A new eudesmane sesquiterpene from *Senecio cannabifolius*

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A new eudesmane sesquiterpene was isolated from the roots of *Senecio cannabifolius*. Its structure was established as 1-oxo-5α, 7αH-eudesma-3-en-15-al on the basis of spectroscopic data, including IR, EI-MS, HR-ESI-MS, 1D and 2D NMR spectroscopy.

Keywords: Compositae, *Senecio cannabifolius*, sesquiterpene, eudesmane

The genus *Senecio* is known as an important source of pyrrolizidine alkaloids.[1,2] Naturally occurring sesquiterpenoids including eremophilanes and eudesmanes are also among their secondary metabolites.[3,4] The plant *Senecio cannabifolius* Less. (Compositae) is distributed mainly in the Northeast and Hebei Province of China, Korea, Japan, and in the far east of the former Soviet Union. It is used as a traditional remedy for treating viral influenza, enteritis, and pneumonia in China.[5] Earlier phytochemical investigation of *S. cannabifolius* have led to the isolation and characterisation of five new lactones,[5,6] and two new monoterpenoid derivatives with antimicrobial activities.[7] Moreover it was reported that the terpene and fatty acid may be associated with the anti-viral activity of the essential oil from *S. cannabifolius*.[8] With the aims of discovering the relationships between the chemical constituents and the biological activity, our attention was drawn to the sesquiterpenoids in the roots of this plant. We now report the isolation and structure elucidation of a new eudesmane sesquiterpene.

Compound **1** was obtained as colourless gum. Its IR spectrum indicated the presence of carbonyl group at 1710 cm^{-1} and double bond at 1645 cm^{-1}. Its EI-MS spectrum exhibited a molecular ion peak at *m/z* 234 $[M]^+$, which combined with the ^1H and ^{13}C NMR (DEPT) data (Table 1), showed that the molecular formula was $C_{15}H_{22}O_2$. This was further confirmed by the quasi molecular ion peak at *m/z* 252.1969 ($[M + NH_4]^+$, $C_{15}H_{26}NO_2$, Calcd 252.1958) in the HR-ESI-MS spectrum. The ^1H NMR spectrum of **1** indicated the presence of a tertiary methyl group at δ_H 1.33 (s, 3H) and an isopropyl group in agreement with signals for two secondary methyl group at δ_H 0.94 (d, J = 6.8 Hz, 6H) and a methine proton at δ_H 1.67 (m, 1H) (Table 1). Moreover the resonances of an olefinic proton at δ_H 6.64 (brd, J = 5.2 Hz, 1H) and an aldehyde proton at δ_H 9.35 (s, 1H) were observed. The ^{13}C NMR (DEPT) spectrum revealed signals for 15 carbons, including a ketone carbonyl at δ_C 212.2 (s) and an α, β-unsaturated aldehyde group at δ_C 192.7 (d), 143.7 (s) and 158.6 (d). The above information established that **1** was a eudesmane sesquiterpene, with a structure similar to that of 5α, 7αH eudesma-3, 11(13)-dien-15-al-12-oic acid,[9] except that the carboxylic acid and terminal double bond were absent, and a carbonyl group was present. In the HMBC plot, the correlations of CH-3, Me-14 and CH_2-2/C-1 suggested the ketone was at C-1. The correlations of CH-3/C-1 and CH-15/C-4 indicated that the double bond was between C-3 and C-4, and that the aldehyde was attached to C-4, (Fig. 2). In the NOESY spectrum, the correlations between H-5 and H-7 suggested that the H-5 and H-7 had an α-orientation (Fig. 2). Hence the structure of **1** was confirmed as 1-oxo-5α,7αH-eudesma-3-en-15-al.

