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Studies on the Constituents of the Cultivated Mulberry Tree. I. Three New Prenylflavones from the Root Bark of *Morus alba* L.[1,2]

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From the benzene extract of the root bark of the cultivated mulberry tree (a variety of *Morus alba* L.), three new prenylflavones, morusin, cyclomorusin, and compound A were isolated. Their structures were shown to be I, II, and III, respectively.

Keywords——morusin; cyclomorusin; prenylflavone; flavone; *Morus alba* L.; mulberry tree; manganese dioxide; 2,3-dichloro-5,6-dicyanobenzoquinone

The root bark of the mulberry tree (*Morus alba* L. and other plants of the genus Morus) has been used as an antiphlogistic, diuretic, and expectorant in the Chinese herb medicine. The constituents of this root bark have been studied by many investigators and some phenolic compounds, triterpenoids, and a glyceride have been isolated.[4] In recent years a series of flavones have been isolated from the heart wood of *Artocarpus* (Moraceae) and the root bark of *Morus* species by Venkataraman and his co-workers.[5]

In the course of our studies on the constituents of the root bark, three new flavone derivatives, morusin (I), cyclomorusin (II), and compound A (III), have been isolated from the benzene extract of the root bark of the cultivated mulberry tree (Ichinose, a variety of *Morus alba* L.). In this paper, the structure determination of these new flavone derivatives is described.

Morusin (I) was obtained as pale yellow prisms, mp 214—216°, M^+ 420, $C_{25}H_{24}O_6$, which gave an intense green color with methanolic ferric chloride and was positive to the Gibbs test as well as to the color reaction test characteristic of flavone derivatives. I gave the absorption bands for hydroxyl, conjugated carbonyl, and benzene ring in the infrared (IR) spectrum. I formed a dimethyl ether (Ia), mp 140—146°, M^+ 448, $C_{27}H_{28}O_6$, on treatment with ethereal diazomethane, and Ia gave a green coloration with methanolic ferric chloride. On prolonged treatment with dimethyl sulfate and potassium carbonate in boiling acetone, a trimethyl ether (Ib), M^+ 462, was obtained as an amorphous solid. Treatment of I with acetic anhydride in pyridine at room temperature yielded a diacetate (Ic), mp 137—138°, M^+ 504, $C_{29}H_{28}O_8$, which gave a green color with ferric chloride and was negative to the Gibbs test. When treated with the same reagents on a water bath, I gave a triacetate (Id), mp 70—75°, M^+ 546, $C_{31}H_{30}O_9$, which was negative to ferric chloride reaction. These findings indicate that I has three phenolic hydroxyl groups and one of them is hydrogen bonded.

1) A preliminary account of this work has been presented: T. Nomura, T. Fukai, S. Yamada, and M. Katayanagi, *Chem. Pharm. Bull.* (Tokyo), **24**, 2898 (1976).
2) Taken from part of the Doctorated thesis presented by T.F. to Hokkaido University (1977).
3) Location: *2-2-1, Miyama, Funabashi-shi, Chiba, 274, Japan.*
4) *a*) T. Tsukamoto and T. Ohtaki, *Yakugaku Zasshi*, **68**, 287 (1948); *b*) T. Uno, *Sanshi Shikenjo Hokoku* (Tokyo), **24**, 437 (1970); *c*) Y. Kondo and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **21**, 2265 (1973); *d*) H. Shibata, I. Mikoshiba, and S. Shimizu, *Agr. Biol. Chem.* (Tokyo), **38**, 1745 (1974).
5) *a*) V.H. Deshpande, P.C. Parthasarathy, and K. Venkataraman, *Tetrahedron Lett.*, **1968**, 1715; *b*) K. Venkataraman, *Phytochemistry*, **11**, 1571 (1972); *c*) V.H. Deshpande, A.V.R. Rao, K. Venkataraman, and P.V. Wakharkar, *Indian J. Chem.*, **12**, 431 (1974); *d*) A.D. Pendse, R. Pendse, A.V.R. Rao, and K. Venkataraman, *ibid.*, **14B**, 69 (1976); *e*) V.H. Deshpande, P.V. Wakharkar, and A.V.R. Rao, *ibid.*, **14B**, 647 (1976).

A dihydroderivative (Ie), mp 200—203°, M^+ 422, $C_{25}H_{26}O_6$, was obtained by hydrogenation in the presence of 3% palladium charcoal, while hydrogenation of I in the presence of Adams catalyst yielded a tetrahydroderivative (If), mp 248—252°, M^+ 424, $C_{25}H_{28}O_6$, showing the presence of two ethylenic bonds.

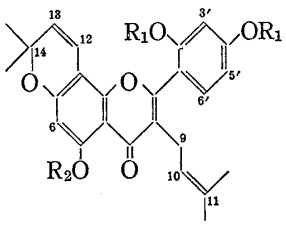
The nuclear magnetic resonance (NMR) spectrum of I indicated the presence of a 2,2-dimethylchromene ring [δ 1.42(9H, s, C_{14}–$CH_3\times2$ and C_{11}–CH_3 overlapping), δ 5.67 (1H, d, J=10 Hz, C_{13}–H), δ 6.53 (1H, d, J=10 Hz, C_{12}–H)] and γ,γ-dimethylallyl group [δ 1.57 (3H, s, C_{11}–CH_3), δ 3.02 (2H, br d, J=8 Hz, C_9–H×2), δ 5.03 (1H, br t, J=8 Hz, C_{10}–H)]. These partial structures were supported by the appearance of a pair of triplet at δ 1.84 (2H, J=7 Hz, C_{13}–H×2), and δ 2.69 (2H, J=7 Hz, C_{12}–H×2) in the dihydroderivative (Ie), and a doublet at δ 0.76 (6H, J=6 Hz, C_{11}–$CH_3\times2$) in the tetrahydroderivative (If).

The ultraviolet (UV) spectrum of I resembled that of mulberrochromene (IV) isolated by Venkataraman, *et al.* from *Morus alba* L.,[5a,b] suggesting that I is a mulberrochromene-type flavone having a γ,γ-dimethylallyl group attached to the 3-position of the pyrone ring[5a] (Table I). This assumption was substantiated by the following data. The NMR spectrum of I showed the absence of the characteristic singlet signal[6] of the 3-position and the chemical

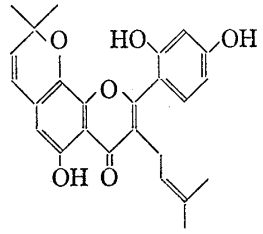
Table I. The UV Spectrum of Prenylflavones

	λ_{max} nm (log ε)				
Morusin (I)[a]	220(sh 4.43),	270(4.60),	300(sh 4.00),	320(sh 3.90),	350(3.81)
Mulberrochromene (IV)[5a]		266(4.51),	300(3.87),		340(3.77)
Cyclomorusin (II)[b]	223(4.45),	255(4.38),	283(4.43),	383(4.19)	
Cyclomulberrochromene (VI)[5a]	219(4.41),	254(4.20),	274(4.21),	370(4.04)	
Compound A (III)[b]	218(4.49),	234(4.49),	278(4.51),	334(4.24)	
VII[a]	219(4.45),	235(4.45),	278(4.47),	334(4.16)	

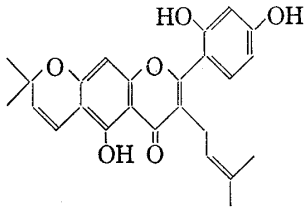
a) Measured in EtOH.
b) Measured in MeOH.



