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A Phenolic Glucoside from *Alangium plantanifolium*

Wen Yan HU[1], Wen Ping XU[2], Jian Gong SHI[1]*, Yong Chun YANG[1], Guang Xiong ZHOU[1]

[1]Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Bejing 100050
[2]Hospital of Jiu Quan District, Gansu Province, Jiuquan District 735000

Abstract: A novel phenolic glucoside was isolated from stem barks of *Alangium plantanifolium*, its structure was elucidated to be 1-*O*-[2-(1-hydroxy-6-oxocyclohex-2-ene-1-carboxymethyl)-phenyl]-4, 6-*O*-[(*S*)-4, 4′, 5, 5′, 6, 6′-hexahydroxydi-phenoyl]-β-D-glucopyranose **1** by spectroscopic methods including 2D NMR techniques.

Keywords: *Alangium plantanifolium*, Alangiaceae, phenolic glucoside, 1-*O*-[2-(1-hydroxy-6-oxocyclohex-2-ene-1-carboxymethyl)-phenyl]-4, 6-*O*-[(*S*)-4, 4′, 5, 5′, 6, 6′-hexahydroxydi-phenoyl]-β-D-glucopyranose.

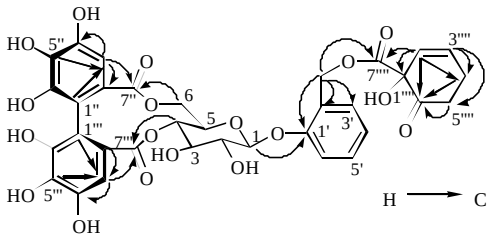
Alangium, the sole genus in the family Alangiaceae, has a variety of about 20 species distributed in the tropical and subtropical area of the Eastern Hemisphere, and 13 species are known to occur in the south of China[1]. *A. plantanifolium* and *A. chinense* are used in chinese traditional medicine for the treatment of rheumatalgia, paralysis, cardianeuria, and wound[2]. Pharmacological studies of the extracts of these two species showed muscular relaxing activity, and anabasine was considered as the active component[3]. We report here structural elucidation of a new phenolic glucoside, 1-*O*-[2-(1-hydroxy-6-oxo-cyclohex-2-ene-1-carboxymethyl)-phenyl]-4, 6-*O*-[(*S*)-4, 4′, 5, 5′, 6, 6′-hexa-hydroxydiphen-oyl]-β-D-glucopyranose **1**, isolated from the ethanolic extract of *A. plantanifolium*.

The ethanolic extract of the air-dried and ground stem barks of *A. plantanifolium* were subjected to column chromatography on silica gel to give compound **1**, white powder, $[\alpha]_D^{18}$ +6.0 (*c* 0.30, MeOH). The IR (KBr, cm^{-1}) spectrum of **1** showed a strong broadened absorption band for hydroxyl groups (3413), bands for conjugated carboxyl groups (1736, 1618), and aromatic rings (1602, 1503, and 1494). The positive FABMS spectrum exhibited quasi-molecular ion peaks at *m/z* 727 $[M+H]^+$ and 749 $[M+Na]^+$, its molecular formula was deduced to be $C_{34}H_{30}O_{18}$ by HRFABMS (found 749.1328, calc. 749.1329). The NMR data (**Table 1**) revealed that **1** is a phenolic glycoside, this was confirmed by HMQC and HMBC experiments. The signals at δ_H 4.99 (d, 1H, *J*=7.5 Hz), and δ_C 102.5, correlated to each other in the HMQC spectrum, were assignable to

* E-mail: shijg@imm.ac.cn

anomeric proton and carbon of the sugar moiety, and the β configuration at the anomeric carbon was suggested by the coupling constant. The chemical shifts and coupling patterns of proton signals for the sugar moiety were in good agreement with those found in strictinin[4], indicating that there is a β-D-glucopyranose unit in **1**. In the aromatic region of the ^{1}H NMR spectrum, four signals at δ 7.25 (br d, 1H, *J*=7.5, H-3′), 6.97 (br dd, 1H, *J*=7.5, and 7.5 Hz, H-4′), 7.28 (br dd, 1H, *J*=8.1, and 7.5 Hz, H-5′), and 7.10 (br d, 1H, *J*=8.1 Hz, H-6′) revealed the presence of an ortho-disubstituted phenyl unit in the molecule of **1**. The protonated carbon signals were assigned by HMQC experiment. The HMBC spectrum (**Figure 1**) showed two- and three-bond correlations from two geminal protons with an AB coupling pattern at δ 5.12 (d, 1H, *J*=12.3 Hz, H-7′a) and 5.39 (d, 1H, *J*=12.3 Hz, H-7′b) to C-1′, C-2′ and C-3′, respectively. These data proved that the ortho-disubstituted phenyl unit is a 2-oxymethylenephenoxy group. Furthermore, in the HMBC spectrum, a three-bond correlation from the anomeric proton to C-1′ established the linkage of 2-oxymethylenephenoxy group and the β-D-glucopyranose moiety.

