

Benzofuranoid Neolignans¹ from *Piper wightii* Miq.

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Eight benzofuranoid neolignans have been isolated from fruits and stems of *Piper wightii* Miq. One of them was found to be a novel compound and another was isolated for the first time from a natural source; on the basis of spectral data (¹H, ¹³C and 2D NMR, NOE, IR, UV, EI MS and CD) their structures were established as (7*S*,8*R*,3'*S*)-Δ⁸-3'-6'-dihydro-3'-methoxy-3,4-methylenedioxy-6'-oxo-8.3',7.0.4'-lignan **5** and (7*S*,8*R*,3'*S*,4'*R*,6'*S*)-Δ⁸-3'-4'-5'-6'-tetrahydro-6'-hydroxy-3,3',4,4'-tetramethoxy-8.3',7.0.4'-lignan **1**, respectively. The other neolignans were found to be kadsurin **B 3**, hancinone **4**, kadsurin **A 6**, piperenone **7**, burchellin **8** and a diastereomer of burchellin, (7*R*,8*S*,1'*S*)-Δ⁸-1',4'-dihydro-5'-methoxy-3,4-methylenedioxy-4'-oxo-8.1',7.0.2'-lignan **9**.

Plants belonging to the genus *Piper* are known to contain biologically active compounds, many of which possess medicinal properties.^{2–5} *Piper wightii* Miq. is a glabrous climber growing wild in the forests of South India. Fruits and stems of *P. wightii* have been under investigation as part of our research programme searching for bioactive compounds in *Piper* species.^{6–13} From stems and fruits of *P. wightii*, we have previously reported the isolation of seven 8.3'-neolignans and three tetrahydrofuranoid lignans.¹¹ This report presents the isolation of eight benzofuran-type neolignans, the highest number yet found in any single *Piper* species. The first pair consists of (7*S*,8*R*,3'*S*,4'*R*,6'*S*)-Δ⁸-3',4',5',6'-tetrahydro-6'-hydroxy-3,3',4,4'-tetramethoxy-8.3',7.0.4'-lignan **1**, known as a synthetic transformation product of an earlier reported neolignan, but new as a natural product, and a known neolignan, kadsurin **B 3**. One compound of the second pair was identified as a new neolignan, (7*R*,8*R*,3'*S*)-Δ⁸-3',6'-dihydro-3'-methoxy-3,4-methylenedioxy-6'-oxo-8.3',7.0.4'-lignan **5** and the other as its known diastereomer, hancinone **4**. The other four compounds were identified as kadsurin **A 6**, piperenone **7**, burchellin **8** and a known diastereomer of burchellin **9**. The absolute stereochemistry of compounds **1**, **4** and **5** was established on the basis of their CD data.

Results and discussion

Repeated flash column chromatography (CC) of the methanolic extract of fruits of *P. wightii* followed by preparative TLC of the selected fractions yielded seven neolignans **1** and **3–8**. Similar treatment of the petrol extract of its stems afforded compounds **3** and **6–9**. Compound **1** showed a molecular ion at *m/z* 390 in its EI mass spectrum; by HRMS this led to a molecular formula of C₂₂H₃₀O₆. The fragments at *m/z* 178 (94%), 165 (16%) and 151 (100%) indicated **1** to be a benzofuran-type neolignan.¹⁴ The IR, UV and ¹H NMR data of **1** were found in agreement with an earlier reported compound obtained by reduction of piperenone with LiAlH₄¹⁵ except for the signal of the hydroxy proton in the ¹H NMR spectrum. This was reported as a singlet at δ 1.64; we observed it at δ 3.29 as a broad singlet and confirmed the assignment from its cross peak with the carbinol proton in the 2D NMR spectrum. The presence of the OH group was confirmed by acetylation; its acetate **2** showed a molecular ion at *m/z* 432 in the EI mass spectrum and a deshielding effect (Δ 1.33 ppm) for the carbinol proton in the ¹H NMR spectrum. The relative configuration of **1** was established from NOE results (Table 1) as follows: 9-H gave an NOE on 7-H (9.0%) and on 2'-H (17.0%), but not on the aromatic or any methoxy protons, thus confirming a *trans* relationship of the methyl (9-H) with the aryl and methoxy group (3'-OMe). The signals at δ 1.90 (1 H, dd) and 2.69 (1 H, dd) in the ¹H NMR spectrum

