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Studies on the Constituents of the Cultivated Mulberry Tree. III.[1] Isolation of Four New Flavones, Kuwanon A, B, C and Oxydihydromorusin from the Root Bark of *Morus alba* L.[2,3]

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The structures of four new flavone derivatives, kuwanon A, B, C and oxydihydromorusin were isolated from the benzene extract of the root bark of the cultivated mulberry tree (a variety of *Morus alba* L.), and were shown to be I, II, III and IV, respectively, on the basis of spectroscopic and chemical evidences. Photooxidative cyclization did not occur with I but with II leading to the formation of a hydroperoxide possessing a dihydrooxepin ring. III was cyclized on photooxidation as II and was converted to morusin (V) by treating with DDQ. On hydration with methanolic hydrochloric acid, V was converted to IV.

Keywords——kuwanon A; kuwanon B; kuwanon C; oxydihydromorusin; *Morus alba* L.; morusin; flavone; photooxidation

The structures of a series of prenylflavones isolated from the root bark of *Morus alba* L., so far a plant of Moraceae family, have been elucidated.[5] In the course of our studies on the constituents of the root bark, four new flavone derivatives, kuwanon A (I), B (II), C (III) and oxydihydromorusin (IV) have been isolated from the benzene extract of the root bark of the cultivated mulberry tree (Ichinose, a variety of *Morus alba* L.). All the flavones were positive to characteristic color reaction for flavones and to methanolic ferric chloride test. In this paper, we report the structure determination of the four new flavone derivatives, I, II, III and IV.

Kuwanon A (I) was obtained as amorphous powder, M+ 420. Treatment of I with ethereal diazomethane yielded a dimethyl ether (Ia), mp 147°, M+ 448, $C_{27}H_{28}O_6$, which gave a violet color with methanolic ferric chloride and was positive to the Gibbs test. I forms a diacetate (Ib), mp 167—169°, M+ 504, $C_{29}H_{28}O_8$, on treatment with acetic anhydride in pyridine at room temperature.

The nuclear magnetic resonance (NMR) spectrum of I showed the characteristic signals for γ,γ-dimethylallyl group [δ 1.45, 1.58 (each 3H, s, C_{11}–CH_3), δ 3.11 (2H, br d, $J=8$ Hz, C_9–H×2), δ 5.13 (1H, m, C_{10}–H)] and 2,2-dimethylchromene ring[5,6] [δ 1.40 (6H, s, C_{14}–CH_3 ×2), δ 5.69 (1H, d, $J=10$ Hz, C_{13}–H), δ 6.75 (1H, d, $J=10$ Hz, C_{12}–H)]. In the low-field region of the spectrum, I showed a sharp single-proton at δ 13.13, which disappeared on addition of D_2O indicating the presence of a chelated hydroxyl group. The *meta*-coupled doublet ($J=2$ Hz) at δ 6.26 and δ 6.32 indicated the phloroglucinolderived A ring, unsubstituted at 6- and 8-positions.[7] The aromatic proton signals at δ 6.68 and δ 7.08 showing

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[1] Part II: T. Nomura, T. Fukai, S. Yamada, and M. Katayanagi, *Chem. Pharm. Bull.* (Tokyo), **26**, 1431 (1978).

[2] A preliminary account of this work has been presented: T. Nomura, T. Fukai, and M. Katayanagi: *Chem. Pharm. Bull.* (Tokyo), **25**, 529 (1977).

[3] Taken from part of the Doctorated thesis presented by T.F. to Hokkaido University (1977).

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[5] T. Nomura, T. Fukai, S. Yamada, and M. Katayanagi: *Chem. Pharm. Bull.* (Tokyo), **26**, 1394 (1978).

[6] V.H. Deshpande, P.C. Parthasarathy, and K. Venkataraman, *Tetrahedron Lett.* **1968**, **1715**.

[7] T.J. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids" Spring-Verlag, Berlin, 1970, Part III.

an *ortho*-coupling (J=9 Hz) indicated the B ring of I substituted at the 2′-, 3′- and 4′-positions.[7] The signals at δ 6.68 and δ 7.08 were assigned to the 5′- and 6′-proton, respectively, because generally the signal of 6′-proton appeares at lower magnetic field than that of 5′-proton.[5,6,7]

The mass spectrum of I gave the fragments at *m/e* 405 (M^+–CH_3), and 365 (M^+–C_4H_7).[8] The peak at *m/e* 153 corresponds to the fragment VII which is expected to arise from the ring A.[9] The ultraviolet (UV) spectrum of I resembled those of morusin (V) and other prenylflavones having a γ,γ-dimethylallyl group attached to the 3-position.[5,6] The NMR spectrum of I was devoid of the characteristic singlet signal[7] of the 3-position and showed the chemical shift of the 6′-proton of the B ring at δ 7.08, *ca.* 0.7 ppm upfield from the corresponding proton of the prenylflavone which has a prenyl group at the position other than the 3-position.[10] These spectral features are characteristic of 3-prenylated flavones.[5,6,11]

