Chinese Chemical Letters Vol. 13, No. 11, pp 1063 – 1066, 2002
http://www.imm.ac.cn/journal/ccl.html

Two New Sesquiterpenes from *Euonymus nanoides*

Hong WANG, Xuan TIAN*, Yao Zu CHEN†

National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000

Abstract: Two new sesquiterpenes,1β-(β-)furancarboxy-4α-hydroxy-6α,13-diacetoxy-9β- cinnamoyloxy-β-dihydroagarofuran(**1**)and1β,6α-di-(α-methyl)-butanoyl-4α-hydroxy-9β-enzoyloxy-13- acetoxy-β-dihydroagarofuran (**2**), were isolated from the seed oil of *Euonymous nanoides*. Their structures were elucidated on the basis of spectral data.

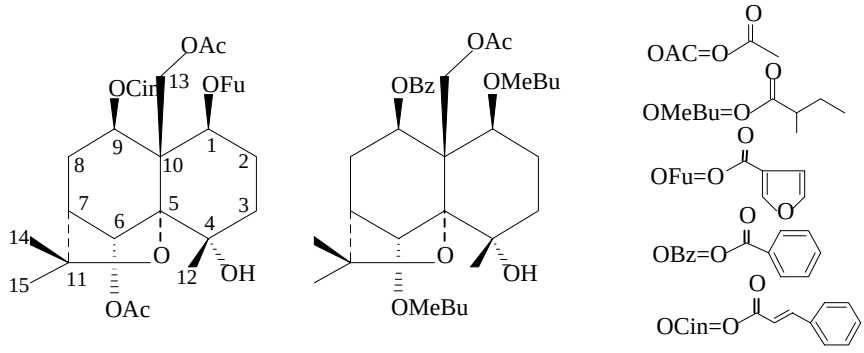
Keywords: Sesquiterpene, β-dihydroagarofuran, *Euonymous nanoides.*

The family *Celastraceae* is a rich source of dihydro-β-agarofuran sesquiterpene esters. In recent years these compounds have been of increasing interest due to their cytotoxic, antitumor-promoting, immunosuppressive, insecticidal, insect-antifeedant activities and for reversing multidrug resistance in cancer cells[1, 2]. In a previous study, we have described the isolation of several dihydro-β-agarofuran from *Euonymus phellomana* Loes[3,4]. Recently, we investigated the chemical constituents of the seed oil of *Euonymous nanoides* (*Celastraceae*). Two new dihydro-β-agarofuran sesquiterpene polyol esters: **1** and **2** (**Figure 1**) have been isolated from the seeds oil of *E. nanoides* growing in Luqu county, Gansu Province of China. In this paper, we deal with the structural elucidation of two new compounds.

Compound **1**, yellow oil, $[\alpha]_D^{20}$ +8.5 (c 0.750, $CHCl_3$), analyzed for $C_{33}H_{38}O_{11}$ by HR-FABMS:*m/z* 611.2494 $[M+1]^+$ (Calcd. For $C_{33}H_{39}O_{11}$: 611.2487). IR spectrum revealed a characteristic ester absorption band at 1732 cm^{-1} and a free hydroxyl absorption band at 3432 cm^{-1}. The NMR spectra suggested the presence of two acetate esters [^{1}H NMR δ 1.79 s, 2.20 s (2×3H); ^{13}C NMR δ 20.6, 21.3, 169.7, 170.8 (2×Ac)], one cinnamo-yloxylate ester [^{1}H NMR δ 6.38 (d, 1H, *J*=15.6Hz), 7.40 (m, 2H), 7.47 (m 1H), 7.55 (m, 2H), 7.70 (d, 1H, *J*=15.6Hz); ^{13}C NMR δ 117.7, 128.8, 130.5, 134.2, 145.8, 165.8], one (β-)furancarboxylate ester [^{1}H NMR δ 6.87 (d, *J*=1.2Hz), 7.41(d ,*J*=1.2Hz), 8.27 (s, 3×1H); ^{13}C NMR δ 109.7, 118.9, 144.0, 148.4, 161.9], and one free hydroxy group (^{1}H NMR δ 2.71 s).

