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Two New Tetranortriterpenoids from *Amoora dasyclada*

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Abstract: Two new tetranortriterpenoids 3-oxo-24, 25, 26, 27-tetranortirucall-7-ene-23(21)- lactone, 3α-hydroxy-24, 25, 26, 27-tetranortirucall-7-ene-23(21)-lactone were isolated from *Amoora dasyclada*. Their structures were elucidated by spectroscopic evidences.

Keywords: *Amoora dasyclada*, tetranortriterpenoid, 3-oxo-24, 25, 26, 27-tetranortirucall-7-ene-23(21)-lactone, 3α-hydroxy-24, 25, 26, 27-tetranortirucall-7-ene-23(21)-lactone.

The genus *Amoora* Roxb.(Meliaceae), found in India and Malaysia, comprises about 25-30 species, 9 of which are distributed in China, 7 species have been found in Yunnan province[1]. The question about if this genus is a valid one has been existed for many years[2, 3]. As the chemotaxonomic marker of the family Meliaceae, tetranortriterpenoid has not been isolated from this genus according to our knowledge [4-6]. However the phytochemical study on the stem of *Amoora dasyclada*(How *et* T. Chen)C.Y.Wu led to the isolation of two new tetranortriterpenoids: 3-oxo-24, 25, 26, 27-tetranortirucall-7-ene-23(21)-lactone **1**, 3α-hydroxy-24, 25, 26, 27-tetranortirucall-7-ene-23(21)-lactone **2**. We hope this work could provide chemical proof for the taxonomy of this genus.

Compound **1**, white needles, its molecular formula of $C_{26}H_{38}O_3$ was concluded from the HRESIMS (cacld. for $C_{26}H_{38}O_3Na$ 421.2718, found 421.2716). It showed the presence of carbonyl group (1708cm^{-1}) and γ-lactone group (1784cm^{-1}) in the IR spectrum. The signals of ^{1}H NMR and ^{13}C NMR spectra indicated there were five methyls δ_C: 12.7(C-19), 21.5(C-29), 22.6(C-18), 24.5(C-28), 27.2(C-30), nine methylenes, four methines δ_C: 39.1(C-20), 48.2(C-9), 51.0(C-17), 52.3(C-5), four quaternary carbons δ_C: 35.1(C-10), 43.7(C-13), 47.8(C-9), 50.7(C-14), one trisubstituted double bond δ_C: 118.7(C-7), 144.8(C-8) and δ_H: 5.28(1H, dd, J=3.2, 6.4, H-7), one ketonyl carbon δ_C: 216.5(C-3). These spectral data were the characteristic of the tirucallane-7-ene system with 3-ketone[7, 8], and the inference was supported by the HMBC (see **Table 3**) and ROSEY experiments. The signal at δ_H 2.70(1H, td, J=14.5, 5.5Hz) was the resonance of H-2β according to the large coupling constant with H-1α (J=14.5Hz), the NOE correlation between H-19 and H-28, H-2β indicated H-28 and H-19 were in axial position (β-bond

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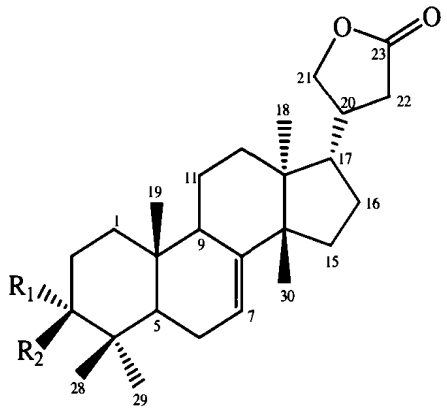

1 R_1, R_2=O

2 R_1=OH, R_2=H

Table 1 The ^{13}C NMR of **1** and **2** ($CDCl_3$, δ_C in ppm)

Carbon	1	2	Carbon	1	2
1	38.4	31.2	14	50.7	50.7
2	34.5	25.4	15	34.1	34.0
3	216.5	76.1	16	27.3	27.3
4	47.8	37.4	17	51.0	51.0
5	52.3	44.5	18	22.6	22.5
6	24.3	23.9	19	12.7	12.9
7	118.7	118.7	20	39.1	39.1
8	144.8	144.9	21	72.4	72.4
9	48.2	48.3	22	34.8	34.6
10	35.1	34.8	23	176.8	177.0
11	17.6	17.3	28	21.5	21.7
12	31.8	31.9	29	24.5	27.7
13	43.7	43.7	30	27.2	27.0

Table 2 ^1H NMR of **1** and **2** ($CDCl_3$, δ_H in ppm, J Hz)

Proton	1	2	Proton	1	2
1	1.92(1H,m)	1.62(1H,m)	16	1.90(1H,m)	1.89(1H,m)
	1.40(1H,m)	1.41(1H,m)		1.30(1H,m)	1.30(1H,m)
2	2.70(1H,td,5.5,14.5)	2.03(1H,m)	17	1.71(1H,m)	1.72(1H,m)
	2.19(1H,m)	1.50(1H,m)	18	0.78(3H,s)	0.82(3H,s)
3		3.44(1H,*br* s)	19	0.95(3H,s)	0.75(3H,s)
5	1.67(1H,m)	1.76(1H,m)	20	2.15(1H,m)	2.50(1H,m)
6	2.06(1H,m)	1.96(1H,m)	21	4.33(1H,t,8.2)	4.37(1H,t,7.9)
	2.24(1H,m)	2.20(1H,m)		3.87(1H,t,9.0)	3.90(1H,t,8.8)
7	5.28(1H,dd,3.2,6.4)	5.25(1H,br s)	22	2.50(1H,m)	2.52(1H,m)
9	2.21(1H,m)	2.28(1H,m)		2.13(1H,m)	2.16(1H,m)
11	1.55(2H,m)	1.55(2H,m)	28	1.06(3H,s)	0.89(3H,s)
12	1.67(1H,m)	1.68(1H,m)	29	0.98(3H,s)	0.91(3H,s)
	1.43(1H,m)	1.40(1H,m)	30	0.97(3H,s)	0.96(3H,s)
15	1.52(2H,m)	1.55(2H,m)			

