Pergamon

Phytochemistry, Vol. 45, No. 5, pp. 1019–1021, 1997
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0031-9422/97 $17.00+0.00

PII: S0031-9422(97)00070-8

SHORT SIDE-CHAIN CYCLOARTANES FROM *TILLANDSIA USNEOIDES*

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(*Received in revised form* 2 *December* 1996)

Key Word Index—*Tillandsia usneoides*; Bromeliaceae; cycloartanes.

Abstract—The short side-chain cycloartanes, 27-*nor*-cycloartan-3,25-dione, 24,25,26,27-*tetranor*-3-oxo-cycloartan-23-al and 25,26,27-*trisnor*-3-oxo-cycloartan-24-al, have been isolated from *Tillandsia usneoides* and identified by spectroscopic and chemical methods. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

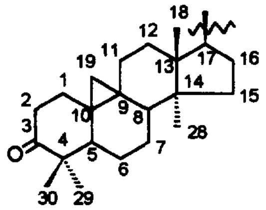
Tillandsia usneoides is a plague which extends into several regions of Argentina. Early work revealed the presence of cycloartanes [1]. As part of our continued interest in cycloartanes of the genus *Tillandsia* [2, 3], we have carried out a chemical investigation of *T. usneoides*. In the present paper, we report the isolation and structural elucidation of four minor components, three of which are novel compounds. Structural elucidation of these compounds was based on spectroscopic analysis and by synthesis of two of them.

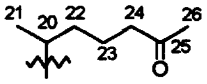
RESULTS AND DISCUSSION

The ^{1}H and ^{13}C NMR spectra of compounds **1**–**3** showed characteristic signals for 3-oxocycloartanes [4, 5].

Compound **1** exhibited a $[M]^+$ at *m/z* 426.3492, corresponding with the molecular formula $C_{29}H_{46}O_2$. The ^{1}H NMR spectrum showed a proton signal at δ 2.13 (3H, *s*), together with the typical signals of a 3-oxocycloartane skeleton, while, in the ^{13}C NMR spectrum, two carbonyl carbons appeared at δ 216.4 (C-3) and 210.9. These data suggested the presence of a methyl ketone group. Taking into account the molecular formula, the structure of compound **1** was assigned as 27-*nor*-cycloartan-3,25-dione. DEPT, COSY ^{1}H-^{1}H and NOESY experiments confirmed the NMR signals for this compound.

The HR mass spectrum of compound **2** showed a $[M]^+$ at *m/z* 384.3027 ($C_{26}H_{40}O_2$). The ^{1}H NMR spectrum showed characteristic H-2, H-19 and H-28 to H-30 signals of a 3-oxocycloartane; the H-21 and H-18 methyl signals were shifted downfield to δ 0.98 (3H, *d*, $J = 6.2$ Hz) and δ 1.05 (6H, *s*, superimposed on H-29), respectively. An aldehyde signal at δ 9.77 was also observed. The ^{13}C NMR spectrum showed a signal at δ 203.4 confirming the presence of an aldehyde. These data indicated that compound **2** possessed a short side-chain with an aldehyde at C-23. This was confirmed by mass spectrometry by a major fragment ion at *m/z* 340, due to the loss of 44 mu. This ion could be formed by a McLafferty rearrangement with migration of H-21 to the C-23 carbonyl oxygen. From this evidence, the structure of compound **2** was deter-





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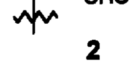

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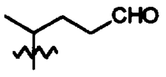

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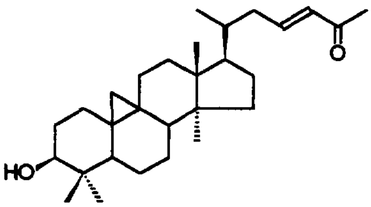

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mined to be 24,25,26,27-*tetranor*-3-oxo-cycloartan-23-al. Reductive ozonolysis of previously isolated 25-hydroxycycloart-23-en-3-one [2], yielded a compound with spectroscopic data identical to those of compound **2**, thus confirming the structure.

