

Communication

A New 3-Benzylchroman Derivative from Sappan Lignum (*Caesalpinia sappan*)

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Abstract: 3'-Deoxy-4-*O*-methylepisappanol, a new 3-benzylchroman derivative, was isolated from Sappan Lignum, together with thirteen known chemical compounds identified as protosappanin A, sappanchalcone, sappanone B, palmitic acid, (+)-(8*S*,8'*S*)-bisdihydrosiringenin, brazilein, 3-deoxysappanchalcone, (+)-lyoniresinol, 3-deoxy-sappanone B, protosappanin B, isoprotosappanin B, 3'-*O*-methylbrazilin and brazilin, respectively. Among these known compounds, this is the first time that (+)-(8*S*,8'*S*)-bisdihydrosiringenin was obtained from the family Caesalpiniaceae.

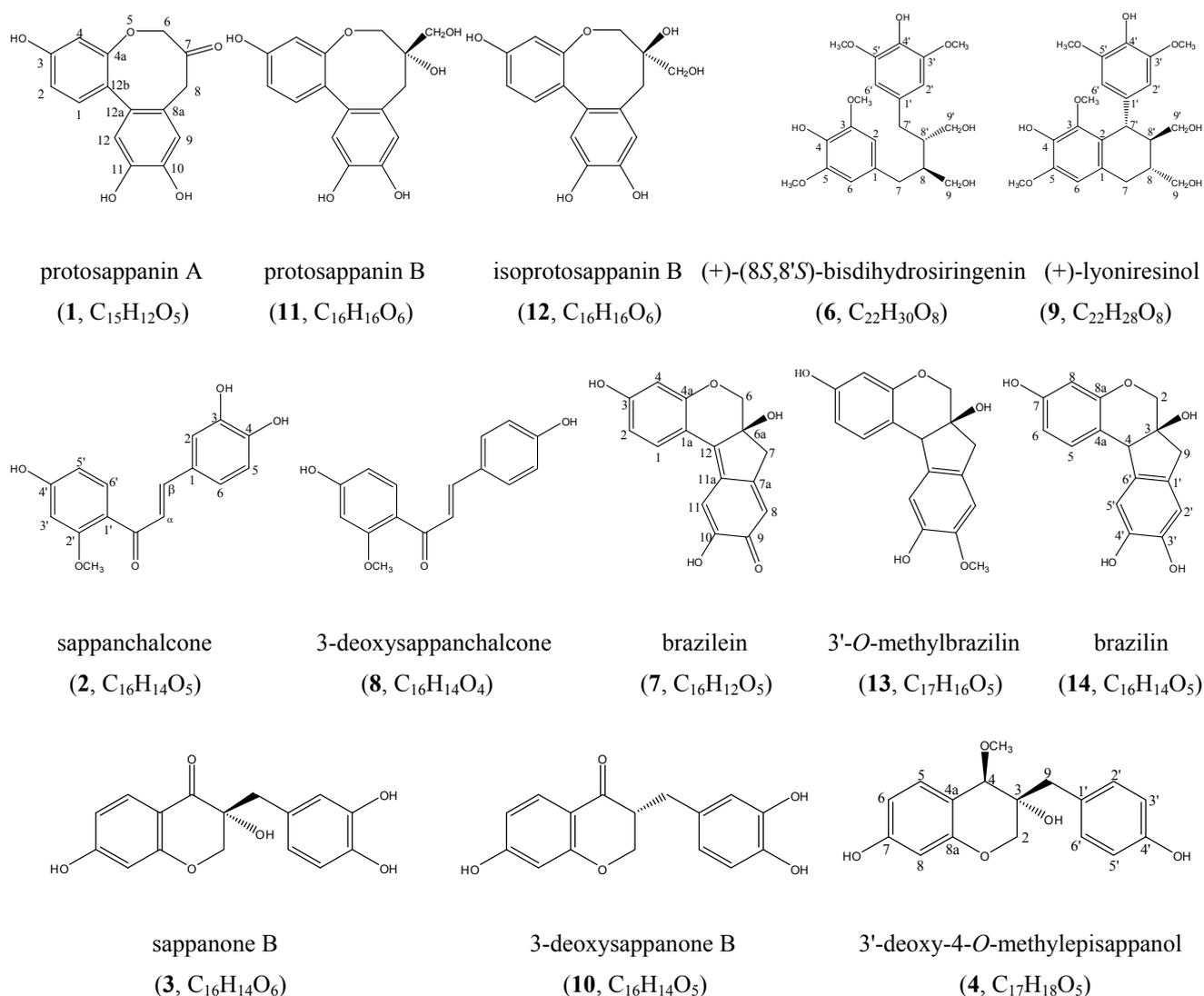
Keywords: Sappan Lignum; chemical compounds; 3'-deoxy-4-*O*-methylepisappanol

