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A SESQUITERPENE LACTONE, SINTENIN, FROM *ACHILLEA SINTENISII*

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Key Word Index—*Achillea sintenisii*; Compositae; sesquiterpene lactone; costunolide; flavonoids.

Abstract—The aerial parts of *Achillea sintenisii* afforded in addition to known compounds a new costunolide, sintenin whose structure was elucidated by spectral methods.

INTRODUCTION

Achillea species have shown antibacterial [1], anti-inflammatory [2], antilarval [3], anti-allergic [4] and anti-irritant [5] activities. In this paper *Achillea sintenisii* Hub.-Mor. (Compositae) was chemically investigated, in addition to flavonoids and terpenoid compounds a new sesquiterpene lactone, sintenin was obtained.

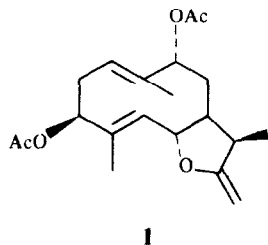
RESULTS AND DISCUSSION

The aerial parts of *A. sintenisii* afforded stigmasterol, α -amyrin, salvigenin, 6-hydroxyluteolin 6,7,3',4'-tetramethyl ether and sintenin (**1**) a new sesquiterpene lactone of the costunolide type. The IR spectrum of **1** showed a γ -lactone band at 1760 cm^{-1} , ester bands at 1720 and 1240 cm^{-1} , unsaturation at 1660 cm^{-1} . The high resolution mass spectrum gave a molecular ion peak at m/z 350 indicating a molecular formula $\text{C}_{19}\text{H}_{26}\text{O}_6$. The ^1H NMR

Table 1. ^1H NMR spectral data of sintenin (400 MHz, CDCl_3)

H	
1	5.24 <i>br dd</i>
3	5.11 <i>dd</i>
5	4.72 <i>br d</i>
6	4.76 <i>dd</i>
7	2.37 <i>ddd</i>
8 β	2.575 <i>ddd</i>
9	5.17 <i>dd</i>
11	2.73 <i>dq</i>
13	1.24 <i>s</i>
14	1.48 <i>s</i>
15	1.71 <i>s</i>
OAc	2.03 <i>s</i>
OAc	2.105 <i>s</i>

J (Hz): $1,2\beta = 12$; $1,2\alpha = 4$;
 $3\alpha,2\beta = 9$; $3\alpha,2\alpha = 5.5$; $5,6 = 8$;
 $6,7 = 12$; $8\beta,9\beta = 10.5$;
 $9\beta,8\alpha = 5$; $11,7 = 7$; $11,13 = 7$.



spectrum exhibited methyl singlets at δ 1.24 (H-13), 1.48 (H-14), 1.71 (H-15) and two acetyl methyl groups as singlets at δ 2.105 and 2.03. The olefinic protons were at δ 5.24 as a double doublet for H-1 and a broadened doublet at δ 4.72 for H-5. The double doublets at δ 5.11 and 5.17 indicated the protons geminal to acetyl groups. The triple doublet at δ 2.37 and double quartet at δ 2.73 indicated H-7 and H-11, respectively. The stereochemistry of the acetyl groups were assigned by using Dreiding models and by measuring J values of H-9 ($J_{9\beta,8\alpha} = 5$ Hz; $J_{9\beta,8\beta} = 10.5$ Hz) and H-3 ($J_{3\alpha,2\beta} = 9$ Hz; $J_{3\alpha,2\alpha} = 5.5$ Hz). The ^1H NMR data of **1** is given in Table 1.

EXPERIMENTAL

Achillea sintenisii was collected from central Turkey (Sivas). A voucher (MARE 572) is deposited in the Herbarium of Faculty of Pharmacy, Univ. of Marmara (Istanbul). Dried and powdered aerial parts of *A. sintenisii* (1.37 kg) was extracted with Et_2O -petrol (1:2) and the extract was treated with MeOH to remove long chain saturated hydrocarbons, the residue was separated by CC (silica gel) the fractions were further separated by prep. TLC. Thus stigmasterol (60 mg), α -amyrin (21 mg), salvigenin (7.3 mg), 6-hydroxyluteolin 6,7,3',4'-tetramethyl ether (15 mg) and sintenin (**1**) (6 mg) were obtained.

Sintenin, 3 β ,9 α -diacetoxycostunolide (**1**): Amorphous, colourless compound. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} 1760 (γ -lactone), 1720, 1240

(-OAc), 1660 C=C), 1450, 1375, 950, ^1H NMR given in Table 1. MS, 70 eV (probe) m/z (rel. int.): 350 $[\text{M}]^+$ ($\text{C}_{19}\text{H}_{26}\text{O}_6$) (0.6), 291 $[\text{M}-\text{OAc}]^+$ (100), 231 $[\text{M}-\text{HOAc}-\text{OAc}]^+$ (60), 203 $[\text{231}-\text{CO}]^+$ (20), 175 $[\text{203}-\text{CO}]^+$ (40), 91 $[\text{C}_7\text{H}_7]^+$ (24).

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ACYCLIC DITERPENES FROM *BIFURCARIA BIFURCATA*

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Key Word Index—*Bifurcaria Bifurcata*; Cystoseiraceae; brown alga; marine diterpenoids; (2E,6E,10E)-12(S)-hydroxy-3,7,11,15-tetramethyl hexadeca-2,6,10,14-tetraenoic acid; (2E,6E,10E,13E)-3,7,11,15-tetramethyl hexadeca-2,6,10,13,15-pentenol.

Abstract—Two new acyclic diterpenes have been isolated from the brown alga *Bifurcaria Bifurcata*. They were characterized by spectral and chemical methods.

INTRODUCTION

We recently described [1] the main product (**1**) from the brown alga *Bifurcaria Bifurcata* collected along Morocco coasts (Oualidia, 1984). Various acyclic diterpenes have been isolated so far from the family of Cystoseiraceae [2-6], but this re-examination of *Bifurcaria Bifurcata* has led to the isolation of two new acyclic diterpenes, one

having an acidic functionality. A few acidic terpenoids have been isolated from marine sources, in particular from marine algae [7].

Silica gel column chromatography of the methanol-chloroform extract of the alga gave a fraction containing **2a** as an impure oil. This fraction was further purified by HPLC to give **2** as an optically active oil. The