Kuwanon B (II) was obtained as pale yellow prisms, mp 250—254°, M^+ 420, $C_{25}H_{24}O_6$. On treatment with ethereal diazomethane, II formed a dimethyl ether (IIa), mp 115—118°, M^+ 448, which gave a violet color with methanolic ferric chloride. Treatment of II with acetic anhydride in pyridine at room temperature yielded a diacetate (IIb), mp 125—127°, M^+ 504.

The mass spectrum of II gave fragments at *m/e* 405 (M^+–CH_3), 365 (M^+–C_4H_7), and 153 (VII) as detected in I. The NMR spectrum of II was similar to that of I except the 5′-proton signal at δ 6.46. The UV spectrum of II resembled that of I. From these data, both kuwanon A (I) and B (II) can be regarded as flavone derivatives having the 2,2-dimethylchromene in the B ring and γ,γ-dimethylallyl group attached to the 3-position of chromone ring.

The changes in chemical shift for 12- and 13-proton when I and II are acetylated (Table I) indicate that the relation of 12-proton in chromene to the hydroxyl group in B ring is *peri* both in I and II. These changes are of the same shift and of the same order of magnitude as those observed by many investigators for a number of similar compounds, in which the hydroxyl group is *peri* to 12-proton.[12] These findings indicate that kuwanon A is represented as I and kuwanon B as II, otherwise kuwanon A as II and kuwanon B as I.

Final proof for the structures of kuwanon A and B was obtained by the photooxidation.[1] When a solution of II in chloroform was irradiated with a high-pressure mercury lamp for 5 hr, kuwanon B hydroperoxide (IIc) was obtained in 60% yield. IIc showed the following data: mp 203°, M^+ 452, NMR spectrum showing the AMX pattern,[1,5] such as 3.00 (1H, dd, J=9 and 16 Hz, C_9–H), 3.67 (1H, dd, J=2 and 16 Hz, C_9–H), 4.83 (1H, dd, J=2 and 9 Hz, C_{10}–H); mass spectrum (MS) *m/e*: 452 (M^+), 436 (M^+–O), 421 (M^+–O–CH_3), 377 (M^+–$C_3H_7O_2$),[5] 153 (VII). On the other hand, this photooxidation did not occur in kuwanon A (I). It is concluded that kuwanon B (II) has the hydroxyl group at the 2′-position, taking into consideration the structural requirement in the case of the photooxidation of morusin (V),[1] where both hydroxyl group at the 2′-position and the isolated double bond in prenyl group attached to the 3-position of the chromone ring are required for this photooxidation. We thus propose the formula (I) for kuwanon A and the formula (II) for kuwanon B.

Kuwanon C (III) was obtained as pale yellow prisms, mp 148—150°, M^+ 422, $C_{25}H_{26}O_6$, which gave a green color with methanolic ferric chloride and was positive to the Gibbs test. The UV spectrum of III resembled that of morusin (V) and other prenylflavones, having

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8) A.V.R. Rao, S.S. Rathi, and K. Venkataraman, *Indian J. Chem.*, **10**, 989 (1972).

9) H. Audier, *Bull. Soc. Chim. France*, **1966**, 2892.

10) P.C. Parthasarathy, P.V. Radhakrishnan, S.S. Rathi, and K. Venkataraman, *Indian J. Chem.*, 7, 101 (1969).

11) A.D. Pendse, R. Pendse, A.V.R. Rao, and K. Venkataraman, *Indian J. Chem.*, **14B**, 69 (1976).

12) *a*) A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, *Tetrahedron Lett.*, **1967**, 4201; *b*) B. Jackson, P.J. Owen, and F. Sheinmann, *J. Chem. Soc.* (*C*), **1971**, 3389.

γ,γ-dimethylallyl group at the 3-position.[5,6] The NMR spectrum of III exhibited the presence of two γ,γ-dimethylallyl groups [δ 1.43 (3H, s, C_{11}–CH_3), δ 1.57 (9H, s, C_{11}–CH_3 and C_{14}–$CH_3 \times 2$), δ 3.12 (2H, br d, $J=8$ Hz, C_9–$H \times 2$), δ 3.35 (2H, br d, $J=8$ Hz, C_{12}–$H \times 2$), δ 5.20 (2H, m, C_{10} and C_{13}–H)], and the aromatic protons of the B ring showed the characteristic ABC pattern of β-resorcylic acid type [δ 6.43 (1H, dd, $J=2$ and 8 Hz, $C_{5'}$–H), δ 6.52 (1H, d, $J=2$ Hz, $C_{3'}$–H), δ 7.20 (1H, d, $J=8$ Hz, $C_{6'}$–H)]. These spectral data suggest that the structure of kuwanon C closely resembles that of mulberrin (VIII).

