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Studies on the Constituents of the Cultivated Mulberry Tree. II.[1] Photo-oxidative Cyclization of Morusin[2,3]

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When a solution of morusin (I) was exposed to bright sunshine or irradiated with a high-pressure mercury lamp, morusin hydroperoxide (III) was obtained in a high yield. This reaction did not occur in the dark. The reaction was dependent on the solvent and proceeded in chloroform or benzene solution whereas the starting material was recovered unchanged in methanol, ethanol or *tert*-butyl alcohol solution. Both of the free hydroxyl group at $C_{2'}$ and the isolated double bond of the γ,γ-dimethylallyl group attached to the 3-position of flavone were found to be required for this photooxidation. Reduction of III gave compound A (II) which had been isolated from the root bark of *Morus alba* L. On the basis of these findings, the structure of morusin hydroperoxide was shown to be III.

Keywords——Photooxidation; morusin; morusin hydroperoxide; hydroperoxide; *Morus alba* L.; dihydrooxepin ring; flavone

In the previous paper,[1] the authors reported the structure determination of three new flavone derivatives, morusin (I), compound A (II), and cyclomorusin, obtained from the root bark of *Morus alba* L. In the present paper, the authors report the formation of morusin hydroperoxide (III) on photooxidation of I, which was found in the course of our studies on the constituents of the root bark.

When a solution of I in chloroform was exposed to bright sunshine or irradiated with a high-pressure mercury lamp or with a tungsten lamp, morusin hydroperoxide (III), mp 204—206°, M^+ 452, $C_{25}H_{24}O_8$, was obtained in *ca.* 80% yield. This reaction did not occur in the dark and was dependent on the solvent, proceeding in chloroform or benzene solution, but in methanol, ethanol or *tert*-butyl alcohol solution the starting material being recovered unchanged. When a solution of morusin diacetate (Ia)[1] or dimethyl ether (Ib),[1] as well as tetrahydromorusin (If),[1] was irradiated in chloroform, photoreaction did not occur and starting material was recovered unchanged. However, when a solution of 12,13-dihydromorusin (Ie)[1] was irradiated, 12,13-dihydromorusin hydroperoxide (IIIf) was obtained. These findings indicate that this photooxidation requires the presence of the isolated double bond in the side chain attached to the 3-position and the hydroxyl groups in B ring. From the following experimental results, it was confirmed that the free hydroxyl group at $C_{2'}$, is required for this photooxidation. Two isomers of morusin monomethyl ether, 2′-O-methyl morusin (Ic), mp 198—199°, M^+ 434, negative to Gibbs test, and 4′-O-methyl morusin (Id), mp 162—164°, M^+ 434, positive to Gibbs test, were obtained by methylation of I with ethereal diazomethane in isopropanol. Additional treatment of Ic or Id with ethereal diazomethane afforded the same dimethyl ether (Ib).[1] The discrimination between the structures of Ic and Id was supported by the results of Gibbs test. When a solution of 2′-O-methyl morusin (Ic) was irradiated, the starting material was recovered unchanged. An irradiation of 4′-O-methyl morusin (Id), however, gave morusin hydroperoxide monomethyl ether (IIIa).

1) Part I: T. Nomura, T. Fukai, S. Yamada, and M. Katayanagi, *Chem. Pharm. Bull.* (Tokyo), **26**, 1394 (1978).
2) A preliminary account of this work has been presented: T. Nomura, T. Fukai, S. Yamada, and M. Katayanagi: *Chem. Pharm. Bull.* (Tokyo), **25**, 1155 (1977).
3) Taken from part of the Doctorated thesis presented by T.F. to Hokkaido University, 1977.
4) Location: *2-2-1, Miyama, Funabashi-shi, Chiba, 274, Japan.*