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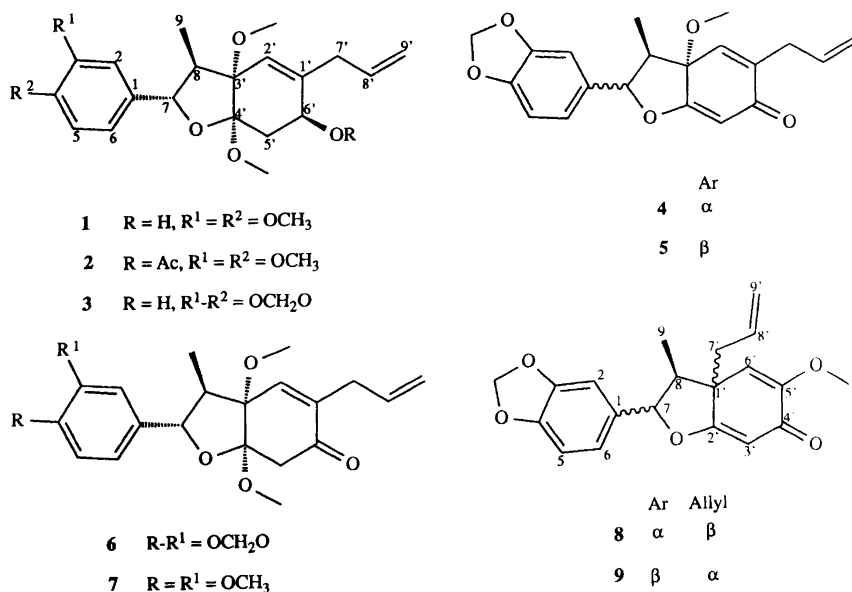


Table 1. NOE results of compound 1.

Proton irradiated	Enhancement (%)													
	9-H	8-H	7-H	9'-H	8'-H	7'-H	6'-H	5'-H _α	5'-H _β	2'-H	4'-OMe	3-OMe and 4-OMe	2-H	5-H and 6-H
9-H	—	13.0	9.0	—	—	—	—	—	—	17.0	—	—	—	—
8-H	2.0	—	—	—	—	—	—	—	—	—	—	—	7.5	+
7-H	1.0	—	—	—	—	—	—	—	—	—	—	—	5.0	+
7'-H	—	—	—	1.0	5.0	—	6.0	—	—	7.0	—	—	—	—
6'-H	—	—	—	—	—	3.0	—	4.5	2.5	—	—	—	—	—
5'-H _α	—	—	1.8	—	—	—	11.0	—	33.0	—	—	—	—	—
5'-H _β	—	—	—	—	—	—	4.5	25.5	—	—	3.0	—	—	—
2'-H	2.0	—	1.0	—	—	2.5	—	—	—	—	—	—	—	—
3'-OMe and 6'-OH	—	+	+	—	—	—	+	+	—	+	—	—	—	—
4'-OMe	—	—	—	—	—	—	—	—	7.0	—	—	—	4.5	+
2-H	—	9.0	5.0	—	—	—	—	—	—	—	—	2.0	—	—
5-H and 6-H	—	+	+	—	—	—	—	—	—	—	—	+	—	—

+ Positive NOE; % NOE could not be calculated because of overlapping signals.

were assigned to 5'-H_α and 5'-H_β, respectively, as 4'-OMe showed an NOE on the signal at δ 2.69 and irradiation of the signal of 6'-OH and 3'-OMe together gave an NOE on the signal at δ 1.90. The observed NOE between 5'-H_α and 6'-H was greater than the NOE between 5'-H_β and 6'-H and on irradiation of the signals of 6'-OH and 3'-OMe together, 7-H underwent an NOE; this was attributed to the 6'-OH group being in the β -position. The absolute configuration was established by inspection of the CD curve and was found similar to that of kadsurin B **3** for which we have established the absolute configuration.¹³ Thus, the structure was assigned as (7*S*,8*R*,3'*S*,4'*R*,6'*S*)- $\Delta^{8',3',4',5',6'}$ -tetrahydro-6'-hydroxy-3,3',4,4'-tetramethoxy-8.3',7.0.4'-lignan **1**.

