Four New Compounds, Ficusal, Ficusesquilignan A, B, and Ficusolide Diacetate from the Heartwood of *Ficus microcarpa*

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Three new lignans, ficusal (1) and ficusesquilignans A (2), B (3) and one new γ-lactone, ficusolide diacetate (4), were isolated from the wood of *Ficus microcarpa* L.f. Their structures were determined by spectral evidence.

Key words *Ficus microcarpa*; Moraceace; ficusal; ficusesquilignan A; ficusesquilignan B; ficusolide diacetate

Ficus microcarpa L.f. (Moraceace) is a popular ornamental plant in Taiwan. Previous chemical studies on this plant, the previous one has been reported on its leaves,[1] in which six terpenoids were observed. The strong vitality of the plant, as well as its antiplatelet activity, prompted us to study the chemical components. We early investigated chemical components of the bark and found two new isoflavones together with twenty-eight components,[2,3] three new compounds from the heartwood,[4,5] and five new triterpenes from the aerial roots.[6] Further chemical studies on the heartwood of the plant were undertaken in our laboratory.

The methanol extract of the heartwood of *F. microcarpa* was concentrated to give a residue which was suspended with water. The suspended aqueous solution was partitioned with *n*-hexane, ethyl acetate, and *n*-BuOH successively. The detailed purification of the ethyl acetate extract by Si gel and HPLC resulted in three new lignans, ficusal (**1**), ficusesquilignans A (**2**) and B (**3**), and one new lactone, ficusolide diacetate (**4**). In this paper, we report the structure of these new compounds.

Ficusal (**1**) was isolated as an oil. It showed positive optical activity and a molecular formula of $C_{18}H_{18}O_6$ by high-resolution mass (HR-MS) spectroscopy. Its IR spectrum revealed the presence of hydroxyl group (3442 cm^{-1}), a conjugated carbonyl group (1679 cm^{-1}) and an aromatic nucleus (1607, 1517 cm^{-1}). The λ_{max} at 235 and 284 nm in its UV spectrum can be assigned to the aromatic–carbonyl conjugated system with two oxygenated substituents.[7] The existence of 18 carbons with 11 directly attached protons was confirmed from ^{13}C-NMR and distortionless enhancement by polarization transfer (DEPT) experiments, and NMR data indicated the presence of a conjugated aldehyde group [δ_C 190.9; δ_H 9.83 (s)]. The chemical shifts (C-1 to C-9, C-2′ to C-6′) in the ^{13}C-NMR spectrum of **1** showed similarities to those of balanophonin (**5**).[8] The ^{1}H-NMR signals due to a methine at δ 5.69 (d, J=6.8 Hz, H-7), a methylene at δ 3.90—3.94 (2H, m, H-9, overlapped with methoxyl signals), and a methine at δ 3.68 (m, H-8), whose chemical shifts were similar to a dehydrodiconiferyl alcohol-type lignan.[8] The stereochemistry between hydroxymethyl and aryl groups was suggested to be *trans*, by the absence of the nuclear Overhauser effect (NOE) correlation between H-8 and H-7. An ABX system [δ_H 6.82 (1H, d, J=8.2 Hz, H-5), 6.88 (1H, dd, J=8.2, 2.4 Hz, H-6), 7.05 (1H, d, J=2.4 Hz, H-2)] was assigned to phenyl protons, and H-7 (δ_H 5.69) exhibited nuclear Overhauser enhancement and exchange spectroscopy (NOESY) correlations with H-2 and H-6. Meanwhile, the H-2 signal has a NOESY correlation with a phenolic methyl group at δ 3.81. A pair of phenyl proton signals with *meta*-coupling (J=1.2 Hz) occurring at δ_H 7.42 (H-6′) and 7.52 (H-2′) showed NOESY correlations with a formyl proton [δ_H 9.83 (1H, s, H-7′)]. All of these data of **1** were similar to those of the balanophonin (**5**) except for an aldehyde group which replaced a propenal group. The assignment was also supported by heteronuclear multiple-quantum coherence (HMQC) and heteronuclear multiple-bond correlation (HMBC) experiments. Accordingly, **1** is 5-formyl-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxy-*trans*-dihydrobenzofuran. The configuration of **1** was shown to be 7*R* and 8*S* due to the optical rotation ($[\alpha]_D$ +3.0°).[9,10]