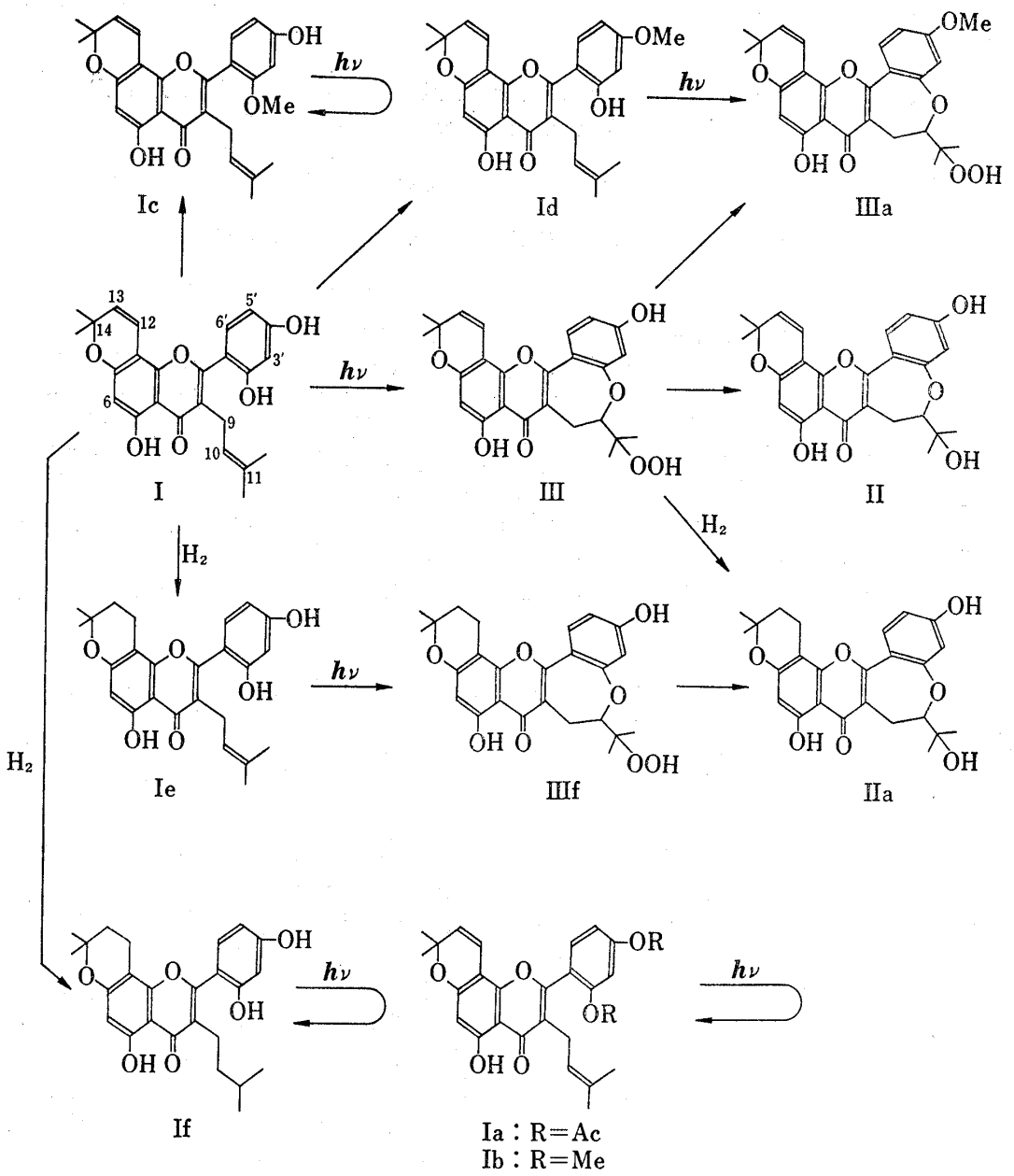
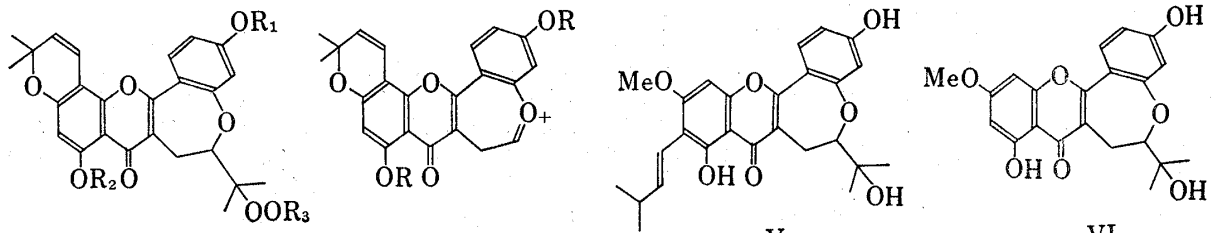


