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Components of *Broussonetia papyrifera* (L.) VENT. I.[1] Structures of Two New Isoprenylated Flavonols and Two Chalcone Derivatives

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Two new isoprenylated flavonols, broussoflavonols A and B, and two isoprenylated chalcones, broussochalcones A and B, were isolated from the benzene extract of the cortex of *Broussonetia papyrifera* (L.) VENT. (Japanese name "Kajinoki," Moraceae). The structures of broussoflavonols A, B, and broussochalcone B were shown to be **1**, **2**, and **4**, respectively, on the basis of spectral evidence, and the structure of broussochalcone A was determined to be **3** on the basis of spectral and chemical evidence.

Keywords——*Broussonetia papyrifera*; Moraceae; isoprenylated flavonol; broussoflavonol A; broussoflavonol B; broussochalcone A; broussochalcone B

We have already reported the isolation and structure determination of a series of natural Diels–Alder type adducts as well as of isoprenylated flavonoids isolated from the root bark of cultivated mulberry tree[2] and the Chinese crude drug "Sāng-Bái-Pi" (Japanese name "Sōhakuhi") imported from the People's Republic of China.[2a,c,3] On the other hand, it was reported that the Chinese crude drug "Sāng-Bái-Pi" obtained in a market had been found to be adulterated with the root barks of *Cudrania tricuspidata* (CARR.) BUR. and *Broussonetia papyrifera* (L.) VENT., both of which belong to the family Moraceae.[4] In the previous papers,[5] we reported the phenolic components of *C. tricuspidata* (CARR.) BUR.

B. papyrifera (L.) VENT. (Japanese name "Kajinoki") is a deciduous tree which is distributed over Southeast Asia, China, and Japan, and its cortex has been used as a raw material for paper and as a Chinese crude drug.[6] In the study of its components, Takasugi *et al.* reported some phenolic phytoalexins from diseased paper mulberry (*Broussonetia papyrifera* (L.) VENT.).[7] In the course of our studies on the constituents of the Morus root bark, we studied the cortex of *B. papyrifera* (L.) VENT. as well as the root bark. In this paper, we report the structure determination of two new isoprenylated flavonols, broussoflavonols A and B, as well as two isoprenylated chalcones, broussochalcones A and B, obtained from the cortex of the plant.

The dried cortex of *B. papyrifera* (L.) VENT. was extracted successively with *n*-hexane and benzene. The benzene extract was fractionated sequentially by column chromatography and preparative thin-layer chromatography (TLC) to give broussoflavonols A (**1**) and B (**2**) and broussochalcones A (**3**) and B (**4**).

Broussoflavonol A (**1**) was obtained as an amorphous powder, $M^+ = 450.1699$, $C_{26}H_{26}O_7$, exhibiting a positive ferric chloride test, magnesium–hydrochloric acid test and sodium molybdate test,[8] but a negative zirconium oxychloride–citric acid test.[9] The infrared (IR) spectrum of **1** suggested the presence of hydroxyl groups [3350, 3250 cm^{-1}], aromatic

rings [1600, 1550 cm^{-1}], and a conjugated carbonyl group [1650 cm^{-1}]. The ultraviolet (UV) spectrum of **1** showed absorption maxima at 232 (sh), 285 (sh), 295, 309 (sh), and 360 nm. The absorption maxima at 295 and 360 nm shifted in the presence of aluminum chloride to 300 and 394 nm, respectively, while these absorption maxima at 300 and 394 nm shifted to 298 and 380 nm on adding hydrochloric acid in the presence of aluminum chloride. In the light of these UV spectra[10] and the results of the color reaction tests,[8,9] **1** seems to be a flavone or 3-*O*-methylflavonol derivative having an *ortho*-dihydroxyl moiety in the structure. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** indicated the presence of a 2,2-dimethylchromene ring [δ 1.47 (6H, s), 5.77 (1H, d, J=10 Hz), 6.70 (1H, d, J=10 Hz)], γ,γ-dimethylallyl group [δ 1.66 (3H, s), 1.81 (3H, s), 3.49 (2H, br d, J=7 Hz), 5.22 (1H, t, J=7 Hz)], methoxyl group [δ 3.88 (3H, s)], and a hydrogen-bonded hydroxyl group [δ 13.29 (1H, s)], while the characteristic singlet signal of the 3-position of the flavone skeleton was not observed.[10] The mass spectrum (MS) of **1** showed significant fragments at m/z 435 ($M^+ - CH_3$), 395 ($M^+ - C_4H_7$, **5**), 231 (**6**), and 137 (**7**) (Chart 1). These results supported the presence of a 2,2-dimethylchromene ring system and a γ,γ-dimethylallyl group in the A ring along with two hydroxyl groups in the B ring.[11] The arrangement of substituents in the B ring

