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Chemical shift assignments of two oleanane triterpenes from *Euonymus hederaceus*[*]

HU He-jiao (胡合姣), WANG Kui-wu (王奎武), WU Bin (吴 斌),
SUN Cui-rong (孙翠荣)[‡], PAN Yuan-jiang (潘远江)[†]
(*Department of Chemistry, Zhejiang University, Hangzhou 310027, China*)
[†]E-mail: panyuanjiang@zju.edu.cn

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Abstract: ^{1}H-NMR and ^{13}C-NMR assignments of 12-oleanene-3,11-dione (compound 1) were completely described for the first time through conventional 1D NMR and 2D shift-correlated NMR experiments using ^{1}H-^{1}HCOSY, HMQC, HMBC techniques. Based on its NMR data, the assignments of 28-hydroxyolean-12-ene-3,11-dione (compound 2) were partially revised.

Key words: *Euonymus hederaceus*, 12-oleanene-3,11-dione, 28-hydroxyolean-12-ene-3,11-dione, 1D-NMR, 2D-NMR, Assignment
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INTRODUCTION

Euonymus hederaceus champ.ex Benth (Celastraceae) has been used as a traditional medical plant (Chang *et al*., 1996). Two compounds, 12-oleanene-3,11-dione and 28-hydroxyolean-12-ene-3,11-dione (Fig.1) were isolated by its phytochemical investigation. The complete ^{1}H and ^{13}C chemical shift assignments of 12-oleanene-3,11-dione are described here for the first time with 1D and 2D NMR, correcting some data in Yuan *et al*.(1994). The ^{13}C assignments of 28-hydroxyolean-12-ene-3,11-dione were partially revised by Shirota *et al*.(1996).

MATERIALS AND METHODS

The barks and stems of *Euonymus hederaceus* champ.ex Benth, collected in October 2003 in Suicang County, Zhejiang Province, were identified by Dr. WU Bin. After crushing them, the obtained powder was extracted thrice by methanol, once a week to give an extract (500 g) after removing methanol. The extract was partitioned between petroleum ether and water. The petroleum ether soluble fraction (33 g) was applied to a silica gel column using petroleum ether and ethyl acetate as a gradient eluent system. Compound 1 and impure compound 2 were obtained when the eluent volume ratios of petroleum ether to ethyl acetate were 10:1 and 6:1, respectively. Compound 2 was further separated and purified by preparative HPLC.

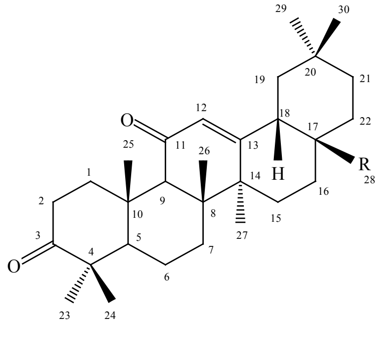

Fig.1 The structure of compounds 1 and 2
Compound 1: R=CH_3; Compound 2: R=CH_2OH

[‡] Corresponding author

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^1H and ^{13}C NMR spectra were measured on Bruker AVANCE DMX 500 NMR, using $CDCl_3$ as solvent and TMS as internal reference.

RESULT AND DISCUSSION

Compound 1 was isolated as white powder of m.p. 241~245 °C, and gave responded positively to the Lieberman-Buchard test for triterpenes. The molecular formula was deduced as $C_{30}H_{46}O_2$ by ESI-MS: 437.2 ($C_{30}H_{46}O_2^-$, $[M\text{-}H]^-$). The ^1H-NMR data (Table 1) showed singlet signals for eight angular methyl groups. The ^{13}C-NMR and DEPT spectra showed 30 signals for eight methyl, nine methylene, four methine and nine quaternary carbons including a keto carbonyl and an α, β-unsaturated keto carbonyl. HMQC experiments revealed ^1H-^{13}C direct correlation between the protons of eight methyl groups and corresponding carbons, and in the observe, olean-type triterpene skeleton was deduced (Mahato and Kundu, 1994). The resonance assignments for eight methyl were at δ_H 1.07, 1.10, 1.27, 1.18, 1.37, 0.85, 0.91, 0.89 to H-23, 24, 25, 26, 27, 28, 29, 30 respectively. The protons of two methyl groups (δ_H 1.10, δ_C 26.5 and δ_H 1.07, δ_C 21.6), and two methylene groups (δ_H 2.95, δ_C