Compound **3** was identified as kadsurin B, an analogue of **1** having a piperonyl unit instead of a veratryl unit. It

was found identical in all respects (spectral and physical data) with the compound reported from *P. schmidtii*.¹³

Compounds **4** and **5** were recognized as diastereomers from the following facts. The compounds showed similar EI mass spectra with the molecular ion at m/z 340 (HR-EIMS gave C₂₀H₂₀O₅) and their ¹³C NMR data were found comparable. In the ¹H NMR spectra all signals except the chemical shifts of a few peaks were also similar. The fragmentation ions in the EI mass spectra and some characteristic signals in the ¹³C NMR spectra indicated them to be neolignans of the mirandin type.¹⁶ The observed chemical shifts of the methyl protons in **4** (δ 0.50) suggested a *trans* and *cis* relationship between the methyl and aryl groups in **4** and **5**, respectively.¹⁶ Compound **4** was found to be a known neolignan, hancinone, with spectral data as published.¹⁷ The CD curve of **4**

matched with the reported CD curve of kadsurinone.¹⁸ Thus, the structure of **4** including the absolute stereochemistry was established as (7*S*,8*R*,3'*S*)- Δ^8 -3',6'-dihydro-3'-methoxy-3,4-methylenedioxy-6'-oxo-8.3',7.0.4'-lignan. The chemical shifts of characteristic signals in the ¹H NMR spectrum of **5** were in close agreement with those of 2-epimirandin A,¹⁶ indicating the relative stereochemistry of **5** to be identical with that of 2-epimirandin A. The only difference between **5** and 2-epimirandin A is that **5** has a piperonyl unit in place of a 3,4,5-trimethoxyphenyl group. The Cotton effects in the CD curve of **5** matched those from reported ORD data of 2-epimirandin A.¹⁶ In conclusion, the structure of **5** including the absolute stereochemistry is (7*S*,8*R*,3'*S*)- Δ^8 -3',6'-dihydro-3'-methoxy-3,4-methylenedioxy-6'-oxo-8.3',7.0.4'-lignan.

The compound of the third pair were found to be kadsurin A **6**⁸ and piperone **7**¹⁵ on the basis of comparison of the spectral data with literature values.

Compound **8** was identified as burchellin^{14,19} and **9** as its diastereomer, (7*S*,8*R*,1'*S*)- Δ^8 -1',4'-dihydro-5'-methoxy-3,4-methylenedioxy-4'-oxo-8.1',7.0.2'-lignan,^{10,20} all the spectral data were identical with the earlier reports.

Experimental

¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker AC 250 or Varian Unity 500 spectrometer at 250 or 500 and 62.9 or 125.7 MHz, respectively. Chemical shifts are reported in δ units with TMS as an internal reference. EI mass spectra were recorded on a Varian MAT 311A, IR spectra on a Perkin Elmer 1720 FT-IR and UV spectra on a Shimadzu UV 160A spectrophotometer. Optical rotations and CD curves were recorded on a Perkin Elmer 141 polarimeter and a custom-built spectrometer, respectively. Silica gel 60 (230–400 mesh, art 9385, Merck) was used for flash CC. TLC and preparative TLC were performed on Merck silica gel 60 F₂₅₄ and silica gel 60 F₂₅₄₊₃₆₆ plates, respectively. Spots were visualized under UV light or by spraying with 10% concentrated H₂SO₄ in ethanol followed by heating at around 120°C for a few minutes. A Delta Pak C₁₈-300 Å (5 cm × 30 cm, 15 μ m) column was used for reversed-phase preparative HPLC with Waters-486 UV detector. Stems and fruits of *Piper wightii* Miq. were collected from Doddabetta forest, Ooty (Tamil Nadu, India) in November 1990 and January 1992, respectively. Voucher specimens have been deposited in the herbarium of the Botanical Survey of India, Southern Circle, TNAU Campus, Coimbatore (Tamil Nadu, India).

