Phenolic Compounds from *Tournefortia sarmentosa*

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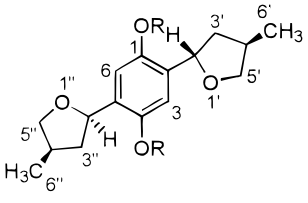
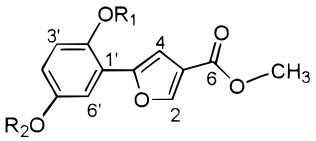
Three new isoprenylbenzenes, tournefolins A (**1**), B (**2**), and C (**3**), and two new 2-ethoxy-4,5-dihydroxybenzoyl compounds, **4** and **5**, together with the known compounds, salicylic acid and allantoin, were isolated from the stems of *Tournefortia sarmentosa*. The structures of new compounds were elucidated as 2-(4*β*-methyltetrahydrofuran-2α-yl)-5-(4*β*-methyltetrahydrofuran-2*β*-yl)-1,4-dihydroxybenzene (**1**), methyl 5-(5-hydroxy-2-methoxyphenyl)-3-furoate (**2**), methyl 5-(2,5-dihydroxyphenyl)-3-furoate (**3**), 2-ethoxy-4,5-dihydroxybenzaldehyde (**4**), and 2-ethoxy-4,5-dihydroxybenzoic acid (**5**), on the basis of spectral and chemical methods. The relative configuration of **1** was determined by single-crystal X-ray crystallography.

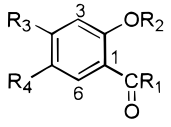
Alkaloids, flavones, triterpenoids, and cinnamates have been found in the genus of *Tournefortia*.[1−4] In Taiwan, *Tournefortia sarmentosa* Lam. (Boraginaceae) has been used as a detoxicant, an antiinflammatory agent, and a circulation promoter to remove blood stasis.[5] Crowley *et al.* have reported the isolation of the pyrrolizidine alkaloid supinine from this plant.[1] As part of our interest in phenolic compounds, a chemical investigation was conducted on the stems of *T. sarmentosa*. In this paper, we report the isolation and structure elucidation of five phenolic compounds (**1**−**5**) along with the two known compounds, salicylic acid and allantoin from the stems of this plant.



1 R=H
6 R=Ac



2 R_1=CH_3, R_2=H
3 R_1=R_2=H
7 R_1= R_2=CH_3



4 R_1=H, R_2=CH_2CH_3, R_3=R_4=OH
5 R_1= R_3=R_4=OH, R_2=CH_2CH_3
8 R_1=H, R_2=CH_2CH_3,
R_3=R_4=OMe
9 R_1=OH, R_2=CH_2CH_3,
R_3=R_4=OAc

Results and Discussion

An 85% EtOH extract from the stems of *T. sarmentosa* was partitioned with ethyl acetate and water. The ethyl acetate-soluble portion was repeatedly separated by Si gel and Sephadex LH-20 column chromatography to yield tournefolins A (**1**), B (**2**), C (**3**), 2-ethoxy-4,5-dihdroxybenzaldehyde (**4**), 2-ethoxy-4,5-dihydroxybenzoic acid (**5**), salicylic acid,[6] and allantoin, with the latter pair identified by direct comparison with authentic samples and published data.[7,8]