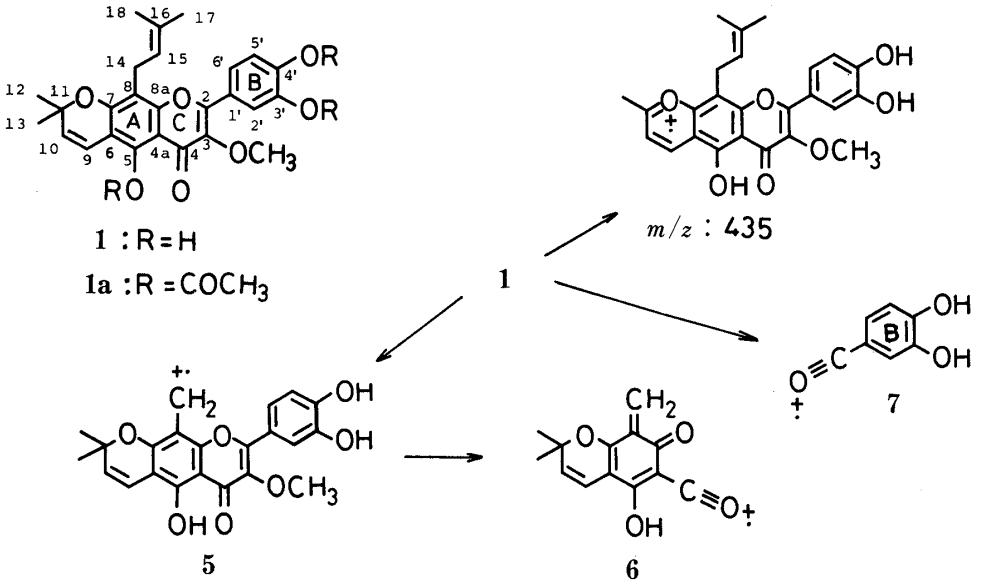


Chart 1

was suggested by the ^{1}H-NMR spectrum, *i.e.*, ABC-type aromatic proton signals [δ 7.06 (1H, d, J=8 Hz), 7.63 (1H, dd, J=1.5, 8 Hz), 7.78 (1H, d, J=1.5 Hz)] indicated that the B ring of **1** was oxygenated in the 3′ and 4′ positions.[10] The linear structure (**1**) for broussoflavonol A was supported by the changes in the chemical shifts of chromene olefinic protons in its triacetate (**1a**) compared with **1** (Table I). These changes are of the same shift and the same magnitude as those reported for similar compounds.[12] In order to corroborate the structure of **1**, the carbon-13 nuclear magnetic resonance (^{13}C-NMR) of **1** was also measured, and all the carbon atoms were assigned by comparing the spectrum with those of model compounds. In the ^{13}C-NMR spectrum of **1**, the chemical shift values of the carbon atoms of the B ring were similar to those of quercetin, and those of the carbon atoms of the C ring and the methoxyl group were in good agreement with those of the relevant carbon atoms of 3-*O*-methylflavonol derivatives.[13] From these results, it was concluded that the structure of broussoflavonol A is represented by the formula (**1**).

Broussoflavonol B (**2**) was obtained as yellow prisms, mp 178—179 °C, M^+=452,1766, $C_{26}H_{28}O_7$, exhibiting a positive ferric chloride test, magnesium–hydrochloric acid test and

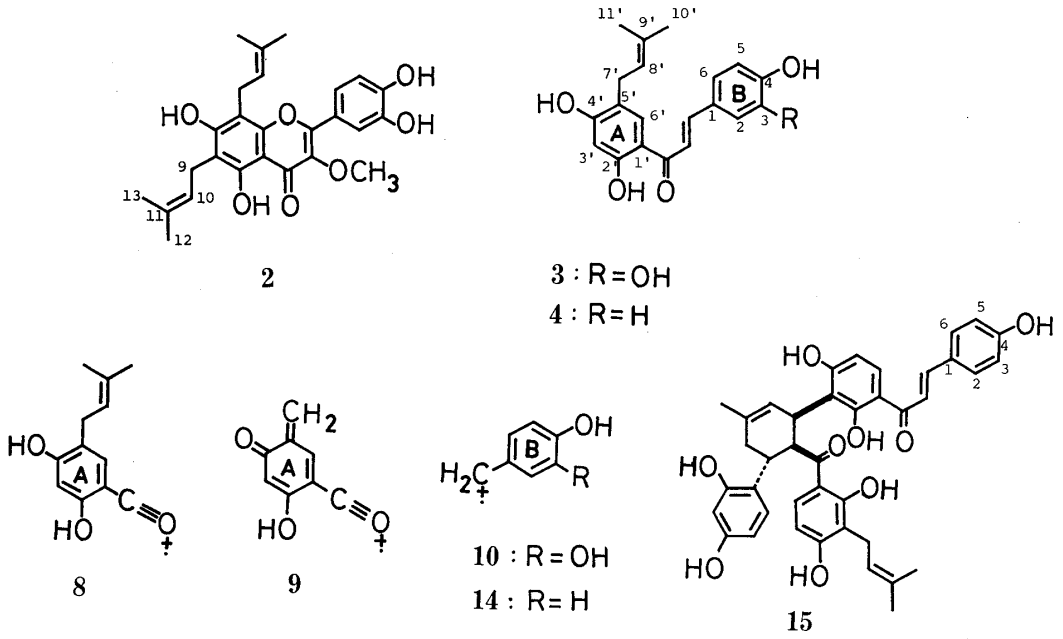


Fig. 1

TABLE I. Chemical Shifts (ppm) for C_9-H and C_{10}-H in **1** and **1a**

Proton	1	1a	Δ
C_9-H	6.70	6.58	+0.12
C_{10}-H	5.77	5.93	−0.16

Measured in acetone-d_6.