Chart 1

Morusin hydroperoxide (III) gave characteristic color reaction for flavones and was negative to Gibbs test. The ultraviolet (UV) spectrum (λ_{max}^{EtOH} 280 and 335 nm) resembled that of compound A (II) rather than I or cyclomorusin.[1] These findings indicated that the side chain in the 3-position cyclized with the 2′-hydroxyl group. Acetylation of III with acetic anhydride in pyridine for 5 min gave the diacetate (IIId), mp 158—159°, M^+ 536, $C_{29}H_{28}O_{10}$, positive to ferric chloride test. The treatment of III with the same reagent for 3 days gave the triacetate (IIIe), mp 147—153.5°, M^+ 578, $C_{31}H_{30}O_{11}$, negative to ferric chloride test. When treated in methanol with ethereal diazomethane, III gave the monomethyl ether (IIIa), mp 187—190°, M^+ 466, $C_{26}H_{26}O_8$, positive to ferric chloride test, and the dimethyl ether (IIIb), mp 228—230°, M^+ 480, negative to ferric chloride test. The infrared (IR) spectrum of IIIb showed the absorption for a hydroperoxyl group at 3300 cm^{-1}. Acetylation of IIIb with acetic anhydride in pyridine gave the dimethyl ether monoacetate (IIIc), mp 150—152°, M^+ 522, which showed absorption for an acetyl peroxyl group at 1780

cm^{-1}.[5] These data indicated the presence of two phenolic hydroxyl groups and a hydroperoxyl group in III. The nuclear magnetic resonance (NMR) spectrum of III showed the signals of the characteristic AMX pattern[1] such as δ 2.59 (1H, dd, J=10 and 18 Hz, C_9–H), δ 3.46 (1H, dd, J=2 and 18 Hz, C_9–H), and δ 4.38 (1H, dd, J=2 and 10 Hz, C_{10}–H). The mass spectrum of III gave fragments at *m/e* 436 (M^+—O)[6], 421 (M^+—O–CH_3), 377 (M^+—$C_3H_7O_2$, IVa), 203 (formed from the ion at 421 by a reverse Diels-Alder reaction).[7] The mass spectra of IIIb and IIIc gave the same fragment at *m/e* 405 (base peak, IVb). From these findings, III can be regarded as a flavone containing a dihydrooxepin ring.[1,8,9] When III was heated in dimethyl sulfoxide, compound A (II) was obtained as well as when treated with sodium borohydride, diphenylsulfide, triphenylphosphine, or trimethylamine in methanol. Hydrogenation of III in the presence of palladium charcoal as catalyst yielded 12,13-dihydro compound A (IIa). From these results, the structure of morusin hydroperoxide is deduced to be III.



IIIb : R_1=R_2=Me, R_3=H
IIIc : R_1=R_2=Me, R_3=Ac
IIId : R_1=R_3=Ac, R_2=H
IIIe : R_1=R_2=R_3=Ac

IVa : R=H
IVb : R=Me

V

VI

Chart 2

As reported by Matsuura and his co-workers,[10] 5-hydroxyflavone derivatives resist photoreaction. They described that the stability to photoreaction is due to hydrogen bonding of the 5-hydroxyl to the 4-carbonyl group and that such an interaction causes an intramolecular hydrogen abstraction in the excited state to yield a tautomer. Although morusin (I) is a flavone derivative which has the intramolecular hydrogen bonding between the 5-hydroxyl and the 4-carbonyl group,[1] the photoreaction occurred in chloroform or benzene solution. In this respect, the photo-oxidative cyclization of morusin (I) is very interesting reaction in the photochemistry of flavonoides.

Furthermore, these results represent the possible models for the biosynthesis of certain uncommon flavonoids such as compound A (II),[1,11] chaplashin (V),[8] and oxyisocyclointegrin (VI),[9] which are supposed to be derived from a 3-prenylflavone precursor.

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10) *a*) T. Matsuura and H. Matsushima, *Tetrahedron*, **24**, 6615 (1968); *b*) T. Matsuura, T. Takemoto, and R. Nakashima, *ibid.*, **29**, 3337 (1973); *c*) R. Nakashima, K. Okamoto, and T. Matsuura, *Bull. Chem. Soc. Jpn.*, **49**, 3355 (1976).
11) In the previous communication,[2] we speculated that compound A (II) was an artifact which was formed from morusin (I) *via* hydroperoxide (III) in the course of isolation. In recent studies, however, II was obtained from methanol extract of the root bark of *Morus alba* L. As described in this paper, the photooxidative cyclization did not occur in the methanol solution and hence this compound may be natural.