Introduction

Sappan Lignum, the dried heartwood of *Caesalpinia sappan* L., has not only been used as a natural dyestuff for a long time [1, 2], but also a Traditional Chinese Medicine for activating blood circulation

and removing stasis [3]. In recent years, the extract of Sappan Lignum has been found to be a potential immunosuppressive agent [4, 5]. The reported main phenolic compounds in Sappan Lignum were divided into to four structural sub-types: *i.e.* brazilin, chalcone, protosappanin and homisoflavonoid. Among the protosappanin derivatives, such as protosappanin B and isoprotosappanin B, 10-*O*-methylprotosappanin B and 10-*O*-methylisoprotosappanin B, as well as protosappanin E1 and protosappanin E2 occur as pairs of epimers. Meanwhile, the homisoflavonoid epimers sappanol and episappanol, 4-*O*-methylsappanol and 4-*O*-methylepisappanol, 3'-*O*-methylsappanol and 3'-*O*-methylepisappanol were successively isolated [6-22]. In continuation of our exploration of the chemical diversity of Sappan Lignum we report in this paper the isolation and identification of the new 3-benzylchroman derivative 3'-deoxy-4-*O*-methylepisappanol (**4**), and thirteen known compounds: protosappanin A (**1**), sappanchalcone (**2**), sappanone B (**3**), palmitic acid (**5**), (+)-(8*S*,8'*S*)-bisdihydrosiringenin (**6**), brazilin (**7**), 3-deoxysappanchalcone (**8**), (+)-lyoniresinol (**9**), 3-deoxysappanone B (**10**), protosappanin B (**11**), isoprotosappanin B (**12**), 3'-*O*-methylbrazilin (**13**) and brazilin (**14**) (Figure 1).

Figure 1. The structures of phenolic compounds from Sappan Lignum.



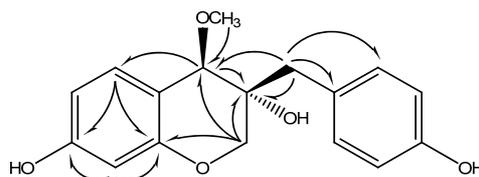
Results and Discussion

Compound **4** was obtained (from MeOH) as a colorless powder with the molecular formula $C_{17}H_{18}O_5$, according to the HREIMS data. Its IR spectrum exhibited bands at 3450 (hydroxyl), 1621 and 1511 cm^{-1} (arom. ring). The $^1\text{H-NMR}$ peaks at δ_{H} 7.16 (2H) and 6.77 (2H), and the $^{13}\text{C-NMR}$ ones at δ_{C} 128.9 (s), 133.8 (d), 116.6 (d) and 158.1 (s), indicated the presence of one 1,4-disubstituted aromatic ring. A 1,2,4-trisubstituted aromatic ring was also inferred from the presence of δ_{H} 6.96 (1H), 6.34 (1H) and 6.28 (1H) in the $^1\text{H-NMR}$ spectra, and δ_{C} 104.5 (d), 108.9 (d), 113.6 (s), 134.3 (d), 157.2 (s) and 160.5 (s) in the $^{13}\text{C-NMR}$ spectra (Table 1).