Tournefolin A (**1**) was isolated as colorless needles from ethanol, mp 205−207 °C, $[\alpha]^{25}_D$ −40 (*c* 1.0, MeOH). It was assigned the molecular formula $C_{16}H_{20}O_4$ based on its HREIMS and ^{13}C NMR spectral data. The IR spectrum showed hydroxyl (3280 and 1180 cm^{-1}) and aromatic ring (1620 and 1520 cm^{-1}) absorptions. The ^1H NMR spectrum (Table 1) showed two methyl groups [δ 1.00 and 1.02 (3H each, d, J = 6.6 Hz, H-6", 6′)], four methylene protons [δ 1.15 and 2.47 (1H each, m, H-3′′), 1.74 and 1.87 (1H each, ddd, J = 12.6, 9.3, 6.6 Hz, H-3′)], two pairs of oxygenated methylene protons [δ 3.29 and 4.04 (1H each, t, J = 7.5 Hz, H-5"), and δ 3.42 and 3.90 (1H each, t, J = 7.5 Hz, H-5′)], two methine protons [δ 2.26 and 2.32 (1H each, m, H-4", 4′)], two oxygenated methine protons [δ 4.91 and 5.01 (1H each, dd, J = 9.3, 6.6 Hz, H-2", 2′)], two singlet phenyl protons [δ 6.76 and 6.68 (1H each, s, H-3, 6)], and two phenolic protons [δ 8.44 and 8.47 (disappeared after D_2O exchange)]. The proton correlations were confirmed from the ^1H-decoupled and $^1H-^1H$ COSY NMR spectra. The ^{13}C NMR and DEPT spectra of **1** (Table 2) exhibited four quaternary aromatic carbons (δ 128.4, 129.0, 145.9, and 146.0), six tertiary carbons (δ 32.5, 34.0, 74.7, 76.0, 111.9, and 112.3), four secondary carbons (δ 40.4, 42.0, 74.4, and 74.1), and two methyl carbons (δ 17.3 and 17.6). Analysis of the HMBC spectral data (see Experimental Section) led to the identification of the connectivity between the two methyl tetrahydrofuran moieties and the benzene ring. Acetylation of **1** with Ac_2O in pyridine yielded diacetate **6** [ν_{max} (KBr), 1760, 1200 cm^{-1}; δ_H 2.38 (6H, s)]. Two singlet phenyl protons shifted to lower fields at δ 7.31 and 7.36 in the ^1H NMR spectrum of the acetate (**6**), indicating that two phenol substituents are adjacent to the phenyl protons. From above results, the planar structure of **1** was assigned as 2,5-bis(4-methyltetrahydrofuran-2-yl)-1,4-dihydroxybenzene. The different ^1H and ^{13}C NMR signal patterns of the two methyltetrahydrofuryl moieties suggested that **1** is an unsymmetrical compound. The relative stereochemistry at C-2′, 2′′, 4′, and 4′′ in the two tetrahydrofuran rings was established by a NOESY experiment (Figure 1). NOEs were observed only between H-2′ and H-6′ indicating that they were *trans* in one tetrahydrofuryl moiety and *cis* in the

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Table 1. ^{1}H NMR Spectral Data for Compounds (**1**−**5**) (in DMSO-d_6, 300 MHz)[a]

proton(s)	**1**	**2**	**3**	**4**	**5**
2		8.39 s	8.35 s		
3	6.76 s			6.49 s	6.50 s
4		7.08 s	7.08 s		
6	6.68 s			7.03 s	7.22 s
1′				4.00 q	4.02 q
				(6.6)	(6.9)
2′	5.01 dd			1.31 t	1.31 t
	(9.3, 6.6)			(6.6)	(6.9)
3′	1.74 ddd	6.96 d	6.77 d		
	(12.6, 9.3, 6.6)	(9.0)	(8.7)		
	1.87 ddd				
	(12.6, 9.3, 6.6)				
4′	2.32 m	6.73 dd	6.59 dd		
		(9.0, 2.4)	(8.7,2.0)		
5′	3.42 t (7.5),				
	3.90 t (7.5)				
6′	1.02 d (6.6)	7.15 d	7.06 d		
		(2.4)	(2.0)		
2″	4.91 dd (9.3, 6.3)				
3″	1.15 m, 2.47 m				
4″	2.26 m				
5″	3.29 t (7.5),				
	4.04 t (7.5)				
6″	1.00 d (6.6)				
OMe		3.79 s, 3.84 s	3.78 s		
OH	8.44 br s	9.09 br s	8.86 br s	9.43 br s	9.48 br s
	8.47 br s		9.53 br s	9.47 br s	9.53 br s
CHO				10.08 s	

[a] Coupling constants (J) in Hz are indicated in parentheses.

Table 2. ^{13}C NMR Spectral Data for Compounds (**1**−**5**) (in DMSO-d_6, 75 MHz)

carbon	**1**	**2**	**3**	**4**	**5**
1	145.9			118.1	110.1
2	129.0	150.9	146.4	159.5	154.8
3	111.9	120.2	120.1	101.4	102.7
4	146.0	108.5	107.9	155.8	153.2
5	128.4	151.0	151.7	140.7	140.8
6	112.3			113.7	119.1
1′		118.1	116.2	65.8	67.3
2′	74.7	148.4	146.4	15.0	15.0
3′	40.4	113.1	116.0		
4′	34.0	115.8	116.9		
5′	74.1	146.9	149.8		
6′	17.6	111.6	110.8		
2″	76.0				
3″	42.0				
4″	32.5				
5″	74.4				
6″	17.3				
OCH_3		51.5, 55.9	51.4		
C═O		162.8	162.9	189.9	168.9