Experimental

All melting points were uncorrected. The NMR spectra were measured with tetramethylsilane as the internal reference. Abbreviations: s=singlet, d=doublet, dd=double doublet, t=triplet, m=multiplet, br=broad, sh=shoulder. The following instruments were used for the physical data: melting points; Mitamura micro-melting point apparatus (a hot-stage type). UV spectra; Shimadzu UV-200 UV Spectrometer. IR spectra; Hitachi IR Spectrometer EPI-G3. NMR spectra; JEAL JNM-4H-100 NMR Spectrometer. Mass spectra; JEAL JMS ISG 2 Mass Spectrometer.

Photooxidation of Morusin (I)——a) On Bright Sunshine: A solution of I (54 mg) in $CHCl_3$ (20 ml) was exposed to bright sunshine in a glass vessel. The formation of a pale yellow crystalline began to precipitate within 4 hr. 7 hr after, the product (47 mg) was filtered off and recrystallized from MeOH to give yellow needles (III), mp 204—206°.

b) On Mercury Lamp: A solution of I (120 mg) in $CHCl_3$ (30 ml) was externally irradiated in a glass vessel with a 100 W high-pressure mercury lamp. A pale yellow crystalline precipitate began to form within 3 hr. 5 hr after, the product (96 mg) was filtered off and recrystallized from MeOH to give yellow needles (III), mp 204—206°.

c) On Tungsten Lamp: A solution of I (23 mg) in $CHCl_3$ (7 ml) was externally irradiated in a glass vessel with a 200 W tungsten lamp for 8 hr. The precipitate was filtered off. Recrystallization from MeOH gave yellow needles (III, 18 mg), mp 204—206°.

d) In Benzene: A solution of I (33 mg) in benzene (10 ml) was irradiated with 100 W high-pressure mercury lamp as described above for 7 hr. The precipitate was filtered off and recrystallization from MeOH gave yellow needles (III, 25 mg), mp 204—206°, $FeCl_3$ (+), Mg–HCl (+), Gibbs test (−). *Anal.* Calcd. for $C_{25}H_{24}O_8$: C, 66.36; H, 5.35. Found: C, 66.37; H, 5.31. UV λ_{max}^{EtOH} nm (log ε): 280 (4.46), 335 (4.42); $\lambda_{max}^{EtOH+AlCl_3}$ 283 (4.39), 320 (sh 4.15), 356 (4.18), 370 (4.42); $\lambda_{max}^{EtOH+NaOMe}$ 267 (4.46), 397 (4.34). IR ν_{max}^{Nujol} cm^{-1}: 3320, 1660, 1635, 1605, 1540. MS *m/e*: 452 (M^+), 436 (M^+-O), 421 (M^+-O-CH_3), 377 ($M^+-O-C_3H_7O$), 203. High resolution MS: Calcd. for $C_{25}H_{24}O_8$: 452.1471. Found: 452.1451; Calcd. for $C_{25}H_{24}O_7$: 436.1522. Found: 436.1522. NMR [$(CD_3)_2CO$] δ: 1.30, 1.46 (each 3H, s, C_{11}–CH_3), 1.48 (6H, s, C_{14}–$CH_3\times2$), 2.59 (1H, dd, J= 10 and 18 Hz, C_9–H), 3.46 (1H, dd, J=2 and 18 Hz, C_9–H), 4.38 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.78 (1H, d, J=10 Hz, C_{13}–H), 6.18 (1H, s, C_6–H), 6.66 (1H, d, J=2 Hz, $C_{3'}$–H), 6.82 (1H, dd, J=2 and 9 Hz, $C_{5'}$–H), 6.86 (1H, d, J=10 Hz, C_{12}–H), 8.01 (1H, d, J=9 Hz, $C_{6'}$–H).

Irradiation of Morusin (I) in Alcohol——A solution of I (10 mg) in 1.5 ml of MeOH, EtOH, or *tert*-BuOH in a Pyrex test tube was externally irradiated with a 100 W high-pressure mercury lamp for 8 hr. After evaporation, the residue was analysed by IR and TLC. The starting material was completely recovered unchanged.

Irradiation of Morusin (I) under N_2——A solution of I (35 mg) in benzene (20 ml) was externally irradiated with 100 W high-pressure mercury lamp under bubbling with N_2 for 10 hr. After evaporation, the residue was analysed by IR and TLC. The starting material was completely recovered unchanged.

Irradiation of Morusin Diacetate (Ia)——A solution of Ia (20 mg) in $CHCl_3$ (7 ml) was irradiated in a glass vessel with 200 W tungsten lamp for 8 hr. After evaporation, the residue was analysed by IR and TLC. 19 mg of the starting material was recovered unchanged.