Table 1. NMR spectral data for (**4**) in acetone- d_6 .

No.	δ_{H}	δ_{C}	HMBC
2	3.82 (1H, <i>d</i> , $J = 11.0$ Hz), 4.10 (1H, <i>d</i> , $J = 11.0$ Hz)	71.2	71.1, 78.8, 157.2
3		71.7	
4	3.60 (1H, <i>s</i>)	78.8	56.9, 71.7, 134.3, 157.2
4a		113.6	
5	6.96 (1H, <i>d</i> , $J = 8.0$ Hz)	134.3	78.8, 157.2, 160.5
6	6.34 (1H, <i>dd</i> , $J = 8.0, 2.0$ Hz)	108.9	104.5, 113.6
7		160.5	
8	6.28 (1H, <i>d</i> , $J = 2.0$ Hz)	104.5	157.2, 160.5
8a		157.2	
9	2.70 (1H, <i>d</i> , $J = 13.5$ Hz), 2.91 (1H, <i>d</i> , $J = 13.5$ Hz)	40.5	71.7, 78.8, 128.9, 133.8
1'		128.9	
2',6'	7.16 (2H, <i>d</i> , $J = 8.5$ Hz)	133.8	40.5, 133.8, 158.1
3',5'	6.77 (2H, <i>d</i> , $J = 8.5$ Hz)	116.6	116.6, 128.9, 158.1
4'		158.1	
4-OCH ₃	3.30 (3H, <i>s</i>)	56.9	78.8

The HMBC correlations (Figure 2) between the proton at δ_{H} 7.16 of the 1,4-disubstituted aromatic ring and the carbon at δ_{C} 40.5, the protons at δ_{H} 2.70 and 2.91 to the carbon at δ_{C} 78.8, the proton at δ_{H} 3.60 to the carbon at δ_{C} 56.9, 71.7, 134.3 and 157.2, and the protons at δ_{H} 3.82 and 4.10 to the carbons at δ_{C} 71.1, 78.8 and 157.2 indicated the presence of a 3,7-dihydroxy-3-(4-hydroxybenzyl)-4-methoxychroman unit. The absolute configuration at the C-3 and C-4 positions of **4** was elucidated by comparison of its $^1\text{H-NMR}$ data and specific rotation with those of 4-*O*-methylsappanol and 4-*O*-methylepisappanol [13, 23]. Thus, the peaks at δ_{H} 3.82 and 4.10 due to the H-2 of **4** were in agreement with those of 4-*O*-methylepisappanol, while the specific rotation of **4** was -21.0 . Consequently, the configuration and structure of **4** was elucidated to be (3*R*,4*R*)-3,7-dihydroxy-3-(4-hydroxybenzyl)-4-methoxychroman, and this compounds has been named 3'-deoxy-4-*O*-methylepisappanol.

Figure 2. Main HMBC correlations of (4).

Conclusions

3'-Deoxy-4-*O*-methylepisappanol (4), the epimer of 3'-deoxy-4-*O*-methylsappanol, is a new compound. (+)-(8*S*,8'*S*)-Bisdihydrosiringenin (6) has been observed in the family Caesalpiniaceae for the first time. Meanwhile, the epimers of protosappanin B (11) and isoprotosappanin B (12) have also been obtained from Sappan Lignum. Besides four main structural sub-types of brazilin, chalcone, protosappanin and homisoflavanoid, phenylpropanoids, including (+)-(8*S*,8'*S*)-bisdihydrosiringenin (6), (+)-lyoniresinol (9), etc., also form another structural sub-type within Sappan Lignum.

