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Chemical Studies on the Constituents of *Polygonum nodosum*

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A new cyclobutane derivative, which may be formed from dehydrokawain by [2+2] cycloaddition, named compound B (**8a**), mp 226—227°C, $C_{28}H_{24}O_6$, and a new flavanonol, named compound C (**10a**), mp 142—143°C, $C_{17}H_{14}O_6$, together with pinobanksin(**1a**), taxifolin(**2a**), quercetin-3β-D-glucopyranoside 2″-gallate(**3**), pinosylvin(**4a**), methyl gallate(**5a**), dehydrokawain(**6**) and compound A(**7a**) were isolated from *Polygonum nodosum* (Polygonaceae). The structures of the new compounds, **8a** and **10a**, were established to be *rel*-1,*trans*-3-bis-(4-methoxy-2-oxopyran-6-yl)-*cis*-2,*trans*-4-diphenyl cyclobutane and (2*R*,3*R*)-3-hydroxy-5-methoxy-6,7-methylenedioxy-flavanone, respectively, on the basis of physicochemical evidence. The structure of **7a** was also established to be *rel*-(1*R*,6*S*,7*S*,8*S*)-5-methoxy-7-phenyl-8-(4-methoxy-2-oxopyran-6-yl)-1-(*E*)styryl-2-oxabicyclo-[4,2,0]-oct-4-en-3-one and this compound was found to be identical with aniba-dimer-A.

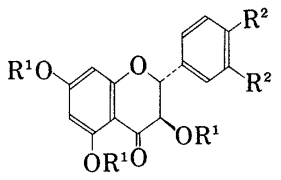
Keywords——*Polygonum nodosum*; Polygonaceae; flavanonol; dehydrokawain dimer; cyclobutane derivative; [2+2] cycloaddition; styrylpyrone derivative; ^{13}C-NMR

The genus *Polygonum* (polygonaceae) contains a large number of species, and several flavonoids and phenolic compounds have been isolated from some of these.[1] However, few studies on the chemical constituents have been carried out. From a chemotaxonomical veiwpoint, we interested in the constituents of the plants of the genus. So far, quercetin, kaempferol, quercetin-3β-D-glucopyranoside, kaempferol-3β-D-glucopyranoside 2″-gallate and quercetin-3β-D-glucopyranoside 2″-gallate (**3**) have been reported[2] as a constituents of *P. nodosum* Pers (Japanese name "Ohinutade"). The present paper describes a further characterization of the constituents of the plant.

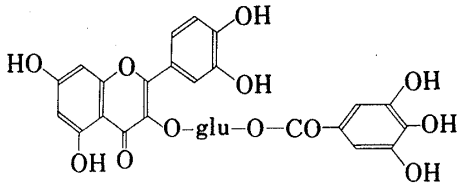
The methanol (MeOH) extract of the aerial part of the plant was fractionated into three fractions, *i.e.*, those soluble in ethyl acetate (AcOEt), *n*-butanol (BuOH) and water. Silica gel column chromatography and preparative thin-layer chromatography (PLC) of the AcOEt fraction gave nine constituents, pinobanksin (**1a**).[3] taxifolin (**2a**),[4] **3**, pinosylvin (**4a**),[5] methyl gallate (**5a**), dehydrokawain (**6**),[6] and compounds A (**7a**), B(**8a**) and C (**10a**).

The compounds **1a** and **2a** gave a tri-(**1b**) and a pentaacetate (**2b**), respectively. The proton nuclear magnetic resonance (^{1}H-NMR) spectra of **1a**, **1b**, **2a** and **2b** indicated that **1a** is pinobanksin and **2a** is taxifolin. The constituent **3** was identical with quercetin-3β-D-glucopyranoside 2″-gallate isolated from the same source as a molluscidal principle.[2] The constituent **4a** gave a diacetate (**4b**) and from the ^{1}H-NMR spectra of **4a** and **4b**, **4a** was concluded to be pinosylvin. The constituent **5a** gave a triacetate (**5b**) and from the spectral data of **5a** and **5b**, **5a** was identified as methyl gallate. The constituent **6** gave the molecular formula $C_{14}H_{12}O_3$. The ^{1}H-NMR spectrum of **6** indicated the presence of a *trans*-styryl group (δ 7.25—7.50 (5H, m), 6.50 (1H, d, J=16 Hz) and 7.42 (1H, J=16 Hz)) and a 4-methoxy-2-oxopyran-6-yl group (δ 3.78 (3H, s), 5.43 (1H, J=2.2 Hz) and 5.90 (1H, J=2.2 Hz)), and **6** was concluded to be dehydrokawain.