The composition of ficusesquilignan A (**2**), was determined to be $C_{31}H_{36}O_{11}$ by HR-FAB-MS. The IR spectrum showed hydroxyl (3407 cm^{-1}) and benzene ring (1597, 1516 cm^{-1}) absorption bands. Comparison of ^{1}H- and ^{13}C-NMR data of **2** with those of the known buddlenol C (**6**)[11] suggested that **2** possesses the same skeletal structure (furofuran and 1-arylglycerol ether linkage) but lacks one phenolic methyl group. The electron impact (EI)-MS (20 eV) of **2** exhibited major fragment peaks at *m/z* 414, 388, 181, 180, 167, 151 and 137. The peaks at *m/z* 137 and 151 are likely to arise from a coniferyl residue and those at *m/z* 167 and 181 from a syringyl (4-OH 3,5-di-OMe phenyl) residue attached to the alicyclic part of a lignan.[11,12] Accurate measurement of the *m/z* 180 peak showed that it could be due to coniferyl alcohol ($C_{10}H_{12}O_3$). The mass measurement showed that the peak at *m/z* 388 had a likely composition of $C_{21}H_{24}O_7$, which is the same as furofurans (Chart 1). The ^{1}H-NMR spectrum showed signals indicating the presence of four aromatic methoxyl groups and eight aromatic protons. This further increases the possibility that **2** consists of two coniferyl and one syringyl phenylpropanoid residue. The ^{1}H- and ^{13}C-NMR (Table 1) signals of glyceryl moiety [δ_H 4.98 (H-7‴), 4.11 (H-8‴), 3.89 (H-9‴); δ_C 72.5 (C-7‴), 87.0 (C-8‴), 60.5 (C-9‴)] indicated that the furofuran unit with phenoxy linked at C-2 of 1-aryl glycerol like buddlenol C (**6**)[11] and carinatidiol (**7**).[8] The ^{13}C-NMR of **2** showed signals at δ 54.0, 54.5, 71.5, 72.1, 85.7, 86.0 which are typical of the furofuran carbons in lignans with 2,6-diequatorial diaryl substitution with different aryl groups.[12] It therefore seems likely that compound **2** consists of a furofuran ring with aromatic attachments, one of which has a coniferylglycerol residue attached to it *via* an ether bridge. Both the ^{1}H- and the ^{13}C-NMR spectra of **2** showed peaks which were similar to those given by syringaresinol except for the absence of a methoxyl