Experimental

General

Melting points were determined using a SGW X-4 micromelting point meter. Optical rotations were measured on a Perkin Elmer 341 polarimeter. UV absorption spectra were measured on a TU-1900 UV spectrophotometer. IR spectra were recorded on an Analect RFX-65A spectrometer. The NMR spectra were measured on a Bruker Avance 500 spectrometer (500 MHz for ¹H and 125 MHz for ¹³C spectra), using TMS as internal standard. HREIMS and EI-MS were recorded on MAT95XP and DSQ spectrometer, respectively. Silica gel (200–300 mesh) and thin layer chromatographic plates were purchased from Qingdao Marine Chemistry Co. Ltd. (Qingdao, China). All analytical grade solvents used were obtained from Tianjin Fuyu Fine Chemical Co. Ltd. (Tianjin, China).

Plant Material

Sappan Lignum was bought from Guangdong Medical Material Company in 2006, and authenticated by Professor Gang Hao from South China Agricultural University. The voucher specimen (Huang, 007) was deposited at Tropical Medicine Institute, Guangzhou University of Chinese Medicine.

Extraction and Isolation

The air-dried and chipped Sappan Lignum (10 Kg) was extracted repeatedly three times under reflux with 95% EtOH. The combined EtOH extract was evaporated under reduced pressure to yield a red residue. After defatting by petroleum ether (60–90 °C), the residue was dissolved in water, then extracted successively with EtOAc and *n*-BuOH, respectively. The combined *n*-BuOH mixture (150 g)

was subjected to silica gel (200~300 mesh) column, and eluted with CHCl₃-MeOH gradient solvents. Combination of similar fractions on the basis of TLC analysis afforded fractions 1 and 2 at 97:3 and 93:7 (v/v), respectively. Fraction 1 (60 g) was chromatographed on a silica gel column eluted with petroleum ether-acetone (80:20, 70:30 and 60:40, v/v) to yield compounds **1** (500 mg), **2** (1 g), **3** (15 mg), **4** (3 mg), **5** (300 mg); **8** (20 mg), **10** (10 mg) and **13** (15 mg), respectively. Fraction 2 (50 g) was separated by repeated chromatography eluting with CHCl₃-MeOH gradients of 93:7, 90:10 and 85:15 (v/v), respectively, to give compounds **6** (15 mg), **7** (1.5 g) and **9** (10 mg), **11** and **12** (100 mg).

Compound characterization

Protosappanin A (**1**): was identified by comparison to literature data [24].

Sappanchalcone (**2**): yellow needles (from MeOH); ¹³C-NMR (acetone-*d*₆) δ: 190.8 (C=O), 123.7 (C-α), 143.3 (C-β), 129.9 (C-1), 117.5 (C-2), 147.3 (C-3), 149.5 (C-4), 116.3 (C-5), 126.6 (C-6), 123.4 (C-1'), 162.7 (C-2'), 101.1 (C-3'), 164.3 (C-4'), 109.7 (C-5'), 134.4 (C-6'), 57.1 (2'-OCH₃). Identified by the match between its ¹H-NMR data and the reported values [23].

Sappanone B (**3**): colorless powder (from MeOH); ¹³C-NMR (acetone-*d*₆) δ: 74.2 (C-2), 74.5 (C-3), 195.4 (C-4), 114.0 (C-4a), 131.2 (C-5), 112.9 (C-6), 166.6 (C-7), 104.6 (C-8), 165.3 (C-8a), 41.8 (C-9), 128.7 (C-1'), 116.6 (C-2'), 146.4 (C-3'), 145.9 (C-4'), 119.7 (C-5'), 124.0 (C-6'). ¹H-NMR data was consistent with those reported [23].

3'-Deoxy-4-O-methylepisappanol (**4**): colorless powder (from MeOH); mp 98-99 °C; $[\alpha]_D^{25} = -21.0$ (c 0.15, MeOH), UV (MeOH) λ_{max} nm (log ε): 284 (3.54), 277 (3.58), 224 (4.04) nm; IR ν_{max}^{KBr} cm⁻¹: 3450 (OH), 3927, 1621 and 1511 (Ar), 1382, 1162 cm⁻¹; ¹H and ¹³C-NMR spectral data were listed in Table 1; EIMS *m/z* (rel. int.): [M]⁺ 302 (3), 272 (4), 153 (100), 123 (40), 107 (47), 77 (18); HREIMS *m/z*: 302.1147 [M]⁺ (calcd for C₁₇H₁₈O₅, 302.1149).