sodium molybdate test,[8] but a negative zirconium oxychloride–citric acid test.[9] The UV spectrum of **2** showed absorption maxima at 264 (sh), 279, and 355 nm which shifted to 286, 312 (sh), 377 and 430 (sh) nm in the presence of aluminum chloride, while hypsochromic shifts were observed on adding hydrochloric acid to the aluminum chloride solution as follows: 268 (sh), 287, 310 (sh), 366, 420 (sh) nm.[10] These UV spectra and the results of color reaction tests were similar to those of **1** suggesting that **2** is a 3-*O*-methylflavonol derivative having an *ortho*-dihydroxyl moiety in the structure. The UV spectrum of **2** exhibited a bathochromic shift of band II in the presence of sodium acetate, while that of **1** showed no change on adding sodium acetate. This result suggests that **2** has a hydroxyl group at the 7-psoition.[10] The ^{1}H-NMR spectrum of **2** indicated the presence of two γ,γ-dimethylallyl groups [δ 1.66 (6H, s), 1.78 (6H, s), 3.44 (2H, br d, J=7 Hz), 3.61 (2H, br d, J=7 Hz), 5.23 (2H, m)], a 1,3,4-trisubstituted phenyl moiety [δ 7.01 (1H, d, J=7.5 Hz), 7.61 (1H, dd, J=2 and 7.5 Hz), 7.76 (1H, d, J=2 Hz)], a methoxy group [δ 3.86 (3H, s)], and a hydrogen-bonded hydroxyl group [δ 13.23 (1H, s)]. In the ^{13}C-NMR spectrum of **2**, the chemical shifts of the carbon atoms, except at the C-6 and C-7 positions, were similar to those of the relevant carbon atoms of **1**. From these results, it was concluded that the structure of broussoflavonol B is represented by the formula (**2**).

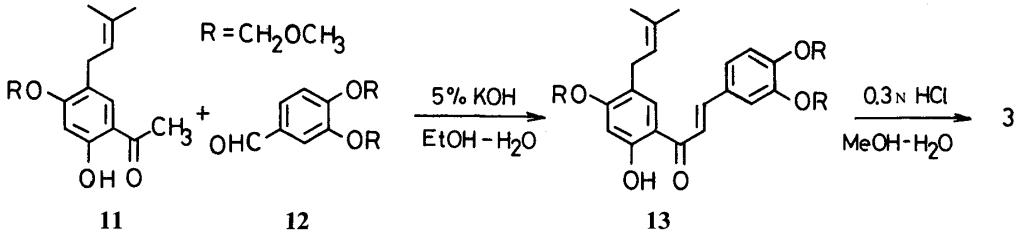
Broussochalcone A (**3**) was obtained as a yellow amorphous powder, M^+=340.1312, $C_{20}H_{20}O_5$, exhibiting a positive ferric chloride test and sodium molybdate test.[8] The IR spectrum of **3** suggested the presence of hydroxyl groups [3400 cm^{-1}], a conjugated carbonyl group [1635 cm^{-1}], and aromatic rings [1610 cm^{-1}]. The UV spectrum of **3** showed absorption maxima at 215, 265, 320 (sh), and 385 nm. The absorption maxima at 265, 320 (sh), and 385 nm shifted in the presence of aluminum chloride to 280, 340 (sh), and 440 nm,

TABLE II. ^{13}C-NMR Chemical Shifts of Broussoflavonols A (**1**) and B (**2**), and Broussochalcones A (**3**) and B (**4**)

Carbon No.	1	1	2	Carbon No.	3	4	15
C-2	152.7	154.3	153.1	C-1	128.3	126.9	127.4
C-3	137.7	139.2	139.0	C-2	116.5	130.8	131.7
C-4	178.4	179.9	179.8	C-3	146.4	116.1	116.7
C-4a	104.4	105.6	106.0	C-4	149.2	160.0	161.0
C-5	153.4	155.1	156.8	C-5	115.8	116.1	116.7
C-6	104.9	106.2	112.0	C-6	123.4	130.8	131.7
C-7	155.9	157.4	160.0	C-1′	114.3	113.6	
C-8	106.9	108.1	107.0	C-2′	163.5	162.5	
C-8a	155.8	156.9	157.7	C-3′	103.5	102.9	
C-1′	120.5	123.2	123.1	C-4′	165.8	164.9	
C-2′	115.8	116.3	116.5	C-5′	121.3	120.6	
C-3′	145.4	146.1	146.2	C-6′	132.2	131.3	
C-4′	148.9	149.3	149.4	C-7′	—[e]	28.5	
C-5′	115.6	116.3	116.5	C-8′	124.0	123.1	
C-6′	121.1	122.0	122.0	C-9′	132.2	131.6	
C-9	115.0	116.3	22.6[a]	C-10′	25.8	25.6	
C-10	128.7	129.1	123.5[b]	C-11′	17.9	17.7	
C-11	77.7	78.7	132.7[c]	C-α	118.5	117.8	
C-12	27.7	28.3	25.8	C-β	145.3	143.9	
C-13	27.7	28.3	18.0[d]	C=O	192.7	191.6	
C-14	21.1	22.1	22.2[a]				
C-15	122.0	123.2	123.1[b]				
C-16	131.1	132.1	132.4[c]				
C-17	25.5	25.9	25.8				
C-18	17.8	18.3	18.2[d]				
OCH_3	59.6	60.2	60.1				
Solvent	DMSO-d_6	Acetone-d_6			Acetone-d_6		

a—*d*) Assignments may be interchanged. *e*) Overlapping with the signals of acetone-d_6.

