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A 3,4-*SECO*-CYCLOARTANE DERIVATIVE FROM *TILLANDSIA USNEOIDES*

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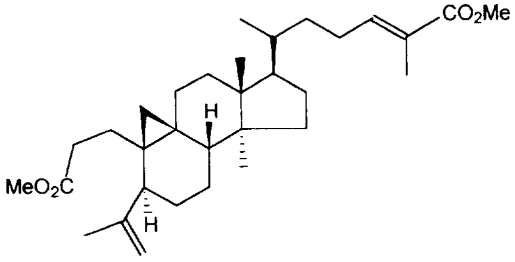
Key Word Index—*Tillandsia usneoides*; Bromeliaceae; cycloartane derivative.

Abstract—From *Tillandsia usneoides* a new 3,4-*seco*-cycloartane has been isolated and identified by spectroscopic methods as dimethyl 3,4-*seco*-cycloart-4(29), 24*E*-diene-3,26-dioate.

INTRODUCTION

Tillandsia usneoides (Bromeliaceae) is an aerial plant which causes the death of other plants where it grows. As it propagates easily, it is considered a pest. Cycloartane derivatives and flavonoid constituents were previously reported [1–3]. We now report the isolation and structure elucidation of a new dimethyl 3,4-*seco* mangiferonate **1**.



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RESULTS AND DISCUSSION

Compound **1** showed in its HR–EI mass spectrum a $[M]^+$ at *m/z* 498.3711 ($C_{32}H_{50}O_4$) and the presence of eight degrees of unsaturation. The ^1H NMR spectrum displayed signals for a cyclopropane methylene (δ0.40 and 0.73, *d*, $J = 4.5$ Hz), two tertiary methyls (δ0.94 and 0.97), one secondary methyl (δ0.91, *d*, $J = 6.5$ Hz) and two vinyl methyls (δ1.69 and 1.83, *bs*). Another two three-proton singlets at δ3.64 and 3.73 were assigned to the methyl protons of carbomethoxy ester functions. Two broad singlets (δ4.72 and 4.80) were ascribed to an sp^2 methylene and a broad double triplet (δ6.76, *bt*, $J = 7.5$ and 1.5 Hz) was due to a conjugated olefinic proton.

The carbon multiplicities were determined by DEPT. The presence of seven methyl, 12 methylene, five methine and eight quaternary carbons was thus established. The signals in the ^{13}C NMR spectrum for a trisubstituted double bond (δ143.2 and 127.2), an ester carbonyl (δ168.8) in conjunction with the signals in the ^1H NMR spectrum at δ6.76, 3.73 and 1.84 were in good agreement with the presence in **1** of the side chain of methyl mangiferonate [4]. Furthermore, the δ values for the C and D ring carbons were the same as those reported for cycloartenol [5].

In order to obtain more information regarding the skeleton of **1**, COSY 45, homonuclear 2DJ, HETCOR and long range optimized HETCOR [6–8] experiments were performed. Table 1 summarizes the results obtained from DEPT and HETCOR correlations. Figure 1 shows COSY connectivities and some important correlations observed in a long range optimized HETCOR experiment. In this experiment the protons of the C-18 methyl group showed correlation with C-13, while the C-28 methyl protons showed long range coupling with C-14. Correlation was also observed between the *O*-methyl protons at δ3.73 and the vinyl methyl protons at δ1.84

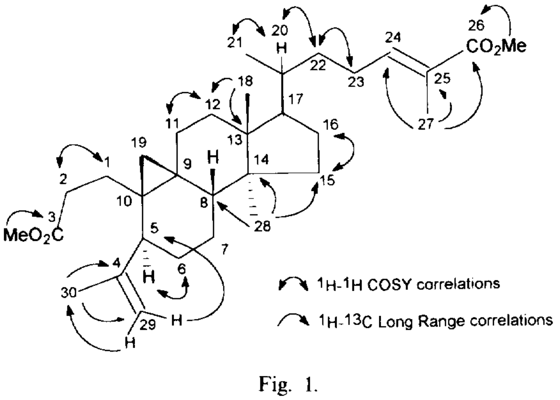

Fig. 1.