Palmitic acid (**5**): identified by comparison to literature data [25].

(+)-(8*S*,8'*S*)-bis-Dihydrosiringenin (**6**): colorless powder (from MeOH); $[\alpha]_D^{25} = +10.0$ (c 0.21, MeOH); ¹H-NMR (pyridine-*d*₅) δ: 2.51 (2H, *m*, H-8 and 8'), 3.11 (2H, *dd*, *J* = 13, 7 Hz, H-7a and 7a'), 3.15 (2H, *dd*, *J* = 13, 7 Hz, H-7b and 7b'), 3.73 (12H, *s*, 3, 3', 5 and 5'-OCH₃), 4.12 (2H, *dd*, *J* = 11, 5 Hz, H-9a and 9a'), 4.19 (2H, *dd*, *J* = 11, 5 Hz, H-9b and 9b'), 6.76 (4H, *s*, H-2, 2', 6 and 6'); ¹³C-NMR (pyridine-*d*₅) δ: 132.1 (C-1 and 1'), 107.5 (C-2 and 2'), 149.0 (C-3 and 3'), 135.4 (C-4 and 4'), 149.0 (C-5 and 5'), 107.5 (C-6 and 6'), 36.4 (C-7 and 7'), 44.3 (C-8 and 8'), 61.3 (C-9 and 9'), 56.3 (3, 3', 5 and 5'-OCH₃). The NMR spectral data were in accordance with those reported [26, 27].

Brazilein (**7**): identified based on its NMR data [18].

3-Deoxysappanchalcone (**8**): yellow needles (from MeOH); ¹³C-NMR (acetone-*d*₆) δ: 190.8 (C=O), 126.6 (C-α), 142.9 (C-β), 129.2 (C-1), 131.9 (C-2 and 6), 117.7 (C-3 and 5), 161.3 (C-4), 123.4 (C-1'),

162.7 (C-2'), 101.1 (C-3'), 164.3 (C-4'), 109.7 (C-5'), 134.4 (C-6'), 57.1 (2'-OCH₃), was confirmed as for its ¹H-NMR spectra, consistent with the reported data [23].

(+)-*Lyoniresinol* (**9**): colorless powder (from MeOH); $[\alpha]_D^{25} = + 2.08$ (*c* 0.24, MeOH); ¹H-NMR (pyridine-*d*₅) δ : 2.24 (1H, *m*, H-8), 2.65 (1H, *m*, H-8'), 3.07 (1H, *m*, H-7a), 3.12 (1H, *m*, H-7b), 3.64 (6H, *s*, 3' and 5'-OCH₃), 3.76 (3H, *s*, 3-OCH₃), 3.77 (3H, *s*, 5-OCH₃), 4.09 (2H, *m*, H-9), 4.17 (2H, *m*, H-9'), 5.06 (1H, *d*, *J* = 5.5 Hz, H-7'), 6.78 (1H, *s*, H-6), 6.93 (1H, *s*, H-6'); ¹³C-NMR (pyridine-*d*₅) δ : 129.5 (C-1), 126.6 (C-2), 147.9 (C-3), 139.4 (C-4), 148.2 (C-5), 107.4 (C-6), 33.8 (C-7), 41.6 (C-8), 66.4 (C-9), 138.4 (C-1'), 107.3 (C-2'), 148.9 (C-3' and 5'), 135.8 (C-4'), 107.3 (C-6'), 42.3 (C-7'), 49.3 (C-8'), 64.1 (C-9'), 59.6 (3-OCH₃), 56.0 (5-OCH₃), 56.4 (3' and 5'-OCH₃) was identified based on analysis of the literature data [27-29].

