105.0339, Calcd for C_7H_5O 105.0340; Found 77.0385, Calcd for C_6H_5 77.0391.

Catalytic Hydrogenation of Hyperenone-A (V)——1) With Wilkinson Complex: Hyperenone-A (V) (5 mg) was hydrogenated in benzene (1 ml) with tristriphenylphosphinerhodium chloride (1 mg) for 12 h. The reaction mixture was purified by preparative TLC with MeOH–$CHCl_3$ (2 : 98) and then recrystallized from ether–hexane to give dihydrohyperenone-A (VI) (4.5 mg), plates, mp 125—127 °C, UV λ_{max} nm (log ε): 236 (4.05) 276 (4.01); IR ν_{max} cm^{-1}: 1650, 1603, 1560. ^{1}H-NMR δ: 0.76 (3H, t, $J=7$ Hz, C$\underline{H}_3$CH$_2$–), 1.38 (3H × 2, s, *tert*-CH_3), 1.84 (2H, q, $J=7$ Hz, CH_3C$\underline{H}_2$–), 4.08 (3H, s, OCH_3), 6.59 (1H, s, $=CH$), 7.50 (3H, m, aromatic protons), 7.74 (2H, m, aromatic protons). MS *m/z* (rel. int. %): 272 (M^+, 40), 257 (M^+-CH_3, 100), 243 ($M^+-C_2H_5$, 40), 241 (M^+-OCH_3, 20), 229 (80), 216 (98), 201 (30), 141 (70), 105 (30), 77 (20). High-resolution MS: Found 272.1423, Calcd for $C_{17}H_{20}O_3$ 272.1412; Found 257.1196, Calcd for $C_{16}H_{17}O_3$ 257.1178; Found 243.0974, Calcd for $C_{15}H_{15}O_3$ 243.1021; Found 241.1192, Calcd for $C_{16}H_{17}O_2$ 241.1123; Found 229.0839, Calcd for $C_{14}H_{13}O_3$ 229.0865; Found 216.0778, Calcd for $C_{13}H_{12}O_3$ 216.0786; Found 201.0579, Calcd for $C_{12}H_9O_3$ 201.0552; Found 141.0554, Calcd for $C_7H_9O_3$ 141.0552; Found 105.0339, Calcd for C_7H_5O 105.0340; Found 77.0377, Calcd for C_6H_5 77.0391.

2) With Adams Catalyst: V (5 mg) was hydrogenated in MeOH (0.5 ml) with PtO_2 (1 mg) for 36 h. After removal of the catalyst by filtration, the reaction mixture was concentrated *in vacuo* and the residue was separated by preparative TLC using acetone–$CHCl_3$ (1 : 99). The most polar band afforded dihydrohyperenone-A (1.9 mg), mp 125—127 °C, identical with the above mentioned VI. The next most polar band gave an octahydro compound (VII) (0.5 mg), oil, UV λ_{max} nm (log ε): 215 (3.62) and 260 (3.51). ^{1}H-NMR δ: 0.71 (3H, t, $J=7$ Hz, C$\underline{H}_3$CH$_2$), 1.30 (3H × 2, s, *tert*-CH_3), 1.79 (2H, q, $J=7$ Hz, CH_3C$\underline{H}_2$), 2.37 (1H, m), 3.91 (3H, s, OCH_3), and 5.91 (1H, s, $=CH$). MS *m/z* (rel. int. %): 278 (M^+, 22), 263 (M^+-CH_3, 95), 249 ($M^+-C_2H_5$, 75), 235 (100), and 222 (65).