† died; *E-mail: xuant@lzu.edu.cn

Figure 1 The structures of **1** and **2**



1 **2**

The ^{1}H NMR (**Table 1**) of **1** showed the presence of three tertiary methyl groups at δ 1.34 (s, H-12), 1.46 (s, H-14), 1.49 (s, H-15). The signals in ^{1}H-^{1}H COSY spectrum at δ 5.66 (d, *J*=4.0Hz, H-1), 5.67 (s, H-6) and 5.28 (d, *J*=6.8Hz, H-9) were assigned to three protons attached to carbon atoms bearing secondary ester groups, while signals at δ 4.42 (d, *J*=12.8Hz, H-13a) and δ 5.04 (d, *J*=12.8Hz, H-13b) were assigned to the two protons attached to carbon atoms bearing primary ester groups. The ^{13}C NMR spectrum (**Table 1**) of the parent skeleton of **1** showed three methyls at δ 24.2, 25.3 and 30.0, three methylene at δ 31.0, 33.6 and 40.5, one mrthylene attached to an oxygen function at δ 66.3, one methane at δ 43.3, three methines attached to an oxygen function at δ 69.0, 69.1 and 70.1, one quaternary carbon at δ 50.8,and three quaternary carbons attached to an oxygen at δ 69.5, 83.7 and 89.7, whose chemical shifts were very similar to those of reported dihydro-β-agarofurans[2,4]. It was determined that compound **1** was a dihydro-β-agarofuran sesquiterpene substituted with two acetates, one β-furancarboxylate, one cinnamoyloxylate ester and one free hydroxyl.

^{1}H-^{13}C long-range correlation spectrum (HMBC) was a useful tool to confirm the location of the ester groups. Thus, the carbonyl signal at δ 161.9 and 165.8 were correlated with the proton signals at δ 5.66 (H-1) and 5.28 (H-9), respectively, revealing that the β-furancarboxylate ester was located at C-1 and cinnamoyloxylate ester was located at C-9. Also, two acetate esters were positioned at C-6 and C-13, respectively, because the carbonyl signals at δ 169.7 and 170.6 were correlated with the proton signals of H-6 and H-13, respectively. As known that in this class of skeleton, H-1 and H-6 have axial stereochemistry[5,6]. From the NOESY spectrum of **1** (**Figure 2**), the correlation between H-1 and H-9 indicated the presence of axial stereochemistry of H-9. From these data, compound **1** was identified as 1β-(β-)furancarboxy-4α-hydroxy-6α, 13-diacetoxy-9β- cinnamoyloxy-β-dihydroagarofuran.

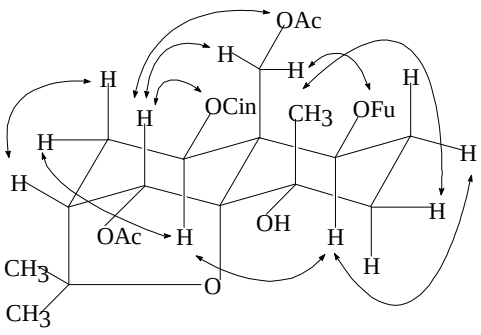
Compound **2**, yellow oil, $[\alpha]_{D}^{20}$ +29.0 (c 0.700, $CHCl_3$), analyzed for $C_{34}H_{48}O_{10}$ by HR-ESIMS: *m/z* 639.3134 $[M+Na]^+$ (Calcd. for $C_{34}H_{48}O_{10}Na$: 639.3140). IR spectrum revealed a characteristic ester absorption band at 1727 cm^{-1} and a free hydroxyl absorption band at 3432 cm^{-1}. The NMR spectra suggested the presence of two α-methyl-butanoate esters [^{1}H NMR δ 0.55t (2×3H), 0.80 d (2×3H, *J*=6.8Hz), 0.92 m

Table 1 The NMR spectral data of compounds **1** and **2** (400MHz, $CDCl_3$)