3-Deoxysappanone B (**10**): colorless powder (from MeOH), $[\alpha]_D^{25} = - 10.0$ (*c* 0.81, MeOH), ¹H-NMR (acetone-*d*₆) δ : 2.55 (1H, *dd*, *J* = 14.0, 10.0 Hz, H-9a), 2.81 (1H, *m*, H-3), 3.07 (1H, *dd*, *J* = 14.0, 10.0 Hz, H-9b), 4.15 (1H, *dd*, *J* = 11.0, 9.0 Hz, H-2a), 4.35 (1H, *dd*, *J* = 11.0, 9.0 Hz, H-2b), 6.37 (1H, *d*, *J* = 2.0 Hz, H-8), 6.56 (1H, *dd*, *J* = 8.0, 2.0 Hz, H-6'), 6.60 (1H, *dd*, *J* = 8.0, 2.0 Hz, H-6), 6.76 (1H, *d*, *J* = 2.0 Hz, H-2'), 6.77 (1H, *d*, *J* = 8.0 Hz, H-5'), 7.73 (1H, *d*, *J* = 8.5 Hz, H-5); ¹³C-NMR (acetone-*d*₆) δ : 71.7 (C-2), 49.1 (C-3), 193.3 (C-4), 115.9 (C-4a), 130.9 (C-5), 112.3 (C-6), 166.0 (C-7), 104.4 (C-8), 165.5 (C-8a), 33.4 (C-9), 132.2 (C-1'), 117.2 (C-2'), 146.9 (C-3'), 145.5 (C-4'), 117.9 (C-5'), 122.3 (C-6') was identified by comparison of its ¹H-NMR data with the reported for this compound [9].

Protosappanin B (**11**) and *isoprotosappanin B* (**12**): colorless powders (from MeOH), were isolated as a 1.2:1 mixture; ¹H-NMR (acetone-*d*₆) δ : 2.54-2.74 (4H, each H *J* = 13 Hz, H-8), 3.16-4.35 (2H, each H *J* = 11 Hz, 7-CH₂OH), 3.16-4.35 (4H, each H *J* = 12 Hz, H-6), 6.48-6.56 (2H, *d*, *J* = 2.5 Hz, H-4), 6.56-6.62 (2H, *dd*, *J* = 8.0, 2.5 Hz, H-2), 6.71-6.84 (4H, *s*, H-9 and 12), 7.00 (2H, *d*, *J* = 8.0 Hz, H-1); ¹³C-NMR (acetone-*d*₆) δ : 134.2/133.3 (C-1), 112.8/112.1 (C-2), 159.8/159.8 (C-3), 109.9/109.1 (C-4), 159.8/160.2 (C-4a), 78.2/76.9 (C-6), 73.7/73.2 (C-7), 43.6/ 40.9 (C-8), 125.9/124.3 (C-8a), 118.4/118.3 (C-9), 145.5/145.7 (C-10), 145.5/145.5 (C-11), 119.9/120.7 (C-12), 131.1/132.6 (C-12a), 129.4/128.3 (C-12b), 66.7/69.1 (7-CH₂OH). The ¹H-NMR data resembled those reported [23].

3'-O-Methylbrazilin (**13**): ¹³C-NMR (acetone-*d*₆) δ : 71.8 (C-2), 78.9 (C-3), 52.4 (C-4), 116.5 (C-4a), 133.0 (C-5), 110.7 (C-6), 156.5 (C-7), 105.0 (C-8), 158.7 (C-8a), 44.0 (C-9), 132.1 (C-1'), 110.5 (C-2'), 148.7 (C-3'), 147.5 (C-4'), 113.1 (C-5'), 139.5 (C-6'), 57.5 (3'-OCH₃). The ¹H-NMR spectral data were identical to those reported [13].

Brazilin (**14**): was identified based on its NMR spectral data, identical to that reported [18].

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Sample Availability: Samples of the compounds are available from the authors.