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Table 1. DEPT multiplicities, ^{13}C NMR, ^{1}H–^{13}C NMR connectivities and J_{HH} of **1**

C	DEPT multiplicity	^{13}C NMR (δ)	^{1}H NMR (δ)	J_{HH} (Hz)
1	CH_2	29.1	2.05, 1.37	
2	CH_2	31.5	2.46, 2.26	
3	-C-	174.4		
4	-C-	149.5		
5	CH	45.9	2.43	*dd*, 13, 4*
6	CH_2	27.8	1.51, 1.08	
7	CH_2	25.1	1.31, 1.06	
8	CH	47.8	1.56	
9	-C-	21.4		
10	-C-	27.2		
11	CH_2	27.1	2.09, 1.26	
12	CH_2	33.1	1.65	
13	-C-	45.3		
14	-C-	49.0		
15	CH_2	35.7	1.30	
16	CH_2	28.1	1.89, 1.24	
17	CH	52.2	1.59	
18	Me	18.1	0.97	*s*
19	CH_2	30.0	0.40 0.73	*d*, 4.5 *d*, 4.5
20	CH	36.0	1.43	
21	Me	18.2	0.91	*d*, 6.5
22	CH_2	35.2	1.55, 1.19	
23	CH_2	25.7	2.0–2.1	
24	CH	143.2	6.76	*dt*, 7.5, 1.5
25	-C-	127.2		
26	-C-	168.8		
27	Me	12.4	1.84	*bs*
28	Me	19.4	0.94	*s*
29	CH_2	111.6	4.80 4.72	*bs* *bs*
30	Me	19.8	1.69	*bs*
C_3OMe	Me	51.5	3.64	*s*
$C_{26}OMe$	Me	51.7	3.73	*s*

*From Homonuclear 2DJ experiment.

with the C-26 carbonyl and between the other *O*-methyl protons (δ3.64) and C-3 carbonyl. Important correlations were also observed between the vinyl methyl at δ1.68 and the carbons C-4 and C-29 and between the broad singlets at δ4.72 and 4.80 and the carbons C-5 and C-30. The δ values of C-5 and H-5, and the coupling constants for H-5 observed in the 2DJ experiment were similar to those reported for schisanlactone B [9] confirming the α position of this proton.

The EIMS fragments were in full accord with those reported for cycloartane derivatives [10] plus those deriving from fragmentation of the side chain.

On the basis of the above spectroscopic studies the structure of **1** was assigned as dimethyl 3,4-*seco*-cycloart-4(29), 24*E*-diene-3,26-dioate.

EXPERIMENTAL

General. The HREIMS was recorded on a VG ZAB-BEQQ mass spectrometer and the EIMS was taken on a triple quadrupole mass spectrometer. NMR spectra were recorded on a Brücker AC200 at 200.1 MHz for ^{1}H and 50.3 MHz for ^{13}C in $CDCl_3$ with TMS as int. standard. The long range HETCOR was optimized for J (^{1}H–^{13}C) = 10 Hz.

Plant material. Tillandsia usneoides was collected at Tigre (Buenos Aires, Argentina) in November, 1993. A voucher specimen no. 17913 is located at the Herbarium of Instituto Darwinion (San Isidro, Buenos Aires).

Extraction and isolation. Fresh plant (7 kg) was extracted at room temp. with EtOH and then with CH_2Cl_2. Water was added to the alcoholic extraction and the soln was extracted with hexane. The hexane layer was added to the CH_2Cl_2 extract and taken to dryness. The oily residue (88 g) was fractionated by dry column flash chromatography on silica gel using hexane and mixts of hexane–CH_2Cl_2 of increasing polarity. The fr. eluted with hexane–CH_2Cl_2, 1:1 (16 g) was further fractionated by the same technique. Subfr. eluted with hexane–CH_2Cl_2, 7:3 (3.6 g) was chromatographed by HPLC (Column: YMC C 18, 5 μm, 22.5 × 2.5 cm; Eluant: MeOH) yielding **1** (120 mg, 2×10^{-3}%).

Compound **1**. Oil. $[\alpha]_D = +63°$ (CH_2Cl_2, $c = 0.132$); UV (CH_2Cl_2) λ_{max} (ε) nm: 234 (5900). GC R_t = 14.93 min (Capillary column: HP-5, 25 m × 0.32 mm, temp: 150–280°, 10 min^{-1}); HREIMS *m/z*: 498.3711 ($C_{32}H_{50}O_4$), requires 498.3709; 483.3472 ($C_{31}H_{47}O_4$), requires 483.3474; EIMS 70 eV, *m/z*: (rel. int.): 498 (18); 483 (54); 455 (6); 451 (12); 385 (5); 343 (6); 330 (7); 315 (5); 301 (4); 249 (29); 217 (15); 175 (45); 161 (56); 95 (100); IR (KBr) ν_{max} cm^{-1}: 2928 (CH); 1740 (CO); 1720 (CO); 1647 (C = C); ^{1}H NMR and ^{13}C NMR: see Table 1.

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