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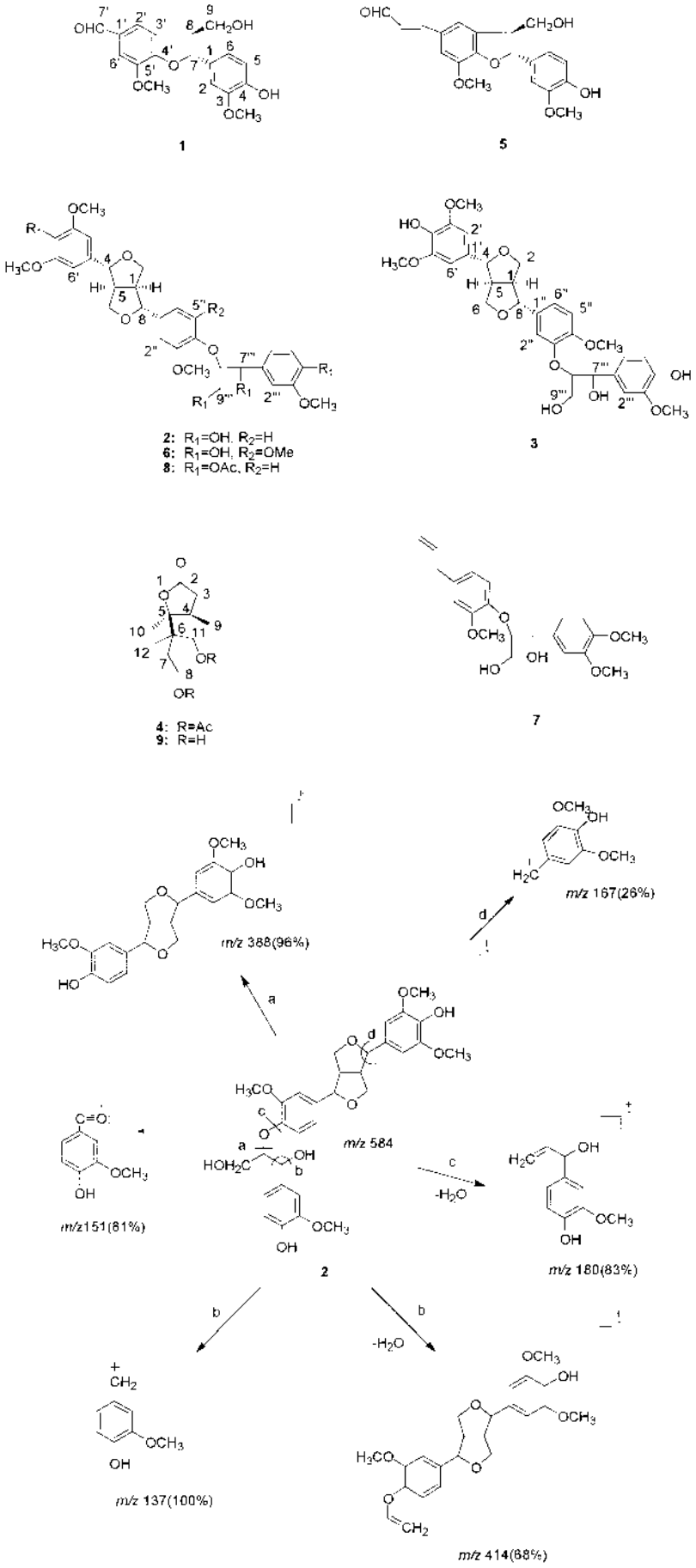
1
5
2: R1=OH, R2=H
6: R1=OH, R2=OMe
8: R1=OAc, R2=H
3
4: R=Ac
9: R=H
7
m/z 388(96%)
m/z 167(26%)
m/z 584
m/z151(81%)
2
m/z 180(83%)
m/z 137(100%)
m/z 414(68%)
a
b
c
d
-H2O

Chart 1

substituent attached to the benzene ring. Thus, the monomethoxyl substituted benzene ring is attached to a coniferylglycerol *via* an ether linkage. Since cleavage upon EI occurs most easily at the ether bridge, it is suggested that the major peaks at *m*/*z* 388 and 180 are formed as shown in Chart 1. The IR spectrum of tetraacetylficusesquilignane A (**8**) (prepared by acetylation) showed strong absorptions at 1763 and 1741 cm^{-1} and the ^{1}H-NMR spectrum showed signals of four acetyl groups at δ 1.96, 2.12, 2.26 and 2.29, along with signals due to four methoxyl groups at δ 3.73, 3.73, 3.78, and 3.82 and eight aromatic protons at δ 6.49—7.00. As mentioned above, the *m*/*z* peaks at 180 and 137 suggest that the aryl attached to the glycerol has two substituents, -OH and -OMe. Two sets of ABX system of phenyl protons [H-2‴, -5‴, -6‴; H-2″, -5″, -6‴] were deduced from their coupling patterns, and the signals at δ 3.82 (3H) and 3.78 (3H) showed NOE correlations with H-2″ and H-2‴, respectively. This result confirmed the location of MeO-3″ and MeO-3‴. H-8‴ also showed an NOE correlation with H-5″ indicating that the coniferylglycerol is attached to C-4″ *via* an ether linkage. The above evidence suggests that ficusesquilignan A has the structure **2**. The coupling constant (J=3.3 Hz) observed between H-7‴ and H-8‴ of the glycerol moiety indicated that it exists as the *erythro* isomer.[10,13]