Compound **3** showed by HREI mass spectrometry $[M]^+$ at *m/z* 398.3192 ($C_{27}H_{42}O_2$), whilst NMR spectra also showed an aldehyde group (^{1}H NMR: δ 9.77 (1H, *t*, $J = 1.5$ Hz); ^{13}C NMR: δ 203.1). These data suggested that compound **3** was an homologue of compound **2**. Reductive ozonolysis of cycloartenone yielded a product whose NMR spectra were identical to those of compound **3**. Thus, the structure of compound **3** was established as 25,26,27-*trisnor*-3-oxo-cycloartan-24-al. The corresponding 3β-hydroxy-derivative has been previously isolated [6].

Compound **4** was identified as 27-*nor*-3β-hydroxycycloart-23-en-25-one by comparison with spectral data (^{1}H and α_D) previously reported [7].

EXPERIMENTAL

General. NMR were recorded at 200 MHz for ^{1}H and 50 MHz for ^{13}C in $CDCl_3$ with TMS as int. standard.

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

Extraction and isolation. Plant material was extracted and fractionated as previously reported [2]. The fr. eluted with hexane–CH_2Cl_2 (1:1) was further fractionated by vacuum chromatography on silica gel using hexane and mixts of hexane–CH_2Cl_2 of increasing polarity. The subfr. eluted with hexane–CH_2Cl_2 (1:4) was chromatographed by HPLC (YMC C18, 5 μm, 22.5 × 2.0 cm; eluant: MeOH) yielding compounds **1**, **4** and a mixt. of **2** and **3**. Compounds **2** and **3** were sepd by HPLC (YMC C18, 5 μm, 250 × 10 mm; eluant: MeCN–H_2O, 9:1) providing **2** (3 mg) and **3** (2 mg). Compound **1** was purified by prep. TLC (CH_2Cl_2) (3 mg) and compound **4** was purified by prep. TLC (CH_2Cl_2–EtOAc, 9:1) (11 mg).

Ozonolysis of 25-*hydroxycycloart*-23-*en*-3-*one* (*and cycloartenone*). A general procedure previously described [8] was applied to CH_2Cl_2 solns of 25-hydroxycycloart-23-en-3-one (and cycloartenone) to obtain pure 24,25,26,27-*tetranor*-3-oxo-cycloartan-23-al (**2**) (and 25,26,27-*trisnor*-3-oxo-cycloartan-24-al (**3**)).

Compound **1**. $[\alpha]_D^{20} = +23°$ ($CHCl_3$, *c* 0.15). HREIMS *m/z*: 426.3492 ($C_{29}H_{46}O_2$), requires 426.3498; EIMS 70 eV, *m/z* (rel. int.): 426 ($[M]^+$, 5), 411 (2), 408 (2), 393 (1), 368 (3), 313 (10), 288 (4), 175 (12), 121 (22), 43 (100); CIMS (CH_4): 455 (7), 427 (100), 409 (42), 313 (34), 207 (44). IR (KBr) ν_{max} cm^{-1}: 2966, 2923, 2857 (CH), 1718 (C=O). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Compound **2**. $[\alpha]_D^{20} = +14°$ ($CHCl_3$, *c* 0.27). HREIMS *m/z*: 384.3027 ($C_{26}H_{40}O_2$), requires 384.3028, EIMS 70 eV, *m/z* (rel. int.): 384 ($[M]^+$, 19), 369 (13), 366 (11), 351 (5), 340 (26), 313 (14), 246 (33), 175 (32),

Table 1. ^{1}H NMR chemical shifts (δ) of compounds **1–3** in $CDCl_3$ (*J* in Hz)