Figure 1 HMBC correlations of **1**



In addition, the ^{1}H NMR spectrum showed two aromatic signals at δ 6.49 (s, 1H, H-3″), and 6.65 (s, 1H, H-3‴), the ^{13}C NMR spectrum showed seven pairs of sp^2 carbon signals including a pair of methine, and six pairs of quaternary carbons among which there was a pair of carbonyl carbons (**Table 1**). These data suggested that there is a hexahydroxydiphenoyl (HHDP) group in the molecule of **1**. A negative Cotton effect at 261 nm and a positive effect at 234 nm in the CD spectrum of **1** showed that the HHDP group possesses a *S* configuration[5]. In the HMBC spectrum, the correlations from H_2-6 to C-7″, and from H-4 to C-7‴ clearly demonstrated that the hydroxyl groups at C-6 and C-4 of the β-D-glucopyranose moiety were esterified by HHDP group. Moreover, the ^{1}H, ^{13}C NMR and DEPT spectral data of **1** (**Table 1**) showed the presence of signals for an additional unit composed of two methylenes, two methines, one carboxyl group, as well as a ketone group and an oxygenated quaternary carbon in the molecule of **1**. The coupling pattern of proton signals of this unit in the ^{1}H NMR spectrum revealed the presence of a partial structure $-CH=CH-CH_2-CH_2-$, which was confirmed by ^{1}H–^{1}H COSY and HMQC experiments. The HMBC experiment (**Figure 1**) unambiguously

established this unit to be a 1-hydroxy-6-oxocyclohex-2-ene-1-carboxyl moiety. The correlation from H_2-7′ to the carboxyl carbon in the HMBC spectrum unequivocally indicated that this unit was esterified at the oxymethylene group of the 2-oxymethylenephenoxy moiety. Accordingly, the structure of **1** was elucidated as 1-*O*-[2-(1-hydroxy-6-oxocyclohex-2-ene-1-carboxymethyl)-phenyl]-4, 6 -*O*-[(*S*)-4, 4′, 5, 5′, 6, 6′-hexahydroxydiphenoyl]-β-D-glucopyranose **1**.

Table 1 NMR Data for compound **1**

No.	H	C	No.	H	C
1	4.99 d (7.5)	102.5 d	5″		137.6 s
2	3.56 dd (7.5, 9.3)	76.0 d	6″		145.0 s
3	3.68 dd (9.3, 9.3)	76.0 d	7″		170.2 s
4	4.90 dd (9.3, 10.2)	73.5 d	1‴		117.2 s
5	3.98 dd (10.2, 6.0)	73.3 d	2‴		126.8 s
6a	3.76 br d (13.2)	64.9 t	3‴	6.65 s	108.8 d
6b	5.15 dd (13.2, 6.0)		4‴		146.0 s
1'		157.0	5‴		137.8 s
2'		126.6	6‴		145.0 s
3'	7.25 br d (7.5)	131.6	7‴		169.9 s
4'	6.97 br dd (7.5, 7.5)	123.9	1⁗		79.5 s
5'	7.28 br dd (7.5, 8.1)	131.6	2⁗	5.72 dt (9.6, 1.5)	129.6 d
6'	7.10 br d (8.1)	116.5	3⁗	6.11 dt (9.6, 3.6)	133.9 d
7′a	5.12 d (12.3)	64.6	4⁗a	2.40 m	27.7 t
7′b	5.39 d (12.3)		4⁗b	2.63 m	
1″		116.9 s	5⁗a	2.45 m	37.4 t
2″		126.6 s	5⁗b	2.85 m	
3″	6.49 s	108.4 d	6⁗		207.9 s
4″		146.0 s	7⁗		171.7 s

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