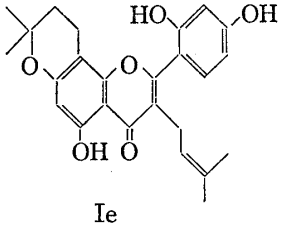
I : $R_1=R_2=H$
Ia: $R_1=CH_3$, $R_2=H$
Ib: $R_1=R_2=CH_3$
Ic: $R_1=Ac$, $R_2=H$
Id: $R_1=R_2=Ac$
Ig: $R_1=CH_3$, $R_2=Ac$



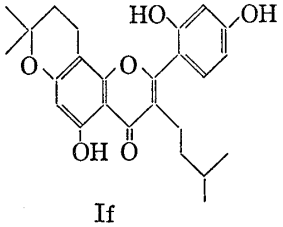
I′



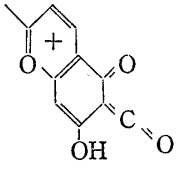
IV



Ie



If



V: *m/e* 203

Chart 1

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

shift of the 6′-proton of the B ring, *ca.* 0.6 ppm upfield from the corresponding proton of the prenylflavone which has no prenyl group at the 3-position.[7] These findings are characteristic feature of 3-prenylated flavones.[5a,d]

The arrangement of substituents in the B ring was assumed by the NMR spectrum of I as follows: a double doublet signal at δ 6.37 (1H, J=2.5 and 7.5 Hz, $C_{5'}$–H), doublet at δ 6.45 (1H, J=2.5 Hz, $C_{3'}$–H), and doublet at δ 7.14 (1H, J=7.5 Hz, $C_{6'}$–H) indicated that the B ring of I was substituted in the 2′- and the 4′-position.

The presence of 2,2-dimethyl chromene ring system in A ring was supported by the mass spectral fragmentation as follows: the mass spectrum (MS) of I gave the fragments at *m/e* 405 (M^+-CH_3) and 203[8] (V, formed from the ion at 405 by a reverse Diels-Alder reaction) which arose from ring A. The above findings suggested the possible structure of morusin to be I or I′. The biogenetic analogy to other prenylflavones suggests that A ring has the phloroglucinol hydroxylation pattern.[5] This assumption was supported by the following data. In the NMR spectrum of 5-acetyl-morusin dimethyl ether (Ig), weak coupling (J= 0.7 Hz) was observed between the aromatic proton in position 6 and the chromene 12-proton. This long-range coupling is considered to be of diagnostic value[9] indicating the 2,2-dimethyl chromene ring as shown in the formula I.

The angular structure (I) for morusin is supported by the consideration of the changes in the chemical shift of chromene olefinic protons in its diacetate (Ic) compared with the triacetate (Id) (Table II). These changes are of the same shift and the same order of magnitude as those observed by many investigators for similar compounds.[8a,9,10] From these results, the structure of morusin could be assigned as I.

Table II. Chemical Shift (ppm) for C_{12}–H and C_{13}–H in Ic and Id[a]

Compound	C_{12}–H	C_{13}–H
Ic	6.52	5.49
Id	6.60	5.59
Δ	−0.08	−0.10

a) Measured in $CDCl_3$.

Cyclomorusin (II) was obtained as yellow prisms, mp 246—248°, M^+ 418, $C_{25}H_{22}O_6$, $[\alpha]_{589}^{20}$ +20° (c=0.15 in MeOH, from optical rotatory dispersion (ORD) measurement), which gave a green color with methanolic ferric chloride and was positive to the color reaction test characteristic of flavone derivatives. II gave an IR spectrum showing the absorption bands for hydroxyl, conjugated carbonyl, and benzene ring. In the UV spectrum, II resembled cyclomulberrochromene[5a] (VI) rather than mulberrochromene[5a] (IV) (Table I).

The NMR spectrum of II indicated the presence of two dimethylallyl groups. One of them is a 2,2-dimethylchromene ring [δ 1.46 (6H, s, C_{14}–$CH_3\times2$), δ 5.79 (1H, d, J=10 Hz, C_{13}–H), δ 6.95 (1H, d, J=10 Hz, C_{12}–H)]. Two vinylic methyls at δ 1.72 and δ 1.98, together with broad doublets (J=10 Hz) at δ 5.49 (C_{10}–H) and 6.24 (C_9–H), suggested that the 2′-hydroxyl group of the B ring in the flavone has been oxidatively cyclized with doubly allylic methylene of a prenyl chain in the 3-position as in cyclomulberrochromene (VI).

7) P.C. Parthasarathy, P.V. Radhakrishnan, S.S. Rathi, and K. Venkataraman, *Indian J. Chem.*, **7**, 101 (1969).
8) *a*) B. Jackson, P.J. Owen, and F. Scheinmann, *J. Chem. Soc.* (*C*), **1971**, 3389; *b*) A.V.R. Rao, S.S. Rathi, and K. Venkataraman, *Indian J. Chem.*, **10**, 989 (1972).
9) A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, *Tetrahedron Lett.*, **1967**, 4201.
10) M. Shabbir, A. Zaman, L. Crombie, B. Tuck, and D.A. Whiting, *J. Chem. Soc.* (*C*), **1968**, 1899.

The aromatic hydrogens of the B ring showed the characteristic ABC pattern of the β-resorcylic acid type [δ 6.46 (1H, d, J=2 Hz, $C_{3'}$–H), δ 6.67 (1H, dd, J=2 and 9 Hz, $C_{5'}$–H), δ 7.82 (1H, d, J=9 Hz, $C_{6'}$–H)].

The single aromatic proton of ring A gave a signal at δ 6.19 as expected for a phloroglucinol ring proton of a flavonoid system.[6] These spectral data suggest that the structure of cyclomorusin closely resembles that of cyclomulberrochromene (VI) rather than mulberrochromene (IV). The structure (II) for cyclomorusin is supported by its mass spectral fragmentation[8b] (Chart 2) and negative Gibbs test.