Irradiation of Morusin Dimethyl Ether (Ib)——A solution of Ib (5 mg) in $CHCl_3$ (2 ml) was irradiated in a glass vessel with 200 W tungsten lamp for 8 hr. TLC and IR analysis of the photolysate revealed that the starting material was completely recovered unchanged.

Irradiation of Tetrahydromorusin (If)——A solution of If (0.5 mg) in $CHCl_3$ (0.5 ml) was irradiated with 200 W tungsten lamp in a Pyrex test tube for 8 hr. TLC and mass spectral analysis revealed that the starting material was recovered unchanged.

When a solution of I in $CHCl_3$ was irradiated in a Pyrex test tube as described in If, III was obtained.

Photooxidation of 12,13-Dihydromorusin (Ie)——A solution of Ie (80 mg) in $CHCl_3$ (20 ml) was exposed to sunshine in a glass vessel. Two days after, a product separated out as a pale yellow crystalline precipitate. The product was filtered and recrystallized from MeOH to give pale yellow needles (IIIf, 47 mg), mp 238—240°. *Anal.* Calcd. for $C_{25}H_{26}O_8$: C, 66.07; H, 5.77. Found: C, 66.19; H, 5.91. UV λ_{max}^{EtOH} nm (log ε); 256 (sh 4.15), 274 (4.24), 290 (sh 4.00), 350 (4.18); $\lambda_{max}^{EtOH+AlCl_3}$ 265 (sh 4.10), 285 (4.29), 363 (4.20), 402 (4.05). IR ν_{max}^{Nujol} cm^{-1}: 3400, 3120, 1660, 1630, 1600. MS *m/e*: 454 (M^+), 438 (M^+-O), 379, 351, 221. NMR (pyridine-d_5) δ: 1.34 (6H, s, C_{14}–$CH_3\times2$), 1.46, 1.67 (each 3H, s, C_{11}–CH_3), 1.80 (2H, t, J=6 Hz, C_{13}–H), 2.80 (2H, t, J= 6 Hz, C_{12}–H), 2.91 (1H, dd, J=10 and 17 Hz, C_9–H), 3.92 (1H, dd, J=1 and 17 Hz, C_9–H), 4.74 (1H, dd, J=1 and 10 Hz, C_{10}–H), 6.48 (1H, s, C_6–H), 6.97—7.20 (2H, m, $C_{3'}$ and $C_{5'}$–H, overlapping with the signal of the solvent), 8.16 (1H, d, J=9 Hz, $C_{6'}$–H), 13.25 (1H, s, OH).

Morusin Monomethyl Ether (Ic and Id)——To a solution of I (28 mg) in isopropanol (0.5 ml) was added excess ethereal diazomethane, and the mixture was allowed to stand at 5° for 12 hr and the solvent was removed *in vacuo*. Preparative TLC of the solid gave 2′-O-methylmorusin (Ic, 1 mg), 4′-O-methylmorusin (Id, 1 mg) and the starting material which was remethylated as above. Finally, the yield of Ic and of Id was 5 mg after repetition of the procedure.

2′-O-Methylmorusin (Ic): mp 198—199° (from ether–*n*-hexane), Gibbs test (−), UV λ_{max}^{MeOH} nm (log ε): 270 (4.47), 300 (3.93), 320 (3.80); $\lambda_{max}^{MeOH+NaOMe}$ 270 (4.47), 300 (3.89), 365 (4.02). IR ν_{max}^{KBr} cm^{-1}: 3300, 1650, 1610, 1590, 1550. MS *m/e*: 434 (M$^+$), 419, 391, 203. NMR [$(CD_3)_2CO$] δ: 1.43, 1.60 (each 3H, br s, C_{11}–CH_3), 1.47 (6H, s, C_{14}–$CH_3\times2$), 3.06 (2H, br d, J=10 Hz, C_9–H×2), 3.83 (3H, s, OCH_3), 5.09 (1H, m, C_{10}–H), 5.63 (1H, d, J=10 Hz, C_{13}–H), 6.17 (1H, s, C_6–H), 6.53—6.66 (3H, m, C_{12}, $C_{3'}$ and $C_{5'}$–H), 7.28 (1H, d, J=9 Hz, $C_{6'}$–H), 13.23 (1H, s, OH).