Ficusesquilignan B (**3**) exhibited a molecular formula of $C_{31}H_{36}O_{11}$, as did **2**, in HR-FAB-MS, and gave an EI-MS (20 eV) spectral fragmentation also similar to that of ficusesquilignan A (**2**): such as *m*/*z* 414, 388, 181, 180, 167, 151 and 137. It also gave similar ^{1}H- and ^{13}C-NMR data (Table 1) to those of ficusesquilignan A (**2**). Therefore, it was shown that **3** has the same skeletal structure as **2**, *i.e.*, a furofuran with two aryl substituents, one of which is attached to an arylglycerol. A difference was seen in the NOESY spectrum where H-8‴ exhibited an NOE correlation with H-2″ [δ 6.86 (1H, d, J=1.6 Hz)] as well as the 4″-OMe having a NOESY correlation with H-5″ [δ 6.89 (1H, d, J=8.4 Hz)]. This indicated that the ether bridge is attached at C-3″, which differs from ficusesquilignan A. Additional proof for structure **3** was obtained using HMBC and HMQC techniques; hence, ficusesquilignan B was presumed to have this structure. The glycerol moiety possessed *threo* stereochemistry as shown by the coupling constant (J=8.7 Hz) observed between H-7″ and H-8‴.[9,13]

The molecular formula of ficusolide diacetate (**4**) was established as $C_{15}H_{24}O_6$ by HR-MS mass spectroscopy. The IR spectrum of **4** exhibited absorption bands at 1774 and 1740 cm^{-1} which suggested the presence of γ-lactone and ester carbonyl groups. The ^{1}H-NMR spectrum of **4** showed two aliphatic acetate (δ_H 2.06, 2.03). Based on the molecular formula $C_{15}H_{24}O_6$ of **4**, its index of hydrogen deficiency (IHD) is four. Ficusolide diacetate (**4**) has $ABXY_3$ system signals, corresponding to H_β-3 [δ 2.28 (dd, J=18.1, 11.2 Hz)], H_α-3 [δ 2.69 (dd, J=18.1, 10.0 Hz)], H-4 [δ 2.84 (ddd, J=11.2, 10.0, 6.8 Hz)], and H_3-9 [δ 1.19 (d, J=6.8 Hz)]. With irradiation at δ 2.84, the signals at δ 2.28, 2.69 and 1.19 collapsed to d, d, and s, respectively. The carbonyl carbon at δ 175.0 showed an HMBC correlation with H-3, so that the C-3–C-4–C-9 moiety was connected to a carbonyl. The moiety (C-4–C-5–C-6) was connected to two singlet methyl groups [δ 1.03 (H_3-12), 1.02 (H_3-10)], an acetoxymethyl [δ 68.7; δ 3.97, 4.00 (1H each, d, J=11.2 Hz), and an acetoxyethyl [δ 29.9, 60.6; δ 2.10, 2.23 (1H each, dt, J=11.6, 6.8 Hz, H-7), 4.13, 4.21 (1H each, dt, J=10.2, 6.8 Hz, H-8)]. Six methylene protons in the acetoxymethyl and acetoxyethyl groups are all nonequivalent as well as expressing HMBC correlations with a quaternary C at δ 42.5. It is concluded that these two groups are linked to an asymmetric C-6 (δ 42.5). Three methyl groups protons are also correlated to C-5 (δ 91.2) in the HMBC spectrum. The signal at δ 1.03 was assigned as H-12 owing to its correlation to C-11 in the HMBC spectrum. Compound **4** was hydrolyzed with 0.5 M sodium hydroxide to afford a product that was identical to ficusolide (**9**)[5] by comparing the ^{1}H- and ^{13}C-NMR spectra. Its relative stereochemistry was confirmed by the NOESY technique. According to the above evidence, the structure of ficusolide diacetate is assigned as **4**.

Table 1. ^{13}C-NMR Data for **2** and **3** ($CDCl_3$, 100 MHz)

C	**2**	**3**
1	54.0 (d)	54.5 (d)
2	71.5 (t)	72.1 (t)
3	—	—
4	86.0 (d)	85.7 (d)
5	54.5 (d)	54.0 (d)
6	72.1 (t)	71.5 (t)
7	—	—
8	85.7 (d)	85.9 (d)
1′	131.2 (s)	132.6 (s)
2′	102.8 (d)	102.7 (d)
3′	153.4 (s)	153.1 (s)
4′	134.2 (s)	134.6 (s)
5′	153.4 (s)	153.1 (s)
6′	102.8 (d)	102.7 (d)
1″	137.8 (s)	137.9 (s)
2″	118.7 (d)	114.3 (d)
3″	146.6 (s)	145.3 (s)
4″	144.8 (s)	146.4 (s)
5″	108.3 (d)	108.6 (d)
6″	114.1 (d)	118.9 (d)
1‴	132.7 (s)	131.9 (s)
2‴	108.6 (d)	109.8 (d)
3‴	146.7 (s)	146.7 (s)
4‴	145.3 (s)	145.4 (s)
5‴	114.3 (d)	114.2 (d)
6‴	118.9 (d)	120.3 (d)
7‴	72.5 (d)	74.1 (d)
8‴	87.0 (d)	89.1 (d)
9‴	60.5 (t)	60.5 (t)
OMe	56.2 (q)	56.2 (q)
	55.9 (q)	55.9 (q)
	56.2 (q)	56.2 (q)
	55.9 (q)	55.9 (q)