Compound A was obtained in two crystalline states, **7a**, mp 185—188°C, and **7b**, mp 207—209°C. The IR spectra (KBr disk) of both crystals were different, but their ^{1}H-NMR spectra were identical. The fragment pattern of the mass spectrum (MS) of compound A is almost superimposable on that of **6** (Fig. 1) and the elemental analysis data of compound A coincide



1a : $R^1=R^2=H$
1b : $R^1=Ac$, $R^2=H$
2a : $R^1=H$, $R^2=OH$
2b : $R^1=Ac$, $R^2=OAc$



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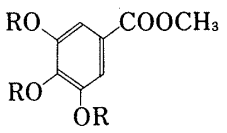
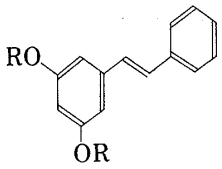
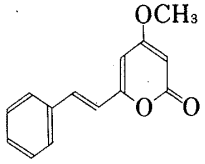


5a : R=H
5b : R=Ac



4a : R=H
4b : R=Ac



6

Chart 1

well with the molecular formula, $C_{14}H_{12}O_3$, of **6**. However, from the ^{1}H-NMR and carbon nuclear magnetic resonance (^{13}C-NMR) spectra the molecular formula of compound A was confirmed to be $C_{28}H_{24}O_6$. Compound A gave a dihydro derivative (**7c**) upon catalytic hydrogenation. From the ^{1}H-NMR and ^{13}C-NMR spectra of compound A and **7c**, the structure of compound A was elucidated. The unusual chemical shifts of a methoxy group (δ 3.30) and a methine proton (δ 3.60), which resonated at higher field than another methoxyl group and other methine protons, can be accounted for by anisotropy of the adjacent *cis*-oriented phenyl group on the cyclobutane ring, as observed in the case of truxinic acid and truxillic acid methyl esters,[7] in which the methoxyl group having an adjacent *trans*-phenyl group resonated at normal field (δ 3.75) but the methoxyl group having an adjacent *cis*-phenyl group did not (δ 3.23) (Chart 2). These unusual chemical shifts and the coupling constants ($J_{7,8}$=9.0, $J_{6,7}$=11.0 Hz) of methine protons on the cyclobutane ring indicated the relative configuration. Thus, the structure of compound A was concluded to be *rel*-(1*R*,6*S*,7*S*,8*S*)-5-methoxy-7-phenyl-8-(4-methoxy-2-oxopyran-6-yl)-1-(*E*)-styryl-2-oxabicyclo[4,2,0]-oct-4-en-3-one. This structure is identical with that of aniba-dimer-A, which has been isolated from Aniba species[8] and whose structure has been confirmed by X-ray analysis by Gottlieb *et al.*[9] They reported that a diastereomer of aniba-dimer-A was synthesized from dehydrokawain by photo-dimerization; its melting point and IR spectrum (KBr disk) were different from those of aniba-dimer-A, but the ^{1}H-NMR spectrum and MS were identical with those of aniba-dimer-A, so that the stereo structure of the synthetic dimer was *rel*-(1*R*, 6*R*, 7*S*, 8*S*)(**7d**). Crysatlline **7a** and **7b** were identical with aniba-dimer-A each other in chloroform solution as judged from the IR spectra. These results indicate that **7a** and **7b** are the same compound and that aniba-dimer-A and the synthetic dimer are also the same compound, differing only in crystalline state.

Compound B (**8a**) was obtained as colorless prisms, mp 226—227°C, $[\alpha]_D$ ±0° (MeOH), showing the same MS fragment pattern (Fig. 1) and elemental analysis data as **6** and **7a**. The ^{1}H-NMR spectrum of **8a** showed the presence of phenyls (δ 7.22 (10H, br s)), a 4-methoxy-2-oxopyran-6-yl moiety (δ 3.68 (6H, s), 5.19 (2H, d, J=2.2 Hz) and 5.81 (2H, J=2.2 Hz)) and two kinds of methine groups (δ 4.28 (2H, m), 4.44 (2H, m)) instead of the *trans* olefinic