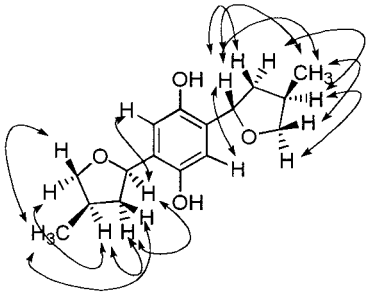

Figure 1. Key NOESY correlations of **1**.

other. X-ray single-crystal analysis (Figure 2) confirmed the relative configuration of compound **1** as proposed above. The asymmetric crystal unit consists of two molecules, one of which is shown in Figure 2.

Compound **2** was obtained as pale yellow needles from methanol. The EIMS displayed a molecular ion peak at *m*/*z*

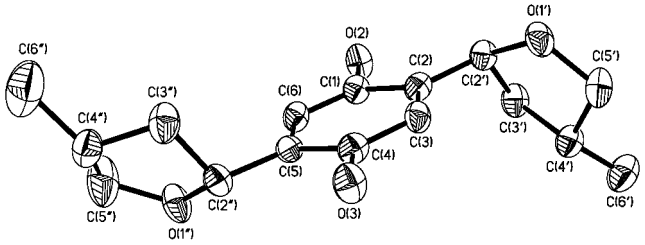

Figure 2. Perspective structure of one of the molecules of tournefolin A (**1**) in the asymmetric crystal unit.

248. Its HREIMS gave *m*/*z* 248.0691 for [M$^+$] corresponding to the molecular formula $C_{13}H_{12}O_5$. The IR spectrum exhibited hydroxyl (3350 and 1200 cm^{-1}), ester (1700 and 1220 cm^{-1}), and aromatic (1615, 1535, and 1510 cm^{-1}) absorptions. The ^{13}C NMR and DEPT spectra of **2** (Table 2) indicated two methoxyl carbons [an alkoxyl methyl (δ 51.5) and a phenolic methyl (δ 55.9)], five aromatic tertiary carbons [δ 108.5, 113.1, 115.8, 111.6, 150.9], five quaternary carbons (δ 118.1, 120.2, 146.9, 148.4, and 151.0), and a conjugated carbonyl (δ 162.8). The ^{1}H NMR spectrum (Table 1) showed two methoxyl groups (δ 3.79 and 3.84), ABX phenyl protons [δ 6.73 (dd, J = 9.0, 2.4 Hz), 6.96 (d, J = 9.0 Hz), 7.15 (d, J = 2.4 Hz)], two singlet furyl protons (δ 7.08 and 8.39), and an exchangeable phenolic proton (δ 9.09). The two low field furyl protons, δ 7.08 and δ 8.39 (corresponding to the signals at δ 108.5 and 150.9), were assigned in turn as the α and β protons, respectively, which were deshielded by an ester carbonyl group. The phenolic methyl (δ 3.84) showed a NOE correlation with the phenyl proton at δ 6.96 in the NOESY spectrum. In addition, long-range correlations were observed in the HMBC spectrum (see Experimental Section) and indicated the structure of **2** to be methyl 5-(5-hydroxy-2-methoxyphenyl)-3-furoate or methyl 5-(3-hydroxy-4-methoxyphenyl)-3-furoate. Methylation of **2** with CH_3I/K_2CO_3 in dry acetone afforded a trimethoxylated product **7** [δ_H 3.84, 3.88 and 3.93 (3H each, s)]. The NOESY spectrum of **7** showed NOE correlations between one of the phenolic methyls (δ 3.84) and two

phenyl protons [δ 7.40 (d, J = 2.0 Hz) and 6.85 (dd, J = 8.4, 2.0 Hz)], and between the other phenolic methyl (δ 3.93) and the phenyl proton at δ 6.91 (d, J = 8.4 Hz). These results permitted the assignment of the structure of **2** as methyl 5-(5-hydroxy-2-methoxyphenyl)-3-furoate.