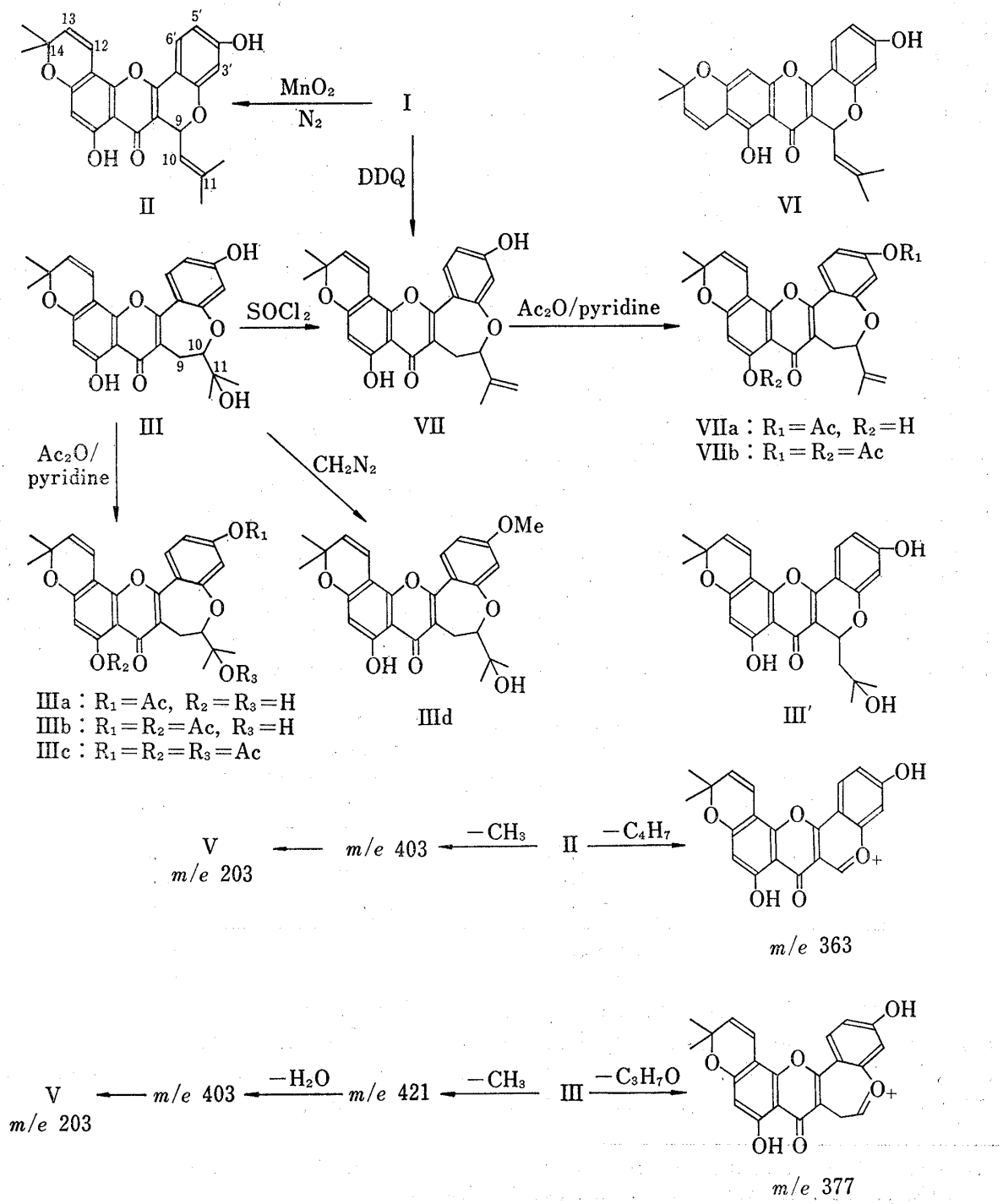


Chart 2

Further evidence supporting the structure of II was obtained by the identity of the IR and the NMR spectrum with those of the compound obtained by the action of manganese dioxide on I in a nitrogen atmosphere.[11]

Compound A (III) was obtained as yellow prisms, mp 258—260°, M^+ 436, $C_{25}H_{24}O_7$, which gave a green color with methanolic ferric chloride and was positive to the color reaction test characteristic of flavone derivatives and negative to the Gibbs test. III gave the absorption bands for hydroxyl, conjugated carbonyl, and benzene ring in its IR spectrum. The UV spectrum of III was distinct from those of mulberrochromene (IV) and cyclomulberrochromene (VI) (Table I).

Treatment of III with acetic anhydride in pyridine at room temperature for 5 min yielded a monoacetate (IIIa), mp 257—258°, M^+ 478, $C_{27}H_{26}O_8$, with a positive ferric chloride reaction. Prolonged treatment of III gave a diacetate (IIIb), mp 249—250°, M^+ 520, $C_{29}H_{28}O_9$ (ν_{max} 3510, 1775, 1760 cm^{-1}), with a negative ferric chloride reaction. When treated with the same reagents on a water bath (60°) for 20 hr, III gave a triacetate (IIIc), mp 218—222°, M^+ 562 (ν_{max} 1770, 1740 cm^{-1}). On treatment with ethereal diazomethane, III forms a monomethyl ether (IIId), mp 227—229°, M^+ 450, $C_{26}H_{26}O_7$, with a positive ferric chloride reaction.

These experimental results suggest the presence of two phenolic hydroxyls and a tertiary alcoholic hydroxyl group.

The NMR spectrum of III showed the presence of a 2,2-dimethylchromene ring [δ 1.48 (6H, s, C_{14}–$CH_3\times2$), δ 5.76 (1H, d, J=11 Hz, C_{13}–H), δ 6.95 (1H, d, J=11 Hz, C_{12}–H)] and four aromatic protons [δ 6.51 (1H, s, C_6–H), δ 7.02 (1H, dd, J=2 and 10 Hz, $C_{5'}$–H), δ 7.05 (1H, d, J=2 Hz, $C_{3'}$–H), δ 8.13 (1H, d, J=10 Hz, $C_{6'}$–H)]. Although the spectrum did not show the signals of γ,γ-dimethylallyl group, the spectrum showed two sharp singlet signals at δ 1.55 and δ 1.58 (each 3H, C_{11}–$CH_3\times2$), and the signals of the characteristic AMX pattern, such as δ 2.96 (1H, dd, J=10 and 16 Hz, C_9–H), δ 3.93 (1H, dd, J=2 and 16 Hz, C_9–H), and δ 4.28 (1H, dd, J=2 and 10 Hz, C_{10}–H). From this finding, it is assumed that the C_5-unit is in the 3-position and this side chain is cyclized with the hydroxyl group at $C_{2'}$. The above results suggest the following two possible formulae (III, III') for compound A (Chart 2). The mass spectrum of III gave fragments at *m/e* 421 (M^+–CH_3), 403 (M^+–CH_3–H_2O), 377[8a] (M^+–C_3H_7O), and 203 (V) (Chart 2). Comparison of the NMR spectra of IIIb and IIIc indicates that the acetylation of the tertiary hydroxyl group at C_{11} caused a down field shift of the H_A-signal (C_{10}–H in IIIb) and shifts to higher field of the H_M- and H_X-signal (C_9–H in IIIb).[12] From these findings, the structure of compound A is assumed to be III.