	1			**2**	
No.	δ_C (DEPT)	δ_H (J_{Hz})	No.	δ_C (DEPT)	δ_H (J_{Hz})
1	70.1 (CH)	5.66 d (4.0)	1	70.0 (CH)	5.57 d (4.0)
2	31.0 (CH_2)	2.31 m, 2.11 m	2	31.1 (CH_2)	2.32 m, 2.15 m
3	40.5 (CH_2)	1.15 m, 0.90 m	3	41.7 (CH_2)	1.50 m, 2.01 m
4	69.5 (C)		4	69.4 (C)	
5	89.7 (C)		5	89.6 (C)	
6	69.1 (CH)	5.67 s	6	70.2 (CH)	5.69 s
7	43.3 (CH)	2.31m	7	43.4 (CH)	2.33m
8	33.6 (CH_2)	2.45 m, 2.07 m	8	33.5 (CH_2)	2.48 m, 2.08 m
9	69.0 (CH)	5.28 d (6.8)	9	68.3 (CH)	5.34 d (6.8)
10	50.8 (C)		10	51.2 (C)	
11	83.7 (C)		11	83.8 (C)	
12	30.0 (CH_3)	1.34 s	12	29.9 (CH_3)	1.34 s
13	66.3 (CH_2)	5.04 d (12.8), 4.42 d (12.8)	13	66.2 (CH_2)	4.87 d (12.8), 4.52 d (12.8)
14	25.3 (CH_3)	1.46 s	14	26.5 (CH_3)	1.43 s
15	24.2 (CH_3)	1.49 s	15	24.4 (CH_3)	1.46 s

(2×1H), 1.20 m (2×1H), 1.90 m (1H), 2.00 m (1H); ^{13}C NMR δ 11.2, 11.6, 15.4, 16.5,25.1, 25.4, 40.6, 40.8, 174.4, 175.2 (2×MeBu)], one acetate ester [^{1}H NMR δ 2.21 s (3H); ^{13}C NMR δ 21.4, 170.5], one benzoate ester [^{1}H NMR δ 7.45 (t, 2H, *J*=7.6Hz), 7.57 (t, 1H, *J*=7.2Hz), 8.05 (d, 2H, *J*=7.6Hz); ^{13}C NMR δ 128.3 (2C), 129.4, 130.2 (2C), 133.3, 165.4] and one free hydroxyl group (^{1}H NMR δ 2.68 s). The NMR data (**Table 1**) for the parent ring system was very similar to those of **1**, suggesting that **2** also contains the 1, 4, 6, 9, 13-pentasubstituted-β-dihydroagarofuran skeleton and the locations of the proton have been confirmed by the ^{1}H-^{1}H COSY spectrum. As with **1**, the free hydroxyl group was at C-4 with equatorial orientation, and the ester group distributions were determined from the HMBC spectrum, which showed cross-peaks between H-9 (5.34 d *J*=6.8Hz) and the carbonyl at δ 165.4 of the benzoate ester, H-13 (4.52, 4.87, each 1H, d, *J*=12.8Hz) and the carbonyl at δ 170.5 of the acetate ester, and H-1 (5.57 d, *J*=4.0Hz), H-6 (5.69 s) and the carbonyls at δ 175.2 and 174.4 of two α-methyl-butanoate esters, respectively. In NOESY spectrum of **2**, the correlation between H-1 and H-9 indicated the presence of axial stereochemistry of H-9. Thus, compound **2** elucidated as 1β, 6α-di-(α-methyl)- butanoyl-4α-hydroxy-9β-benzoyloxy- 13-acetoxy-β-dihydroagarofuran.

Figure 2 The NOESY correlations of **1**



Acknowledgments

We would like to thank Prof. Ji-zhou Sun of Department of Biology, Lanzhou University for the authentication of the plant.

References

1. Z. B. M. Tincusi, I. A. Jimenez, A. G. Ravelo, R. Missico, *J. Nat. Prod.*, **1998**, *61*, 1520.
2. H. Wang, X. Tian, L. Yang, Y. Z. Chen, *Chin. Chem. Lett.*, **2000**, *11*, 331.
3. H. Wang, L. Yang, X. Tian, Y. Z. Chen, *Pharmazie*, **2001**, *56*, 889.
4. N. Wakabayashi, W. J. Wu, R. M. Waters, R. E. Redfern, G. D. M. Jr, A. B. Demilo, W. R. Lusby, D. Andrzejewski, *J. Nat. Prod.*, **1988**, *51*, 537.
5. H. C. Huang, C. C. Shen, C. F. Chen, Y. C. Wu, Y. H. Kuo, *Chem. Pharm. Bull.*, **2000**, *48*, 1079.
6. W. Wu, M. Wang, J. Zhu, W. Zhou, Z. Hu, Z. Ji, *J. Nat. Prod.*, **2001**, *64*, 364.

Received 21 January, 2002