Compound **3** yielded a molecular formula $C_{12}H_{10}O_5$ from its HREIMS and ^{13}C NMR data. The IR absorption bands at 3250, 1710, 1620, 1525, 1215, 1190, and 1140 cm^{-1} discerned the presence of phenol and ester groups in **3**. The UV and ^1H and ^{13}C NMR data of **3** (Tables 1 and 2) were similar to those of compound **2** except for the presence of two hydroxyl groups (δ_H 8.86 and 9.53, disappeared after D_2O exchange) in place of a hydroxyl and a methoxyl group in **2**. Methylation of **3** as described for **2** afforded **7**. Thus, the structure of compound **3** was established as methyl 5-(2,5-dihydroxyphenyl)-3-furoate.

Compound **4** was obtained as colorless needles from ethanol, mp 140−141 °C. On the basis of its HREIMS and ^{13}C NMR data, the molecular formula $C_9H_{10}O_4$ was established. The presence of hydroxyl, aldehyde, and aromatic groups was revealed by its IR spectrum. Compound **4** with six phenyl carbon signals (Table 2) and two singlet phenyl protons (δ 6.49 and 7.03) (Table 1) could be assigned as a 1,2,4,5-tetrasubstituted benzene. Its ^1H NMR data showed the presence of an aldehyde group at δ 10.08. The UV characteristic absorptions, and the ^1H and ^{13}C NMR (δ_c 189.9) spectra indicated that an aldehyde was conjugated with the benzene ring. Dimethyl ether **8** [δ 3.84 and 3.88] was obtained from **4** by methylation. The NOESY spectrum of **8** showed NOE correlations as follows: the phenyl proton at δ 6.46 had correlations with the methoxyl (δ 3.88) and the methylene protons (δ 4.13), the other phenyl proton at δ 7.29 showed correlations with the methoxyl (δ 3.84) and the aldehyde proton (δ 10.31), and the aldehyde proton also had correlations with the methylene protons. These data established **4** as 2-ethoxy-3,4-dihydroxybenzaldehyde, unambiguously.

The EIMS of **5** gave a molecular ion at m/z 198, consistent with a molecular formula of $C_9H_{10}O_5$. The ^{13}C NMR data of **5** were very similar to those of **4** except that the carbonyl group signal shifted to higher field at δ 168.9. IR absorption bands at 3260−2500 and 1680 cm^{-1} indicated the presence of a carboxylic acid instead of an aldehyde in **5**. One of the phenyl protons *ortho* to the carboxylic acid was shifted downfield to δ 7.22, and methylene protons (δ 4.02) showed a NOE correlation only with the other proton (δ 6.50). Acetylation of **5** yielded diacetate **9** [ν_{max} 3450, 3250−2500, 1735, 1210 cm^{-1}; δ_H 2.28 and 2.29 (3H each, s)]. The presence of a NOE correlation between two acetyl groups indicated two hydroxyl groups occurring in an *ortho* arrangement. Based on the above data, the structure of **5** was elucidated as 2-ethoxy-3,4-dihydroxybenzoic acid.

Experimental Section

General Experimental Procedures. Melting points were determined on Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were recorded on a JASCO DIP-370 polarimeter. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. UV spectra were measured on a Hitachi U-3200 spectrophotometer. NMR spectra were run on Bruker AC-300 and AMX-500 spectrometers. Mass spectra (EIMS and HREIMS) were taken on a JEOL JMS-100 and JEOL SX-102A instrument, respectively. The X-ray crystallographic data were collected on a Siemens Smart CCD diffractometer using graphic-monochromated Mo Kα radiation.

Plant Material. The stems of *T. sarmentosa* Lam. were collected from Kaohsiung Hsien, Taiwan, Republic of China, in August 1997. The plant was identified by comparison with the voucher specimens already deposited at the Herbarium of the Department of Botany, National Taiwan Unversity, Taipei, Taiwan, Republic of China. (No: TAI 175693, collected on April 1, 1979).

Extraction and Isolation. The stems of *T. sarmentosa* (10 kg) was extracted with EtOH (each 50 mL, × 3) at 50 °C. The EtOH extract was evaporated under reduced pressure. The concentrate was taken up in H_2O, and partitioned successively with EtOAc and *n*-BuOH (each 1 L, × 3). The EtOAc-soluble fraction (65 g) was subjected to column chromatography over Si gel using a gradient from chloroform−methanol. The fractions (5−20% methanol) rich in phenolic compounds were passed over a Si gel column and eluted with 5−10% methanol to yield three fractions. Each fraction was further purified using a Sephadex LH-20 column (MeOH), to afford **1** (186 mg), **2** (76 mg), **3** (65 mg), **4** (35 mg), and **5** (25 mg). The fractions from 25% to 50% methanol eluate were further subjected to Sephadex LH-20 column chromatography (MeOH) to yield salicylic acid[6] (1.72 g) and allantoin[7,8] (3.24 g).