H	**1**	**2**	**3**
2	2.30 *ddd* (13.5, 4.0, 2.5)	2.30 *m*	2.30 *m*
	2.71 *dt* (13.5, 6.5)	2.71 *dt* (13.8, 6.6)	2.71 *dt* (13.5, 6.6)
18	0.99 *s*	1.05 *s*	1.00 *s*
19 exo	0.57 *d* (4.0)	0.58 *d* (4.4)	0.57 *d* (4.4)
endo	0.79 *d* (4.0)	0.79 *d* (4.4)	0.79 *d* (4.4)
21	0.89 *d* (6.5)	0.98 *d* (6.2)	0.89 *d* (6.5)
23	1.4–1.65 *m*	9.77 *bs*	
24	2.39 *m*		9.77 *bt* (1.6)
26	2.13 *s*		
28	0.90 *s*	0.91 *s*	0.91 *s*
29	1.05 *s*	1.05 *s*	1.05 *s*
30	1.10 *s*	1.10 *s*	1.10 *s*

Table 2. ^{13}C NMR chemical shifts (δ) of compounds **1–3** in $CDCl_3$

C	1	2	3
1	33.4	33.4	33.4
2	37.4	37.4	37.5
3	216.4	216.4	216.4
4	50.2	50.2	50.2
5	48.5	48.4	48.4
6	21.5	21.5	21.6
7	25.9	25.8	25.9
8	47.9	47.8	47.9
9	21.0	21.0	21.0
10	26.0	26.0	26.0
11	26.7	26.6	26.7
12	32.8	32.7	32.8
13	45.4	45.5	45.4
14	48.8	48.9	48.8
15	35.6	35.5	35.6
16	28.1	28.4	28.3
17	52.1	52.2	52.2
18	18.1*	18.1	18.1*
19	29.6	29.5	29.5
20	35.7	31.9	35.7
21	18.2*	19.6	18.0*
22	35.9	51.1	28.1
23	21.5	203.4	41.2
24	44.3		203.1
25	210.9		
26	24.9		
28	19.3	19.3	19.3
29	22.2	22.2	22.2
30	20.8	20.8	20.8

* May be interchanged.

147 (67), 121 (57), 55 (100); CIMS (CH_4): 413 (8), 385 (100), 341 (26), 313 (33). IR (KBr) ν_{max} cm^{-1}: 2923, 2873, 2720 (CH), 1718 (C = O), 1707 (C = O). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Compound **3**. $[\alpha]_D^{20} = +20°$ ($CHCl_3$ *c* 0.21). HR-EIMS *m/z*: 398.3192 ($C_{27}H_{42}O_2$), requires 398.3185, EIMS 70 eV, *m/z* (rel. int.): 398 ($[M]^+$, 6), 383 (4), 380 (5), 365 (2), 355 (1), 313 (10), 260 (10), 175 (12), 55 (100); CIMS (CH_4): 427 (9), 399 (100). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Compound **4**. ^{1}H NMR: δ 6.80 (*ddd*, $J = 15.7$, 8.4 and 6.2 Hz, H-23), 6.07 (*d*, $J = 15.7$ Hz, H-24), 3.29 (*dd*, $J = 4.5$ and 10.5 Hz, H-3), 2.37 (*dd*, $J = 14.2$ and 6.2 Hz, H-22), 2.24 (*s*, H-26), 0.99 (*s*, H-18), 0.97 (*s*, H-29), 0.91 (*d*, $J = 6.0$ Hz, H-21), 0.90 (*s*, H-28), 0.81 (*s*, H-30), 0.57 (*d*, $J = 4.4$ Hz, H-19), 0.33 (*d*, $J = 4.4$, H-19). ^{13}C NMR: δ 198.4 (C-25), 147.5 (C-23), 132.5 (C-24), 78.8 (C-3), 52.2 (C-17), 48.9 (C-14), 48.0 (C-8), 47.1 (C-5), 45.5 (C-13), 40.5 (C-4), 39.6 (C-22), 36.2 (C-20), 35.5 (C-15), 32.8 (C-12), 32.0 (C-1), 30.4 (C-2), 29.9 (C-19), 28.2 (C-16), 26.9 (C-26), 26.2 (C-10), 26.4 (C-11), 26.0 (C-7), 25.4 (C-29), 21.1 (C-6), 19.9 (C-9), 19.3 (C-28), 18.7 (C-21), 18.1 (C-18), 14.0 (C-30).

Acknowledgements—We thank UMYMFOR (CONICET-FCEN, UBA), CONICET (Argentina) and Fundación Antorchas for financial support.

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