4′-O-Methylmorusin (Id): mp 162—164° (from benzene), Gibbs test: green, UV λ_{max}^{MeOH} nm (log ε): 270 (4.47), 300 (3.92), 320 (3.77); $\lambda_{max}^{MeOH+NaOMe}$ 270 (4.47), 300 (3.88), 365 (3.88). IR ν_{max}^{KBr} cm^{-1}: 3300, 1650, 1610, 1600, 1550. MS *m/e*: 434 (M$^+$), 419, 391, 203. NMR [$(CD_3)_2CO$] δ: 1.47 (9H, br s, C_{11}–CH_3 and C_{14}–$CH_3\times2$), 1.58 (3H, br s, C_{11}–CH_3), 3.12 (2H, br d, J=9 Hz, C_9–H×2), 3.85 (3H, s, OCH_3), 5.11 (1H, m, C_{10}–H), 5.63 (1H, d, J=10 Hz, C_{13}–H), 6.17 (1H, s, C_6–H), 6.56—6.68 (3H, m, C_{12}, $C_{3'}$ and $C_{5'}$–H), 7.32 (1H, d, J=9 Hz, $C_{6'}$–H), 13.24 (1H, s, OH).

Additional treatment of Ic or Id with ethereal diazomethane yielded respective dimethyl ether. The compound obtained here wes identified (TLC, mixed mp, and IR) with morusin dimethyl ether (Ib) prepared from morusin (I).[1)]

Photooxidation of 4′-O-Methylmorusin (Id)——A solution of Id (2 mg) in $CHCl_3$ (0.2 ml) in a Pyrex test tube was irradiated with a 100 W high-pressure mercury lamp for 5 hr. The crystalline precipitate was collected and recrystallized from MeOH to give yellow needles (IIIa, 1.1 mg). The compound obtained here was identified (TLC, mixed mp, and IR) with the monomethyl ether (IIIa) obtained from III.

Irradiation of 2′-O-Methylmorusin (Ic)——A solution of Ic (5 mg) in $CHCl_3$ (0.5 ml) in a Pyrex test tube was irradiated for 5 hr as described in Id. TLC and IR analysis revealed that the starting material was completely recovered unchanged.

Morusin Hydroperoxide Monomethyl Ether (IIIa) and Dimethyl Ether (IIIb)——To a solution of III (45 mg) in MeOH (10 ml) was added excess ethereal diazomethane, and the mixture was allowed to stand overnight at 5° and the solvent was removed under a reduced pressure. Preparative TLC of the solid gave monomethyl ether (IIIa, 26 mg) and dimethyl ether (IIIb, 3 mg).

Monomethyl Ether (IIIa): mp 187—190°, *Anal.* Calcd. for $C_{26}H_{26}O_8$: C, 66.94; H, 5.62. Found: C, 66.99; H, 5.46. UV λ_{max}^{MeOH} nm (log ε): 215 (4.25), 236.5 (4.25), 279 (4.27), 337 (3.99); $\lambda_{max}^{MeOH+AlCl_3}$ 225 (4.26), 283.5 (4.29), 359 (4.07), 423.5 (3.72); $\lambda_{max}^{MeOH+NaOMe}$ 286 (4.34), 387 (3.55). IR ν_{max}^{Nujol} cm^{-1}: 3280, 1655, 1635, 1605. MS *m/e*: 466 (M$^+$), 450, 435, 391, 377, 203. NMR ($CDCl_3$) δ: 1.28, 1.39 (each 3H, s, C_{11}–CH_3), 1.50 (6H, s, C_{14}–$CH_3\times2$), 2.55 (1H, dd, J=10 and 17 Hz, C_9–H), 3.58 (1H, dd, J=2 and 17 Hz, C_9–H), 3.88 (3H, s, OCH_3), 4.43 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.60 (1H, d, J=10 Hz, C_{13}–H), 6.22 (1H, s, C_6–H), 6.63—6.82 (3H, m, C_{12}, $C_{3'}$ and $C_{5'}$–H), 7.96 (1H, d, J=9 Hz, $C_{6'}$–H), 12.79 (1H, s, OH).