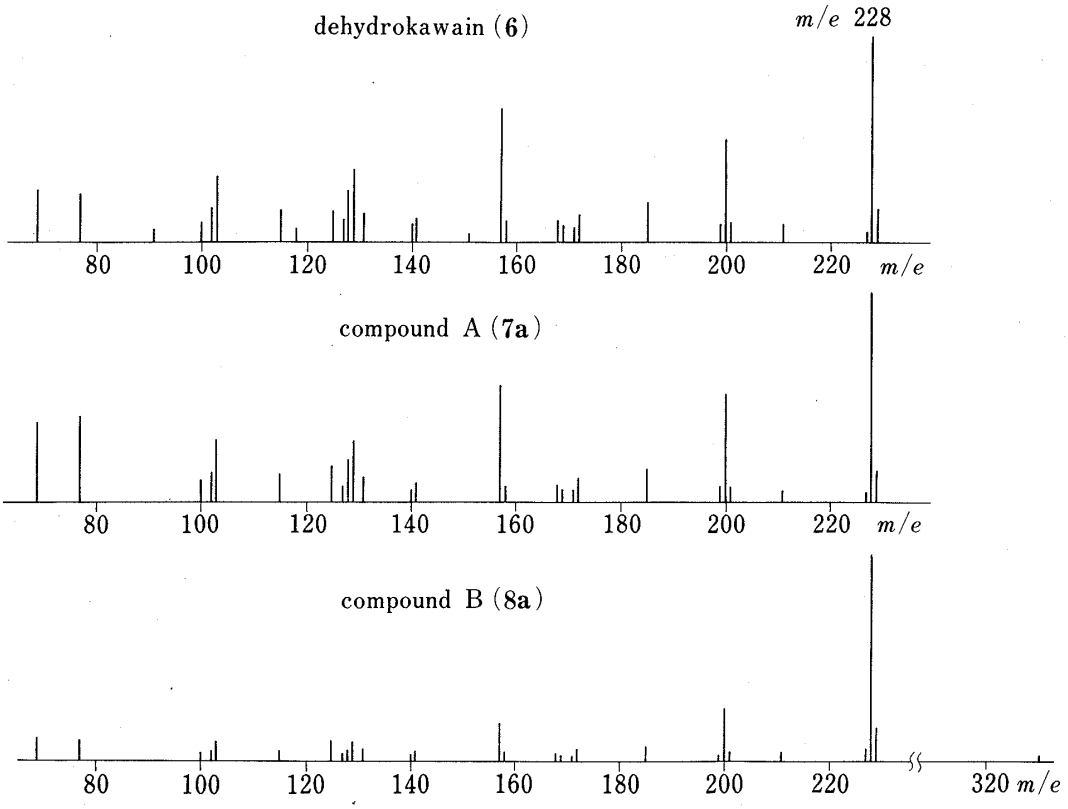
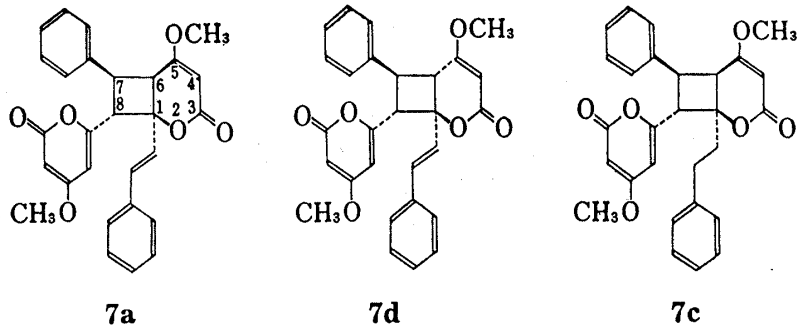


Fig. 1. Mass Spectra of **6**, **7a** and **8a**



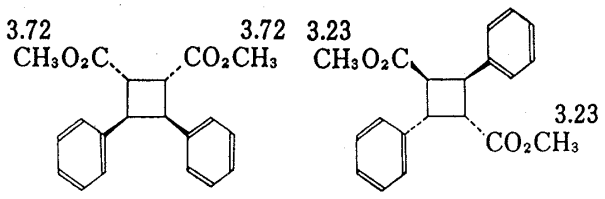


Chart 2

group of **6**. The presence of the two kinds of methin groups was also supported by the ^{13}C-NMR spectrum (δ 43.6 (d) and 45.0 (d)) of **8a**. Thus, **8a** was considered to be a cyclobutane derivative formed by dimerization of dehydrokawain at the styryl olefinic moiety, and so the molecular formular was considered to be $C_{28}H_{24}O_6$, the same as that of **7a**. This was confirmed by the fact that the molecular ion peak of **8a** could be detected at *m/e* 456 (below 0.5%) in the enlarged spectrum. Similar cyclobutane derivatives of natural products, truxinic and truxillic acid derivatives, are well known.[11] In such compounds, head-to-head and head-to-tail dimers