Unequivocal evidences for the structure (III) of kuwanon C were obtained as follows: when a solution of III in chloroform was irradiated with a high-pressure mercury lamp for 10 hr, kuwanon C hydroperoxide (IIIa) was obtained in 30% yield in analogy with morusin (V)[1] and kuwanon B (II). Kuwanon C hydroperoxide (IIIa), mp 162—163°, M^+ 454, gave a green color with methanolic ferric chloride and was negative to the Gibbs test. In the NMR spectrum of IIIa, the AMX pattern, such as δ 2.93 (1H, dd, $J=10$ and 18 Hz, C_9–H), δ 3.77—4.10 (3H, dd and br d overlapping, C_9–H and C_{12}–$H \times 2$), δ 4.78 (1H, dd, $J=2$ and 10 Hz, C_{10}–H), showed the presence of dihydrooxepin ring.[1,5] However, the other prenyl unit is in the form of a γ,γ-dimethylallyl group as shown by the signals at δ 3.77—4.10 (benzylic and allylic methylene) and one proton multiplet at δ 5.62. The mass spectrum of IIIa gave fragments at m/e 438 (M^+–O), 395 (M^+–O–C_3H_7), 379 (M^+–$C_3H_7O_2$).[1,8] Treatment of III with 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) yielded morusin (V) and compound VI.[5,13] From the consideration of these results, we propose the formula (III) as the structure of kuwanon C.

Oxydihydromorusin (IV)[14] was obtained as yellow needles, mp 215—216°, M^+ 438, $C_{25}H_{26}O_7$. The UV spectrum of IV [$\lambda_{\max}^{\mathrm{MeOH}}$ nm: 206, 225, 242, 269.5, 300 (sh), 350 (sh)] closely resembles that of morusin (V). The NMR spectrum of IV exhibited the presence of a γ-hydroxyisoamyl chain [δ 1.39 (12H, s, C_{11}–$CH_3 \times 2$ and C_{14}–$CH_3 \times 2$), 2.00—2.30 (2H, m, C_{10}–$H \times 2$), 2.98—3.28 (2H, m, C_9–$H \times 2$)]. The other signals closely resembled those of V.[5] The mass spectrum of IV gave fragments at m/e 423 (M^+–CH_3), 420 (M^+–H_2O), 405 (M^+–CH_3–H_2O), 379 (M^+–C_3H_7O), 365[8] (M^+–C_4H_9O), 203[5] (formed from the ion at 423 or 405 by a reverse Diels-Alder reaction). From these data, the structure of oxydihydromorusin was deduced as formula IV. Final proof for the structure (IV) assigned to oxydihydromorusin was obtained by comparing the mixed melting point with that of compound (IV) obtained by the action[15] of 4% methanolic hydrogene chloride on morusin (V). From these results, the structure of oxydihydromorusin could be assigned as IV.

TABLE I. Chemical Shift (ppm) for C_{12}–H and C_{13}–H in I, Ib, II and IIb[a]

Compound	C_{12}–H	C_{13}–H
I	6.75	5.69
Ib	6.53	5.88
Δ	+0.22	−0.19
II	6.77	5.72
IIb	6.46	5.90
Δ	+0.31	−0.18

[a] measured in $(CD_3)_2CO$

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13) V.H. Deshpande, A.V.R. Rao, S. Srinivasan, and K. Venkataraman, *Indian J. Chem.*, **10**, 681 (1972).

14) Recently, Hikino and his co-workers [C. Konno, Y. Oshima, and H. Hikino, *Planta medica*, **32**, 118 (1977)] obtained the same compound, which named morusinol, from the crude drug "Sohakuhi."

15) *a*) T. Saitoh and S. Shibata, *Chem. Pharm. Bull.* (Tokyo), **17**, 729 (1969); *b*) M. Komatsu, T. Tomimori, K. Hatayama, and N. Mikuriya, *Yakugaku Zasshi*, **90**, 463 (1970).