Table III. Chemical Shift (ppm) for the Protons of the AMX Pattern in IIIb and IIIc[a]

Compound	H_A	H_M	H_X
IIIb	4.28	3.95	2.83
IIIc	4.68	3.57	2.75
Δ	−0.40	+0.38	+0.08

a) Measured in pyridine-d_5.

The assumption was supported by the following data: treatment of III with thionyl chloride in pyridine did not give cyclomorusin (II) but a dehydrated product (VII), mp 266—272°, M^+ 418, $C_{25}H_{22}O_6$. The UV spectrum of VII resembled that of III and was distinct from that of II (Table I). VII afforded a monoacetate (VIIa), mp 227—232°, M^+ 460,

11) A preliminary account of this reaction has been communicated in the earlier paper: T. Nomura, T. Fukai, and M. Katayanagi, *Heterocycles*, **6**, 1847 (1977).

12) K. Tori and T. Komeno, *Tetrahedron*, **21**, 309 (1965).

$C_{27}H_{24}O_7$, on treatment with acetic anhydride in pyridine. When treated with the same reagents on a water bath, VII gave a diacetate (VIIb), mp 195—197°, M^+ 502, which showed no IR absorption in the hydroxyl region and was negative to the ferric chloride reaction. The NMR spectrum of VII showed the presence of only three methyl groups [δ 1.49 (6H, s, C_{14}–$CH_3\times2$), δ 1.88 (3H, s, C_{11}–CH_3)] and the terminal methylene group [δ 4.93 and 5.06 (each 1H, s, C_{11}=CH_2)]. The structure of the dehydrated product is suggested to be of VII. Further evidence supporting the structure of VII was obtained by comparing its IR and NMR spectral data, and mixed melting point with those of compound (VII) obtained by the action of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) on I. In the light of DDQ reactions discussed in the earlier papers by Venkataraman and his co-workers,[5b,13] it is most likely that the action of DDQ on I does not lead I to II but to VII. From these results, the structure of compound A could be assigned as III.

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. 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 pectra; JEAL·JNM-4H-100 and Varian HA 100 D NMR Spectrometers. MS; JEAL JMS ISG 2 Mass Spectrometer. ORD; JASCO ORD/UV-5 Spectrometer.

Isolation of Prenylflavones——The dry root bark (2.7 kg), collected in the neighborhood of Akabori, Gunma Prefecture, was finely cut and extracted with *n*-hexane and then with benzene. Evaporation of the *n*-hexane and the benzene solution to dryness yielded 32 and 63 g of the residue, respectively. The *n*-hexane extract (20 g) was chromatographed on silica gel (400 g) using benzene as an eluent, and α-amyrin acetate (550 mg) was obtained. The benzene extract was dissolved in the minimal amount of MeOH, and allowed to stand until 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, washed with water, dried and solvent evaporated to give a nonphenolic material. The 5% aqueous NaOH solution was acidified with dilute HCl and extracted with ether. The ether solution was then washed with water, dried, and the solvent evaporated to give a mixture of phenolic material (10 g). The phenolic material was chromatographed on silica gel (400 g) using benzene–MeOH as an eluent, and each fraction was checked by thin-layer chromatography (TLC). The fraction eluted with benzene and benzene containing 0.5% MeOH was evaporated, and the residue was dissolved in MeOH, allowed to stand until beturinic acid (400 mg) separated. From the methanolic mother liquor, cyclomorusin (II, 3 mg) and morusin (I, 1.1 g) were obtained by using preparative TLC (ether: $CHCl_3$=1: 4, silica gel). Further elution of the silica gel column with benzene containing 1% MeOH gave compound A (III, 20 mg).

Morusin (I)——I was recrystallized from ether–*n*-hexane to give pale yellow prisms, mp 214—216°, $FeCl_3$ (+), Mg–HCl (+), Zn–HCl (+), Gibbs test (+). *Anal.* Calcd. for $C_{25}H_{24}O_6$: C, 71.41; H, 5.75. Found: C, 71.49; H, 5.83. UV λ_{max}^{EtOH} nm (log ε): 206 (4.49), 220 (sh 4.43), 270 (4.60), 300 (sh 4.00), 320 (sh 3.90), 350 (3.81); $\lambda_{max}^{EtOH+AcONa+H_3BO_3}$ 270 (4.62), 300 (sh 4.04), 320 (sh 3.97), 350 (sh 3.87); $\lambda_{max}^{EtOH+AlCl_3}$ 279 (4.63), 338 (3.89), 415 (3.79); $\lambda_{max}^{EtOH+NaOMe}$ 267 (4.59), 371 (4.04). IR ν_{max}^{Nujol} cm^{-1}: 3250, 1660, 1600. MS *m/e*: 420 (M^+), 405 (M^+-CH_3), 377, 256, 203. NMR [in $(CD_3)_2SO$] δ: 1.42 (9H, br s, $C_{14}-CH_3\times2$ and C_{11}–CH_3), 1.57 (3H, br s, C_{11}–CH_3), 3.02 (2H, br d, J=8 Hz, C_9–H×2), 5.03 (1H, br t, J=8 Hz, C_{10}–H), 5.67 (1H, d, J=10 Hz, C_{13}–H), 6.21 (1H, s, C_6–H), 6.37 (1H, dd, J=2.5 and 7.5 Hz, $C_{5'}$–H), 6.45 (1H, d, J=2.5 Hz, $C_{3'}$–H), 6.53 (1H, d, J=10 Hz, C_{12}–H), 7.14 (1H, d, J=7.5 Hz, $C_{6'}$–H), 9.78, 9.85, 13.17 (each 1H, s, OH, disappeared on addition of D_2O).

Morusin Dimethyl Ether (Ia)——To a solution of I (38 mg) in MeOH (5 ml) was added excess ethereal diazomethane, and the mixture was allowed to stand at −10° for 12 hr and treated as usual. The product was then purified by preparative TLC and crystallized from MeOH to give pale yellow needles (Ia, 11 mg), mp 140—146°, $FeCl_3$ (+), Gibbs test (−). *Anal.* Calcd. for $C_{27}H_{28}O_6$: C, 72.30; H, 6.29. Found: C, 72.18; H, 6.46. UV λ_{max}^{EtOH} nm (log ε): 209 (4.62), 234 (4.46), 273 (4.60), 300 (sh 3.75), 345 (sh 3.15); $\lambda_{max}^{EtOH+AlCl_3}$ 209 (4.60), 230 (4.49), 284.5 (4.63), 330 (sh 3.63), 415 (3.67). IR ν_{max}^{Nujol} cm^{-1}: 1650, 1630, 1580. MS *m/e*: 448 (M^+), 433, 405, 203. NMR (in $CDCl_3$) δ: 1.48 (9H, br s, $C_{14}-CH_3\times2$ and C_{11}–CH_3), 1.64 (3H, br s, C_{11}–CH_3), 3.06 (2H, br d, J=6 Hz, C_9–H×2), 3.82, 3.91 (each 3H, s, OCH_3), 5.09 (1H, br t, J=6 Hz, C_{10}–H), 5.47 (1H,

13) *a*) V.H. Deshpande, A.V.R. Rao, R. Srinivasan, and K. Venkataraman, *Indian J. Chem.*, **10**, 681 (1972); *b*) A.V.R. Rao, S.S. Rathi, and K. Venkataraman, *ibid.*, **10**, 905 (1972).

d, J=10 Hz, C_{13}–H), 6.27 (1H, s, C_6–H), 6.59 (3H, m, C_{12}, $C_{3'}$ and $C_{5'}$–H), 7.28 (1H, d, J=9 Hz, $C_{6'}$–H), 13.11 (1H, s, OH, disappeared on addition of D_2O).