The least polar band afforded a hexahydro compound (VIII) (0.4 mg), oil, UV λ_{max} nm (log ε): 209 (3.98) and 270 (3.31); IR ν_{max} cm^{-1}: 1740 and 1715. ^{1}H-NMR δ: 0.82 (3H, t, $J=7$ Hz, C$\underline{H}_3$CH$_2$), 1.01, 1.03 (each 3H, s, *tert*-CH_3), 1.40 (2H, q, $J=7$ Hz, CH_3C$\underline{H}_2$), 2.70—3.00 (4H, m, C_6H_5–C$\underline{H}_2$C$\underline{H}_2$–CO), 3.46 (1H, s, CO–CH–CO), 3.65 (3H, s, OCH_3), and 7.14—7.26 (5H, m, aromatic protons). MS: see Fig. 1. High-resolution MS: Found 276.1706, Calcd for $C_{17}H_{24}O_3$ 276.1725; Found 206.0917, Calcd for $C_{12}H_{14}O_3$ 206.0943; Found 133.0658, Calcd for C_9H_9O 133.0653; Found 105.0695, Calcd for C_8H_9 105.0704; Found 91.0552, Calcd for C_7H_7 91.0547; Found 71.0848, Calcd for C_5H_{11} 71.0860.

3) With Pd–C: In the same manner as above, hydrogenation of V (5 mg) with 10% Pd–C (1 mg) was carried out in MeOH (0.5 ml) for 9 h, and two products were detected by TLC. The reaction mixture was separated by preparative TLC with AcOEt–hexane (1 : 9) as the eluent and the lower band gave the hexahydro compound (VIII) (0.9 mg), which was identical with the sample (VIII) obtained in 2). The upper band gave another hexahydro compound (IX) (0.4 mg), colorless oil, UV λ_{max} nm (log ε): 212 (3.86) 256 (1.96); IR ν_{max} cm^{-1}: 1715. ^{1}H-NMR δ: 0.86 (3H, t, $J=7$ Hz, C$\underline{H}_3$CH$_2$), 1.05, 1.12 (3H × 2, s, *tert*-CH_3), 1.55 (2H, m, CH_3C$\underline{H}_2$), 2.54, 3.01 (each 1H, dd, $J=3$, 17 Hz and $J=13$, 17 Hz, respectively, CO–CH_2), 2.74 (1H, d, $J=3$ Hz, CO–CH), 3.57 (3H, s, OCH_3), 5.16 (1H, d, $J=3$ Hz, O–C$\underline{H}$–OCH_3), 5.18 (1H, dd, $J=3$, 13 Hz, C_6H_5–C$\underline{H}$–O), and 7.35—7.60 (5H, m, aromatic protons). MS *m/z* (rel. int. %): 276 (M^+, 1), 245 (M^+-OCH_3, 5), 216 ($M^+-HCO_2CH_3$, 45), 175 ($M^+-OCH_3-C_5H_{10}$, 75), 104 (90), 99 (100), 77 (41). High-resolution MS: Found 276.1655, Calcd for $C_{17}H_{24}O_3$ 276.1725; Found 245.1478, Calcd for $C_{16}H_{21}O_2$ 245.1541; Found 216.1521, Calcd for $C_{15}H_{20}O$ 216.1514; Found 175.0813, Calcd for $C_{11}H_{11}O_2$ 175.0759; Found 104.0605, Calcd for C_8H_8 104.0626; Found 99.0784, Calcd for $C_6H_{11}O$ 99.0810; Found 77.0390, Calcd for C_6H_5 77.0391.

Hydrolysis and Decarboxylation of the Hexahydro Compound VIII——To a solution of VIII (0.3 mg) in MeOH (0.1 ml) was added 2% NaOH–H_2O (0.1 ml) and the mixture was heated in a water bath for 15 min. The mixture was then made acidic by the addition of 5% HCl (0.1 ml) and heated for 30 min. After evaporation of the solvent, the product was taken up in CH_2Cl_2 and examined by GC-MS. MS: see Fig. 1. High-resolution MS: Found 218.1639, Calcd for $C_{15}H_{22}O$ 218.1670; Found 148.0828, Calcd for $C_{10}H_{12}O$ 148.0888; Found 133.0664, Calcd for C_9H_9O 133.0653; Found 105.0708, Calcd for C_8H_9 105.0704; Found 91.0534, Calcd for C_7H_7 91.0547; Found 71.0849, Calcd for C_5H_{11} 71.0860.

