A New Diterpenoid from the Seeds of *Caesalpinia sappan* Linn

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Abstract: A new cassane-type diterpene, named Phangininoxy A (1) and one known Phanginin A (2) were isolated from the exact of seeds of *Caesalpinia sappan* Linn. Their structures were elucidated by spectroscopic methods, mainly 1D and 2D NMR.

Keywords: *Caesalpinia sappan*; cassane; diterpene; NMR.

1. Plant Source

Chromatographic separation of the CH₂Cl₂ extract of seeds of *Caesalpinia sappan* Linn have led to the isolation of a new diterpene, named Phangininoxy A (1) and one known diterpene Phanginin A (2) (Figure 1).

The seeds of *C. sappan* Linn were collected in Guangxi province, P. R. China, in October 2007, and identified by Jin-Gui Shen of Shanghai Institute of Materia Medica. A voucher specimen was deposited at the herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

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2. Previous Studies

*Caesalpinia sappan* L is a large perennial shrub or small tree of the Fabaceae family. The plants are widely distributed in Southeast Asia [1]. Several species of the genus *Caesalpinia* were used in different systems of traditional medicine for the treatment of a variety of diseases, including liver disorders, fevers, ulcers of the mouth and throat [2].

So far, diterpenoids [3-7] and flavones [8-10] were isolated from the genus *Caesalpinia* as their major secondary metabolites. These compounds exhibit various biological activities including antioxidant, cytotoxic, anti-inflammatory, antimalarial, and antiviral activities [11-13].

3. Present Study

Air-dried seeds (1.0 kg) of *C. sappan* were extracted with CH$_2$Cl$_2$ at room temperature. The crude extracts were evaporated under reduced pressure to afford brownish CH$_2$Cl$_2$ (0.13 Kg) extract. The crude extract was further purified by QCC using petroleum ether as eluent and increasing polarity with acetone to give nine fractions (C1–C4). Fraction C2 (870 mg) was further purified by CC with petroleum ether-acetone (3:1, v/v) to give 2 (56 mg). Fraction C3 (3.12 g) was subjected to CC with ether-acetone (2:1, v/v) to afford four subfractions (C3a–C3d). Subfraction C3b (84.5 mg) was separated by preparative HPLC (C-18 column; CH$_3$CN/H$_2$O, from 5% to 95% in 30 min; flow 3 mL/min; 220 nm), 1 (26.3 mg) was obtained.

*Phangininoxy A* (1). White amorphous powder. IR(KBr): 3423, 2923, 2867, 1718, 1635, 1457, 1265, 1126, [90 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): 7.26 (d, J = 1.5 Hz, H-16), 6.20 (d, J = 1.5 Hz, H-15), 5.45 (s, H-20), 5.19 (d, J = 4.8 Hz, H-11), 4.20 (dd, J = 2.8 and 12.7 Hz, H-19b), 4.08 (d, J = 12.7 Hz, H-19a), 3.65 (s, 18-OMe), 2.76 (m, H-14), 2.58 (m, H-2b), 2.25 (m, H-1b), 2.19 (m, H-5), 2.12 (m, H-3), 2.01 (m, H-2a), 1.72 (m, H-6), 1.70 (m, H-7b), 1.32 (m, H-1a), 1.25 (m, H-7a), 0.96 (d, J = 7.1 Hz, H-17). $^{13}$C NMR (100 MHz, CDCl$_3$): 174.3, C-18; 147.8, C-12; 143.1, C-16; 128.9, C-13; 109.1, C-15; 104.4, C-20; 71.0, C-11; 69.9, C-19; 51.5, OMe; 46.1, C-5; 44.8, C-4; 43.2, C-9; 40.7, C-10; 38.3, C-8; 37.6, C-3; 33.7, C-1; 31.7, C-14; 28.0, C-7; 23.6, C-6; 20.3, C-2; 13.9, C-17. HREIMS: m/z 358.1776 [M$^+$] (calcd for C$_{21}$H$_{26}$O$_5$, 358.1781).

*Phanginin A* (2). White amorphous powder. $^1$H NMR (400 MHz, CDCl$_3$): 7.19(s, H-16), 6.20(s, H-15), 5.03(s, H-20), 4.38(d, J = 11.6 Hz, H-19a), 3.75(d, J = 11.6 Hz, H-19e), 3.65(s, OMe), 2.58 (m, H-14), 0.96(d, J = 7.0 Hz, H-17). $^{13}$C NMR (100 MHz, CDCl$_3$): 175.6, C-18; 149.3, C-12; 140.3, C-16; 122.4, C-13; 109.7, C-15; 97.3, C-20; 61.6, C-19; 51.5, OMe; 45.5, C-4; 45.1, C-5; 42.2, C-9; 38.5, C-10; 37.7, C-1; 36.6, C-8; 35.4, C-3; 31.4, C-14; 29.4, C-7; 23.5, C-6; 22.4, C-11; 20.8, C-2; 16.7, C-17. EIMS: m/z 360[M$^+$], 342, 254, 198, 145, 108.
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Compound 1 was obtained as white amorphous powder. Its molecular formula was determined as C_{21}H_{26}O_{4} by HR-EI mass spectrum (m/z 358.1776 [M]^{+}, calcd. 358.1781). The IR spectrum displayed absorption bands for ester (1718 cm^{-1}) and furan ring (1635 and 1457 cm^{-1}) groups. The ^{13}C NMR and DEPT spectrum of 1 revealed 21 carbon signals, which were ascribed to an ester carbonyl δ_{C} 174.3, a 1,2-disubstituted furan ring (δ_{C} 109.1, 128.9, 143.1 and 147.8), two methyls, six methylenes, six methines, and two quaternary carbons. The ^{1}H NMR spectrum of 1 indicated a methyl at δ_{H} 0.96 (d, J = 7.1), a methoxyl at δ_{H} 3.65 (s), a hemiacetal proton at δ_{H} 5.45 (s), and two furan ring protons at δ_{H} 6.20 (d, J = 1.5) and 7.26 (d, J = 1.5).

By comparison of the spectroscopic data of 1 with those of known compound-Phanginin A (2) [6], 1 has the same substructure as 2 concerning the A-D rings. One major difference between these two compounds was the chemical shift of C-11. In comparison with the corresponding resonance δ_{C} 22.4 in compound 2, the C-11 in compound 1 shifted up-field to δ_{C} 71.0, which was indicative of an oxymethine and not a methylene. The connection between C-11 and C-20 via the oxygen atom to form a five-membered ring was confirmed by the key HMBC correlations between H-20 (δ_{H} 5.45) and C-11 (δ_{C} 71.0). Thus the planar structure of 1 was established.

Considering its biogenetic relationship, such elucidation was wholly consistent with those of naturally-occurred cassane-type diterpene. As for the relative stereochemistry of C-11, coupling constant (J = 4.8 Hz) of H-11 (δ_{H} 5.19) indicated that H-11 is oriented similar direction of H-9, and H-9 located at axial position (splitting pattern dd, J = 4.7 and 12.5 Hz). The relative configuration of 1 was further confirmed by a ROESY experiment. The key correlations of H-9 (δ_{H} 1.85) with H-20 (δ_{H} 5.45) and H-11 (δ_{H} 5.19) indicated the stereochemistry of H-11 (α) and H-20 (α), respectively (Fig. 1). Therefore the structure of 1 was established.

References


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