Extraction and isolation. Fruits (0.82 kg) were extracted in a Soxhlet apparatus first with petrol (60–80°C) and then with methanol. Crushed and dried stems (1.35 kg) were extracted successively with petrol (60–80°C), dichloromethane and methanol. The extracts were concentrated *in vacuo*. The methanolic extract of fruits was subjected

to CC and afforded upon elution with chloroform–petrol (9:1) a major fraction (10 g), which was further fractionated by flash CC into 25 fractions using a gradient solvent system of petrol and chloroform with increasing order of polarity. Compound **3** was isolated from fractions 8 and 9 by crystallisation from petrol–chloroform and the mother-liquor afforded compound **8** by preparative TLC in petrol–ethyl acetate (9:1). Compound **1** was purified from fraction 16 by reversed-phase HPLC, eluting with 38% aqueous ethanol. Compounds **6** and **7** were isolated from fraction 18 when subjected first to preparative TLC and then to reversed-phase HPLC using 32% aqueous ethanol as the eluant. Fraction 6 was further subjected to flash CC; fraction 12 of a total of 46 fractions afforded directly pure **5**. Preparative TLC of fraction 13 (from the latter separation) gave **4** by elution with ethyl acetate–petrol (5:95). The petrol extract of stems was flash chromatographed with a gradient solvent system of petrol and ethyl acetate with increasing amounts of the latter. Compound **3** and **6–9** were isolated from different fractions by repetitive preparative TLC or by crystallization.

(7*S*,8*R*,3'*S*,4'*R*,6'*S*)- Δ^8 -3',4',5',6'-tetrahydro-6'-hydroxy-3,3',4,4'-tetramethoxy-8.3',7.0.4'-lignan (**1**) Colourless viscous mass (23 mg) (lit.¹⁵ m.p. 72.5–73.5°C). $[\alpha]_D^{25}$ –228.0 (MeOH; *c* 0.30). UV and IR data were identical with literature values.¹⁵ MS (EI, 70 eV), *m/z* (%): 390 (18, *M*⁺), 359 (10), 358 (28), 343 (19), 317 (9), 287 (96), 246 (26), 224 (10), 211 (96), 210 (26), 181 (12), 178 (94), 165 (16), 151 (100), 149 (14), 137 (8), 107 (8), 91 (20), 77 (14), 57 (18), 43 (14) and 41 (22) (Found $[M]^+$ 390.2033. C₂₂H₃₀O₆ requires 390.2042). ¹H NMR: δ 0.94 (3 H, d, *J* 6.9 Hz, 9-H₃), 1.90 (1 H, dd, *J* 4.9, 14.6 Hz, 5'-H _{α}), 2.69 (1 H, dd, *J* 1.6, 14.7 Hz, 5'-H _{β}), 2.75 (1 H, m, 8-H), 3.09 (2 H, t, *J* 8.2 Hz, 7'-H₂), 3.28 (3 H, s, 3'-OMe), 3.29 (1 H, br s, 6'-OH), 3.57 (3 H, s, 4'-OMe), 3.87 and 3.89 (3 H each, s, 3-OMe, 4-OMe), 4.08 (1 H, dd, *J* 3.8, 10.4 Hz, 6'-H), 4.19 (1 H, d, *J* 10.4 Hz, 7-H), 5.17 (2 H, m, 9'-H), 5.41 (1 H, s, 2'-H), 5.92 (1 H, m, 8'-H), 6.82 (2 H, m, 5-H, 6-H) and 6.92 (1 H, br s, 2-H). ¹³C NMR: δ 9.2 (C-9), 34.1 (C-5'), 39.0 (C-7'), 48.8 (C-8'), 48.9 (OMe-3'), 51.8 (OMe-4'), 55.7 and 55.9 (OMe-3, OMe-4), 65.8 (C-6'), 81.2 (C-3'), 85.0 (C-7), 104.4 (C-4'), 110.0 (C-2), 110.6 (C-5), 117.2 (C-9'), 120.1 (C-2'), 120.2 (C-6), 132.6 (C-1), 135.3 (C-8'), 146.2 (C-1'), 149.1 and 149.3 (C-3, C-4); CD (MeOH; *c* 7.3 mg/100 ml: 230–400): $[\theta]_{230}^{\max}$ +2819, $[\theta]_{234}$ 0, $[\theta]_{234}^{\min}$ –10041, $[\theta]_{270}^{\max}$ –4228, $[\theta]_{294}^{\min}$ –5284, $[\theta]_{300}$ –5108, $[\theta]_{319}$ 0, $[\theta]_{332}^{\max}$ +1409, $[\theta]_{349}$ +1233, $[\theta]_{371}$ +1057 and $[\theta]_{400}$ 0.

