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Two New Sesquiterpenes from *Euonymus nanoides*

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Abstract: Two new dihydroagarofuran sesquiterpenes with a novel substitution pattern: 1α-(α-methyl)-butanoyl-2α, 15-diacetoxy-4β-hydroxy-9β-(β-)furancarboxy-β-dihydroagarofuran (**1**) and 1α, 2α-di-(α-methyl)-butanoyl-4β-hydroxy-9β-(β-)furancarboxy-15-acetoxy-β-dihydro–agarofuran (**2**) were isolated from *Euonymus nanoides*. Their structures were elucidated by means of ^{1}H and ^{13}C NMR spectroscopic studies, including 2D NMR technique.

Keywords: *Euonymus nanoides*, Celastraceae, sesquiterpene, β-dihydroagarofuran.

Various dihydroagarofuran sesquiterpenes have been isolated from many species of the Celastraceae[1, 2]. In recent years these compounds have been increasing interest due to their insecticid, cytotoxic, antitumor-promoting, immunosuppressive, insect-antifeedant activities and for reversing multidrug resistance in cancer cells[3, 4]. In our previous study, the isolation of two dihydro-β-agarofuran have been described from *Euonymus nanoides* (Celastraceae)[2]. Resently, we have also found two novel dihydro-β-agarofuran sesqui -terpene polyol esters (**Figure 1**)[2] which displayed a substitution pattern hitherto unreported on a dihydro-β-agarofuran skeleton with 1α, 2α, 4β, 9β and 15 substituents from *Euonymus nanoides*. In this paper, we deal with the structural elucidation.

Compound **1**, colorless gum, $[\alpha]_D^{20}$ +38 (*c* 1.17, $CHCl_3$), has the molecular formula $C_{29}H_{40}O_{11}$ (HR-ESIMS:*m/z* 565.2642 $[M+1]^+$, calcd. for $C_{29}H_{40}O_{11}$ 565.2643) and its IR spectrum indicated the presence of ester and hydroxyl groups. The ^{1}H, ^{13}CNMR spectra and DEPT (**Table**) established this compound has three quaternary methyl groups, four methylenes, four methines, four quarternary carbons and two acetates, one (α-methyl)-butanoate, one (β-) furancarboxylate and one hydroxyl group. Its parent structure is a dihydroagarofuran sesquiterpene polyester.

The ring protons could be unequivocally assigned from its homonuclear COSY and chemical shift correlated spectral data. An AB quartet at δ_H 4.53 and 4.79 was assigned to two protons (H-15a, H-15b) attached the carbon atom bearing primary ester group[5-7]. From a comparison of the ^{1}HNMR data for **1** and known sesquiterpene[5-7], the signal at δ_H 5.50 (ddd, J=3.4, 3.4 and 3.4Hz) was assigned to H_{eq}-2 in the dihydroagafuran skeleton from the coupling constants, and this proton was coupled with the signal at

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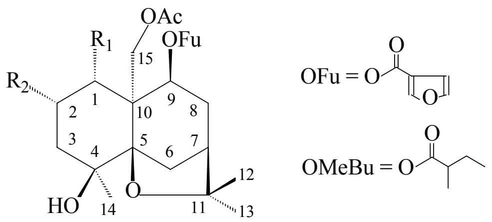
δ_H 5.58 (d, J=3.4Hz), assigned to H_{ax}-1 or H_{ax}-3. The assignment of H_{ax}-1 for this signal is more likely, because all the sesquiterpenes with a dihydroagafuran skeleton isolated from Celastraceae have an equatorial ester on C-1 [8, 9]. A doublet at δ_H 5.23 (J=6.6Hz) was assigned to H_{eq}-9. The tertiary hydroxy group responsible for the signal at δ_H 2.63 is placed at C-4, since compound **1** has three tertiary methyl groups.

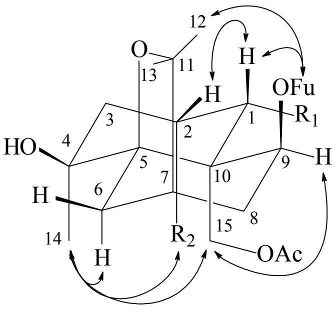
Figure 1 The structure of **1** and **2**



1 R_1 = OMeBu, R_2 = OAc **2** R_1 = OMeBu, R_2 = OmeBu

The chemical shifts for the carbons attached to protons were assigned according to HMQC experiment and the chemical shifts of known ring protons. As the quaternary carbons could be assigned by HMBC method. HMBC showed the correlations between H-15 and H-2 with the carboxylic carbon of two acetate groups, H-1 coupled with the carboxylic carbon of α-methyl-butanoate and H-9 with the carboxylic carbon of β-furan -carboxylate.