respectively, while hypsochromic shifts were observed on adding hydrochloric acid to the aluminum chloride solution as follows: 270, 330 (sh), 391 nm. From these UV spectra[10] and the results of the sodium molybdate test,[8] **3** seems to be a chalcone derivative having an *ortho*-dihydroxyl moiety in the structure. The ^{1}H-NMR spectrum of **3** indicated the presence of a γ,γ-dimethylallyl group [δ 1.74 (6H, s), 3.32 (2H, br d, J=7.5 Hz), 5.37 (1H, br t, J=7.5 Hz)], a 1,3,4-trisubstituted phenyl moiety [δ 6.94 (1H, d, J=8 Hz), 7.23 (1H, dd, J=2 and 8 Hz), 7.34 (1H, d, J=2 Hz)], a 1,2,4,5-tetrasubstituted phenyl moiety [δ 6.43 (1H, s), 7.98 (1H, s)], and α and β protons in the chalcone skeleton [δ 7.70 (1H, d, J=15 Hz), 7.78 (1H, d, J=15 Hz)], as well as a hydrogen-bonded hydroxyl group [δ 13.75 (1H, s)]. The MS of **3** showed significant fragments at *m/z* 205 (**8**), 149 (**9**), and 123 (**10**), to supporting the presence of a γ,γ-dimethylallyl group in the A ring along with two hydroxyl groups in the B ring.[11] From these results, the formula (**3**) was suggested for broussochalcone A. The ^{13}C-NMR spectrum was analyzed by comparison with those of model compounds as shown in Table II.[13] To confirm the structure, compound (**3**) was prepared according to the procedure shown in Chart 2. Condensation of 2-hydroxy-4-methoxymethoxy-5-*C*-prenyl acetophenone (**11**) with 3,4-dimethoxymethoxybenzaldehyde (**12**) in alkaline solution gave a chalcone (**13**) which was converted into **3**.[5c,14] The compound (**3**) thus obtained was shown to be identical with broussochalcone A by IR spectral comparison. From these results, the structure of broussochalcone A was determined as formula (**3**).



11 12 13

Chart 2

Broussochalcone B (**4**) was obtained as yellow needles, mp 168—170 °C, $M^+ = 324.1378$, $C_{20}H_{20}O_4$, exhibiting a positive ferric chloride test, but a negative sodium molybdate test.[8] The UV spectrum of **4** showed absorption maxima at 229 (sh), 263 (sh), 297 (sh), 307 (sh), and 375 nm which shifted to 240, 280 (sh), 324 (sh), 338 (sh), 384, and 433 nm in the presence of aluminum chloride, while no hypsochromic shift was observed on adding hydrochloric acid to the aluminum chloride solution. The ^{1}H-NMR spectrum of **4** indicated the presence of a γ,γ-dimethylallyl group [δ 1.72 (6H, s), 3.26 (2H, d, $J=7$ Hz), 5.32 (1H, br t, $J=7$ Hz)], a 1,4-disubstituted phenyl moiety [δ 6.92 (2H, d, $J=8$ Hz), 7.65 (2H, d, $J=8$ Hz)], a 1,2,4,5-tetrasubstituted phenyl moiety [δ 6.40 (1H, s), 7.90 (1H, s)], and α and β protons in the chalcone skeleton [δ 7.68 (1H, d, $J=15$ Hz), 7.80 (1H, d, $J=15$ Hz)], as well as a hydrogen-bonded hydroxyl group [δ 13.49 (1H, s)]. The MS of **4** showed fragment ions at m/z 205 (**8**), 149 (**9**), and 107 (**14**). The ^{13}C-NMR spectrum was analyzed by comparison with those of **3** and kuwanon R (**15**).[15] The chemical shift values of the carbon atoms of the A ring of **4** were similar to those of the corresponding carbon atoms of **3**, and those of the carbon atoms of the B ring were similar to those of the corresponding carbon atoms of **15** (Table II). From these results, it was concluded that the structure of broussochalcone B is represented by the formula (**4**).

Experimental

All melting points are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were measured with tetramethylsilane (TMS) as an internal reference. Chemical shifts are expressed in ppm downfield from TMS, and coupling constants (J) in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, sh = shoulder, infl. = inflection. The following instruments were used: melting points; Mitamura's micromelting point apparatus (hot-stage type), UV spectra; Hitachi 340 UV spectrometer, IR spectra; Hitachi 295 spectrometer, ^{1}H-NMR spectra; JEOL JNM 4H-100 and Hitachi R-900 FT NMR spectrometers, ^{13}C-NMR spectra; Hitachi R-900 FT NMR and JEOL GX-400 FT NMR spectrometers, mass spectra; JEOL JMS 01SG-2 and Hitachi RMU mass spectrometers. For TLC and preparative TLC, Wakogel B-5FM was used, and for column chromatography, Wakogel C-200.