may be formed. In the case of the head-to-head dimer, which has been synthesized from **6** by photo dimerization,[10] three typical fragments at *m/e* 228, 180 and 276 due to the ions **9a**, **9b** and **9c**, respectively (Fig. 2), appeared. The appearance of a base peak corresponding to the ion **9a** and disappearance of fragments **9b** and **9c** in **8a** indicated **8a** to be a head-to-tail dimer (Fig. 2). Five possible structures, **8a**, **8b**. **8c**, **8d**, and **8e**, were considered. The coupling pattern of the methine protons on the cyclobutane ring was expected to be AA'BB' type[12] in the case of **8a**, A_2B_2 type in the cases of **8b** and **8c**, and a more complex type in the cases of **8d** and **8e**. In the ^{1}H-NMR spectrum of compound B (measured at 200 MHz) four methine protons appeared as an AA'BB' type signal consisting of at least sixteen symmetrical peaks. These results indicated that the structure of compound B is *rel*-, *trans*-3-bis[6-(4-methoxy-2-pyronyl)]-*cis*-2, *trans*-4-diphenyl cyclobutane (**8a**).

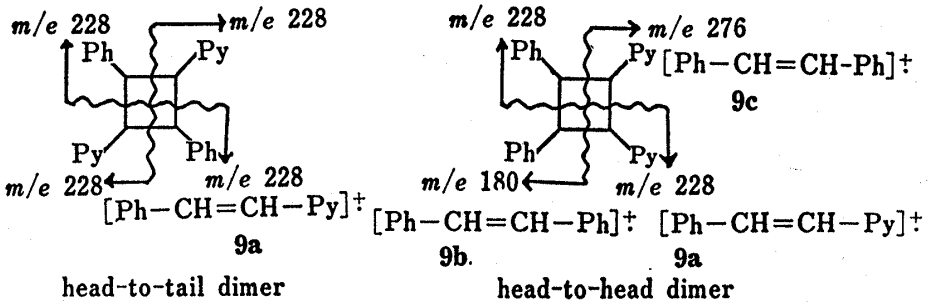


Fig. 2. The Predicted Mass Fragments of Head-to-Tail and Head-to-Head Dimers

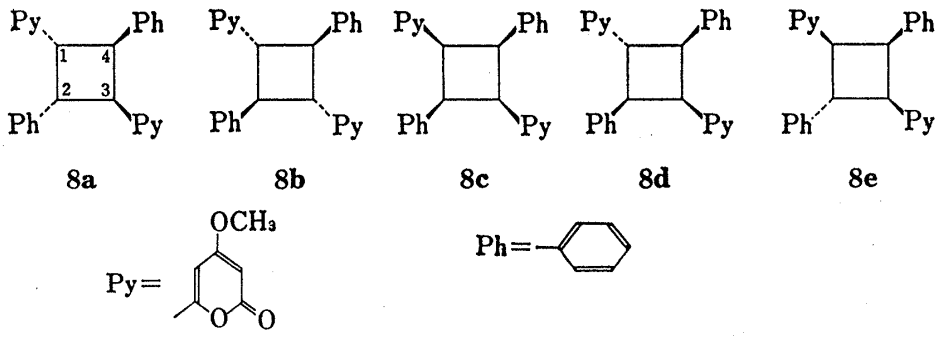
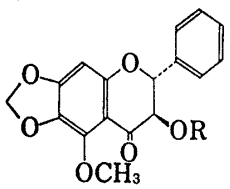
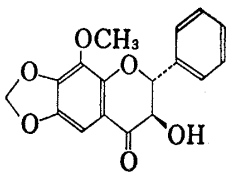


Chart 3

Compound C (**10a**) was obtained as colorless needles, mp 142—143°C, $C_{17}H_{14}O_6$, $[\alpha]_D$ +29.0° (MeOH), and gave a monoacetate (**10b**), mp 98—100°C, $C_{19}H_{16}O_7$. The ^{1}H-NMR spectrum of **10a** showed the presence of a phenyl (δ 7.2—7.6 (5H, m)), a methoxyl (δ 4.07 (3H, s)), a methylenedioxy (δ 5.90 (2H, s)), an alcoholic hydroxyl (δ 3.92 (1H, d, J=2.8 Hz)), two methine groups (δ 4.34 (1H, dd, J=12.0, 2.8 Hz) and 4.97 (1H, d, J=12.0 Hz)) and an aromatic proton (δ 6.17 (1H, s)). The ^{1}H-NMR spectrum of **10b** showed a new acetyl signal, and the hydroxy proton was lost. One of the two methine protons was also shifted to lower field (δ 5.65). These observations indicated that **10a** is a flavanonol derivative having a methoxyl group and a methylenedioxy group on ring A. It has been reported that the carbon chemical shift of a methoxyl group situated between substituents such as hydroxyl, alkoxyl, acyloxyl acyl and other groups on a benzene ring is shifted to lower field (to near 60 ppm).[13] Since the methoxyl group of **10a** resonated at δ 60.4 ppm, the substitution pattern on ring A was considered to be 6,7-methylenedioxy-5-methoxy (**10a**) or 6,7-methylenedioxy-8-methoxy (**10c**). In the ^{13}C-NMR spectrum of **10a** the sp^2 carbon appearing at the highest field (δ 93.1 ppm) showed a doublet peak under off-resonance conditions and was assigned to carbon having O-functional groups on both *ortho* positions. Thus the structure of compound C was