Figure 2 The NOESY correlations of **1** and **2**



1 R_1 = OMeBu, R_2 = OAc **2** R_1 = OMeBu, R_2 = OmeBu

From the NOESY spectrum of **1** (**Figure 2**), the correlations between H-1 and H-2, H-15 with H-9 and H-14 indicated the presence of equatorial stereochemistry of H-2, H-9 and OH. Thus, compound **1** was identified as 1α-(α-methyl)-butanoyl-2α, 15-diace -toxy-4β-hydroxy-9β-(β-) furancarboxy-β-dihydroagarofuran.

Compound **2**, colorless gum, $[\alpha]_D^{20}$ +42 (*c* 1.00, $CHCl_3$), has the molecular formula $C_{32}H_{46}O_{11}$ (HR-ESIMS:*m/z* 624.3371 $[M+NH_4]^+$, calcd. for $C_{32}H_{46}O_{11}$ 624.3378) contained two (α-methyl)-butanoyl, one acetyl, one (β-) furancarboxyl ester and one hydroxy based on the spectral analysis. The ^{13}CNMR spectral data (**Table**) were very similar to that of **1** except the ester groups' signals. The ^{1}HNMR spectrum of compound **2** was almost the same as that of **1**, except one acetic ester was substituted by (α-methyl)-butanoyl ester. By HMBC and NOESY, compound **2** was concluded as 1α, 2α-di-(α-methyl)-butanoyl-4β-hydroxy-9β-(β-)furancarboxy-15-acetoxy-β-dihydro-agarofuran.

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

	1		2	
No.	δ_C (DEPT)	δ_H (J_{Hz})	δ_C (DEPT)	δ_H (J_{Hz})
1	69.8 (CH)	5.58d (3.4)	69.8 (CH)	5.62d (3.4)
2	68.6 (CH)	5.50ddd (3.4, 3.4, 3.4)	69.7 (CH)	5.52ddd (3.4, 3.4, 3.4)
3	40.5 (CH_2)	2.05m, 2.13m	40.7 (CH_2)	2.01m
4	69.4 (C)		69.3 (C)	
5	89.8 (C)		89.8 (C)	
6	31.0 (CH_2)	2.12m, 2.46m	31.0 (CH_2)	2.08m , 2.43m
7	43.3 (CH)	2.18m	43.3 (CH)	2.17m
8	33.4 (CH_2)	2.16m, 2.30m	33.4 (CH_2)	2.13m, 2.30m
9	69.5 (CH)	5.23d (6.6)	68.3 (CH)	5.22d (6.8)
10	51.1 (C)		51.0 (C)	
11	83.7 (C)		83.6 (C)	
12	24.2 (CH_3)	1.42s	24.2 (CH_3)	1.43s
13	30.0 (CH_3)	1.33S	29.9 (CH_3)	1.33s
14	25.1 (CH_3)	1.43s	25.0 (CH_3)	1.44s
15	65.7 (CH_2)	4.53d (12.8), 4.79d (12.8)	66.2 (CH_2)	4.47d (12.8), 4.86d (12.8)
OH		2.63s		2.63s
15-OAc	21.4 (CH_3),170.4(C)	2.19s	21.4 (CH_3),170.4(C)	2.18s
2-OAc	21.1(CH_3),169.5 (C)	2.09s		
1-OMeBu	11.3(CH_3),15.7(CH_3), 25.6 (CH_2),40.8(CH), 174.6 (C)	0.68t (7.2), 0.90d (7.2), 1.09m, 1.36 m, 2.03m	11.3(CH_3),15.5(CH_3), 25.6 (CH_2),40.8(CH), 174.6(C)	0.68t (7.2), 0.92m, 1.04m, 1.35m, 2.01m
2-OMeBu			11.6(CH_3),16.5 (CH_3), 26.5(CH_2),41.7(CH), 175.2 (C)	0.92m, 1.20d (6.8), 1.50m, 1.75m, 2.40m
9-OFu	109.9(CH),118.9(C), 143.7(CH),148.7 (CH),162.0 (C)	6.73s,7.41s, 8.01s	109.9(CH),118.9(C), 143.6(CH),148.8 (CH),162.0 (C)	6.73s,7.41s,8.02s

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