Isolation of Broussolfavonols A (1) and B (2), and Broussochalcones A (3) and B (4)——The dried cortex (3.50 kg) of *Broussonetia papyrifera* (L.) VENT., collcted in the Botanical Gardens, Faculty of Science, University of Tokyo, Japan, in June 1984, was finely cut and extracted with *n*-hexane and then with benzene. Evaporation of the *n*-hexane and the benzene extracts to dryness yielded 51.5 and 47.5 g of residue, respectively. The benzene extract was dissolved in MeOH, and the MeOH extract (28.0 g) was chromatographed on silica gel (340 g) using benzene–$(CH_3)_2CO$ as an eluent, each fraction being monitored by TLC. The fraction eluted with benzene containing 3% $(CH_3)_2CO$ was evaporated to give the residue (3.23 g). This residue (3.23 g) was fractionated by preparative TLC (*n*-hexane : $(CH_3)_2CO = 2:1$, *n*-hexane : AcOEt = 3 : 2, *n*-hexane : $Et_2O = 2:3$, benzene : $Et_2O = 4:1$) to give broussoflavonol A (**1**, 4 mg). The same fraction was fractionated by preparative TLC (*n*-hexane : $(CH_3)_2CO = 2:1$, *n*-hexane : AcOEt = 3 : 2, benzene : $Et_2O = 4:1$) to give broussoflavonol B (**2**, 162 mg). The same fraction was also fractionated by preparative TLC (*n*-hexane : $(CH_3)_2CO = 2:1$, *n*-hexane : AcOEt = 3 : 2) to give broussochalcone B (**4**, 39 mg). The fraction eluted with benzene containing 5% $(CH_3)_2CO$ was evaporated to give the residue (1.54 g). This residue (1.54 g) was fractionated by preparative TLC (*n*-hexane : $(CH_3)_2CO = 2:1$; *n*-hexane : $Et_2O = 2:3$; benzene : AcOEt = 2 : 1; benzene: MeOH = 10 : 1) to give broussochalcone A (**3**, 12 mg).

Broussoflavonol A (1)——Compound **1** was obtained as a yellow amorphous powder, $FeCl_3$ test (+), Mg–HCl test (+), Na_2MoO_4 (+), $ZrOCl_2$–citric acid test (−). UV λ_{max}^{EtOH} nm (log ε): 232 (sh 4.31), 285 (sh 4.31), 295 (4.36), 309 (sh 4.18), 360 (4.18); $\lambda_{max}^{EtOH+AlCl_3}$: 232 (sh 4.31), 300 (4.27), 394 (4.09); $\lambda_{max}^{EtOH+AlCl_3+HCl}$: 242 (sh 4.24), 267 (sh 4.05), 298

(4.25), 310 (sh 4.24), 335 (sh 4.11), 380 (4.15); $\lambda_{max}^{EtOH+NaOAc}$: 285 (sh 4.31), 295 (4.35), 363 (4.08), 420 (sh 4.00). IR $\nu_{max}^{KBr}cm^{-1}$: 3350 (br), 3250 (sh), 1650, 1600, 1550. High-resolution MS, Calcd for $C_{26}H_{26}O_7$ (M^+), *m/z* 450.1677. Found: *m/z* 450.1699; Calcd for $C_{25}H_{24}O_7$, *m/z* 435.1442. Found: *m/z* 435.1451; Calcd for $C_{23}H_{19}O_7$, *m/z* 407.1130. Found: *m/z* 407.1175; Çalcd for $C_{22}H_{19}O_7$ (**5**), *m/z* 395.1129. Found: *m/z* 395.1158; Calcd for $C_{13}H_{11}O_4$ (**6**), *m/z* 231.0656. Found: *m/z* 231.0627; Calcd for $C_7H_5O_3$ (**7**), *m/z* 137.0239. Found: *m/z* 137.0270. ^{1}H-NMR ($(CD_3)_2CO$, 100 MHz) δ: 1.47 (6H, s, C_{11}-$CH_3\times2$), 1.66 (3H, s, C_{16}-CH_3), 1.81 (3H, s, C_{16}-CH_3), 3.49 (2H, br d, $J=7$, C_{14}-H×2), 3.88 (3H, s, C_3-OCH_3), 5.22 (1H, t, $J=7$, C_{15}-H), 5.77 (1H, d, $J=10$, C_{10}-H), 6.70 (1H, d, $J=10$, C_9-H), 7.06 (1H, d, $J=8$, $C_{5'}$-H), 7.63 (1H, dd, $J=1.5$ and 8, $C_{6'}$-H), 7.78 (1H, d, $J=1.5$, $C_{2'}$-H), 13.29 (1H, s, C_5-OH). ^{13}C-NMR: Table II.

Broussoflavonol A Triacetate (1a)——Broussolfavonol A (**1**, 15 mg) was acetylated with Ac_2O (0.3 ml) and pyridine (0.1 ml) at room temperature for 6 h. The reaction mixture was treated as usual, and purified by preparative TLC (*n*-hexane : Et_2O = 1 : 1) to give **1a** (3 mg). Compound **1a** was obtained as an amorphous powder, negative to the $FeCl_3$ test. MS *m/z*: 576 (M^+), 534, 519, 477, 449. ^{1}H-NMR ($(CD_3)_2CO$, 90 MHz) δ: 1.49 (6H, s, C_{11}-$CH_3\times2$), 1.67, 1.81 (each 3H, s, C_{16}-CH_3), 2.33 (6H, s, $C_{3'}$-$OCOCH_3$ and $C_{4'}$-$OCOCH_3$), 2.39 (3H, s, $C_{5'}$-$OCOCH_3$), 3.58 (2H, br d, $J=7$, C_{14}-H×2), 3.82 (3H, s, C_3-OCH_3), 5.22 (1H, t, $J=7$, C_{15}-H), 5.93 (1H, d, $J=10$, C_{10}-H), 6.58 (1H, d, $J=10$, C_9-H), 7.43 (1H, d, $J=8.5$, $C_{5'}$-H), 7.94 (1H, d, $J=2.5$, $C_{2'}$-H), 8.01 (1H, dd, $J=2.5$, $C_{6'}$-H).