(7*S*,8*R*,3'*S*,4'*R*,6'*S*)- Δ^8 -3',4',5',6'-Tetrahydro-6'-acetoxy-3,3',4,4'-tetramethoxy-8.3',7.0.4'-lignan (**2**) Compound **1** (5 mg) was refluxed in acetic anhydride (1 ml) and pyridine (0.2 ml) for 4 h. The resulting mixture was poured into ice-cold water, extracted with ethyl acetate and the extract was dried over Na₂SO₄. Upon removal of the solvent, the resulting oily residue was subjected to

preparative. TLC in ethyl acetate–benzene (3:7) to afford the corresponding acetate **2** as an oil (4.0 mg). $[\alpha]_{\text{D}}^{22} - 32.3$ (CHCl₃; *c* 0.16). UV (MeOH) λ_{max} : 225 and 278. IR (KBr) ν_{max} : 3440, 2926, 2854, 1734, 1639, 1609, 1515, 1464, 1423, 1374, 1321, 1240, 1203, 1163, 1132, 1101 and 1050. MS (EI, eV) *m/z* (%): 432 (8, *M*⁺), 391 (16), 372 (6), 331 (32), 299 (15), 287 (100), 271 (10), 240 (14), 181 (12), 179 (18), 165 (19), 151 (62), 149 (8), 91 (11), 83 (7), 71 (10), 57 (13), 43 (27) and 41 (8). ¹H NMR: δ 0.91 (3 H, d, *J* 6.9 Hz, 9-H₃), 1.89 (1 H, dd, *J* 5.5, 15.2 Hz, 5'-H_x), 2.02 (3 H, s, COCH₃), 2.60 (1 H, m, 8-H), 2.63 (1 H, dd, *J* 1.6, 15.2 Hz, 5'-H_β), 2.93 (2 H, t, *J* 8.0 Hz, 7'-H₂), 3.27 (3 H, s, 3'-OMe), 3.53 (3 H, s, 4'-OMe), 3.87 and 3.88 (3 H each, s, 3-OMe, 4-OMe), 4.22 (1 H, d, *J* 10.8 Hz, 7-H), 5.15 (2 H, m, 9'-H), 5.41 (1 H, d, *J* 5.0 Hz, 6'-H), 5.60 (1 H, s, 2'-H), 5.95 (1 H, m, 8'-H), 6.83 (2 H, m, 5-H, 6-H) and 6.96 (1 H, br s, 2-H).

