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A New Cassane-type Diterpene and Other Constituents from *Caesalpinia minax*

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Caesalpinia minax Hance (Fabaceae) is a medicinal plant growing in the tropical and subtropical regions of southeast Asia. Its seeds, known as "kushilian", have been long used in Chinese traditional medicine for the treatment of dysentery and sore diseases.[1] Recent studies showed that the cassane-type diterpenes of genus *Caesalpinia* displayed significant biological activities such as antimalarial,[2] antibacterial,[3] antihelmintic,[4] antiproliferative and antineoplasmic activities.[5,6] As a part of our exploration on the medicinal plant, the $CHCl_3$ extract of the seeds of this plant was studied. One new cassane-type diterpene, named 1α,7β-diacetoxy-5α-hydroxy-12α-methoxycass-13(15)-en-16,12-olide-17β-carboxylate, along with ten known compounds (Figure 1) were isolated. In this paper, we report the isolation and structure elucidation of the new compound.

Compound **1** was isolated as a white amorphous powder with a $[\alpha]_D^{20}$ as −12.0 (c = 0.1, MeOH). HR-ESI-MS gave a quasi-molecular ion peak at m/z 531.2191 $[M + Na]^+$ (*Calcd* 531.2206) in the positive-ion mode. In conjunction with the analyses of ^1H and ^{13}C-APT (Table 1) spectra, the molecular formula of compound **1** was deduced as $C_{26}H_{36}O_{10}$. The IR spectrum showed hydroxyl absorption at 3479 cm^{-1} and carbonyl absorption at 1738 cm^{-1} (lactone). The UV absorption maximum was 202 nm along with the IR absorption band at 1738 cm^{-1}, indicating the presence of an α,β-

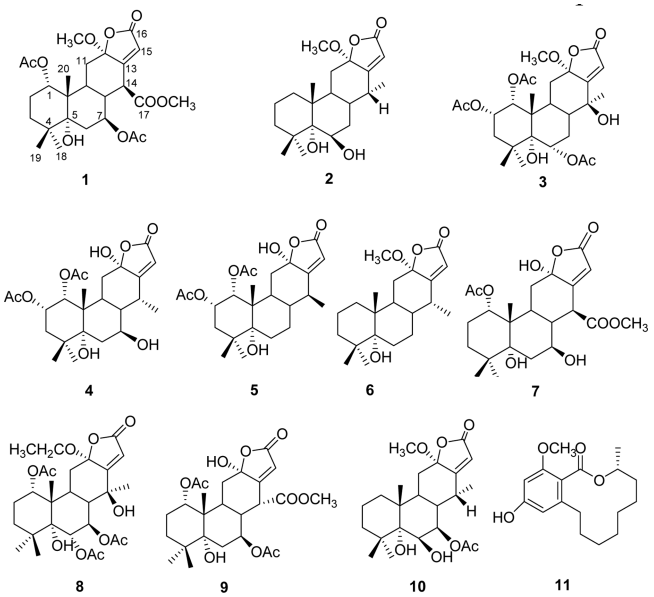

Figure 1. Structures of Compounds **1**-**11**.

[a]These authors contributed equally to this work.

Table 1. NMR data (600 MHz) for compounds **1** in $CDCl_3$

Position	δ_C, type	δ_H (J in Hz)
1	74.9, CH	4.86 s
2	22.9, CH_2	1.72-1.76, m
		1.92-1.99, m
3	30.1, CH_2	1.13-1.17, m
		1.76-1.80, m
4	38.6, C	
5	78.4, C	
6	32.4, CH_2	1.56-1.60, m
		2.02-2.05, m
7	74.8, CH	5.21, m
8	44.1, CH	2.21-2.23, m
9	36.0, CH	2.81, td (10.8, 2.4)
10	43.6, C	
11	36.1, CH_2	1.53-1.58, m
		2.15-2.17, m
12	106.8, C	
13	163.1, C	
14	48.9, CH	3.18, d (10.8)
15	118.0, CH	5.81, s
16	168.7, C	
17	171.0, C	
18	28.1, CH_3	1.02, s
19	24.7, CH_3	1.11, s
20	17.7, CH_3	1.03, s
1-O<u>C</u>OCH_3	169.9, C	
1-OCO<u>C</u>H_3	21.4, CH_3	2.00, s
7-O<u>C</u>OCH_3	169.2, C	
7-OCO<u>C</u>H_3	21.3, CH_3	2.11, s
14-COO<u>C</u>H_3	52.3, CH_3	3.78, s
12-O<u>C</u>H_3	50.7, CH_3	3.16, s

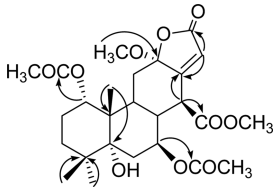

Figure 2. HMBC correlations of compound **1**.