Dimethyl Ether (IIIb): mp 228—230°, $FeCl_3$ (−), UV λ_{max}^{EtOH} nm (log ε): 229 (4.50), 239 (4.46), 277.5 (4.47), 360 (4.14); $\lambda_{max}^{EtOH+AlCl_3}$ 218.5 (4.59), 277.5 (4.47), 360 (4.14). IR ν_{max}^{Nujol} cm^{-1}: 3300, 1630, 1615, 1590. MS *m/e*: 480 (M$^+$), 465, 449, 405. NMR ($CDCl_3$+pyridine-d_5) δ: 1.45 (3H, s, C_{11}–CH_3), 1.52 (9H, s, C_{11}–CH_3 and C_{14}–$CH_3\times2$), 2.66 (1H, dd, J=10 and 18 Hz, C_9–H), 3.66 (1H, dd, J=2 and 18 Hz, C_9–H), 3.82, 3.92 (each 3H, s, OCH_3), 4.51 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.60 (1H, d, J=10 Hz, C_{13}–H), 6.27 (1H, s, C_6–H), 6.64 (1H, d, J=2.5 Hz, $C_{3'}$–H), 6.75 (1H, dd, J=2.5 and 9 Hz, $C_{5'}$–H), 6.81 (1H, d, J=10 Hz, C_{12}–H), 7.90 (1H, d, J=9 Hz, $C_{6'}$–H).

Morusin Acetylperoxide Dimethyl Ether (IIIc)——Acetylation of IIIb (2 mg) with acetic anhydride (0.5 ml) and pyridine (0.2 ml) by keeping at room temperature for 5 min, was followed by usual work-up. Recrystallization from MeOH afforded colorless needles (IIIc, 1.3 mg), mp 150—152°. IR ν_{max}^{Nujol} cm^{-1}: 1780, 1640, 1615. MS *m/e*: 522 (M$^+$), 480, 462, 405.

4′-Acetylmorusin Acetylperoxide (IIId)——Acetylation of III (40 mg) with acetic anhydride (2.5 ml) and pyridine (1 ml) by keeping at room temperature for 5 min, was followed by usual work-up. Recrystallization from MeOH afforded yellow needles (IIId, 32 mg), mp 158—159°, $FeCl_3$ (+). *Anal.* Calcd. for $C_{29}H_{28}O_{10}$: C, 64.92; H, 5.26. Found: C, 64.65; H, 5.15. UV λ_{max}^{EtOH} nm (log ε): 234 (4.62), 276 (4.68); $\lambda_{max}^{EtOH+AlCl_3}$ 235 (4.65), 284 (4.70). IR ν_{max}^{Nujol} cm^{-1}: 1780, 1765, 1660, 1640, 1615. MS *m/e*: 536 (M$^+$), 521, 478, 418, 403, 377, 361, 333, 203. NMR ($CDCl_3$) δ: 1.46 (3H, s, C_{11}–CH_3), 1.48 (9H, s, C_{11}–CH_3 and C_{14}–$CH_3\times2$), 2.03, 2.35 (each 3H, s, OAc), 2.66 (1H, dd, J=10 and 18 Hz, C_9–H), 3.49 (1H, dd, J=2 and 18 Hz, C_9–H), 4.42 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.62 (1H, d, J=10 Hz, C_{13}–H), 6.28 (1H, s, C_6–H), 6.72 (1H, d, J=10 Hz, C_{12}–H), 6.93—7.08 (2H, m, $C_{3'}$ and $C_{5'}$–H), 7.99 (1H, d, J=9 Hz, $C_{6'}$–H), 12.74 (1H, s, OH).

5,4′-Diacetylmorusin Acetylperoxide (IIIe)——Acetylation of III (40 mg) with acetic anhydride (2 ml) and pyridine (1 ml) by keeping at room temperature for 3 days, was followed by usual work-up. Recrystallization from MeOH afforded colorless needles (IIIe, 18 mg), mp 147—153.5°, $FeCl_3$ (−). *Anal.* Calcd. for $C_{31}H_{30}O_{11}$: C, 64.35; H, 5.22. Found: C, 64.42; H, 5.12. UV λ_{max}^{EtOH} nm (log ε): 233 (4.64), 271 (4.58), 325 (4.24); $\lambda_{max}^{EtOH+AlCl_3}$ 236 (4.86), 270 (4.78), 321 (4.42). IR ν_{max}^{Nujol} cm^{-1}: 1770, 1630, 1620, 1600, 1590, 1210. MS *m/e*: 578 (M$^+$), 536, 518, 493, 426, 403. NMR ($CDCl_3$) δ: 1.44, 1.46 (each 3H, s, C_{11}–CH_3), 1.51 (6H, s, C_{14}–$CH_3\times2$), 2.01, 2.32, 2.43 (each 3H, s, OAc), 2.55 (1H, dd, J=10 and 18 Hz, C_9–H), 3.49 (1H, dd, J=2 and 18 Hz, C_9–H), 4.35 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.71 (1H, d, J=10 Hz, C_{13}–H), 6.48 (1H, s, C_6–H), 6.82 (1H, d, J=10 Hz, C_{12}–H), 6.94 (1H, d, J=2 Hz, $C_{3'}$–H), 6.98 (1H, dd, J=2 and 9 Hz, $C_{5'}$–H), 7.98 (1H, d, J=9 Hz, $C_{6'}$–H).