Morusin Trimethyl Ether (Ib)——A mixture of I (54 mg), Me_2SO_4 (1 ml), anhyd. K_2CO_3 (1 g), and acetone (10 ml) was refluxed overnight, and the reaction mixture was worked up as usual. The amorphous trimethyl ether (Ib, 32 mg) resisted crystallization but indicated only one spot on TLC. IR ν_{max}^{Nujol} cm^{-1}: 1655, 1635, 1610, 1585. MS *m/e*: 462 (M^+), 447, 431, 419, 233, 217, 202. UV λ_{max}^{EtOH} nm (log ε): 237 (4.27), 268 (4.34), 285 (sh 4.06), 330 (sh 3.68); $\lambda_{max}^{EtOH+AlCl_3}$ 235 (4.29) 268 (4.37), 285 (sh 4.11), 330 (sh 3.74). NMR (in $CDCl_3$) δ: 1.40, 1.58 (each 3H, br s, C_{11}–CH_3), 1.45 (6H, s, C_{14}–$CH_3\times2$), 3.02 (2H, br d, J=7 Hz, C_9–H×2), 3.78, 3.82, 3.86 (each 3H, s, OCH_3), 5.15 (1H, m, C_{10}–H), 5.43 (1H, d, J=10 Hz, C_{13}–H), 6.26 (1H, s, C_6–H), 6.55 (1H, d, J=2 Hz, $C_{3'}$–H), 6.56 (1H, dd, J=2 and 9 Hz, $C_{5'}$–H), 7.25 (1H, d, J=9 Hz, $C_{6'}$–H).

Morusin Diacetate (Ic)——A mixture of I (113 mg), acetic anhydride (2 ml) and pyridine (1 ml) was kept at room temperature for 5 min, and then poured into ice water. The solid was collected and recrystallized from ether–*n*-hexane to give the diacetate (Ic, 100 mg), mp 137—138°, $FeCl_3$ (+), Gibbs test (−). *Anal.* Calcd. for $C_{29}H_{28}O_8$: C, 69.04; H, 5.59. Found: C, 69.00; H, 5.76. UV λ_{max}^{EtOH} nm (log ε): 234 (4.27), 270 (4.54), 354 (3.69); $\lambda_{max}^{EtOH+AlCl_3}$ 279 (4.62), 338 (4.87), 415 (3.77). IR ν_{max}^{Nujol} cm^{-1}: 1770, 1660, 1590, 1470. MS *m/e*: 504 (M^+), 489, 471, 461, 203. NMR (in $CDCl_3$) δ: 1.43 (9H, br s, C_{14}–$CH_3\times2$ and C_{11}–CH_3), 1.62 (3H, br s, C_{11}–CH_3), 2.11, 2.32 (each 3H, s, OAc), 3.07 (2H, br d, C_9–H×2), 5.08 (1H, m, C_{10}–H), 5.49 (1H, d, J=10 Hz, C_{13}–H), 6.27 (1H, s, C_6–H), 6.52 (1H, d, J=10 Hz, C_{12}–H), 7.11 (1H, d, J=2 Hz, $C_{3'}$–H), 7.12 (1H, dd, J=2 and 9 Hz, $C_{5'}$–H), 7.46 (1H, d, J=9 Hz, $C_{6'}$–H), 12.85 (1H, s, OH, disappeared on addition of D_2O).

Morusin Triacetate (Id)——A solution of I (51 mg), pyridine (1 ml), and acetic anhydride (0.1 ml) was heated at 90° for 2 hr. Conventional work-up gave its triacetate (Id, 65 mg), which was recrystallized from ether to give colorless needles, mp 70—75°, $FeCl_3$ (−). *Anal.* Calcd. for $C_{31}H_{30}O_9\cdot1/2H_2O$: C, 67.02, H, 5.62. Found: C, 66.86; H, 5.52. IR ν_{max}^{Nujol} cm^{-1}: 1780, 1640, 1630, 1610. UV λ_{max}^{EtOH} nm (log ε): 235 (4.47), 262 (4.53), 318 (3.86); $\lambda_{max}^{EtOH+AlCl_3}$ 235 (4.49), 261.5 (4.53), 318 (3.91). MS *m/e*: 546 (M^+), 504, 489, 287, 245, 203. NMR (in $CDCl_3$) δ: 1.34, 1.57 (each 3H, br s, C_{11}–CH_3), 1.44 (6H, s, C_{14}–$CH_3\times2$), 2.09, 2.30, 2.42 (each 3H, s, OAc), 3.01 (2H, br d, C_9–H×2), 5.05 (1H, m, C_{10}–H), 5.59 (1H, d, J=10 Hz, C_{13}–H), 6.46 (1H, s, C_6–H), 6.60 (1H, d, J=10 Hz, C_{12}–H), 7.10 (1H, d, J=2.5 Hz, $C_{3'}$–H), 7.10 (1H, dd, J=2.5 and 9 Hz, $C_{5'}$–H), 7.46 (1H, d, J=9 Hz, $C_{6'}$–H).

12,13-Dihydromorusin (Ie)——I (103 mg) in 2-ethoxyethanol (50 ml) was hydrogenated over 3% Pd–C (55 mg) as a catalyst. One mol of H_2 were absorbed during 2 hr. After removal of the catalyst, the solvent was evaporated *in vacuo*. Recrystallization of the residue from H_2O–MeOH yielded a dihydrocompound (Ie, 80 mg), mp 200—203°. *Anal.* Calcd. for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20. Found: C, 71.45; H, 6.33. IR ν_{max}^{KBr} cm^{-1}: 3350, 1660, 1610. UV λ_{max}^{MeOH} nm (log ε): 264 (4.25), 303 (sh 3.83), 320 (3.83); $\lambda_{max}^{MeOH+AlCl_3}$ 275.5 (4.31), 333 (3.79), 370 (3.72). MS *m/e*: 422 (M^+), 405, 389, 379, 322. NMR [in $(CD_3)_2CO$] δ: 1.37 (6H, s, C_{14}–$CH_3\times2$), 1.46, 1.58 (each 3H, br s, C_{11}–CH_3), 1.84 (2H, t, J=7 Hz, C_{13}–H×2), 2.69 (2H, t, J=7 Hz, C_{12}–H×2), 3.14 (2H, br d, J=8 Hz, C_9–H×2), 5.11 (1H, m, C_{10}–H), 6.11 (1H, s, C_6–H), 6.61 (2H, m, $C_{3'}$ and $C_{5'}$–H), 7.23 (1H, d, J=9 Hz, $C_{6'}$–H), 12.88 (1H, s, OH).