butenolide ring.[7] The olefinic proton signal at δ_H 5.81 (s, H-15) and olefinic carbon signals at δ_C 118.0 (C-15), 163.1 (C-13) also confirmed the presence of an α,β-butenolide ring, combined with the three methyl signals at δ_H 1.02 (s, H_3-18), 1.03 (s, H_3-20), 1.11 (s, H_3-19) which are typical signals for cassane-type diterpenes. Therefore, the basic skeleton of **1** was cassane diterpenoid lactone-type. The data above were similar to those of 1α,7β-diacetoxy-5α,12α-dihydroxy-cass-13(15)-en-16,12-olide-17β-carboxylate (**9**),[14] except for the hydroxy group in **9** which was replaced by methoxy group in **1**. All carbon-bond protons were assigned from HSQC spectrum. The HMBC correlations (Figure 2) observed between δ_H 4.86 (s, H-1) and δ_C 169.9 (1-OCO), between δ_H 5.21 (m, H-7) and δ_C 169.2 (7-OCO), between δ_H 3.18 (d, *J*=10.6, H-14), δ_H 3.78 (s, 14-$COOCH_3$) and δ_C 171.0, and between δ_H 3.16 (s, 12-OCH_3) and δ_C 106.8 indicated that the acetyl groups were at C-1 and C-7, carboxymethyl group at C-14 and methoxy group at C-12. The relative configuration of compound **1** was determined on the basis of NOESY spectrum. The NOEs from H_3-20 to H-1 (δ_H 4.86, s), H-8 (δ_H 2.21-2.23, m), H-11_{ax} (δ_H 2.15-2.17, m) and H_3-19 (δ_H 1.11, s), from H_3-18 to H-7 (δ_H 5.21, m), H-9 (δ_H 2.81, td, *J* = 10.8, 2.4), and from H-9 to 12-OCH_3 (δ_H 3.16 s), H-14 (δ_H 3.18 d, *J* = 10.8) indicated that rings A and B have a chair conformation with *trans*-fused ring junction and thus confirmed the relative configuration at C-1, C-7, C-10, C-12 and C-14. The circular dichroism (CD) showed a strong negative cotton effect with the γ-lactone chromophore at λ_{max}232 nm indicated that the chirality at C-12 was *R*.[8] Combined with the NOESY spectrum, compound **1** was characterized as 1α, 7β-diacetoxy-5α-hydroxy-12α-methoxycass-13(15)-en-16, 12-olide-17β-carboxylate.

The known compounds were identified as 6β-hydroxy-neocaesalpin E (**2**),[9] Neocaesalpin W (**3**),[10] Neocaesalpin C (**4**),[11] Neocaesalpin J (**5**),[12] 12,16-epoxy-5α-hydroxy-12α-methoxycassa-13-(15)-en-16-one (**6**),[13] Neocaesalpin N (**7**),[12] 12α-ethoxyl-1α,6α,7β-triacetoxy-5α,14β-dihydroxy-cass-13(15)-en-16,12-olide (**8**),[14] 1α,7β-diacetoxy-5α,12α-dihydroxy-cass-13(15)-en-16,12-olide-17β-carboxylate (**9**),[14] 7β-acetoxy-6β-hydroxyneocaesalpin E (**10**)[9] and lasiodiplodin (**11**).[15] Among them, compounds **2-4**, **6** and **10** were reported for the first time from this plant and compound **11** has not been reported in any species of the genus *Caesalpinia*.

Experimental Section

Plant Material. The seeds of *C. minax* were collected in September 2008 from Nanning, Guangxi Province, China and identified by Prof. Jing-Quan Yuan, Department of Pharmaceutical Chemistry, Guangxi Botanical Garden of Medicinal Plant. A voucher specimen (NO. 21648) was deposited at the Guangxi Botanical Garden of Medicinal Plant, Nanning, Guangxi province, China.

1α,7β,-Diacetoxy-5α-Hydroxy-12α-Methoxycass 13 (15)-en-16,12-olide-17β-Carboxylate (1): white amorphous powder. $[\alpha]_D^{20}$ −12.0 (*c* = 0.1 MeOH); IR (KBr) cm^{-1} 3479, 1738 cm^{-1}; UV λ_{max} (MeOH) nm (log ε): 202 (3.49); CD (MeOH, Δε) λ_{max} (log ε) 232 (−6.87) nm; ^1H and ^{13}C-APT ($CDCl_3$): see Table 1; HR-ESI-MS *m/z*: 531.2191 $[M + Na]^+$ (*Calcd for* 531.2206).

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Supporting Information. General experimental procedures, the isolation details and spectra data of compound **1** are available as Supporting Information.

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