(7*S*,8*R*,3'*S*,4'*R*,6'*S*)- Δ^8 -3',4',5',6'-Tetrahydro-6'-hydroxy-3,4-methylenedioxy-3',4'-dimethoxy-8.3',7.O.4'-lignan (*kadsurin B*, **3**) Colourless crystals (500 mg from fruits, 100 mg from stems), m.p. 101–102°C (lit.¹³ m.p. 101–102°C). $[\alpha]_{\text{D}}^{22} - 218.4$ (MeOH; *c* 0.4) {lit.¹³ $[\alpha]_{\text{D}}^{22} - 217.1$ (MeOH; *c* 0.47)}. All spectral data (¹H and ¹³C NMR, IR, UV, EI mass and CD) were identical with those reported for our isolated compound from *Piper schmidtii*.¹³

(7*S*,8*R*,3'*S*)- Δ^8 -3',6'-Dihydro-3'-methoxy-3,4-methylenedioxy-6'-oxo-8.3',7.O.4'-lignan (*hancinone 4*) Viscous oil (7 mg) (lit.¹⁷ m.p. 79–80°C). $[\alpha]_{\text{D}}^{22} + 18.0$ (CHCl₃; *c* 0.15) {lit.¹⁷ $[\alpha]_{\text{D}}^{15} + 30.1$ (CHCl₃; *c* 0.013)}. ¹H NMR, EI mass, UV and IR spectral data were comparable to the published data.¹⁷ CD (MeOH; *c* 4.4 mg/100 ml: 230–400): $[\theta]_{230}^{\text{max}} + 43487$, $[\theta]_{239}^{\text{min}}$ 0, $[\theta]_{254}^{\text{min}}$ - 102144, $[\theta]_{280}^{\text{min}}$ - 22249, $[\theta]_{292}^{\text{min}}$ 0, $[\theta]_{298}^{\text{max}}$ + 4045, $[\theta]_{304}^{\text{min}}$ 0, $[\theta]_{312}^{\text{min}}$ - 3034, $[\theta]_{320}^{\text{min}}$ 0, $[\theta]_{352}^{\text{max}}$ + 38431, $[\theta]_{386}^{\text{max}}$ + 6068 and $[\theta]_{400}^{\text{min}}$ 0.

(7*R*,8*R*,3'*S*)- Δ^8 -3',6'-Dihydro-3'-methoxy-3,4-methylenedioxy-6'-oxo-8.3',7.O.4'-lignan (**5**) Oil (4.3 mg). $[\alpha]_{\text{D}}^{22} - 38.8$ (MeOH; *c* 0.42). UV (MeOH) λ_{max} : 230 and 290 nm. IR (KBr) ν_{max} : 3436, 3307, 2919, 2851, 1733, 1672, 1645, 1625, 1505, 1494, 1447, 1379, 1256, 1183, 1040 and 936. MS (EI, eV) *m/z* (%): 340 (5, *M*⁺), 309 (4), 271 (3), 269 (2), 243 (4), 178 (8), 165 (22), 162 (74), 149 (34), 135 (45), 115 (40), 104 (58), 103 (74), 91 (75), 77 (100), 69 (94), 65 (64), 55 (56), 51 (36), 43 (88), 41 (98) and 39 (62). (Found $[M]^+$ 340.1303. C₂₀H₂₀O₅ requires 340.1311). ¹H NMR: δ 0.49 (3 H, d, *J* 7.4 Hz, 9-H₃), 2.65 (1 H, m, 8-H), 3.13 (2 H, m, 7'-H₂), 3.16 (3 H, s, 3'-OMe), 5.10 (2 H, m, 9'-H₂), 5.85 (1 H, m, 8'-H), 5.90 (1 H, s, 5'-H), 6.0 (2 H, s, OCH₂O), 6.06 (1 H, d, *J* 4.5 Hz, 7-H), 6.25 (1 H, t, *J* 1.2 Hz, 2'-H), 6.71 (2 H, m, 2-H, 5-H) and 6.80 (1 H, m, 6-H). ¹³C NMR: 9.7 (C-9), 33.4 (C-7'), 47.3 (C-8), 51.4 (3'-OMe), 82.2 (C-3'), 88.1 (C-7), 101.2 (OCH₂O), 104.1 (C-5'), 106.3 (C-2), 108.3 (C-5), 117.2 (C-9'), 119.0 (C-6), 130.4 (C-1), 132.1 (C-2'), 135.2 (C-8'), 143.4 (C-1'), 147.3 and 147.9 (C-3, C-4), 173.0