10a : R=H
10b : R=Ac



10c

Chart 4

concluded to be **10a**, not **10c**. The streochemistry at C-2 and C-3 was determined to be 2*R*, 3*R* from the coupling constant (J=12.0 Hz) of the methine protons and the positive optical rotation.[14]

Truxinic acid and truxillic acid derivatives are well known as natural dimers having a cyclobutane ring, considered to be formed through [2+2] cycloaddition, and recently other such natural compounds have been reported.[15] These natural compounds are optically inactive in general, and **7a** and **8a** are also optically inactive. This is the first report of isolation of such dehydrokawain derivatives from Polygonaceae plants.

The coexistence of flavanonols **1a** and **10a**, stilbene derivative **4a**, and styrylpyrone derivatives **6**, **7a** and **8a**, which contain phenyl groups is interesting from a biogenetic standpoint. These compounds may be biosynthesized through a common C_6H_5–C_3 unit which is then elongated by the addition of acetate units.

Experimental

All melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IRA-2 machine, and UV spectra were recorded on a Hitachi model 200-10 spectrometer. Optical rotations were determined on a JASCO DIP-180 automatic polarimeter. ^{1}H-NMR spectra were recorded on Hitachi R-24B (60 MHz), Hitachi R-22 (90 MHz) and JEOL FX-200 (200 MHz) machines with tetramethylsilane (TMS) as an internal standard (δ value). ^{13}C-NMR spectra were recorded on a JEOL FX-100 machine with TMS as an internal standard (δ value). MS were recorded on a JMS-01SG-2 mass spectrometer. Thin layer chromatography (TLC) was carried out on Kieselgel GF_{254} (Merck) and precoated Kieselgel $60F_{254}$ (Merck), and PLC was carried out on Kieselgel PF_{254} (Merck, 200×200×0.75 mm). Column chromatography was carried out on Kieselgel type 60 (Merck).

Isolation of Constituents——Aerial parts (fresh 10 kg) of *Polygonum nodosum*, collected at Shizuoka city, Japan, on August 1980, were extracted with boiling MeOH. The MeOH extract was concentrated under reduced pressure. The residue was suspended in water, and extracted with AcOEt to give 250 g of AcOEt extract. The water layer was extracted with BuOH to give the BuOH extract (100 g) and water layer. The AcOEt extract was chromatographed on a silica gel column with a benzene–AcOEt gradient system as the developer. The resultant eluates were recombined on the basis of their TLC pattern to give seventeen fractions, fr. 1—17. Fr. 10 (21 g) was chromatographed repeatedly on a silica gel column and/or subjected to PLC to give pinobanksin (**1a**) (70 mg), pinosylvin (**4a**) (270 mg), dehydrokawain (**6**) (100 mg), compound A (550 mg) as crystals (**7b**) and compound C (**10a**) (2.2 g). Fr. 11 (23 g) was also chromatographed on a silica gel column and/or subjected to PLC to give taxifolin (**2a**) (120 mg), methyl gallate (**5a**) (250 mg), compound A (1.2 g) as crystals (**7a**) and compound B (**8a**) (700 mg). Fr. 15 gave quercetin-3β-D-glucopyranoside 2″-gallate (**3**) (4.6 g) upon filtration.

Pinobanksin (**1a**)——Colorless needles from $CHCl_3$, mp 171—174°C. $[\alpha]_D$ +6.1 (c=0.45, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3460, 3120, 1650, 1620, 1480, 1285,1178. ^{1}H-NMR (δ in CD_3OD): 4.48 (1H, d, J=12.0 Hz, at C-2), 5.03 (1H, d, J=12.0 Hz, at C-3), 5.90 (2H, s, at C-6 and 7), 7.25—7.52 (5H, m, phenyl). ^{13}C-NMR (δ in $CDCl_3$): 72.5 (d), 83.5 (d), 96.0 (d) 96.9 (d), 100.5 (s), 127.6 (d), 128.6 (d), 129.2 (d), 136.5 (s), 163.0 (s), 163.6 (s), 167.5 (s), 196.0 (s).