10,11,12,13-Tetrahydromorusin (If)——I (43 mg) in MeOH (50 ml) was hydrogenated over PtO_2 (7 mg) as a catalyst. Two mol of H_2 were absorbed during 10 hr. After removal of the catalyst, the solvent was evaporated *in vacuo*, and the residue was recrystallized from H_2O–MeOH to pale yellow prisms (If, 13 mg), mp 248—252°, M^+ 424. *Anal.* Calcd. for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.90; H, 6.50. IR ν_{max}^{KBr} cm^{-1}: 3300, 3220, 1660, 1610. UV λ_{max}^{MeOH} nm (log ε): 263 (4.22), 315 (3.79); $\lambda_{max}^{MeOH+AlCl_3}$ 276 (4.17), 330 (3.75), 379 (3.67). NMR [in $(CD_3)_2CO$] δ: 0.76 (6H, d, J=6 Hz, C_{11}–$CH_3\times2$), 1.34 (6H, s, C_{14}–$CH_3\times2$), 1.20—1.50 (3H, m, C_{10}–H×2 and C_{11}–H, overlapping with the signal at δ 1.34), 1.85 (2H, t, J=7 Hz, C_{13}–H×2), 2.43 (2H, t, J=7 Hz, C_9–H×2), 2.68 (2H, t, J=7 Hz, C_{12}–H×2), 6.08 (1H, s, C_6–H), 6.52 (2H, m, $C_{3'}$ and $C_{5'}$–H), 7.24 (1H, d, J=8 Hz, $C_{6'}$–H), 12.97 (1H, s, OH).

5-Acetyl-Morusin Dimethyl Ether (Ig)——A mixture of Ia (35 mg), acetic anhydride (1 ml), and pyridine (0.5 ml) was kept at 5° for 10 days, subjected to the ordinary work-up and recrystallization from ether–*n*-hexane to give 5-acetyl-morusin dimethyl ether (Ig, 15 mg), mp 125—127°, $FeCl_3$ (−). *Anal.* Calcd. for $C_{29}H_{30}O_7$: C, 71.00; H, 6.16. Found: C, 70.98; H, 6.15. UV λ_{max}^{MeOH} nm (log ε): 206 (4.62), 239 (4.57), 263 (4.49), 319 (4.01); $\lambda_{max}^{MeOH+AlCl_3}$ 207 (4.63), 239 (4.58), 263 (4.51), 319 (4.02). IR ν_{max}^{Nujol} cm^{-1}: 1770, 1630, 1600, 1565. MS *m/e*: 490 (M^+), 448, 433, 405. NMR (in $CDCl_3$) δ: 1.33, 1.58 (each 3H, br s, C_{11}–CH_3), 1.47 (6H, s, C_{14}–$CH_3\times2$), 2.47 (3H, s, OAc), 3.03 (2H, br d, J=6 Hz, C_9–H×2), 3.80, 3.89 (each 3H, s, OCH_3), 5.12 (1H, br t, J=6 Hz, C_{10}–H), 5.58 (1H, d, J=10 Hz, C_{13}–H), 6.48 (1H, d, J=0.7 Hz, C_6–H), 6.53 (1H, d, J=2 Hz, $C_{3'}$–H), 6.55 (1H, dd, J=2 and 9 Hz, $C_{5'}$–H), 6.68 (1H, dd, J=0.7 and 10 Hz, C_{12}–H), 7.28 (1H, d, J=9 Hz, $C_{6'}$–H).

Cyclomorusin (II)——II was recrystallized from MeOH to give yellow prisms, mp 246—248°, $FeCl_3$ (+), Mg–HCl (+), Gibbs test (−). *Anal.* Calcd. for $C_{25}H_{22}O_6$: C, 71.76; H, 5.30. Found: C, 71.87; H, 5.50. UV λ_{max}^{MeOH} nm (log ε): 223 (4.45), 255 (4.38), 283 (4.43), 383 (4.19); $\lambda_{max}^{MeOH+AlCl_3}$ 229 (4.51), 265 (4.35), 285 (4.41), 379 (4.24), 429 (3.84); $\lambda_{max}^{MeOH+NaOMe}$ 270 (4.47), 409 (4.41). IR ν_{max}^{KBr} cm^{-1}: 3500, 1660, 1620, 1590. MS *m/e*: 418 (M^+), 403, 385, 363, 348, 347, 203. NMR [in $(CD_3)_2CO$] δ: 1.46 (6H, s, C_{14}–$CH_3\times2$), 1.72, 1.98 (each 3H, br s, C_{11}–CH_3), 5.49 (1H, br d, J=10 Hz, C_{10}–H), 5.79 (1H, d, J=10 Hz, C_{13}–H), 6.19 (1H, s, C_6–H), 6.24 (1H, br d,

J=10 Hz, C_9–H), 6.46 (1H, d, J=2 Hz, $C_{3'}$–H), 6.67 (1H, dd, J=2 and 9 Hz, $C_{5'}$–H), 6.95 (1H, d, J=10 Hz, C_{12}–H), 7.82 (1H, d, J=9 Hz, $C_{6'}$–H), 12.73 (1H, s, OH).

MnO_2-oxidation of Morusin (I)——To a solution of I (90 mg) in dry benzene (60 ml) was added commercial MnO_2 (1.5 g) under N_2, and whole solution was kept out of contact with air at room temperature for 5 days. MnO_2 was filtered off and washed with MeOH. The filtrate and washings were combined and evaporated to dryness. The residue was then purified by preparative TLC (ether: $CHCl_3$=1: 4, silica gel) and crystallized from ether–*n*-hexane to give pale yellow prisms (39 mg). NMR spectrum showed that the products were mixture of II and VII. The mixture was recrystallized repeatedly from MeOH to give yellow prisms (II, 9 mg), mp 246—248°, and yellow needles (VII, 5 mg), mp 266—272°. The compound (II) obtained here was identified (IR and NMR) with cyclomorusin (II).

