Chinese Chemical Letters Vol. 13, No. 11, pp 1067 – 1068, 2002 1067
http://www.imm.ac.cn/journal/ccl.html

A New Pseudo Sesquiterpenoid from the Seeds of Koelreuteria paniculata

Wen Han LIN*, Hai Ming LEI, Hong Zheng FU, Jun LI

National Research Laboratories of Natural and Biomimetic Drugs, Peking University, Beijing 100083

Abstract: From the seeds of medicinal plant *Koelreuteria paniculata*, a new pseudo sesquiterpenoid with novel skeleton namely paniculoid **1** was isolated. The structure of **1** was established on the basis of extensive 2D NMR spectroscopy in conjugation with MS and IR spectral analysis.

Keywords: *Koelreuteria Paniculata*, seeds, paniculoid, structural elucidation.

The species *Koelreuteria paniculata* Laxm (Sapindaceae) widely distributed in Northern China close to mountain area in Beijing suburb. The previous works[1,2] reported that the plant possesses the activities for anti-tumour, anti-oxidation, antibiosis, and the seeds mainly contained flavonoids and galloyl derivatives and possesses the activity for insecticide. In the systematic study on the plant phytochemically, a new pseudo sesquiterpenoid with novel skeleton namely paniculoid **1** was isolated from the ethyl acetate extract of the seeds by using silica gel column chromatography. This report intended to describe its structural elucidation.

Paniculoid **1** was obtained as colorless amorphous powder. Its molecular formula $C_{15}H_{18}O_3$ was proposed due to the molecular ion peak *m/z* 246 [M^+] in EIMS spectrum and the ^1H, ^{13}C NMR spectra as well as DEPT data. The IR absorptions at 1742 and 1710 cm^{-1} suggested the presence of two carbonyl groups. The ^{13}C NMR and DEPT spectra displayed two methyl groups (δ_C 15.42, 16.72); five methylene groups (δ_C 21.57, 29.00, 30.68, 31.32, and 32.71); two methine groups (δ_C 43.34 and 138.34); as well as six quaternary carbons (δ_C 46.38, 121.59, 130.10, 158.55, 167.72 and 170.92). ^1H NMR spectrum showed two methyl groups at δ 0.80 (d, 3H, J=6.6 Hz) and 1.81 (s, 3H); one olefinic proton at δ_H 6.90 (brs), and the signals of remained protons overlapped around 0.84-2.68 ppm. In HMBC spectrum, methyl protons δ_H 1.81 (s) correlated with carbonyl carbon δ_C 170.92 (C-3), olefinic carbons δ_C158.55 (C-5) and 121.59 (C-4); olefinic proton δ_H 6.90 (brs, H-9) correlated with carbonyl carbon δ_C 167.72 (C-1), 158.55 (C-5), 46.38 (C-7) and 21.57 (C-8). Moreover, the HMBC spectrum showed the correlations of methylene protons at C-6 (δ 2.68, d, J=17.0 Hz; 2.46,d, J=17.0 Hz) with C-4, C-5, C-7 and C-11(δ_C 43.34); and methylene protons at C-8 (δ_H 2.45, d, J=16.5 Hz, 2.23, brd, J=16.5 Hz) with δ138.34 (d, C-9), 130.10 (s, C-10), C-7 and C-11. These results led to conclude a 4-methyl-7, 8-dihydroisochromene-1,3-dione subunit. In 2D TOCSY spectrum, the proton correlations generated from methyl protons δ_H 0.80 (d,

J=6.6 Hz, H-15) to H-11(δ 1.82, m), H-12(δ 1.18, m; 1.23, m), H-13 (δ 2.00, m; 1.72, m), H-14 (δ 2.10, m; 1.52, m), in association with HMBC correlations of H-11, H-12, H-13, H-14 as well as H-15 with C-7, indicating a five membered spiral ring at C-7, and the methyl group CH_3-15 was deduced at C-11 due to the long range correlations of H-15 with C-7, C-11 and C-12. Therefore, the entire structure was determined as showed in **Figure 1**. The stereochemistry of **1** was proposed due to the NOESY spectrum. The NOE correlation of Me-15 with H-8α (δ_H 2.23) and H-9 implied that Me-15 was spatial close to H-8α and H-9. The NOE evidence in association with Dreding structure modeling supposed that the Me-15 was in β-configuration and C-7 was in R configuration. The ^{1}H and ^{13}C NMR data showed in **Table 1**

Figure 1 The proposed structure and main NOE correlations of compounds 1

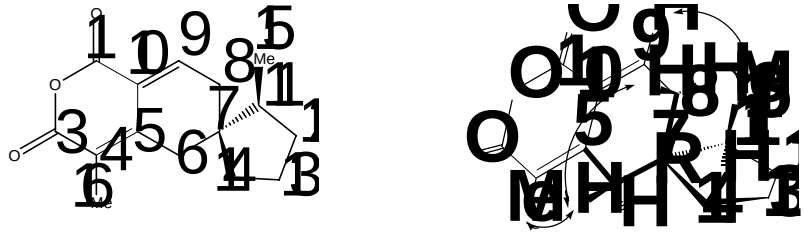

Table 1 ^{1}H and ^{13}C NMR Data of Compound 1

Position	δ_C	δ_H	HMBC (H→C)
1	167.72, s		
3	170.92, s		
4	121.59, s		
5	158.55, s		
6	30.68, t	2.68 (6α), d, 17.0; 2.46 (6β),	C-4, C-5, C-7, C-8, C-10, C-11, C-14
7	46.38, s	d, 17.0	
8	21.57, t		C-6, C-7, C-9, C-10, C-11, C-14
9	138.34, d	2.45 (8β), d, 16.5; 2.23 (8α),	C-1, C-5, C-7, C-8, C-10,
10	130.10, s	brd, 16.5	
11	43.34, d	6.90, brs	C-6, C-7, C-8, C-11, C-12, C-13, C-14, C-15
12	31.32, t		C-7, C-11, C-13, C-14, C-15
13	29.00, t	1.82, m	C-7, C-11, C-12, C-14
14	32.71, t	1.18, m; 1.23, m	C-6, C-7, C-8, C-11, C-12, C-13
15	16.72, q	1.72, m; 2.00, m	C-7, C-11, C-12
16	15.42, q	1.52, m; 2.10, m	C-3, C-4, C-5
		0.80, d, 6.6, 1.81, s	

in DMSO-d6

Acknowledgment

This project is supported by the National Natural Science Foundation of China (No.29732040).

References

1. X.F.Yang, H.M.Lei, H.Z.Fu, G.E.Ma, W.H. Lin, *Acata Pharm. Sin.*, **2000**,*35* (4), 279.
2. X.F.Yang, H.M.Lei, H.Z.Fu, G.E.Ma, W.H. Lin, *Acata Pharm. Sin.*, **1999**,*34* (6), 457.

Received 22 January, 2002