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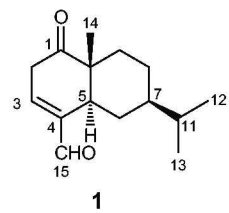
Table 1 ^1H, ^{13}C and DEPT data of compound **1** ($CDCl_3$, δ in ppm, TMS)[a]

No.	δ_H	δ_C	DEPT
1	–	212.2	C
2	2.54 (m, 2H)	38.9	CH_2
3	6.64 (brd, 5.2, 1H)	158.6	CH
4	–	143.7	C
5	2.21 (dd, 10.8, 4.8, 1H)	53.1	CH
6α	1.44 (m, 1H)		
6β	1.87 (m, 1H, overlapped)	25.0	CH_2
7	1.81 (m, 1H, overlapped)	55.8	CH
8	1.58 (m, 2H)	26.8	CH_2
9α	2.43 (ddd, 14.4, 10.8, 3.6, 1H)	35.1	CH_2
9β	2.86 (ddd, 14.4, 5.4, 5.4, 1H)		
10	–	59.6	C
11	1.67 (m, 1H)	32.3	CH
12	0.94, (d, 6.8, 3H)	19.4	CH_3
13	0.94, (d, 6.8, 3H)	21.9	CH_3
14	1.33 (s, 3H)	19.6	CH_3
15	9.35 (s, 1H)	192.7	CH

[a]Measured at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR.



1

Fig. 1 The structure of compound **1**.

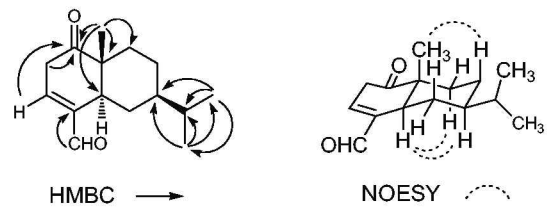


Fig. 2 The key HMBC and NOESY correlations of **1**.

Experimental

Optical rotations were measured on a Perkin-Elmer 341 polarimeter. The IR spectrum was recorded with a Bruker Vertex 70 FT-IR spectrometer in KBr. ^1H, ^{13}C NMR (DEPT) and 2D NMR were recorded on Varian Mercury plus-400 spectrometer with TMS as internal reference. EI-MS and HR-ESI-MS spectra were obtained respectively on HP-5988A GC/MS and Bruker APEX II instruments using the direct insertion probe method. Silica gel (200–300 and 300–400 mesh) used for column chromatography (CC) were supplied by Qingdao Marine Chemical Factory in China. The purity of the samples were checked on TLC (silica gel, GF_{254} and RP-18) under UV light at 254 nm or by heating after spraying with 5% H_2SO_4 in C_2H_5OH.

Plant material

The roots of *Senecio cannabifolius* were collected from Changbai Mountains, Tonghua, People's Republic of China in September 2008. The specimens were identified by Associate Prof. Hong Zhao (Marine College, Shandong University at Weihai). A voucher specimen (No. CB2008021) was deposited in the Herbarium of Laboratory of Botany, Research Centre of Medical Chemistry & Chemical Biology, Chongqing Technology and Business University.

Extraction and isolation

The air-dried roots of *Senecio cannabifolius* (480 g) were pulverised and extracted with CH_3OH three times (6 days each time) at room temperature. The extract was concentrated under reduced pressure to afford a residue (39 g). This residue was suspended in water (150 mL), and the suspension was extracted successively with hexane and $CHCl_3$. The $CHCl_3$ soluble fraction was concentrated under reduced pressure to yield a residue (3.2 g). This residue was subjected to silica gel column chromatography (200–300 mesh, 50 g) with a gradient of hexane–acetone (15:1, 5:1) as the eluent. Three fractions were collected following TLC analysis. Fraction 2 (hexane–acetone 10:1, 0.7 g) was subjected to a silica-gel column with petroleum ether (b.p. 60–90 °C)–acetone (12:1) as the eluent to yield compound **1** (1.2 mg). There were no significant spots found in fractions 1 and 3.

1-oxo-5α,7αH-eudesma-3-en-15-al (**1**): $C_{15}H_{22}O_2$, Colourless gum. $[\alpha]_D^{18}$ –20 (*c* 0.2, $CHCl_3$). IR (KBr) ν_{max}/cm^{-1}: 3417, 2877, 1710, 1645. EI-MS *m/z* (rel. int.): 234 (17, $[M]^+$), 219 (6), 205 (2), 191 (16), 173 (7), 163 (29), 149 (19), 123 (56), 107 (41), 93 (32), 91 (62), 83 (60), 77 (57), 69 (39), 55 (44), 53 (40), 43 (100), 41 (70). HR-ESI-MS: *m/z*: 252.1969 ($[M + NH_4]^+$, $C_{15}H_{26}NO_2^+$; Calcd 252.1958). ^1H, ^{13}C NMR and DEPT data see Table 1.

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