Compound A (III)——III was recrystallized from MeOH–AcOEt to give yellow prisms, mp 258—260°, $FeCl_3$ (+), Mg–HCl (+), Gibbs test (−), $[\alpha]_{589}^{20}$ 0° (c=0.15 in MeOH, from ORD measurement). *Anal.* Calcd. for $C_{25}H_{24}O_7$: C, 68.80; H, 5.54. Found: C, 68.76; H, 5.85. IR ν_{max}^{Nujol} cm^{-1}: 3500 (sh), 3400, 3200, 1660, 1630, 1600. UV λ_{max}^{MeOH} nm (log ε): 218 (4.49), 234 (4.49), 278 (4.51), 334 (4.24); $\lambda_{max}^{MeOH+AlCl_3}$ 224 (4.53), 260.5 (4.41), 284 (4.54), 360 (4.33), 417 (4.02); $\lambda_{max}^{MeOH+NaOMe}$ 265 (4.56), 393 (4.42). MS *m/e*: 436 (M^+), 421 (M^+-CH_3), 403 ($M^+-CH_3-H_2O$), 377, 363, 203. NMR (in pyridine-d_5) δ: 1.48 (6H, s, C_{14}–$CH_3\times2$), 1.55, 1.58 (each 3H, s, C_{11}–CH_3), 2.96 (1H, dd, J=10 and 16 Hz, C_9–H), 3.93 (1H, dd, J=2 and 16 Hz, C_9–H), 4.28 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.76 (1H, d, J=11 Hz, C_{13}–H), 6.51 (1H, s, C_6–H), 6.95 (1H, d, J=11 Hz, C_{12}–H), 7.02 (1H, dd, J=2 and 10 Hz, $C_{5'}$–H), 7.05 (1H, d, J=2 Hz, $C_{3'}$–H), 8.13 (1H, d, J=10 Hz, $C_{6'}$–H), 12.70 (1H, s, OH).

Compound A Monoacetate (IIIa)——Acetylation of III (27 mg) with acetic anhydride (2 ml) and pyridine (0.7 ml) by keeping at room temperature for 5 min, was followed by usual work-up. Crystallization from MeOH afforded yellow needles (IIIa, 20.5 mg), mp 257—258°, $FeCl_3$ (+). *Anal.* Calcd. for $C_{27}H_{26}O_8\cdot1/2H_2O$: C, 66.52; H, 5.57. Found: C, 66.81; H, 5.64. IR ν_{max}^{Nujol} cm^{-1}: 3440, 1755, 1660, 1640, 1610, 1565. UV λ_{max}^{EtOH} nm (log ε): 211 (4.49), 233 (4.48), 279 (4.50), 325 (sh 4.02); $\lambda_{max}^{EtOH+AlCl_3}$ 210 (4.48), 233 (4.45), 284.5 (4.50), 347 (4.08), 420 (3.71); $\lambda_{max}^{EtOH+NaOMe}$ 269 (4.44), 308.5 (4.29), 353 (4.26), 387 (4.22). MS *m/e*: 478 (M^+), 463 (M^+-CH_3), 421, 405, 377, 333, 256, 203. NMR (in pyridine-d_5) δ: 1.47 (6H, s, C_{14}–$CH_3\times2$), 1.55, 1.56 (each 3H, s, C_{11}–CH_3), 2.23 (3H, s, OAc), 2.87 (1H, dd, J=10 and 17 Hz, C_9–H), 3.88 (1H, dd, J=2 and 17 Hz, C_9–H), 4.30 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.66 (1H, d, J=10 Hz, C_{13}–H), 6.51 (1H, s, C_6–H), 6.86 (1H, d, J=10 Hz, C_{12}–H), 7.05—7.28 (2H, m, $C_{3'}$ and $C_{5'}$–H, overlapping with the signal of the solvent), 8.13 (1H, d, J=10 Hz, $C_{6'}$–H), 13.25 (1H, s, OH).

Compound A Diacetate (IIIb)——Acetylation of III (15 mg) with acetic anhydride (2 ml) and pyridine (0.7 ml) by keeping overnight at room temperature, was followed by ordinary work up. Crystallization from MeOH, afforded the collorless needles (IIIb, 11 mg), mp 249—250°, $FeCl_3$ (−). *Anal.* Calcd. for $C_{29}H_{28}O_9\cdot H_2O$: C, 64.67; H, 5.62. Found: C, 64.33; H, 5.44. IR ν_{max}^{Nujol} cm^{-1}: 3510, 1775, 1760, 1630, 1620, 1575. UV λ_{max}^{EtOH} nm (log ε): 233 (4.61), 271 (4.53), 326 (4.18); $\lambda_{max}^{EtOH+AlCl_3}$ 233 (4.60), 270 (4.54), 326 (4.21). MS *m/e*: 520 (M^+), 505 (M^+-CH_3), 478, 463, 445, 421, 405, 377, 333. NMR (in pyridine-d_5) δ: 1.47 (6H, s, C_{14}–$CH_3\times2$), 1.53, 1.54 (each 3H, s, C_{11}–CH_3), 2.26, 2.51 (each 3H, s, OAc), 2.83 (1H, dd, J=10 and 15 Hz, C_9–H), 3.95 (1H, dd, J=2 and 15 Hz, C_9–H), 4.28 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.76 (1H, d, J=10 Hz, C_{13}–H), 6.80 (1H, s, C_6–H), 6.89 (1H, d, J=10 Hz, C_{12}–H), 7.05—7.25 (2H, m, $C_{3'}$ and $C_{5'}$–H, overlapping with the signal of the solvent), 8.08 (1H, d, J=10 Hz, $C_{6'}$–H).

Compound A Triacetate (IIIc)——A solution of IIIb (8 mg), pyridine (1 ml), and acetic anhydride (3 ml) was heated at 60° for 20 hr. Conventional work-up gave compound A triacetate (IIIc, 4.1 mg), which was recrystallized from MeOH to colorless needles, mp 218—222°, $FeCl_3$ (−). IR ν_{max}^{Nujol} cm^{-1}: 1770, 1740, 1670, 1635, 1575. UV λ_{max}^{EtOH} nm (log ε): 232 (4.53), 269 (4.47), 324 (4.11); $\lambda_{max}^{EtOH+AlCl_3}$ 232 (4.54), 269 (4.49), 324 (4.13). MS *m/e*: 562 (M^+), 520, 506, 445, 403, 377, 361, 333, 203. NMR (in pyridine-d_5): 1.48 (6H, s, C_{14}–$CH_3\times2$), 1.68, 1.72 (each 3H, s, C_{11}–CH_3), 1.92, 2.27, 2.50 (each 3H, s, OAc), 2.75 (1H, dd, J=10 and 18 Hz, C_9–H), 3.57 (1H, dd, J=2 and 18 Hz, C_9–H), 4.68 (1H, dd, J=2 and 10 Hz, C_{10}–H), 5.79 (1H, d, J=10 Hz, C_{13}–H), 6.84 (1H, s, C_6–H), 6.93 (1H, d, J=10 Hz, C_{12}–H), 7.20—7.40 (2H, m, $C_{3'}$ and $C_{5'}$–H, overlapping with the signal of the solvent), 8.12 (1H, d, J=9 Hz, $C_{6'}$–H).