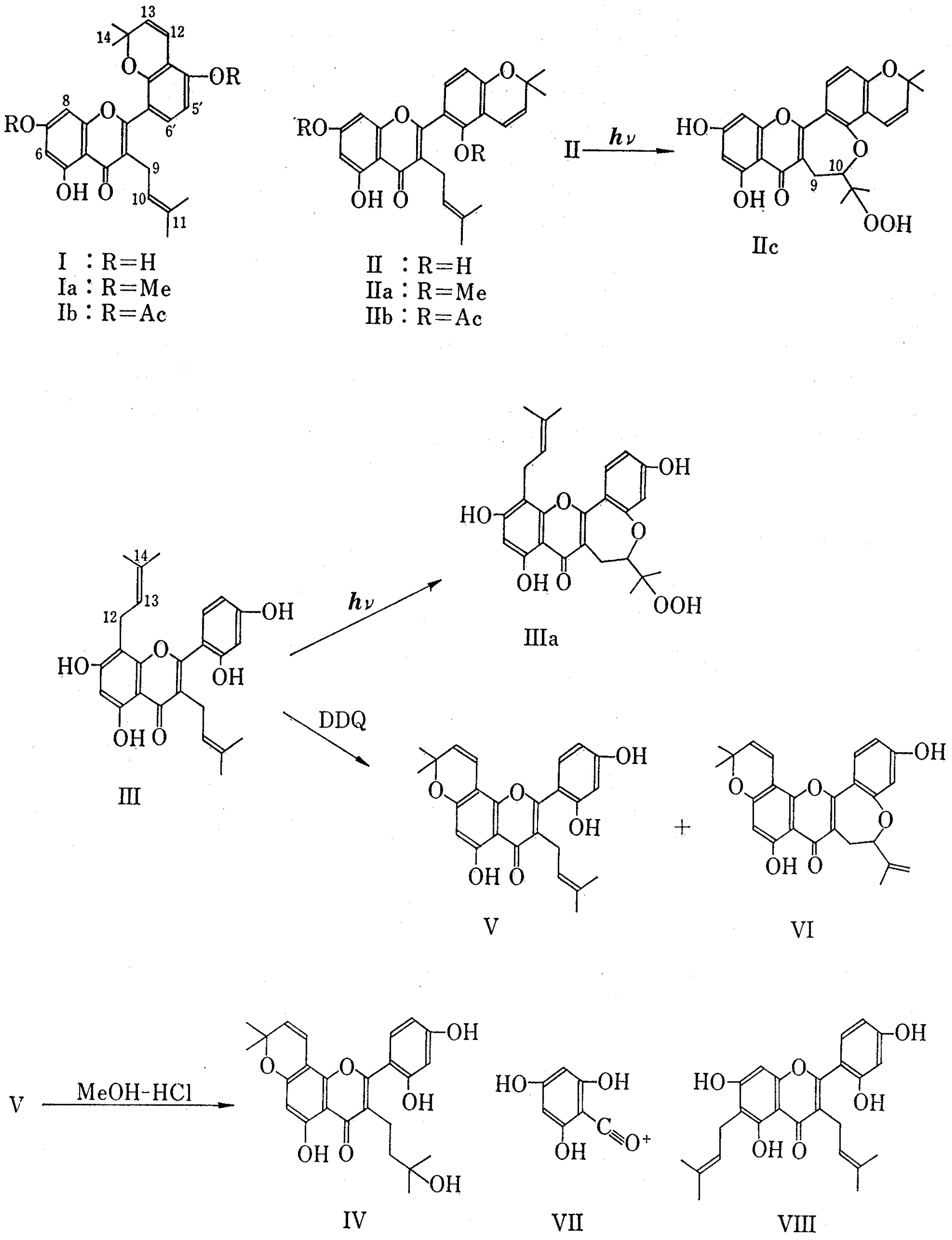

Chart 1

Experimental

All melting points were uncorrected. The NMR spectra were measured with tetramethylsilan as the internal reference. Abbreviations: s=singlet, d=doublet, dd=double doublet, t=triplet, m=multiplet, br=broad, sh=shoulder. The general experimental procedures used are described in Part I.[5]

Isolation of Prenylflavones——The dry root bark (2.7 kg), collected in the vicinity of Akabori, Gunma Prefecture, was finely cut and extracted with *n*-hexane and then with benzene. The benzene extract (63 g) was dissolved in a minimal amount of MeOH, and allowed to stand until a semi-solid mass (30 g) separated. The methanolic mother liquor was evaporated and the residue was dissolved in ether. The ether solution was extracted successively with 5% aqueous $NaHCO_3$, 5% aqueous Na_2CO_3, and 5% aqueous NaOH, and treated as usual. The NaOH–soluble fraction (10 g) was chromatographed on silica gel (350 g) using benzene–MeOH as an eluent, and each fraction was checked by thin–layer chromatography (TLC). The fraction eluted with benzene containing 0.5% MeOH gave morusin (V, 1.1 g). The mother liquor of V contained V, kuwanon A (I), and kuwanon B (II), which were separated by preparative TLC (solvent system; ether: $CHCl_3$=1: 4 and MeOH: benzene=1: 9, these solvent systems being used repeatedly. silica gel). Further elution of the silica gel column with benzene containing 1% MeOH gave kuwanon C (III, 12 mg), and gave oxydihydromorusin (IV, 11 mg) with benzene containing 2% MeOH.

