



Terpenoid from the liverwort *Scapania bolandeli*

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Abstract

A clerodane-type diterpenoid was isolated from *Scapania bolandeli*, and its structure was determined by extensive NMR spectroscopic techniques. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *Scapania bolandeli*; Hepaticae; Clerodane; Diterpenoid

1. Introduction

Liverworts are known to be a rich source of sesqui- and diterpenoids (Asakawa, 1995; Asakawa, 1982; Zinsmeister, Becker & Eicher, 1991; Huneck, 1982). In this paper, we report the isolation and identification of a new clerodane-type diterpenoid from *Scapania bolandeli*.

2. Results and discussion

From the ether extracts of *Scapania bolandeli*, a new clerodane-type diterpenoid (**1**) was isolated. **1** gave an $[M + Na]^+$ ion peak at m/z 429.2267 in the HR-FAB⁺ mass spectrum corresponding to a molecular formula of C₂₃H₃₄O₆. The IR spectrum exhibited the presence of a hydroxy group (3390 cm⁻¹), and carbonyl groups (1722 and 1638 cm⁻¹ *br*). The ¹H-NMR spectrum displayed signals for two vinylic protons (δ_H 5.69 and 6.29) and five quaternary methyl groups (δ_H 0.78, 1.39, 2.06, 2.18 and 3.73). The ¹³C-NMR spec-

trum of **1** showed the presence of six methyls, five methylenes, five methines and seven quaternary carbons indicating the presence of three carboxyl groups (δ_C 168.2, 170.8 and 171.3) and two oxygenated aliphatic carbons (δ_C 51.7 and 67.5) in the molecule. Based on this spectroscopic evidence, these oxygens corresponded to two ester groups and a free carboxyl group. The combined data of ¹H- and ¹³C-NMR spectral assignments with ¹H–¹H COSY, ¹H–¹³C COSY, DEPT, NOESY and COLOC experiments revealed the complete structure of **1**. The ¹H–¹H COSY experiment revealed the substructures C (10) H–C (1) H₂–C (2) H–C (3) H, C (6) H₂–C (7) H₂–C (8) H–C (17) H₃, and C (11) H₂–C (12) H₂. The long-range correlations observed by COLOC revealed the connectivities of all segments as shown in Fig. 1. NOESY data supported this result and led to the relative configuration shown. NOEs were observed between H-1 α and 19-Me, H-1 α and 20-Me, H-8 and H-10, 19-Me and 20-Me. These observations required the methyl groups C-5, C-8 and C-9 to be in the α -position. The NOE between H-12 and H-14 indicated the geometric isomerism at the C-13/C-14 double bond in an E configuration. Additional NOE between H-2 and H-3 indicated that the acetoxy group at C-2 was axial. For a better understanding of the NOE correlations and H–H couplings, the conformation of **1** is shown in Fig. 1.

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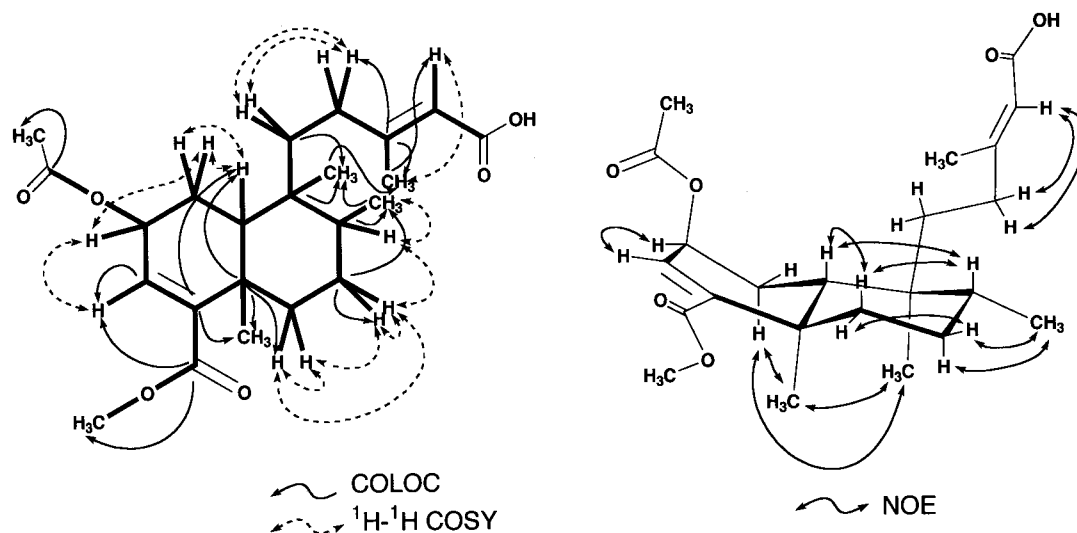
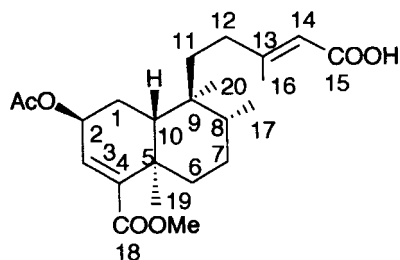