Broussoflavonol B (2)——Compound **2** was crystallized from C_6H_6–$(CH_3)_2CO$ to give pale yellow prisms (162 mg), mp 178—179 °C, $FeCl_3$ (+), Mg–HCl (+), Na_2MoO_4 (+), $ZrOCl_2$–citric acid (−). UV λ_{max}^{EtOH} nm (log ε): 264 (sh 4.23), 279 (4.25), 355 (4.19); $\lambda_{max}^{EtOH+AlCl_3}$: 286 (4.28), 312 (sh 3.93), 377 (4.10), 430 (4.06); $\lambda_{max}^{EtOH+AlCl_3+HCl}$: 268 (sh 4.14) 287 (4.20), 310 (sh, 4.00), 366 (4.20), 420 (sh 3.86); $\lambda_{max}^{EtOH+NaOAc}$: 279 (4.29), 374 (4.11), 420 (sh 4.02). IR $\nu_{max}^{KBr}cm^{-1}$: 3500, 3450, 3210 (br), 1635, 1605, 1560. High-resolution MS, Calcd for $C_{26}H_{28}O_7$ (M^+), *m/z* 452.1833. Found: *m/z* 452.1776; Calcd for $C_{23}H_{22}O_7$, *m/z* 410.1364. Found: *m/z* 410.1305; Calcd for $C_{23}H_{21}O_7$, *m/z* 409.1286. Found: *m/z* 409.1240; Calcd for $C_{22}H_{21}O_7$, *m/z* 397.1287. Found: *m/z* 397.1232; Calcd for $C_{18}H_{13}O_7$, *m/z* 341.0660. Found: *m/z* 341.0597. ^{1}H-NMR ($(CD_3)_2CO$, 100 MHz) δ: 1.66 (6H, s, C_{11} and C_{16}-CH_3), 1.78 (6H, s, C_{11} and C_{16}-CH_3), 3.44 (2H, br d, $J=7$, C_{14}-H×2), 3.61 (2H, br d, $J=7$, C_9-H×2), 3.86 (3H, s, C_3-OCH_3), 5.23 (2H, m, C_{10} and C_{15}-H), 7.01 (1H, d, $J=7.5$, $C_{5'}$-H), 7.61 (1H, dd, $J=2$ and 7.5, $C_{6'}$-H), 7.76 (1H, d, $J=2$, $C_{2'}$-H), 13.23 (1H, s, C_5-OH). ^{13}C-NMR: Table II.

Broussochalcone A (3)——Compound **3** was obtained as a yellow amorphous powder, $FeCl_3$ (+), Mg–HCl (−), Na_2MoO_4 (+). UV λ_{max}^{EtOH} nm (log ε): 215 (4.52), 265 (3.97), 320 (sh 3.92), 385 (4.24); $\lambda_{max}^{EtOH+AlCl_3}$: 215 (4.51), 280 (3.85), 340 (sh 3.89), 390 (infl. 4.10), 440 (4.21); $\lambda_{max}^{EtOH+AlCl_3+HCl}$: 215 (4.51), 270 (3,87), 330 (sh 3.92), 391 (4.23), 420 (sh 4.20). IR $\nu_{max}^{KBr}cm^{-1}$: 3400, 1635, 1610. High-resolution MS, Calcd for $C_{20}H_{20}O_5$ (M^+), *m/z* 340.1312. Found: *m/z* 340.1312; Calcd for $C_{12}H_{13}O_3$ (**8**), *m/z* 205.0865. Found: *m/z* 205.0895; Calcd for $C_8H_5O_3$ (**9**), *m/z* 149.0238. Found: *m/z* 149.0202. EI-MS *m/z*: 340 (M^+), 205 (**8**), 187, 163, 161, 149 (**9**), 136, 123 (**10**). ^{1}H-NMR ($(CD_3)_2CO$, 100 MHz) δ: 1.74 (6H, s, $C_{9'}$-$CH_3\times2$), 3.32 (2H, br d, $J=7.5$, $C_{7'}$-H×2), 5.37 (1H, br t, $J=7.5$, $C_{8'}$-H), 6.43 (1H, s, $C_{3'}$-H), 6.94 (1H, d, $J=8$, C_5-H), 7.23 (1H, dd, $J=2$ and 8, C_6-H), 7.34 (1H, d, $J=2$, C_2-H), 7.70 (1H, d, $J=15$, C_α-H), 7.78 (1H, d, $J=15$, C_β-H), 7.98 (1H, s, $C_{6'}$-H), 13.75 (1H, s, $C_{2'}$-OH). ^{13}C-NMR: Table II.