Table 1 ^1H-NMR, ^{13}C-NMR, HMQC, HMBC for compound 1 and compound 2

Atom number	Compound 1			Compound 2
	δ_C	δ_H	HMBC (carbon)	δ_C
C-1	240.0t[b]	2.95m, 1.41m	C-9, C-25	040.0t
C-2	234.5t[e]	2.60m, 2.35m	/	234.2t
C-3	217.4s[e]	/	C-1, C-2, C-23, C-24	217.4s
C-4	248.0s[e]	/	C-2, C-23	048.0s
C-5	255.6d[e]	1.28	C-7, C-25, C-24	055.7d
C-6	219.0t[e]	1.54, 1.03	/	19.1t
C-7	232.3t[e]	1.64, 1.45	C-6, C-26	32.3t
C-8	245.5s[e]	/	C-6, C-27	45.5s
C-9	261.2d[e]	2.44 1H s	C-12, C-25, C-26	61.3d
C-10	236.9s[e]	/	C-6, C-9, C-25	36.9s
C-11	199.7s[e]	/	C-9	199.6s
C-12	128.2d[e]	5.62 1H s	C-18	128.4d
C-13	171.3s[e]	/	C-18	170.2s
C-14	243.7s[e]	/	C-9, C-26, C-12	43.8s
C-15	226.7t[e]	1.18, 1.81br	C-27	26.2t
C-16	226.6t[e]	0.98, 2.09	C-22, C-28	21.6t[a]
C-17	232.6s[e]	/	C-15, C-21	37.0s
C-18	247.9d[e]	2.14m	C-12, C-28	43.0d
C-19	245.5t[e]	1.64, 1.10	C-30, C-29, C-21	45.3t
C-20	231.3s[e]	/	C-30	31.3s
C-21	234.7t[e]	1.37, 1.18	C-22, C-30	34.1t
C-22	236.7t[e]	1.45, 1.31	C-28	30.9t[a]
C-23	21.6q[e]	1.07 3H s	C-24	21.7q
C-24	26.7q[e]	1.10 3H s	C-23	26.5q
C-25	215.9q[e]	1.27 3H s	C-9	15.9q
C-26	218.9q[e]	1.18 3H s	C-9	18.7q
C-27	223.6q[e]	1.37 3H s	C-15	23.6q
C-28	229.0q[e]	0.85 3H s	C-16, C-22	69.9q
C-29	23.3q[e]	0.91 3H s	C-19, C-30	23.8q
C-30	33.8q[e]	0.89 3H s	C-21, C-29	33.3q

[a]: The assignments are different from those in Shirota *et al.*(1996); [e]: The assignments are different from those in Yuan *et al.*(1994); [b]: Multiplicities by DEPT experiments in parentheses; s: quaternary; d: CH; t: CH_2; q: methyl C atom; m: Multiplicities by ^1H-NMR experiment; br: broad form Multiplicities by ^1H-NMR experiment

40.0 and δ_H 2.60, δ_C 34.5) had ^1H-^{13}C long-range correlation with the carbon at δ_C 217.4, establishing the carbonyl to be C-3. The hydrogen signal appearing at δ_H 5.62 (s), corresponding to the only present olefinic hydrogen atom correlates to the carbon atom at δ_C 128.3 in the HMQC spectrum. The olefinic C-13 atom was quaternary and appeared at 171.3, and a keto C-atom appearing at 199.7 suggested that compound 1 had an olean-12-ene-11-ketone skeleton (Shirota *et al*., 1996). These assumptions were confirmed by the HMQC and HMBC spectra, for the H-12 olefinic proton (δ_H 5.62) indicated ^1H-^{13}C long range correlations with the methine carbons C-9 (δ_C 61.2), C-14 (δ_C 43.7); the H-9 proton (δ_H 2.44) with C-11 (δ_C 199.7); the H-18 proton (δ_H 2.14) with C-13 (δ_C 29.02) in the HMBC spectrum (Table 1). Therefore, compound 1 was considered to be 12-oleanene-3,11-dione. It was isolated in 1970 (Govindachari *et al*., 1970). The ^{13}C-NMR assignments for this compound have not reported until 1994 (Yuan *et al*., 1994). In this study, the ^1H- and ^{13}C-NMR assignments for compound 1 were carried out on the basis of DEPT, HMQC, ^1H-^1H COSY (homonuclear correlation spectroscopy) and HMBC experiments. Our result revises some assignments in Yuan *et al*.(1994).

Compound 2 has the molecular formula $C_{30}H_{46}O_3$ and similar chemical shifts with the compound 1, and was different from the compound 1 in that one tertiary methyl group signal at δ_C 29.02 disappeared and one methylene connecting to hydroxyl appeared at δ_C 69.9. We determined the structure of compound 2 to be 28-hydroxyolean-12-ene-3,11-dione by comparing the NMR data to data in Shirota *et al*.(1996). The γ-effect was supposed to result in C-16, C-18, C-22 in the upfield shifts of $0\sim9\times10^{-6}$ (Mahato and Kundu, 1994) when the hydroxyl group replaced the 28-methyl group in the carbon assignments of compound 1, so that, the assignments of this compound in Shirota *et al*.(1996) were partially revised (Table 1).

Researching the ^{13}C-NMR rule of the triterpenoids is helpful for deducing structures of unknown analogs; the complete assignments of compound 1 and assignment corrections for compound 2 to some extent offer scientific material for future research.

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