Pinobanksin Triacetate (**1b**)——An amorphous solid. ^{1}H-NMR (δ in $CDCl_3$): 1.95 (3H, s, Ac at C-3), 2.25 (3H, s, Ac at C-7), 2.34 (3H, s, Ac at C-5), 5.35 (1H, d, J=12.0 Hz, at C-2), 5.75 (1H, d, J=12.0 Hz, at C-3), 6.54 (1H, d, J=2.0 Hz, at C-8), 6.73 (1H, d, J=2.0 Hz, at C-6), 7.26—7.43 (5H, m, phenyl).

Taxifolin (**2a**)——Colorless needles from benzene–AcOEt, mp 234—237°C. $[\alpha]_D$ +28.5° (c=0.35, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3540, 3380, 1630, 1585, 1450, 1362, 1255, 1061. ^{1}H-NMR (δ in CD_3OD): 4.42 (1H, d, J=12.0 Hz, at C-2), 4.90 (1H, d, J=12.0 Hz, at C-3), 5.84 (2H, s, at C-6 and 8), 6.6—7.0 (3H, m, at C-2′, 5′

and 6′). *Anal.* Calcd for $C_{15}H_{12}O_7$: C, 59.2; H, 3.98. Found: C, 59.17; H, 4.23. MS *m/e*: 304 (M^+) for $C_{15}H_{12}O_7$.

Taxifolin Pentaacetate (2b)——An amorphous solid, ^{1}H-NMR (δ in $CDCl_3$): 2.04 (3H, s, Ac at C-3), 2.30 (9H, s, Ac at C-3′, 4′ and 7), 2.38 (3H, s, Ac at C-5), 5.45 (1H, d, J=12.0 Hz, at C-3), 5.65 (1H, d, J=12.0 Hz, at C-3), 6.55 (1H, d, J=2.0 Hz, at C-8), 6.72 (1H, d, J=2.0 Hz, at C-6), 7.27—7.35 (3H, m, at C-2′, 5′ and 6′).

Quercetin-3β-D-glucopyranoside 2″-Gallate (3)——Yellow needles from $CHCl_3$–MeOH, mp 208—210°C, IR ν_{max}^{KBr} cm^{-1}: 3200, 1710, 1660, 1605, 1235, 1200. ^{1}H-NMR (δ in CD_3OD): 5.70 (1H, d, J=8.0 Hz, at C-1″), 6.10 (1H, d, J=2.0 Hz, at C-8), 6.25 (1H, d, J=2.0 Hz, at C-6), 6.75 (1H, d, J=9.5 Hz, at C-5′), 7.08 (2H, s, on gallate), 7.42 (1H, dd, J=9.5, 2.0 Hz at C-6′), 7.50 (1H, d, J=2.0 Hz at C-2′). Identical with an authentic sample.

Pinosylvin (4a)——Colorless needles from $CHCl_3$, mp 156°C, IR ν_{max}^{KBr} cm^{-1}: 3400, 3300, 1610, 1590, 1155. MS *m/e*: 212 (M^+) for $C_{14}H_{12}O_2$. ^{1}H-NMR (δ in $CDCl_3$): 6.21 (1H, t, J=2.0 Hz at C-4), 6.48 (2H, d, J=2.0 Hz, at C-2 and 6), 6.95 (2H, s, at C-7 and 8), 7.10—7.50 (5H, m, phenyl).

Pinosylvin Diacetate (4b)——Colorless needles from MeOH, mp 86—87°C. IR ν_{max}^{KBr} cm^{-1}: 1758, 1602, 1575, 1210, 1188. ^{1}H-NMR (δ in $CDCl_3$): 2.20 (6H, s, Ac), 6.65 (1H, t, J=2.0 Hz, at C-4), 6.85 (2H, s, at C-7 and 8), 6.94 (2H, d, J=2.0 Hz, at C-2 and 6), 7.05—7.35 (5H, m, phenyl).

Methyl Gallate (5a)——Colorless needles from $CHCl_3$, mp 200—203°C. IR ν_{max}^{KBr} cm^{-1}: 3480, 3300, 1692, 1618, 1318, 1200, 1140. ^{1}H-NMR (δ in CD_3OD): 3.78 (3H, s, CH_3O–CO–), 7.00 (2H, s, at C-2 and 3). Identical with an synthetic sample.