Broussochalcone B (4)——Compound **4** was crystallized from $CHCl_3$ to give yellow needles, mp 168—170 °C, $FeCl_3$ (+), Mg–HCl (−), Na_2MoO_4 (−). UV λ_{max}^{EtOH} nm (log ε): 229 (sh 4.26), 263 (sh 3.99), 297 (sh 4.00), 307 (sh 4.11), 375 (4.52); $\lambda_{max}^{EtOH+AlCl_3}$: 240 (4.21), 280 (sh 3.83), 324 (sh 4.07), 338 (sh 4.19), 384 (4.45), 433 (4.53). IR $\nu_{max}^{KBr}cm^{-1}$: 3350 (br), 1640, 1610, 1550, 1510. High-resolution MS, Calcd for $C_{20}H_{20}O_4$ (M^+), *m/z* 324.1365. Found: *m/z* 324.1378. EI-MS *m/z*: 324 (M^+), 205, 149, 107. ^{1}H-NMR ($(CD_3)_2CO$, 90 MHz) δ: 1.72 (6H, s, $C_{9'}$-$CH_3\times2$), 3.26 (2H, d, $J=7$, $C_{7'}$-H×2), 5.32 (1H, br t, $J=7$, $C_{8'}$-H), 6.40 (1H, s, $C_{3'}$-H), 6.92 (2H, d, $J=8$, C_3 and C_5-H), 7.65 (2H, d, $J=8$, C_2 and C_6-H), 7.68 (1H, d, $J=15$, C_α-H), 7.80 (1H, d, $J=15$, C_β-H), 7.90 (1H, s, $C_{6'}$-H), 13.49 (1H, s, C_2-OH). ^{13}C-NMR: Table II.

2-Hydroxy-4-methoxymethoxy-5-*C*-prenylacetophenone (11)——A mixture of 5-*C*-prenyl-resoacetophenone (500 mg),[14] methoxymethyl chloride (0.5 ml), and K_2CO_3 (5 g) in dry $(CH_3)_2CO$ (25 ml) was refluxed for 15 min, then H_2O (50 ml) was added and the mixture was allowed to stand for 30 min. The solvent was evaporated off under reduced pressure and the product was purified by preparative TLC (*n*-hexane: $(CH_3)_2CO$ = 4 : 1) to give an oily substance (**11**, 520 mg). MS *m/z*: 264 (M^+), 219, 165. UV λ_{max}^{EtOH} nm (log ε): 230 (4.10), 273 (4.04), 326 (3.69); $\lambda_{max}^{EtOH+AlCl_3}$: 229 (4.07), 236 (sh 4.04), 274 (3.94), 296 (3.79), 327 (3.56), 375 (sh 3.10). IR $\nu_{max}^{KBr}cm^{-1}$: 1640 (sh), 1635, 1620 (sh), 1580. High-resolution MS, Calcd for $C_{15}H_{20}O_4$, *m/z* 264.1364. Found: *m/z* 264.1368. ^{1}H-NMR ($(CD_3)_2CO$, 90 MHz) δ: 1.72 (6H, s), 2.41 (3H, s), 3.25 (2H, br d, $J=7.5$), 3.38 (3H, s), 5.15 (2H, s), 5.29 (1H, t, $J=7.5$), 6.53 (1H, s), 7.44 (1H, s), 12.51 (1H, s).

3,4-Dimethoxymethoxybenzaldehyde (12)——A mixture of protocatechualdehyde (500 mg), methoxymethyl chloride (0.5 ml), and K_2CO_3 (5 g) in dry $(CH_3)_2CO$ (25 ml) was refluxed for 15 min, then H_2O was added. The mixture was allowed to stand for 30 min and evaporated under reduced pressure. The product was purified by preparative TLC (*n*-hexane : $(CH_3)_2CO$ = 4 : 1) to give an oily substance (**12**, 370 mg). MS *m/z*: 226 (M^+), 150. UV λ_{max}^{EtOH} nm (log ε): 225 (4.11), 270 (3.99), 305 (sh 3.70); $\lambda_{max}^{EtOH+AlCl_3}$: 225 (3.98), 270 (3.71), 305 (sh 3.40). IR $\nu_{max}^{KBr}cm^{-1}$: 1700 (sh), 1680, 1590, 1580, 1500. ^{1}H-NMR ($(CD_3)_2CO$, 100 MHz) δ: 3.29 (6H, s), 5.07, 5.11 (each 2H, s), 7.08 (1H, d, $J=8$), 7.19 (1H, dd, $J=2$ and 8), 7.44 (1H, d, $J=2$), 9.64 (1H, s).