Experimental

General Procedures Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker AM-300 spectrometer. Two dimensional (2D) NMR spectra were run on a Varian Unity 400 spectrometer. EI-MS, HR-MS, and HR-FAB-MS were taken on a Finnigan TSQ-46C, JEOL 5X-10-2A, and JEOL JMS-HX110, respectively, and UV and specific rotations were taken on a Hitachi S-3200 spectrometer and a JASCO DIP-180 digital polarimeter, respectively. Extracts were chromatographed on silica gel (Merck 3374, 70—230 mesh) and purified on a semi-preparative normal-phase HPLC column (250×10 mm, 7 μm, LiChrosorb Si 60).

Plant Material The heartwood of *Ficus microcarpa* L.f. was collected

on the campus of the National Taiwan University and was identified by Prof. Shao-Shun Ying, Department of Forestry, National Taiwan University, and a voucher specimen has been deposited at the Herbarium of the Department of Botany, National Taiwan University, Taipei, Taiwan.

Extraction and Isolation The heartwood of *F. microcarpa* was crushed to give 7.0 kg (air-dried) of raw material, which was extracted with MeOH (60 l) three times (7 d each time) at room temperature. The combined extracts were evaporated *in vacuo* to give a black residue (58.8 g) that was suspended in water (500 ml). Then, the aqueous solution was partitioned with hexane (500 ml×3), EtOAc (500 ml×4), and *n*-BuOH (500 ml×3), successively. The EtOAc extract (13.3 g) was chromatographed by Si gel column chromatography (hexane–EtOAc and EtOAc–MeOH solvent system). Crude compounds **2**, **3** and **4** were eluted by hexane–EtOAc (1 : 4), and crude **1** eluted by hexane–EtOAc (2 : 5). Further purification by HPLC gave **1** (2.5 mg), **2** (2.0 mg), **3** (2.6 mg), and **4** (2.5 mg) using hexane–EtOAc–iso-PrOH (1 : 1 : 0.2), acetone–CH_2Cl_2–iso-PrOH (1 : 3 : 0.2), acetone–CH_2Cl_2–iso-PrOH (1 : 3 : 0.2), and hexane–EtOAc–CH_2Cl_2–iso-PrOH (5 : 1 : 2 : 0.2), respectively. Compound **2** (2.0 mg) was acetylated with Ac_2O and pyridine in the usual way and purified by HPLC using acetone–CH_2Cl_2–iso-PrOH (1 : 10 : 0.2) to give tetraacetate (**8**) (1.9 mg).

Ficusal (**1**): Pale yellow oil. $[\alpha]_D^{25}=+3.0°$ (c=0.18, $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 235 (4.60), 284 (4.15). IR ν_{max}^{KBr} cm^{-1}: 3442 (OH), 1679 (C=O, conjugated), 1607, 1517 (benzene ring), 1321, 1130. ^{1}H-NMR (acetone-d_6, 400 MHz), see text. ^{13}C-NMR (acetone-d_6, 100 MHz) δ: 190.9 (s, C-7′), 154.8 (s, C-4′), 148.4 (s, C-4), 147.6 (s, C-3), 145.8 (s, C-5′), 133.3 (s, C-1), 132.3 (s, C-1′), 131.1 (s, C-3′), 121.4 (d, C-2′), 119.8 (d, C-6), 115.7 (d, C-5), 113.3 (d, C-6′), 110.6 (d, C-2), 89.8 (d, C-7), 64.1 (t, C-9), 56.3, 56.2 (3H each, s, OMe), 53.8 (d, C-8). EI-MS (70 eV) *m/z* (rel. int. %): 330 (M^+, 88), 317 (45), 312 (100), 300 (57), 297 (34), 280 (34), 267 (40). HR-EI-MS *m/z*: 330.1098 (Calcd for $C_{18}H_{18}O_6$: 330.1103).