Kuwanon A (I)——I was obtained as amorphous powder (20 mg). Although only one spot was detected on TLC (ether: $CHCl_3$=1: 4 and benzene: MeOH=9: 1, silica gel), I could not be isolated as a crystalline form, $FeCl_3$ (+), Mg–HCl (+), Zn–HCl (+), Gibbs test (+). UV λ_{max}^{EtOH} nm (log ε): 208 (4.49), 260.5 (4.26), 283 (sh 4.11), 325 (sh 3.93); $\lambda_{max}^{EtOH+AlCl_3}$ 208 (4.54), 269 (4.33), 373 (3.81); $\lambda_{max}^{EtOH+NaOMe}$ 267.5 (4.35), 327 (4.11), 370 (sh 4.00). IR ν_{max}^{Nujol} cm^{-1}: 3250 (br), 1660, 1620, 1590. MS *m/e*: 420 (M^+), 405 (M^+-CH_3), 377, 365, 364, 321, 153, 152. NMR [in $(CD_3)_2CO$] δ: 1.40 (6H, s, $C_{14}-CH_3\times 2$), 1.45, 1.58 (each 3H, s, $C_{11}-CH_3$), 3.11 (2H, br d, J=8 Hz, $C_9-H\times 2$), 5.13 (1H, m, $C_{10}-H$), 5.69 (1H, d, J=10 Hz, $C_{13}-H$), 6.26 (1H, d, J=2 Hz, C_6-H), 6.32 (1H, d, J=2 Hz, C_8-H), 6.68 (1H, d, J=9 Hz, $C_{5'}-H$), 6.75 (1H, d, J=10 Hz, $C_{12}-H$), 7.08 (1H, d, J=9 Hz, $C_{6'}-H$), 13.13 (1H, s, OH).

Kuwanon A Dimethyl Ether (Ia)——To a solution of I (10 mg) in MeOH (0.5 ml) was added excess ethereal diazomethane and the mixture was allowed to stand overnight at −10° and the solvent was removed *in vacuo*. The product was then purified by preparative TLC and crystallized from MeOH to give pale yellow prisms (4 mg), mp 147°, $FeCl_3$ (+), Gibbs test (+). UV λ_{max}^{MeOH} nm (log ε): 231 (4.47), 260 (4.39), 325 (3.99); $\lambda_{max}^{MeOH+AlCl_3}$ 269 (4.46), 320 (3.95), 376 (3.90); $\lambda_{max}^{MeOH+NaOMe}$ 270 (4.40), 362 (3.68). IR ν_{max}^{Nujol} cm^{-1}: 1665, 1645, 1630, 1590. MS *m/e*: 448 (M^+), 433, 405, 393, 167. *Anal.* High-resolution MS: Calcd. for $C_{27}H_{28}O_6$ (M^+, *m/e*): 448.1855. Found: 448.1890. NMR (in $CDCl_3$) δ: 1.41 (6H, s, $C_{14}-CH_3\times 2$), 1.45, 1.58 (each 3H, s, $C_{11}-CH_3$), 3.12 (2H, br d, J=8 Hz, $C_9-H\times 2$), 3.84, 3.88 (each 3H, s, OCH_3), 5.12 (1H, m, $C_{10}-H$), 5.75 (1H, d, J=10 Hz, $C_{13}-H$), 6.33 (1H, d, J=2 Hz, C_6-H), 6.45 (1H, d, J=2 Hz, C_8-H), 6.71 (1H, d, J=9 Hz, $C_{5'}-H$), 6.73 (1H, d, J=10 Hz, $C_{12}-H$), 7.26 (1H, d, J=9 Hz, $C_{6'}-H$), 13.05 (1H, s, OH).