Condensation of 11 and 12 (Formation of 13)[14]——A mixture of **11** (420 mg) and **12** (180 mg) dissolved in EtOH (2 ml) was treated with 25% KOH solution (0.5 ml). The mixture was allowed to stand overnight at room temperature, then the solution was acidified to pH 2 with dil. HCl and extracted with Et_2O. The Et_2O layer was treated as usual and the solvent was evaporated off. The product was purified by preparative TLC (*n*-hexane : $(CH_3)_2CO$ = 4 : 1) to give **13** (91 mg) as yellow prisms, mp 65—68 °C. *Anal.* Calcd for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.12; H, 6.90. MS *m/z*: 472 (M^+), 249, 235, 217, 207, 203, 175, 148. UV λ_{max}^{EtOH} nm (log ε): 240 (sh 3.98), 256 (3.94), 305 (sh 4.03), 365 (4.35); $\lambda_{max}^{EtOH+AlCl_3}$ 243 (sh 3.98), 267 (sh 3.79), 314 (sh 4.01), 374 (4.30), 440 (sh 4.09). IR ν_{max}^{KBr} cm^{-1}: 1640, 1605, 1580 (sh), 1570. ^{1}H-NMR ($(CD_3)_2CO$, 100 MHz) δ: 1.73, 1.74 (each 3H, s), 3.27 (2H, br d, *J* = 7), 3.44, 3.45, 3.49 (each 3H, s), 5.10—5.36 (1H, m), 5.23 (4H, s), 5.29 (2H, s), 6.58 (1H, s), 7.13 (1H, d, *J* = 8), 7.39 (1H, dd, *J* = 2 and 8), 7.53 (1H, d, *J* = 2), 7.76 (2H, s), 7.91 (1H, s), 13.22 (1H, s, OH).

Conversion of 13 to 3[5c]——A mixture of **13** (50 mg), MeOH (2.5 ml), and 3 N HCl (0.5 ml) was refluxed for 20 min and extracted with Et_2O. The Et_2O layer was treated as usual and evaporated. The residue was chromatographed on Sephadex LH-20 with MeOH as an eluent to give **3** (14 mg). The compound thus obtained was shown to be identical with broussochalcone A by IR spectral comparison.

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References and Notes

1) This paper forms Part XXVI of "Constituents of the Cultivated Mulberry Tree." Part XXV: T. Fukai, Y. Hano, K. Hirakura, T. Nomura, J. Uzawa, and K. Fukushima, *Chem. Pharm. Bull.*, **33**, 3195 (1985).
2) *a*) T. Nomura, *Kagaku No Ryoiki*, **36**, 596 (1982) and references cited therein; *b*) T. Nomura and T. Fukai, *Heterocycles*, **15**, 1531 (1981); *c*) T. Nomura, Abstracts of Papers, The 20th Symposium on Phytochemistry, Tokyo, January 1984, p. 1 and references cited therein.
3) *a*) Y. Hano and T. Nomura, *Heterocycles*, **20**, 1071 (1983) and references cited therein; *b*) Y. Hano, M. Itoh, N. Koyama, and T. Nomura, *ibid.*, **22**, 1791 (1984); *c*) Y. Hano, T. Fukai, H. Kohno, K. Hirakura, T. Nomura, and J. Uzawa, *ibid.*, **22**, 2729 (1984).
4) Y. Zhen-ying, *Chinese J. Pharmaceutical Analysis*, **1**, 94 (1981).
5) *a*) T. Fujimoto, Y. Hano, and T. Nomura, *Planta Med.*, **50**, 218 (1984); *b*) T. Fujimoto, Y. Hano, T. Nomura, and J. Uzawa, *ibid.*, **50**, 161 (1984); *c*) T. Fujimoto and T. Nomura, *Heterocycles*, **22**, 997 (1984).
6) *a*) "Zhong Yao Do Ci Dian," Vol. 2, ed. by Jiang Su New Medical, Shanghai, 1977, p. 1502; *b*) K. Akamatsu, "Wakanyaku," Ishiyaku Shuppan, Tokyo, 1970, p. 511.
7) *a*) M. Takasugi, M. Anetai, T. Masamune, A. Shirata, and K. Takahashi, *Chem. Lett.*, **1980**, 339; *b*) M. Takasugi, Y. Kumagai, S. Nagao, T. Masamune, A. Shirata, and K. Takahashi, *ibid.*, **1980**, 1459; *c*) M. Takasugi, N. Niino, S. Nagao, M. Anetai, T. Masamune, A. Shirata, and K. Takahashi, *ibid.*, **1984**, 689; *d*) M. Takasugi, N. Niino, M. Anetai, T. Masamune, A. Shirata, and K. Takahashi, *ibid.*, **1984**, 693.
8) K. Takeda and K. Hayashi, "Shyokubutsu Shikiso," ed. by K. Hayashi, Yokendo, Tokyo, 1980, p. 179.
9) T. Okamoto and T. Murakami, "Tennenbutsu Kagaku," Hirokawa Shoten, Tokyo, 1973, p. 249.
10) T. J. Mabry, K. R. Markham, and M. B. Thomas, "The Spectrometric Identification of Flavonoids," Springer–Verlag, Berlin, 1970.
11) T. J. Mabry and K. R. Markham, "The Flavonoids," Part 1, ed. by J. B. Harborne, T. J. Mabry, and H. Mabry, Academic Press Inc., New York, 1975, pp. 79—126.
12) A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, *Tetrahedron Lett.*, **1967**, 4201.
13) K. R. Markham and V. M. Chari, "The Flavonoids: Advances in Research," ed. by J. B. Harborne and T. J. Mabry, Chapman and Hall, London, 1982, pp. 19—134.
14) K. Kyogoku, K. Hatayama, S. Yokomori, M. Shio, and M. Komatsu, *Chem. Pharm. Bull.*, **21**, 1192 (1973).
15) S. Ueda, J. Matsumoto, and T. Nomura, *Chem. Pharm. Bull.*, **32**, 350 (1984).