Fig. 1. ^1H – ^1H , ^{13}C – ^1H and NOE correlations of compound **1**.



1

3. Experimental

3.1. General

^1H -NMR: 270 MHz in CDCl_3 and C_6D_6 ; ^{13}C -NMR: 67.8 MHz in CDCl_3 , solvent peaks as the international standard. Bond types were distinguished by DEPT. ^1H connectivities were determined by means of ^1H – ^1H COSY and homodecoupling. One bond and long-range heteronuclear ^1H – ^{13}C connectivities were determined by ^1H – ^{13}C COSY and COLOC, respectively. Standard pulse sequences were used in NOESY. IR: KBr pellet, UV and optical rotations: EtOH and CHCl_3 , respectively.

3.2. Plant materials

Scapania bolandeli (14.5 g DW) was collected at Yatugatake Mt. Nagano prefecture, Japan, in July, 1997. The sample was identified by T. Furuki. A voucher specimen is deposited at the Department of Bioresource Science, Obihiro University of Agriculture and Veterinary Medicine.

3.3. Extraction and isolation

The ether extracts (410 mg) of *S. bolandeli* were divided into seven fractions by vacuum liquid chromatography (VLC) on silica gel using a *n*-hexane–EtOAc gradient. Fr. 4 was separated by HPLC (SiO_2 , *n*-hexane–EtOAc 4:1) to give **1** (5.5 mg).

Table 1

^1H -NMR (400 MHz) and ^{13}C -NMR (67.8 MHz) spectral data for **1**

C		H	
1	24.7	α 2.05	<i>dd</i> , <i>J</i> = 4.0, 14.7 Hz
		β 2.29	<i>dd</i> , <i>J</i> = 8.6, 14.7 Hz
2	67.5	5.60	<i>dt</i> , <i>J</i> = 4.0, 8.6 Hz
3	133.2	6.29	<i>d</i> , <i>J</i> = 4.0 Hz
4	144.0		
5	36.9		
6	36.7	α 1.13	<i>m</i>
		β 2.44	<i>m</i>
7	28.2	α 1.28	<i>m</i>
		β 1.12	<i>m</i>
8	37.2	1.44	<i>m</i>
9	39.8		
10	48.5	1.62	<i>m</i>
11	35.7	1.44, 1.59	<i>m</i>
12	34.6	2.01 (2H)	<i>m</i>
13	163.8		
14	114.9	5.69	<i>s</i>
15	171.3		
16	19.4	2.18	<i>brs</i>
17	19.2	0.79	<i>d</i> , <i>J</i> = 6.6 Hz
18	168.2		
19	34.2	1.39	<i>s</i>
20	15.9	0.78	<i>s</i>
COOCH ₃	51.7	3.73	<i>s</i>
CH ₃ COO	21.2	2.06	<i>s</i>
CH ₃ COO	170.8		

3.4. *Compound 1 2β-acetoxy-19-carboxymethyl-cleroda-3,13-dien-15-oic acid*

$[\alpha]_D = +32.82^\circ$ (*c* 0.275); HR-FABMS Found $[M + Na]^+$ 429.2267; $C_{23}H_{34}O_6Na$ requires 429.2253. UV λ_{max} nm (log ϵ): 208 (4.63), 294 (3.29); IR ν_{max}^{KBr} cm^{-1} 3390, 1722, 1638, 1434, 1375, 1231, 1037, 756; 1H - and ^{13}C -NMR spectral data: Table 1.

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