Kuwanon A Diacetate (Ib)——A mixture of I (4 mg), acetic anhydride (0.2 ml) and pyridine (0.1 ml) was kept at room temperature for about 3 min, and then the product was purified by preparative TLC (ether: $CHCl_3$=1: 4, silica gel) and crystallized from MeOH to give pale yellow prisms (3.1 mg), mp 167—169°. UV λ_{max}^{MeOH} nm (log ε): 224 (4.56), 258.5 (4.39), 327 (3.99): $\lambda_{max}^{MeOH+AlCl_3}$ 268 (4.46), 310 (3.87), 383 (3.86); $\lambda_{max}^{MeOH+NaOMe}$ 268 (4.46), 345 (4.03). IR ν_{max}^{Nujol} cm^{-1}: 1770, 1650, 1630, 1610, 1210. MS *m/e*: 504 (M^+), 489, 461, 406, 167. *Anal.* High-resolution MS: Calcd. for $C_{29}H_{28}O_8$ (M^+, *m/e*): 504. 1783. Found: 504.1805. NMR [in $(CD_3)_2CO$] δ: 1.41 (9H, br s, $C_{14}-CH_3\times 2$ and $C_{11}-CH_3$), 1.58 (3H, s, $C_{11}-CH_3$), 2.29, 2.35 (each 3H, s, OAc), 3.13 (2H, br d, J=8 Hz, $C_9-H\times 2$), 5.10 (1H, m, $C_{10}-H$), 5.88 (1H, d, J=10 Hz, $C_{13}-H$), 6.53 (1H, d, J=10 Hz, $C_{12}-H$), 6.60 (1H, d, J=2 Hz, C_6-H), 6.79 (1H, d, J=2 Hz, C_8-H), 6.84 (1H, d, J=9 Hz, $C_{5'}-H$), 7.32 (1H, d, J=9 Hz, $C_{6'}-H$), 13.21 (1H, s, OH).

Kuwanon B (II)——II was recrystallized from MeOH to give pale yellow prisms (13 mg), mp 250—254°, $FeCl_3$ (+), Mg–HCl (+), Zn–HCl (+), Gibbs test: green. *Anal.* Calcd. for $C_{25}H_{24}O_6$: C, 71.41; H, 5.75. Found: C, 71.22; H, 5.93. UV λ_{max}^{MeOH} nm (log ε): 234 (4.49), 260 (4.38), 280 (sh 4.10), 330 (sh 4.00); $\lambda_{max}^{MeOH+AlCl_3}$ 214 (4.52), 269 (4.44), 376 (3.94); $\lambda_{max}^{MeOH+NaOMe}$ 268 (4.44), 310 (4.02), 359 (4.09). IR ν_{max}^{Nujol} cm^{-1}: 3300, 1650, 1620. MS *m/e*: 420 (M^+), 405 (M^+-CH_3), 403, 377, 365, 351, 321, 153. NMR [in $(CD_3)_2CO$] δ: 1.42, 1.58 (each 3H, s, $C_{11}-CH_3$), 1.47 (6H, s, $C_{14}-CH_3\times 2$), 3.12 (2H, br d, J=6 Hz, C_9-H), 5.11 (1H, br t, J=6 Hz, $C_{10}-H$), 5.72 (1H, d, J=10 Hz, $C_{13}-H$), 6.26 (1H, d, J=2 Hz, C_6-H), 6.31 (1H, d, J=2 Hz, C_8-H), 6.46 (1H, d, J=9 Hz, $C_{5'}-H$), 6.77 (1H, d, J=10 Hz, $C_{12}-H$), 7.08 (1H, d, J=9 Hz, $C_{6'}-H$), 13.07 (1H, s, OH).

Kuwanon B Dimethyl Ether (IIa)——To a solution of II (12.5 mg) in MeOH (0.5 ml) was added excess ethereal diazomethane and the mixture was allowed to stand overnight at −10° and the solvent was removed *in vacuo*. The product was then purified by preparative TLC and crystallized from MeOH to give pale yellow prisms (4.9 mg), mp 115—118°, $FeCl_3$ (+). UV λ_{max}^{EtOH} nm (log ε): 213 (4.57), 235 (4.60), 261 (4.51), 320 (sh 4.08); $\lambda_{max}^{EtOH+AlCl_3}$ 215 (4.62), 270.5 (4.54), 315 (sh 4.06), 375 (3.82); $\lambda_{max}^{EtOH+NaOMe}$ 267 (4.76), 358 (3.86). IR ν_{max}^{Nujol} cm^{-1}: 1665, 1615, 1580, 1500. MS *m/e*: 448 (M^+), 433, 417, 405, 393, 375, 361, 167. NMR [in $(CD_3)_2CO$] δ: 1.40, 1.58 (each 3H, s, $C_{11}-CH_3$), 1.47 (6H, s, $C_{14}-CH_3\times 2$), 3.12 (2H, br d, J=6 Hz, $C_9-H\times 2$), 3.73, 3.90 (each 3H, s, OCH_3), 5.11 (1H, m, $C_{10}-H$), 5.88 (1H, d, J=10 Hz, $C_{13}-H$), 6.33 (1H, d, J=2 Hz, C_6-H), 6.50 (1H, d, J=2 Hz, C_8-H), 6.67 (1H, d, J=10 Hz, $C_{12}-H$), 6.69 (1H, d, J=9 Hz, $C_{5'}-H$), 7.22 (1H, d, J=9 Hz, $C_{6'}-H$).