Compound A Monomethyl Ether (IIId)——To a solution of III (9 mg) in MeOH (0.5 ml) was added excess ethereal diazomethane, and the mixture was allowed to stand at −10° for 12 hr and treated as usual. The product was purified by preparative TLC (ether: $CHCl_3$=1: 4, silica gel) and crystallized from MeOH to give yellow needles (IIId, 3.2 mg), mp 227—229°, $FeCl_3$ (+). *Anal.* Calcd. for $C_{26}H_{26}O_7$: C, 69.32; H, 5.82. Found: C, 69.32; H, 5.85. IR ν_{max}^{Nujol} cm^{-1}: 3570, 3420, 1660, 1640, 1610, 1550. UV λ_{max}^{EtOH} nm (log ε): 207 (4.46), 221 (4.46), 238 (4.46), 282 (4.61), 336 (4.20); $\lambda_{max}^{EtOH+AlCl_3}$ 208 (4.49), 232 (4.42), 249 (sh 4.36), 291 (4.53), 354 (4.26). MS *m/e*: 450 (M^+), 435, 417, 391, 377, 203. NMR (in pyridine-d_5) δ: 1.49 (6H, s, C_{14}–$CH_3\times2$), 1.57, 1.59 (each 3H, s, C_{11}–CH_3), 2.89 (1H, dd, J=9 and 18 Hz, C_9–H), 3.73 (3H, s, OCH_3), 3.94 (1H, dd, J=2 and 18 Hz, C_9–H), 4.28 (1H, dd, J=2 and 9 Hz, C_{10}–H), 5.68 (1H, d, J=10 Hz, C_{13}–H), 6.52 (1H, s, C_6–H), 6.86 (1H, d, J=10 Hz, C_{12}–H), 6.93 (2H, m, $C_{3'}$ and $C_{5'}$–H), 8.09 (1H, d, J=9 Hz, $C_{6'}$–H).

Cyclodehydrogenation of Morusin (I)——A mixture of I (110 mg) and DDQ (110 mg) in dry benzene (30 ml) was refluxed for 2 hr. The reaction mixture was filtered and the filtrate was concentrated. The residue on separation by preparative TLC (ether: $CHCl_3$=1: 4, silica gel) gave the cyclized product in pure form. On crystallization from ether–*n*-hexane, yellow needles (VII, 16.2 mg), mp 266—272°, $FeCl_3$ (+), Gibbs test

(−), were obtained. *Anal.* Calcd. for $C_{25}H_{22}O_6 \cdot 1/2H_2O$: C, 70.25; H, 5.41. Found: C, 70.61; H, 5.37. IR ν_{max}^{Nujol} cm^{-1}: 3200, 1665, 1640, 1615. UV λ_{max}^{EtOH} nm (log ε): 219 (4.45), 235 (4.45), 278 (4.47), 334 (4.16); $\lambda_{max}^{EtOH+AlCl_3}$ 226.5 (4.49), 261.5 (4.38), 284 (4.54), 358.5 (4.28), 424 (3.97); $\lambda_{max}^{EtOH+NaOMe}$ 271 (4.50), 309 (4.35), 351 (4.31), 389 (4.27). MS *m/e*: 418 (M^+), 403 ($M^+ - CH_3$), 385, 363, 203. NMR (in pyridine-d_5) δ: 1.49 (6H, s, C_{14}–$CH_3 \times 2$), 1.88 (3H, s, C_{11}–CH_3), 2.88—3.15 (2H, m, C_9–H × 2), 4.83 (1H, m, C_{10}–H), 4.93, 5.06 (each 1H, br s, C_{11}=CH_2), 5.49 (1H, d, J=10 Hz, C_{13}–H), 6.49 (1H, s, C_6–H), 6.92 (1H, d, J=10 Hz, C_{12}–H), 7.05—7.20 (2H, m, $C_{3'}$ and $C_{5'}$–H, overlapping with the signal of the solvent), 8.19 (1H, d, J=9 Hz, $C_{6'}$–H).

Acetylation of VII (Formation of VIIa)——Acetylation of VII (10 mg) with acetic anhydride (0.6 ml) and pyridine (0.3 ml) by keeping at room temperature for 5 min, was followed by ordinary work-up. Recrystallization from MeOH, afforded the monoacetate (VIIa, 7 mg), mp 227—232°, $FeCl_3$ (+). *Anal.* Cacld. for $C_{27}H_{24}O_7$: C, 70.42; H, 5.25. Found: C, 70.11; H, 5.27. IR ν_{max}^{Nujol} cm^{-1}: 1760, 1665, 1610, 1220. UV λ_{max}^{EtOH} nm (log ε): 232 (4.54), 279.5 (4.60), 325 (sh 4.01); $\lambda_{max}^{EtOH+AlCl_3}$ 233 (4.48), 285 (4.59), 345.5 (4.13), 426.5 (3.82). MS *m/e*: 460 (M^+), 445, 403, 203. NMR (in $CDCl_3$) δ: 1.49 (6H, s, C_{14}–$CH_3 \times 2$), 1.89 (3H, s, C_{11}–CH_3), 2.33 (3H, s, OAc), 2.90 (1H, dd, J=9 and 15 Hz, C_9–H), 3.15 (1H, dd, J=2 and 15 Hz, C_9–H), 4.23 (1H, dd, J=2 and 9 Hz, C_{10}–H), 4.95, 5.06 (each 1H, br s, C_{11}=CH_2), 5.58 (1H, d, J=10 Hz, C_{13}–H), 6.27 (1H, s, C_6–H), 6.73 (1H, d, J=10 Hz, C_{12}–H), 6.97 (2H, m, $C_{3'}$ and $C_{5'}$–H), 7.91 (1H, d, J=9 Hz, $C_{6'}$–H).

Acetylation of VII (Formation of VIIb)——A solution of VII (10 mg), pyridine (1 ml), and acetic anhydride (2 ml) was kept on a water bath (80°) for 20 min. Ordinary work-up and recrystallization from MeOH afforded the diacetate (VIIb, 2.5 mg), mp 195—197°, $FeCl_3$ (−). IR ν_{max}^{Nujol} cm^{-1}: 1760, 1650, 1630, 1610. UV λ_{max}^{EtOH} nm (log ε): 219 (4.47), 231.5 (4.41), 272.5 (4.30), 355 (3.95); $\lambda_{max}^{EtOH+AlCl_3}$ 219.5 (4.52), 272 (4.33), 355 (4.04). MS *m/e*: 502 (M^+), 460, 445.

Dehydration of Compound A with $SOCl_2$——To a solution of III (35 mg) in dry pyridine (1 ml) was added gradually $SOCl_2$ (0.5 ml) with stirring in an ice-bath and then ice-water was added to the mixture. The solid thus obtained was purified by preparative TLC (ether: $CHCl_3$=1: 4, silica gel) and crystallized from ether–*n*-hexane to give yellow needles (VII, 6 mg), mp 266—272°. The compound obtained here was identified (TLC, mixed mp, IR, and NMR) with the product (VII) of cyclodehydrogenation of I described above.

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