Triacetate of 5a (5b)——Colorless needles from MeOH, mp 121°C. IR ν_{max}^{KBr} cm^{-1}: 1762, 1710, 1608, 1420, 1320, 1200, 1180, 1160. ^{1}H-NMR (δ in $CDCl_3$): 2.25 (9H, s, Ac), 3.83 (3H, s, CH_3O–CO–), 7.65 (2H, s, at C-2 and 6).

5,6-Dehydrokawain (6)——Colorless needles from ethanol, mp 136—138°C. UV λ_{max}^{MeOH} nm (log ε): 266 (3.84), 320 (3.93), 380 (3.83). IR ν_{max}^{KBr} cm^{-1}: 1720, 1628, 1600, 1544, 1400, 1252, 1145. ^{1}H-NMR (δ in $CDCl_3$): 3.78 (3H, s, CH_3O), 5.43 (1H, d, J=2.2 Hz, at C-3), 5.93 (1H, d, J=2.2 Hz, at C-5), 6.50 (1H, d, J=16 Hz, at C-8), 7.42 (1H, d, J=16 Hz, at C-7), 7.25—7.50 (5H, m, phenyl).

Compound A (7a)——Colorless needles from AcOEt, mp 185—188°C. $[\alpha]_D$ ±0° (c=0.21, $MeOH_3$). UV λ_{max}^{MeOH} nm (log ε): 206 (4.77), 251 (4.54), 283 (3.95), 292 (3.88). IR λ_{max}^{KBr} cm^{-1}: 1720, 1710, 1645, 1625, 1569, 1460, 1445, 1400, 1262, 1250, 1245, 1145. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1710, 1643, 1625, 1568, 1455, 1415, 1396, 1256, 1242, 1142. ^{1}H-NMR (δ in $CDCl_3$): 3.30 (3H, s, CH_3O), 3.60 (1H, d, J=11.0 Hz, at C-6), 3.70 (3H, s, CH_3O), 4.20 (1H, d, J=9.0 Hz, at C-8), 4.40 (1H, dd, J=11.0 and 9.0 Hz, at C-7), 5.32 (1H, s, at C-4), 5.35 (1H, d, J=2.2 Hz, at C-3′), 5.94 (1H, d, J=2.2 Hz, at C-5′), 6.60 (1H, d, J=16.0 Hz, at C-7″), 7.00 (1H, d, J=16.0 Hz, at C-8″), 7.20—7.50 (10H, m, phenyl×2). ^{13}C-NMR (δ in $CDCl_3$): 39.2 (d), 45.7 (d), 54.4 (d), 55.4 (q), 55.9 (q), 79.4 (s), 88.6 (d), 91.7 (d), 102.6 (d), 124.3 (d), 126.8 (d), 127.5 (d), 127.8 (d), 128.2 (d), 128.4 (d), 128.6 (d), 131.4 (d), 135.5 (s), 135.8 (s), 158.6 (s), 163.8 (s), 164.5 (s), 169.8 (s), 170.4 (s). MS *m/e*: 228 (M^+×1/2). *Anal.* Calcd for $C_{28}H_{24}O_6$: C, 73.67; H, 5.30. Found: C, 73.52; H, 5.30. The crystals **7b**, mp 207—209°C, IR ν_{max}^{KBr} cm^{-1}: 1720, 1640, 1570, 1455, 1395, 1263, 1248, 1150, 1102. The crystals, **7a** and **7b**, gave identical IR spectra in $CHCl_3$ solution.

Catalytic Hydrogenation of 7a——A solution of **7a** (60 mg) in MeOH (12 ml) was shaken with Pd-C (5%) (20 mg) in an H_2 atmosphere for 10 h, then the reaction mixture was filtered. The filtrate was concentrated to give a crystalline product, which was recrystallized from AcOEt to give colorless needles, **7c** (35 mg), mp 169—171°C. IR ν_{max}^{KBr} cm^{-1}: 1720, 1640, 1570, 1454, 1397, 1261, 1246, 1150. ^{1}H-NMR (δ in $CDCl_3$): 2.23 (2H, m, CH_2 at C-8″), 2.76 (2H, m, CH_2 at C-7″), 3.24 (3H, s, CH_3O), 3.28 (1H, d, J=9.0 Hz, at C-6), 3.76 (3H, s, CH_3O), 4.02 (1H, d, J=11.0 Hz, at C-8), 4.13 (1H, dd, J=11.0, 9.0 Hz, at C-7), 5.27 (1H, s at C-4), 5.40 (1H, d, J=2.2 Hz, at C-3′), 5.95 (1H, d, J=2.2 Hz, at C-5′), 7.10—7.45 (10H, m, phenyl×2). ^{13}C-NMR (δ in $CDCl_3$): 29.4 (t), 36.2 (t), 39.2 (d), 43.9 (d), 53.0 (d), 55.2 (q), 55.9 (q), 79.9 (s), 88.7 (d), 91.1 (d), 102.8 (d), 126.2 (d), 127.4 (d), 127.7 (d), 128.3 (d), 128.5 (d), 135.5 (d), 140.5 (s), 158.6 (s), 163.8 (s), 165.1 (s), 170.0 (s), 170.4 (s). *Anal.* Calcd for $C_{28}H_{26}O_6$: C, 73.35; H, 5.72. Found: C, 73.70; H, 5.72.