Kuwanon B Diacetate (IIb)——A mixture of II (2 mg), acetic anhydride (0.2 ml), and pyridine (0.1 ml) was kept at room temperature for about 3 min, and then the product was purified by preparative TLC and crystallized from ether–*n*-hexane to give pale yellow prisms (1 mg), mp 125—127°, $FeCl_3$ (+). UV λ_{max}^{EtOH} nm (log ε): 233 (4.62), 262 (4.43), 322 (4.07); $\lambda_{max}^{EtOH+AlCl_3}$ 225 (4.56), 269.5 (4.46), 326 (3.92), 383 (3.93); $\lambda_{max}^{EtOH+NaOMe}$ 268.5 (4.53), 359 (4.17). IR ν_{max}^{Nujol} cm^{-1}: 1780, 1770, 1655, 1610. MS *m/e*: 504 (M^+), 461, 447, 445. NMR [in $(CD_3)_2CO$] δ: 1.47 (9H, br s, $C_{14}-CH_3\times 2$ and $C_{11}-CH_3$), 1.62 (3H, s, $C_{11}-CH_3$), 2.15, 2.28 (each 3H, s, OAc), 3.13 (2H, br d, J=8 Hz, $C_9-H\times 2$), 5.15 (1H, m, $C_{10}-H$), 5.90 (1H, d, J=10 Hz, $C_{13}-H$), 6.46 (1H, d, J=10 Hz, $C_{12}-H$), 6.56 (1H, d, J=2 Hz, C_6-H), 6.72 (1H, d, J=2 Hz, C_8-H), 6.85 (1H, d, J=9 Hz, $C_{5'}-H$), 7.37 (1H, d, $J=9$ Hz, $C_{6'}$–H).

Photooxidation of Kuwanon A (I) and Kuwanon B (II)——a) Kuwanon A (I): A solution of I (2 mg) in $CHCl_3$ (0.2 ml) was externally irradiated in a Pyrex test tube with a 100 W high-pressure mercury lamp for 7 hr. After evaporation, the residue was analysed by IR and TLC. The starting material was completely recovered unchanged.

b) Kuwanon B (II): A solution of II (8 mg) in $CHCl_3$ (0.5 ml) was externally irradiated in a Pyrex test tube with a 100 W high-pressure mercury lamp. The formation of a pale yellow crystalline began to precipitate within 3 hr. 5 hr after, the product (5 mg) was collected and recrystallized from ether to give pale yellow needles, mp 203°, $FeCl_3$ (+). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ε): 210 (4.38), 268 (4.32), 290 (sh 4.04), 350 (4.14); $\lambda_{\max}^{\text{MeOH+AlCl}_3}$ 210 (4.48), 278 (4.26), 360 (4.08), 396 (4.08); $\lambda_{\max}^{\text{MeOH+NaOMe}}$ 233 (4.35), 276 (4.40), 377 (4.07). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3400, 3200, 1655, 1620, 1600. MS *m/e*: 452 (M^+), 436 (M^+-O), 421, 403, 377, 153. NMR (in pyridine-d_5) δ: 1.41, 1.43 (each 3H, s, C_{14}–CH_3), 1.52, 1.64 (each 3H, s, C_{11}–CH_3), 3.00 (1H, dd, $J=9$ and 16 Hz, C_9–H), 3.67 (1H, dd, $J=2$ and 16 Hz, C_9–H), 4.83 (1H, dd, $J=2$ and 9 Hz, C_{10}–H), 5.76 (1H, d, $J=$ 9 Hz, $C_{5'}$–H), 6.72 (1H, d, $J=2$ Hz, C_6–H), 6.80 (1H, d, $J=2$ Hz, C_8–H), 7.92 (1H, d, $J=9$ Hz, $C_{6'}$–H).

Kuwanon C (III)——III was recrystallized from ether–benzene to give pale yellow prisms, mp 148—150°, $FeCl_3$ (+), Mg–HCl (+), Zn–HCl (+), Gibbs test (+). *Anal.* Calcd. for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20. Found: C, 70.89; H, 6.35. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 210 (4.63), 264.5 (4.49), 315 (4.06); $\lambda_{\max}^{\text{EtOH+AlCl}_3}$ 274.5 (4.55), 335 (4.02), 387 (3.93); $\lambda_{\max}^{\text{EtOH+NaOMe}}$ 276 (4.56), 320 (sh 4.10), 373 (4.20). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3370, 1660, 1630, 1610, 1560. MS *m/e*: 422 (M^+), 407 (M^+-CH_3), 405, 389, 379, 367, 323. NMR [in $(CD_3)_2CO$] δ: 1.43 (3H, s, C_{11}–CH_3), 1.57 (9H, br s, C_{11}–CH_3 and C_{14}–$CH_3\times2$), 3.12 (2H, br d, $J=8$ Hz, C_9–H×2), 3.35 (2H, br d, $J=8$ Hz, C_{12}–H×2), 5.20 (2H, m, C_{10} and C_{13}–H), 6.31 (1H, s, C_6–H), 6.43 (1H, dd, $J=2$ and 8 Hz, $C_{5'}$–H), 6.52 (1H, d, $J=2$ Hz, $C_{3'}$–H), 7.20 (1H, d, $J=8$ Hz, $C_{6'}$–H), 13.05 (1H, s, OH).