Catalytic Hydrogenation of Mysorenone-A (XI)——1) With Adams Catalyst: Mysorenone-A (XI) (3 mg) was hydrogenated with PtO_2 (1 mg) in MeOH (0.3 ml) for 12 h and the reaction mixture was separated by preparative

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TLC using AcOEt–hexane (1 : 9) as the eluent. The more polar fraction gave dihydromysorenone-A (XII) (0.9 mg), oil, UV λ_{max} nm (log ε): 217 (3.13), 252 (3.08), 319 (3.59). ^{1}H-NMR δ: 0.88 (3H, t, J=7 Hz, C$\underline{H}_3$CH$_2$), 1.09, 1.10 (each 3H, s, *tert*-CH$_3$), 1.47 (2H, q, J=7 Hz, CH$_3$C$\underline{H}_2$), 3.37 (1H, s, CO–CH–CO), 3.72 (3H, s, OCH$_3$), 6.47 (1H, s, =CH), 7.50 (3H, m, aromatic protons), 7.93 (2H, m, aromatic protons), and 16.22 (1H, s, enolic OH). MS m/z (rel. int. %): 290 (M^+, 1), 259 ($M^+ - OCH_3$, 2), 220 (McLafferty fragment, 65), 188 (McLafferty fragment $-OCH_3$, 30), 160 (75), 147 (100), 143 (8), 105 ($C_6H_5CO^+$, 95), 77 (30). The less polar fraction afforded octahydromysorenone-A (XIII) (0.6 mg), oil, UV λ_{max} nm (log ε): 282 (3.40). ^{1}H-NMR δ: 0.88 (3H, t, J=7 Hz, C$\underline{H}_3$CH$_2$), 1.04, 1.06 (each 3H, s, *tert*-CH$_3$), 1.40 (2H, q, J=7 Hz, CH$_3$C$\underline{H}_2$), 2.20 (1H, m), 3.34 (1H, s, CO–CH–CO), 3.70 (3H, s, CO$_2$CH$_3$), 5.76 (1H, s, =CH), and 15.70 (1H, s, enolic OH). MS m/z (rel. int. %): 296 (M^+, 1), 265 ($M^+ - OCH_3$, 5), 226 (McLafferty fragment, 60), 194 (60), 153 (95), 143 (100), 111 (97), and 83 (97).

2) With Pd–C: XI (5 mg) was hydrogenated with 10% Pd–C (1 mg) in MeOH (1 ml) for 12 h, and after removal of the catalyst, the mixture was separated by preparative TLC with benzene. The less polar fraction gave a deoxo product (VIII) (1.5 mg), oil, MS m/z: 276 (M^+, $C_{17}H_{24}O_3$), which was identical with the hexahydro product (VIII) obtained from hyperenone-A in all respects. The more polar fraction gave a tetrahydro compound (XIV) (1.5 mg), oil, IR ν_{max} cm^{-1}: 3500, 1740, 1710. ^{1}H-NMR δ: 0.86 (3H, t, J=7 Hz, C$\underline{H}_3$CH$_2$), 1.08 (3H×2, s, *tert*-CH$_3$), 1.44 (2H, q, J=7 Hz, CH$_3$C$\underline{H}_2$), 2.93 (2H, d, J=6 Hz, CO–CH$_2$), 3.22 (1H, d, J=3 Hz, CH–O$\underline{H}$), 3.50 (1H, s, CO–CH–CO), 3.70 (3H, s, CO$_2$CH$_3$), 5.19 (1H, dt, J=3, 6 Hz, C$\underline{H}$–OH), 7.30—7.40 (5H, m, aromatic protons). MS m/z (rel. int. %): 274 ($M^+ - H_2O$, 1), 204 (McLafferty fragment, 25), 144 (20), 131 (100), 103 (25), 77 (15).

Lithium Aluminum Hydride Reduction of Compound-C (XV)——Excess of lithium aluminum hydride was added to a solution of XV (0.5 mg) in dry ether (0.1 ml) and the mixture was stirred for 1 h at room temperature. After decomposition of the excess reagent by addition of a small amount of H_2O, the precipitate was removed by filtration and washed thoroughly with ether. The ether solution was concentrated to give a small amount of oily residue (a mixture of XVI and XVII). This was examined by GC and GC-MS, and peak 2 was identified as α,β-dihydroxyethylbenzene (XVI) by direct comparisons with an authentic sample.[10]

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