(C-4') and 187.4 (C-6'). CD (MeOH; *c* 10.3 mg/100 ml: 230–400): $[\theta]_{230}^{\text{max}} + 19964$, $[\theta]_{242}^{\text{min}}$ 0, $[\theta]_{246}^{\text{min}}$ - 18429, $[\theta]_{254}^{\text{min}}$ - 35760, $[\theta]_{265}^{\text{min}}$ - 18429, $[\theta]_{275}^{\text{min}}$ 0, $[\theta]_{282}^{\text{max}}$ + 5485, $[\theta]_{289}^{\text{min}}$ 0, $[\theta]_{295}^{\text{min}}$ - 18429, $[\theta]_{306}^{\text{min}}$ - 39929, $[\theta]_{325}^{\text{min}}$ - 18429, $[\theta]_{336}^{\text{min}}$ 0, $[\theta]_{354}^{\text{max}}$ + 12286, $[\theta]_{382}^{\text{min}}$ + 2413, $[\theta]_{390}^{\text{min}}$ + 1316 and $[\theta]_{400}^{\text{min}}$ 0.

(7*S*,8*R*,3'*S*,4'*R*)- Δ^8 -3',4',5',6'-Tetrahydro-3,4-methylenedioxy-3',4'-dimethoxy-6'-oxo-8.3',7.O.4'-lignan (*kadsurin A*, **6**) Oil (5 mg from fruits, 50 mg from stems). $[\alpha]_{\text{D}}^{22} - 102.0$ (CHCl₃; *c* 0.24) {lit.⁸ $[\alpha]_{\text{D}}^{22} - 104.4$ (CHCl₃; *c* 0.46)}. It was found identical in all respects (¹H and ¹³C NMR, EI mass, UV and IR) with our earlier isolated sample from *P. schmidtii*.⁸

(7*S*,8*R*,3'*S*,4'*R*)- Δ^8 -3',4',5',6'-Tetrahydro-3,4-methylenedioxy-3',4'-dimethoxy-6'-oxo-8.3',7.O.4'-lignan (*piperenone*, **7**) Solid mass (5 mg from stems) (lit.¹⁵ m.p. 86–88°C). $[\alpha]_{\text{D}}^{22} - 135.5$ (MeOH; *c* 0.14) {lit.¹⁵ $[\alpha]_{\text{D}}^{22} - 129.0$ (MeOH; *c* 1.16)}. It was identified by comparison of its spectral data (¹H and ¹³C NMR, EI mass, UV and IR) with literature data.^{13,15}

(7*S*,8*S*,1'*R*)- Δ^8 -1',4'-Dihydro-5'-methoxy-3,4-methylenedioxy-4'-oxo-8.1',7.O.2'-lignan (*burchellin*, **8**) Oil (14 mg from fruits, 15 mg from stems). $[\alpha]_{\text{D}}^{22} + 23.8$ (CHCl₃; *c* 0.29) {lit.¹⁹ $[\alpha]_{\text{D}}^{22} + 42.0$ (CHCl₃; *c* 0.0060)}. All spectral data (¹H and ¹³C NMR, EI mass, UV, IR and CD) were identical with those reported.^{14,19}

(7*R*,8*S*,1'*S*)- Δ^8 -1',4'-Dihydro-5'-methoxy-3,4-methylenedioxy-4'-oxo-8.1',7.O.2'-lignan (**9**) Oil (16 mg from fruits, 3 mg from stems). $[\alpha]_{\text{D}}^{22} - 67.4$ (MeOH; *c* 0.49) {lit.¹⁰ $[\alpha]_{\text{D}}^{22} - 56.7$ (MeOH; *c* 0.53)}. Spectral data (¹H and ¹³C NMR, EI mass, UV, IR and CD) were identical with those reported.^{10,20}

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