Tournefolin A (1): colorless needles (MeOH); mp 205−207 °C; $[\alpha]^{25}_D$ −40 (*c* 1.0, MeOH); IR (KBr) ν_{max} 3280, 1620, 1520, 1415, 1180, 895, 850 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 298 (3.80), 222 (3.87) nm; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HMBC correlations: H-3/C-1, C-2, C-2′, C-4, C-5; H-6/ C-1, C-2, C-2″, C-4, C-5; H-2′/C-1, C-2, C-3, C-3′, C-4′, C-5′; H-3′/C-2, C-2′, C-4′, C-5′, C-6′; H-5′/C-2′, C-3′, C-4′, C-6′; H-6′/C-3′, C-4′, C-5′; H-2″/C-4, C-5, C-6, C-3″, C-4″, C-5″; H-3″/C-2″, C-3″, C-4″, C-5″ C-5; H-5″/ C-2″, C-3″, C-4″, C-6″; H-6″/C-3″, C-4″, C-5″; EIMS m/z 278 [M]$^+$ (100), 247 (18), 229 (26), 217 (9), 201 (10), 187 (7), 175 (18), 161 (10), 85 (17); HREIMS m/z 278.1514 (calcd for $C_{16}H_{22}O_4$, 278.1519).

Tournefolin B (2): pale yellow needles (MeOH); mp 180−182 °C; IR (KBr) ν_{max} 3350, 1700, 1615, 1535, 1510, 1220, 1200, 1150, 1030, 760 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 325 (3.78), 274 (4.00), 266 (4.12), 261 sh (4.09), 228 sh (3.94) nm; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HMBC correlations: H-3′/ C-1′, C-2′, C-4′, C-5′; H-6′/C-1′, C-2′, C-4′, C-5′, C-5; H-2/C-3, C-4, C-5, C-6; OC*H*$_3$/C-6; OC*H*$_3$/C-2′; EIMS m/z 248 [M]$^+$ (100), 233 (31), 217 (10), 205 (18), 173 (20), 101 (13), 83 (11), 65 (10); HREIMS m/z 248.0691 (calcd for $C_{13}H_{12}O_5$, 248.0685).

Tournefolin C (3): pale yellow needles (MeOH); mp 195−196 °C; IR (KBr) ν_{max} 3250, 1710, 1620, 1525, 1215, 1190, 1140, 1030, 1000 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 327 (3.81), 276 (4.02), 265 (4.12), 261 sh (4.09), 227 sh (3.95) nm; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HMBC correlations O*H*-2′/ C-1′, C-2′, C-3′; O*H*-5′/ C-4′, C-5′, C-6′; H-2/ C-3, C-4, C-5, C-6; H-4/C-1, C-3, C-5, C-6; H-3′/C-1′, C-2′, C-4′, C-5′; H-4′/C-2′, C-3′, C-5′, C-6′; H-6′/ C-1′, C-2′, C-3, C-4′, C-5, C-5′; EIMS m/z 234 [M]$^+$ (100), 219 (4), 205 (45), 202 (22), 177 (15), 146 (20), 118 (11), 102 (12), 89 (7), 63 (5); HREIMS m/z 234.0519 (calcd for $C_{12}H_{10}O_5$, 234.0525).

2-Ethoxy-4,5-dihydroxybenzaldehyde (4): colorless needles (MeOH); mp 140−141 °C; IR (KBr) ν_{max} 3420, 3200, 1660, 1620, 1510, 1200, 1140, 1040 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 355 (3.88), 279 (3.78), 240 (3.90), 208 (3.96) nm; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS m/z 182 [M]$^+$ (27), 154 (23), 153 (70), 84 (95), 66 (100); HREIMS m/z 182.0585 (calcd for $C_9H_{10}O_4$, 182.0579).

2-Ethoxy-4,5-dihydroxybenzoic acid (5): colorless needles (MeOH); mp 165−166 °C; IR (KBr) ν_{max} 3420, 3260−2500, 1680, 1630, 1595, 1530, 1220, 1180, 1030 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 356 sh (3.12), 306 (3.78), 254 (3.91) nm; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS m/z 198 [M]$^+$ (37), 154 (43), 152 (100), 126 (85), 69 (17); HREIMS m/z 198.0523 (calcd for $C_9H_{10}O_5$, 198.0528).

