SESQUITERPENE LACTONES FROM Dendroseris neriifolia

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Abstract - A new eudesmanolide, dendroserin ,was isolated from the aerial part of Dendroseris neriifolia Hook. and Arn. together with 8 α -hydroxy-achillin, a known sesquiterpene lactone. The structures were elucidated by spectroscopic methods.

INTRODUCTION.

Dendroseris D. Don is a South American genus, endemic to the Juan Fernandez Islands. The genus is variable morphologically, both in its floral and vegetative parts. The considerable morphological diversity among the species is reflected by the recognition of three subgenera: Dendroseris, Phoenicoseris and Rea.[1]

As part of a chemical systematic study of genus Dendroseris, we describe the isolation and structure elucidation of 8α -hydroxyachillin[2,3] and of the new sesquiterpene lactone named, dendroserin, from the leaves of Dendroseris neriifolia (subgenus, Rea) both reported for the first time to Dendroseris.

RESULTS AND DISCUSSION.

The methanolic extract of the aerial parts was fractioned with $CHCl_3$. The $CHCl_3$ soluble fraction was chromatographed on a silica gel. The column chromatography gave a mixture of known pentacyclic triterpenes reported earlier for another member of Lactuceae[4]. They are lupeol, taraxasterol, ursolic and betulinic acid, and the sterols β-sitosterol and stigmasterol.

Two sesquiterpene lactones isolated from Dendroseris neriifolia were dendroserin (1) and 8α -hydroxyachillin (2). These compounds have not been reported before from this genus, but they are closely related to lactones from the tribe

Lactuceae[5].

The ^1H nmr spectrum of (1) (Table 1) was in part close to that of 4-epi-arbusculin A[6]. The presence of the corresponding 8-desacetyl-11β, 13- dihydro derivative followed from the upfield shift of the H-8 signal and the replacement of the exomethylene protons (H-13) by signal at δ 1.77 dq and 0.98 d (3H). The configuration at C-11 followed from the coupling (J=12 Hz) which indicates a trans-diaxial orientation of the protons at C-7 and C-11.

Table 1. ^1H nmr spectral data of compound (1) dendroserin (400 MHz, δ -values).

$CDCl_3/C_6D_6$ 1:1	
H - 1α	3.21 dd
H - 2α	1.40 dddd
H - 2β	1.33 dddd
H - 3α	1.49 ddd
H - 3β	1.65 br d
H - 5α	1.45 d
H - 6	3.88 t
H - 7α	1.25 ddd
H - 8α	1.45 m
H - 8β	1.01 dddd
H - 9α	0.83 ddd
H - 9β	1.65 br d
H - 11	1.77 dq
H - 13	0.98 d
H - 14	0.67 s
H - 15	1.15 s
CH	3.25 s

J (Hz): Compound 1 : 1α ,2α =4; 1α,2β =11;2α,2β=2β,3α=3α,3β =10; 2α ,3α=2α,3β=2β, 3β∿4; 5,6=11;6,7=10;7,8β =7,11=8β,9α =12;7,8α =8α,9α =8α ,9β =8β ,9β∿ 3.5;8α ,8β = 9α ,9β =12; 11,13=7.

EXPERIMENTAL

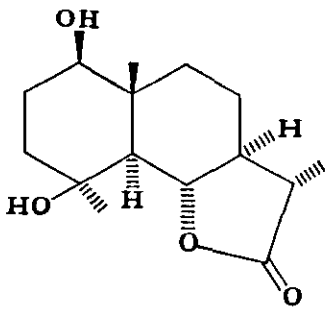
Extraction and isolation- Aerial parts were collected during the expeditions to the Juan Fernandez Islands (Chile) in January and November 1980 from Masatierra (Populations: 5169, 5179, 5129 and 5405 respectively). The plant material was air-dried in the field. Vouchers are deposited at the Herbarium of the Ohio State University, U.S.A., with duplicates at the Herbarium of the Universidad de Concepción, Chile.

The air-dried plant material (620.0 g) was extracted with MeOH for 3 days at 20°C and the solvent removed in vacuo. The extract (77.2 g) was fractionated with petrol ether, $CHCl_3$, EtOAc, and n-BuOH.

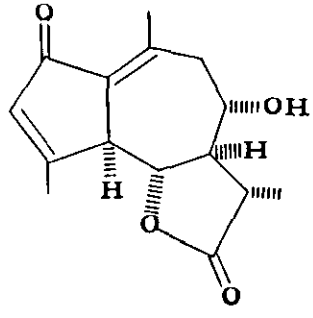
The $CHCl_3$ extract (8.3 g) was chromatographed on a silica gel column using petrol ether-$CHCl_3$ (50:50 v/v), $CHCl_3$, and $CHCl_3$-EtOAc (50:50 v/v) as eluents. *The compounds isolated were crystallized from the same solvent mixture used to* eluate them from the column. Fraction 127-133 ($CHCl_3$ - EtOAc, 75:25) gave 88.5 mg of compound (2) and fraction 147-153 ($CHCl_3$ - EtOAc, 60:40) gave 3.0 mg of compound (1).

Compound (1). Dendroserin. Colourless needles (MeOH), mp 178-182°C, uv λ_{max}^{MeOH} 216 nm, ms m/z (rel.int): 268 M $^+$(0.4), 253.144 (M - Me)$^+$(44) (calc. for $C_{14}H_{21}O_4$ 253.144), 235 253-H_2O $^+$(8), 217 235-H_2O $^+$(8), 101 (96), 95 (84), 81 (72), 72 (100).

Compound (2). 8α-Hydroxyachillin. Colourless needles (MeOH), mp 161-162°C, ir ν_{max}^{Nujol} 3520 (OH), 1770 (γ-lactone), 1680 (C=C C=O) cm^{-1}, uv λ_{max}^{MeOH} 255 nm. (log ε 4.22).



(1)



(2)

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