Formation of Compound A (II) from Morusin Hydroperoxide (III)——a) To a solution of III (40 mg) in MeOH (30 ml) was added gradually sodium borohydride (50 mg). The mixture was acidified with dilute acetic acid, and the solid was collected and recrystallized from MeOH–ethyl acetate to give yellow prisms (II, 33 mg), mp 258—260°.

b) A mixture of III (42 mg), MeOH (15 ml), ether (0.5 ml), and diphenylsulfide (2 ml) was kept at room temperature for 2 days. After concentrating the mixture *in vacuo*, benzene was added and the insoluble material was filtered. The product was crystallized from MeOH–ethyl acetate to give yellow prisms (II, 25 mg), mp 258—260°.

c) A mixture of III (40 mg), MeOH (15 ml), triphenylphosphine (20 mg) was kept at room temperature for 3 days and the solvent was removed *in vacuo*. The product was purified by preparative TLC and crystallized from MeOH–ethyl acetate to give yellow prisms (II, 38 mg), mp 258—260°.

d) A mixture of III (40 mg), MeOH (15 ml), and 30% aqueous trimethylamine (0.7 ml) was kept at room temperature. 2 days after, the mixture was acidified with dilute HCl, and the solid was collected and recrystallized from MeOH–ethyl acetate to give yellow prisms (II, 25 mg), mp 258—260°.

e) A solution of III (48 mg) in dimethyl sulfoxide (3 ml) was kept at 80° for 14 hr. After the solvent was removed *in vacuo*, the residue was crystallized from MeOH–ethyl acetate to give yellow prisms (II, 29 mg), mp 258—260°.

All the compounds obtained in a)—e) were identified (TLC, mixed mp, and IR) with compound A (II).

Formation of 12,13-Dihydro Compound A (IIa) from 12,13-Dihydromorusin Hydroperoxide (IIIf)——To a solution of IIIf (22.5 mg) in MeOH (30 ml) was added gradually sodium borohydride (25 mg). Immediately, the mixture was acidified with dilute acetic acid, and the solid was collected and crystallized from MeOH to give pale yellow needles (IIa, 11,8 mg), mp 281—285°. The compound obtained here was identified (TLC, mixed mp, and IR) with IIa from III as described below.

Catalytic Hydrogenation of Morusin Hydroperoxide (III)——III (70 mg) in EtOH (50 ml) was hydrogenated over 3% Pd–C (40 mg) as a catalyst. After removal of the catalyst, the solvent was evaporated *in vacuo*. Recrystallization of the residue from MeOH gave pale yellow needles (IIa, 54.5 mg), mp 281—285°. *Anal.* Calcd. for $C_{25}H_{26}O_7 \cdot 1/2H_2O$: C, 67.10; H, 6.08. Found: C, 67.34; H, 6.17. UV λ_{max}^{EtOH} nm (log ε): 255 (sh 4.22), 274 (4.34), 300 (sh 4.03), 350 (4.25); $\lambda_{max}^{EtOH+AlCl_3}$ 265 (sh 4.14), 285 (4.34), 300 (sh 4.14), 362 (4.25), 400 (4.11). IR ν_{max}^{Nujol} cm^{-1}: 3380, 3140, 1650, 1615, 1605. MS *m/e*: 438 (M^+), 423, 405, 381, 380, 379, 351. NMR (pyridine-d_5) δ: 1.35 (6H, s, C_{14}–$CH_3 \times 2$), 1.57, 1.59 (each 3H, s, C_{11}–CH_3), 1.81 (2H, t, $J=7$ Hz, C_{13}–$H \times 2$), 2.81 (2H, t, $J=7$ Hz, C_{12}–$H \times 2$), 3.01 (1H, dd, $J=10$ and 16 Hz, C_9–H), 4.00 (1H, dd, $J=2$ and 16 Hz, C_9–H), 4.31 (1H, dd, $J=2$ and 10 Hz, C_{10}–H), 6.48 (1H, s, C_6–H), 7.10—7.35 (2H, m, $C_{3'}$ and $C_{5'}$–H), 8.16 (1H, d, $J=9$ Hz, $C_{6'}$–H), 13.27 (1H, s, OH). The crystals thus prepared were identified (TLC, mixed mp, and IR) with IIa from IIIf as described above.

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