Acetylation of 1. A solution of **1** (5 mg) in pyridine (0.5 mL) and Ac_2O (0.5 mL) was left at room temperature overnight. The solvent and excess reagent were removed using a high-vacuum pump. Recrystallization from EtOH gave **6** (4 mg) as colorless needles (MeOH): mp 175−176 °C; IR (KBr) ν_{max} 1760, 1500, 1200, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.13 and 1.15 (3H each, d, J = 6.0 Hz, H-6″, 6′), 1.47 (1H, m, H-3″), 1.93−2.05 (2H, m, H-3′), 2.38 (6H, s, OAc), 2.38−2.58 (3H, m, H-3″, 4″, 4′), 3.50 (1H, t, J = 7.5 Hz, H-5″), 3.60 (1H, t, J = 7.5 Hz, H-5′), 4.12 (1H, t, J = 7.5 Hz, H-5′), 4.25 (1H, t,

J = 7.5 Hz, H-5″), 5.03 (1H, dd, J = 9.6, 9.3 Hz, H-2′), 5.15 (1H, dd, J = 9.3, 9.0 Hz, H-2″), 7.31 (1H, s, H-6), 7.36 (1H, s, H-3).

Methylation of 2 and 3. To a stirred solution of **2** or **3** (each of 5 mg) in dry acetone (0.5 mL) were added 0.5 mL of methyl iodide and 20 mg of K_2CO_3. The mixture was stirred overnight at room temperature. After filtration, evaporation under vacuum and purification by preparative thin-layer chromatography, each reaction mixture gave same product, **7** (2 mg) as colorless needles (EtOH); mp 141−142 °C; IR (KBr) ν_{max} 1730, 1620, 1535, 1510, 1215, 1150, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.84, 3.88 and 3.93 (3H each, s, OMe), 6.85 (1H, dd, J = 8.4, 2.0 Hz, H-4′), 6.91 (1H, d, J = 8.4, H-3′), 7.24 (1H, s, H-4), 7.40 (1H, d, J = 2.0 Hz, H-6′), 8.04 (1H, s, H-2).

Methylation of 4. Compound **8** (3 mg) was prepared from **4** (5 mg) using a method similar to that employed for the preparation of **7**, and **8** exhibited: colorless needles (EtOH); mp 87−88 °C (EtOH); IR (KBr) ν_{max} 1680, 1625, 1530, 1220, 1140, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.47 (3H, t, J = 7.2 Hz, H-2′), 3.84 and 3.88 (3H each, s, OMe), 4.13 (2H, q, J = 7.2 Hz, H-1′), 6.46 (1H, s, H-3), 7.29 (1H, s, H-6), and 10.31 (1H, s, CHO).

Acetylation of 5. Compound **9** (3 mg) was prepared from **5** (5 mg) by a method similar to the preparation of **6**, and **9** exhibited: colorless needles (EtOH); mp 110−112 °C (EtOH); IR (KBr) ν_{max} 3450, 3250−2500, 1735, 1615, 1510, 1210, 1150, 1015 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55 (3H, t, J = 7.2 Hz, H-2′), 2.28 and 2.29 (3H each, s, OAc), 4.29 (2H, q, J = 7.2 Hz, H-1′), 6.95 (1H, s, H-3), and 7.97 (1H, s, H-6).

X-ray Crystal Structure Analysis of Tournefolin A (1).[9] A colorless crystal of **1** with dimensions 0.10 × 0.20 × 0.20 mm was selected for X-ray analysis. Structure analysis was performed by using the SHELXTL program on PC.[10] Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. The compound crystallized in the monoclinic space group $P2_1$, a = 11.2630 (2) Å, b = 13.1540 (2) Å, c = 11.5340 (2) Å, β = 117.578(10)°, V = 1514.65 (4) Å^3, Z = 4, D_{calc} = 1.221 g/cm^3, λ = 0.71073 Å, μ(Mo Kα) = 0.087 mm^{-1}, F(000) = 600, and T = 296 K. The SMART program was used to make data corrections. A total of 16 058 reflections, collected in the range 1.99≤ θ ≤ 25.0°, yielded 5311 unique reflections. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 values for 4984 reflections with $I > 2\sigma(I)$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined using ariding mode. The final indices were R = 0.0691, R_w = 0.1576 with goodness-of-fit = 1.093. Scattering factors were taken from the *International Tables for X-ray Crystallography*.[11]

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