Ficusesquilignan A (**2**): Pale yellow oil. $[\alpha]_D^{27}=-11.1°$ (c=0.17, $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 235 (3.87), 280 (3.50). IR ν_{max}^{KBr} cm^{-1}: 3407 (OH), 1597, 1516 (benzene ring, C=C), 1453, 1276, 1240, 1122, 1035. ^{1}H-NMR ($CDCl_3$, 300 MHz), see text. ^{13}C-NMR, see Table 1. FAB-MS *m/z*: 584 (M^+). EI-MS (20 eV) *m/z* (rel. int. %): 414 ($M^+-C_8H_{10}O_4$, 68), 388 (96), 357 (6), 193 (29), 181 (49), 180 (83), 167 (26), 151 (81), 137 (100). HR-FAB-MS *m/z*: 584.2264 (Calcd for $C_{31}H_{36}O_{11}$: 584.2258).

Tetraacetylficusesquilignan A (**8**) Prepared by Acetylation of **2**: Pale yellow oil. $[\alpha]_D^{27}=-10.3°$ (c=0.20, $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 225 (sh, 3.85), 272 (3.37). IR ν_{max}^{KBr} cm^{-1}: 1763, 1741 (ester, C=O), 1593, 1509 (benzene ring, C=C), 1464, 1220, 1198, 1125, 1046. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.00 (1H, d, J=9.2 Hz, H-5‴), 6.98 (1H, d, J=2.0 Hz, H-2″), 6.96 (1H, d, J=1.0 Hz, H-2‴), 6.94 (1H, dd, J=9.2, 1.0 Hz, H-6‴), 6.90 (1H, d, J=8.0 Hz, H-5″), 6.87 (1H, dd, J=8.0, 2.0 Hz, H-6″), 6.49 (2H, s, H-2′, 6′), 6.06 (1H, d, J=3.2 Hz, H-7‴), 4.79 (1H, d, J=5.2 Hz, H-8), 4.69 (1H, d, J=6.4 Hz, H-4), 4.59 (1H, m, H-8‴), 4.46 (1H, dd, J=11.4, 5.4 Hz, H_a-9‴), 4.27 (1H, dd, J=8.8, 7.5 Hz, H_α-6), 4.25 (1H, dd, J=11.4, 2.4 Hz, H_b-9‴), 4.24 (1H, dd, J=8.8, 7.3 Hz, H_α-2), 3.90 (2H, dd, J=8.8, 6.8 Hz, H_β-2, H_β-6), 3.82, 3.78, 3.73, 3.73 (3H each, MeO-3″, 3‴, 3′, 5′), 3.09 (1H, m, H-1), 3.04 (1H, m, H-5), 2.29, 2.26, 2.12, 1.96 (3H each, OAc). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 170.7, 169.4, 169.0, 168.8 (s, $\underline{C}OCH_3$), 153.4 (s, C-3′, 5′), 151.3 (s, C-4‴), 150.9 (s, C-3″), 140.2 (s, C-1″), 139.6 (s, C-3‴), 139.3 (s, C-4″), 137.3 (s, C-1′), 136.2 (s, C-1‴), 135.1 (s, C-4′), 122.8 (d, C-5″), 122.4 (d, C-5‴), 119.4 (d, C-6‴), 117.9 (d, C-6″), 111.8 (d, C-2‴), 110.1 (d, C-2″), 103.0 (d, C-2′, 6′), 85.9 (d, C-4), 85.5 (d, C-8), 80.8 (d, C-8‴), 74.1 (d, C-7‴), 72.1 (t, C-6), 71.9 (t, C-2), 54.4 (d, C-1, 5), 62.7 (t, C-9‴), 56.1, 56.1, 56.0, 56.0 (q, CH_3O-3′, 5′, 3″, 3″), 21.0, 20.7, 20.7, 20.6 (q, CH_3CO). FAB-MS *m/z*: 752 (M^+). HR-FAB-MS *m/z*: 752.2686 (Calcd for $C_{39}H_{44}O_{15}$: 752.2680).