form). Because the presence of the double bond between C-7 and C-8, the ring B turned to twist-chair form and ring C became twist-boat form, the NOE correlation between H-9 and H-18, H-5 revealed their *cis*-relationship (α-bond form). The signals of the ester group δ_C: 72.4(C-21), 176.8(C-23), the methylene δ_C: 34.7(C-22) and the methine δ_C: 39.0(C-20) suggested the side chain was a γ-lactone, and C-17 was attached with C-20, this was confirmed by HMBC correlations: H-17 with C-20, C-21; H-20 with C-17, C-21, C-23; H-22 with C-17, C-20, C-21; H-21 with C-17, C-20, C-22, C-23, besides the H-17 showed NOE correlation with H-30. Accordingly **1** was identified as 3-oxo-24, 25, 26, 27-tetranortirucall-7-ene-23(21)- lactone.

Compound **2**, white needles, was established to have a molecular formula of $C_{26}H_{40}O_3$ by HRESIMS (calcd. for $C_{26}H_{40}O_3Na$ 423.5900, found 423.5897). The IR spectrum indicated the presence of hydroxyl group (3442cm^{-1}) and γ-lactone (1774cm^{-1}), the ^{1}H NMR and ^{13}C NMR spectra of it (see **Table 1** and **2**) were in good agreement with those of **1**, except the ketonyl carbon was replaced by a methine carbon δ_C: 76.1(C-3), HMQC indicated the corresponding proton signal is δ_H: 3.44(1H, *br*s), these revealed a hydroxyl substitution at C-3. Although there was no useful information obtained about the stereochemistry of C-3 in the ROSEY spectrum, the resonance of H-3 was observed as a broad singlet at obviously lower field due to the stronger deshielding by the axial 3α-OH than the equatorial 3β-OH[9], so **2** was elucidated as 3α-hydroxy-24, 25, 26, 27-tetranortirucall- 7-ene-23 (21)-lactone.

Table 3 HMBC spectral data of **1** and **2**

Proton	1	2
1	C-2, 3, 5, 10, 19	C-2, 3, 5, 10, 19
2	C-1, 3, 10, 4	C-1, 3, 10, 4
3		C-1, 2, 4, 5, 28, 29
5	C-1, 3, 4, 6, 7, 9, 10, 19, 28, 29	C-1, 3, 4, 6, 7, 9, 10, 19, 28, 29
6	C-4, 5, 7, 8, 10	C-4, 5, 7, 8, 10
7	C-5, 6, 8, 9, 14	C-5, 6, 8, 9, 14
9	C-8, 10, 11,	C-8, 10, C-11
11	C-9, 10, 12, 13	C-9, 10, 12, 13
12	C-11, 13, 17, 18,	C-11, 13, 17, 18
15	C-8, 13, 14, 16, 17, 30	C-8, 13, 14, 16, 17, 30
16	C-13, 14, 15, 17, 20	C-13, 14, 15, 17, 20
17	C-12, 13, 16, 18, 20, 21	C-12, 13, 16, 18, 20, 21
18	C-12, 13, 14, 17	C-12, 13, 14, 17
19	C-1, 5, 9, 10	C-1, 5, 9, 10
20	C-17, 21, 23	C-17, 21, 23
21	C-17, 20, 22	C-17, 20, 22, 23
22	C-17, 20, 21, 23	C-17, 20, 21, 23
28	C-3, 4, 5, 29	C-3, 4, 5, 29
29	C-3, 4, 5, 28	C-3, 4, 5, 28
30	C-8, 13, 14, 15	C-8, 13, 14, 15

Compond **1:** white needles from Me_2CO, $C_{26}H_{38}O_3$, mp 188-189℃; $[\alpha]^{27}_D$ –88.11(*c* 0.244, $CHCl_3$); IR (KBr) ν: 2952, 2364, 1784, 1708, 1472, 1457, 1386, 1178, 1037, 1020, 993cm^{-1}; EIMS *m/z*: 398[M^+](23), 383(100), 365(17), 341(3), 323(4), 297(5), 271(3), 259(4), 245(8), 199(7), 185(14), 173(13), 159(16), 149(20), 145(19), 133(27), 119(34), 105(42), 95(35), 91(34), 81(33), 79(28), 69(27), 55(41).

Compound **2:** white needles from Me_2CO, $C_{26}H_{40}O_3$, mp 268-269℃; $[\alpha]^{27}_D$ –55.29 (*c* 0.208, $CHCl_3$); IR (KBr) ν: 3442, 2941, 1774, 1630, 1442, 1468, 1386, 1364, 1191, 1017, 995cm^{-1}; EIMS *m/z*: 400[M^+](7), 385(12), 367(38), 260(62), 245(17), 187(32), 175(32), 159(31), 145(41), 133(83), 119(95), 105(100), 95(90), 91(87), 81(82), 67(41), 55(68).

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