Compound B (8a)——Colorless needles from AcOEt, mp 226—227°C. $[\alpha]_D$ ±0° (C=0.39,MeOH). UV λ_{max}^{MeOH} nm (log ε): 207 (4.74), 287 (4.13). IR ν_{max}^{KBr} cm^{-1}: 1720, 1640, 1560, 1447, 1400, 1253, 1132. ^{1}H-NMR (δ in $CDCl_3$): 3.67 (6H, s, CH_3O×2), 4.28 (2H, m, CH×2 on cyclobutane ring), 4.44 (2H, m, CH×2 on cyclobutane), 5.19 (2H, d, J=2.2 Hz, at C-3′ and C-3″), 5.74 (2H, d, J=2.2 Hz, at C-5′ and C-5″), 7.20—7.40 (10H, m, phenyl×2). ^{13}C-NMR (δ in $CDCl_3$): 43.6 (d), 45.0 (d), 55.7 (q), 87.7 (d), 101.4 (d), 127.1 (d), 127.3 (d), 128.5 (d), 137.3 (s), 162.6 (s), 163.8 (s), 170.4 (s). MS *m/e*: 456 (M^+) (0.5% below), 228 (M^+×1/2) (100%). *Anal.* Calcd for $C_{28}H_{24}O_6$: C, 73.67; H, 5.30. Found: C, 73.41; H, 5.30.

Compound C (10a)——Colorless needles from AcOEt, mp 142—143°C. $[\alpha]_D$+29.0° (c=0.5, MeOH). UV λ_{max}^{Nujol} nm (log ε): 208 (4.28), 243 (4.16), 283 (3.95), 341 (3.50). IR ν_{max}^{KBr} cm^{-1}: 3520, 3480, 1668, 1620, 1610, 1498, 1475, 1440, 1243, 1162, 1115, 1092. ^{1}H-NMR (δ in $CDCl_3$): 3.96 (1H, d, J=2.0 Hz, OH), 4.34 (1H, dd, J=12.0 and 2.0 Hz, at C-3), 4.97 (1H, d, J=12.0 Hz, at C-2), 4.09 (3H, s, CH_3O), 5.90 (2H, s, O–CH_2–O), 6.17 (1H, s, at C-8), 7.20—7.60 (5H, m, phenyl). ^{13}C-NMR (δ in $CDCl_3$): 60.4 (q), 72.8 (d), 83.4 (d), 93.1 (d), 101.7 (t), 105.3 (s), 127.4 (d), 128.6 (d), 129.1 (d), 131.3 (s), 136.3 (s), 142.7 (s), 155.6 (s), 160.3 (s), 191.2 (s). MS *m/e*: 314 (M^+). *Anal.* Calcd for $C_{17}H_{14}O_6$: C, 64.77; H, 4.52. Found: C, 64.96; H, 4.49.

Acetate (10b) of 10a——10a (400 mg) was acetylated with Ac_2O-Pyr at room temperature and the reaction mixture was poured into ice-water. The resulting precipitates were filtered off and recrystallized from MeOH to give colorless needles (**10b**) (300 mg), mp 98—100°C. IR ν_{max}^{KBr} cm^{-1}: 1750, 1685, 1620, 1480, 1225. ^{1}H-NMR (δ in $CDCl_3$): 2.00 (3H, s, CH_3CO), 4.05 (3H, s, CH_3O), 5.25 (1H, d, J=12.0 Hz, at C-2), 5.63 (1H, d, J=12.0 Hz, at C-3), 5.89 (2H, s, O–CH_2–O), 6.18 (1H, s, at C-8), 7.20—7.50 (5H, m, phenyl). MS *m/e*: 356 (M^+). *Anal.* Calcd for $C_{19}H_{16}O_6$: C, 64.04; H, 4.53. Found: C, 63.87; H, 4.65.

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