Photooxidation of Kuwanon C (III)——A solution of III (10 mg) in $CHCl_3$ (1 ml) was externally irradiated in a Pyrex test tube with a 100 W high-pressure mercury lamp for 10 hr. The crystalline precipitate was collected and recrystallized from ether to give pale yellow prisms (3 mg), mp 162—163°, $FeCl_3$ (+), Gibbs test (−). UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 209 (4.58), 273.5 (4.25), 344 (4.09); $\lambda_{\max}^{\text{EtOH+AlCl}_3}$ 209 (4.58), 282 (4.25), 302 (4.04), 350 (4.14): $\lambda_{\max}^{\text{EtOH+NaOMe}}$ 282 (4.31), 381.5 (4.05), 401 (4.25). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3200, 1660, 1620. MS *m/e*: 454 (M^+), 438 (M^+-O), 436, 421, 395, 379, 323. NMR (in pyridine-d_5) δ: 1.47, 1.68, 1.72, 1.92 (each 3H, s, C_{11}–$CH_3\times2$ and C_{14}–$CH_3\times2$), 2.93 (1H, dd, $J=10$ and 18 Hz, C_9–H), 3.77—4.10 (3H, m, C_9–H and C_{12}–H×2), 4.78 (1H, dd, $J=2$ and 10 Hz, C_{10}–H), 5.62 (1H, m, C_{13}–H).

Cyclodehydrogenation of Kuwanon C (III)——A mixture of III (10 mg) and DDQ (10 mg) in dry benzene (4 ml) was refluxed for 2 hr. The mixture was evaporated *in vacuo* and the residue was purified by preparative TLC (ether: $CHCl_3=1:4$, silica gel) to give morusin (V, 0.6 mg) and VI (1 mg). The compounds obtained here were identified (TLC, mixed mp, and IR) with the authentic samples.[5]

Oxydihydromorusin (IV)——IV was recrystallized from MeOH to give yellow needles, mp 215—216°, $FeCl_3$ (+), Mg–HCl (+), Gibbs test (+). *Anal.* Calcd. for $C_{25}H_{26}O_7\cdot CH_3OH$: C, 66.37; H, 6.43. Found: C, 66.41; H, 6.29. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ε): 206 (4.38), 225 (4.26), 242 (4.26), 269.5 (4.44), 300 (sh 3.82), 350 (sh 3.64); $\lambda_{\max}^{\text{MeOH+AlCl}_3}$ 206 (4.42), 227 (4.34), 278.5 (4.47), 336 (3.76), 409 (3.61); $\lambda_{\max}^{\text{MeOH+NaOMe}}$ 269.5 (4.41), 370 (3.81). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3380, 1660, 1640, 1630, 1600, 1560. MS *m/e*: 438 (M^+), 423, 420, 405, 379, 365, 203. NMR (in pyridine-d_5) δ: 1.39 (12H, s, C_{11}–$CH_3\times2$ and C_{14}–$CH_3\times2$), 2.00—2.30 (2H, m, C_{10}–H×2), 2.98—3.28 (2H, m, C_9–H×2), 5.47 (1H, d, $J=10$ Hz, C_{13}–H), 6.46 (1H, s, C_6–H), 6.70 (1H, d, $J=10$ Hz, C_{12}–H), 6.87 (1H, dd, $J=2$ and 7.5 Hz, $C_{5'}$–H), 7.10 (1H, d, $J=2$ Hz, $C_{3'}$–H), 7.54 (1H, d, $J=7.5$ Hz, $C_{6'}$–H).

Formation of Oxydihydromorusin (IV) from Morusin (V)——A mixture of V (50 mg), MeOH (8 ml) and conc. hydrochloric acid (1 ml) was refluxed for 5 hr. After standing at room temperature, the crude solid was collected and washed with water. The solid was purified by preparative TLC (ether: $CHCl_3=1:4$, silica gel) to give two products. The minor product (0.5 mg) was identified (TLC, mixed mp, and mass spectrum) with oxydihydromorusin (IV). No further investigation of the major product (6 mg, M^+ 452) was carried out.

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