Ficusesquilignan B (**3**): Pale yellow oil. $[\alpha]_D^{27}=-8.0°$ (c=0.24, $CHCl_3$); UV λ_{max}^{MeOH} nm (log ε): 240 (3.86), 279 (3.47). IR ν_{max}^{KBr} cm^{-1}: 3436 (OH), 1592, 1516 (benzene ring, C=C), 1462, 1273, 1233, 1124, 1033. ^{1}H-NMR ($CDCl_3$, 300 MHz), see text. ^{13}C-NMR, see Table 1. FAB-MS *m/z*: 584 (M^+). EI-MS (20 eV) *m/z* (rel. int. %): 414 ($M^+-C_8H_{10}O_4$, 30), 388 (80), 280 (26), 208 (29), 181 (25), 180 (20), 167 (8), 151 (32), 137 (25), 118 (50), 83 (100). HR-FAB-MS *m/z*: 584.2252 (Calcd for $C_{31}H_{36}O_{11}$: 584.2258).

Ficusolide Diacetate (**4**): Amorphous. $[\alpha]_D^{25}=-1.8°$ (c=0.23, $CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 1774 (C=O), 1740 (C=O), 1421, 1369, 1234, 1040. ^{1}H-NMR ($CDCl_3$, 400 MHz), see text. ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 175.0 (s, C-2), 170.8 (s, 2×$CH_3\underline{C}O$), 91.2 (s, C-5), 68.7 (t, C-11), 60.6 (t, C-8), 42.5 (s, C-6), 37.2 (t, C-3), 33.4 (d, C-4), 29.9 (t, C-7), 20.9 (q, $\underline{C}H_3CO$), 20.9 (q, $\underline{C}H_3CO$), 20.6 (q, C-10), 20.6 (q, C-12), 16.4 (q, C-9). EI-MS (20 eV) *m/z* (rel. int. %): 300 (M^+, 2), 280 (1), 241 (2), 213 (4), 185 (5), 171 (6), 153 (4), 125 (100), 115 (6). HR-EI-MS *m/z*: 300.1584 (Calcd for $C_{15}H_{24}O_6$: 300.1573).

Hydrolysis of 4 in 0.5 M NaOH Compound **4** (2 mg) was dissolved in 0.5 M NaOH methanolic solution (2 ml) for 2 h under stirring. After removing of methanol, the reaction mixture was extracted with EtOAc (5 ml×3) and purified to afford **9** (1.2 mg, yield 83.3%): Amorphous, $[\alpha]_D^{20}=+2.5°$ (c=0.20, $CHCl_3$). EI-MS (70 eV) *m/z* (rel. int. %): 216 (M^+, 76), 198 (33), 187 (95), 177 (71), 154 (100), 137 (89), 107 (38). HR-EI-MS *m/z*: 216.1358 (Calcd for $C_{11}H_{20}O_4$: 216.1362).

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References

1) Higa M., Yogi S., Hokama K., *Bull. Coll. Sci. Univ. Ryukyus*, **13**, 75—86 (1987).
2) Li Y. C., Kuo Y. H., *J. Nat. Prod.*, **60**, 292—293 (1997).
3) Kuo Y., H. Li Y. C., *J. Chin. Chem. Soc.*, **44**, 321—325 (1997).
4) Li Y. C., Kuo Y. H., *Phytochemistry*, **49**, 2417—2419 (1998).
5) Kuo Y. H., Li Y. C., *Chem. Pharm. Bull.*, **47**, 299—301 (1999).
6) Kuo Y. H., Chiang Y. M., *Chem. Pharm. Bull.*, **47**, 498—500 (1999).
7) Tsai I. L., Su M. J., Duh C. Y., Chen I. S., *Phytochemistry*, **43**, 1261—1263 (1996).
8) Mitsumasa H., Koube T., Ito K., Murata H., *Chem. Pharm. Bull.*, **30**, 1525—1527 (1982).
9) Kawanishi K., Uhara Y., Hashimoto Y., *Phytochemistry*, **22**, 2277—2280 (1983).
10) Kikuchi T., Matsuda S., Kadota S., Tai T., *Chem. Pharm. Bull.*, **33**, 1444—1451 (1985).
11) Duffield A. M., *J. Heterocycl. Chem.*, **4**, 16—21 (1967).
12) Houghton P. J., *Phytochemistry*, **24**, 819—826 (1985).
13) Popoff T., Theander O., *Acta Chem. Scand. Ser. B*, **31**, 329—337 (1977).