Asian Journal of Chemistry Vol. 18, No. 4 (2006), 3092–3096

^{1}H and ^{13}C Assignments of Passiflorine from *Passiflora edulis*

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Two cycloartanol-type saponins isolated from *Passiflora edulis* were identified as passiflorine and its C-31 epimer by NMR techniques. Complete ^{1}H and ^{13}C assignments of passiflorine have not previously been published. The identification of this compound by NMR methods will be discussed and full ^{1}H and ^{13}C assignments for both epimers are given.

Key Words: NMR, Passiflorine, *Passiflora edulis*.

INTRODUCTION

Passiflora edulis Sims belonging to Passifloracea is a woody climber, native of Brazil, now cultivated in all parts of the world, chiefly for its edible fruits and ornamental flowers. This plant is with deeply three-lobed leaves and white flowers often tinted with purple colour. Two cycloartanol-type saponins isolated from *Passiflora edulis* were identified as passiflorine and its C-31 epimer by NMR techniques. Complete ^{1}H and ^{13}C assignments of passiflorine have not previously been published. The identification of this compound by NMR methods will be discussed and full ^{1}H and ^{13}C assignments for both epimers are given.

EXPERIMENTAL

Plant Material: The plant *Passiflora edulis* Sims was collected at Coonoor, Nilgiris, India. The air-dried leaves were ground and extracted with 70% MeOH for 7 d, and then the MeOH was removed under vacuum. A portion of the resulting aqueous extract was dried to allow quantitation; this indicated that 1 kg of dried plant material yielded 50 g of extract.

Isolation and Purification: The aqueous concentrate was extracted with petroleum ether (60–80°C), Et_2O and EtOAc. The EtOAc extract yielded a yellow powder (5 g) which was subjected to chromatography on a cellulose column with elution by water and an increasing percentage of AcOH. The fraction eluted with 30% AcOH gave a yellow powder which was recrystallized from MeOH to yield passiflorine as white crystals.

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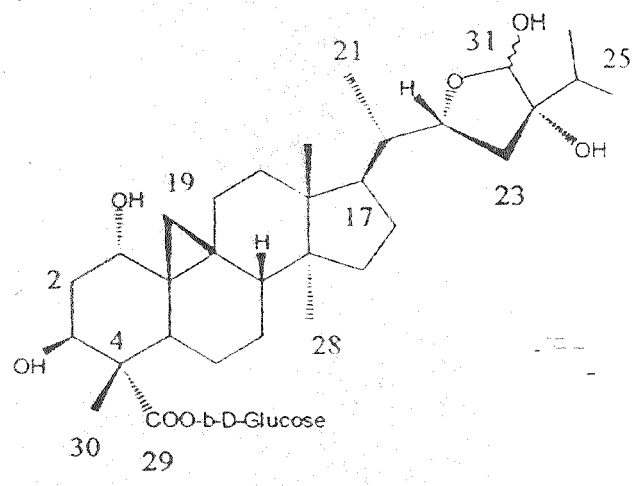
NMR spectra were recorded in various deuterated solvents (pyridine-d_5) on a Varian Unity 400 NMR instrument at 399.951 MHz for ^{1}H and 100.578 MHz for ^{13}C, using standard Varian pulse sequence programs. LRMS were taken on a VG 7070 E-HF at VPI & SU. Other conditions were as previously described[6].

RESULTS AND DISCUSSION

Passiflorine (1): White crystals; m.p. 183°C; $C_{37}H_{60}O_{12}$, FABMS (neg.) m/z 533 $[M\text{-}C_6H_{11}O_5]^-$; ^{1}H NMR (Table-1); ^{13}C NMR (Table-2); HMBC (Table-1); ROESY (Table-1).

During a phytochemical investigation of the plant *Passiflora edulis*, the known triterpenoid passiflorine **(1)** was isolated and identified by NMR methods, including COSY, HMQC, HMBC and ROESY. Passiflorine has a cycloartanol skeleton with an unusual five-membered hemi-acetal ring in its side chain. The structure of **1** was determined in the original work[2] by degradation of the aglycone followed by several reactions to identify the functional groups and the stereochemistry at C-22 and C-24 was assigned as 22R and 24S. The compound was identified as a mixture of epimers at the C-31 position. The structure of the methyl ester of its aglycone, passifloric acid methyl ester, was later confirmed by X-ray crystallography[1].



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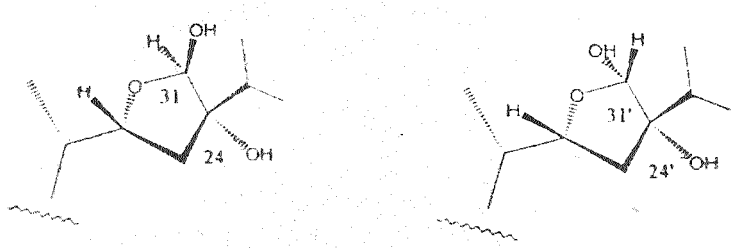

1a **1b**

Fig. 1

TABLE-1
^{1}H-NMR, HMBC AND ROESY DATA FOR PASSIFLORINE (1)

	^{1}H	^{13}C	1a HMBC Correlations	NOE Correlations
1	3.85, br s	72.4 (d)	C-3, C-5, C-10, C-19	H-2α, H-2β, H-11β, H-19b
2α	2.42, br d, J = 11.6	38.4 (t)	C-4, C-10	H-1, H-3
2β	2.23, m			H-1,30-CH_3
3	5.58, br d, J = 8.8	70.8 (d)	C-4, C-30	H-5
4		56.4 (s)		
5	3.36, m	37.7 (d)	C-4, C-6, C-10, C-30	H-3
6α	1.83, m	23.1 (t)		
6β	1.12, m			H-19a
7α	1.42, m	27.7 (t)		
7β	1.83, m			
8	1.42	48.3 (d)		H-18, H-19a
9		20.9 (s)		
10		30.1 (s)		
11α	2.72, m	26.1 (t)	C-9, C-10	H-28
11β	1.40, m			H-1, H-19b
12α	1.70, m	33.1 (t)		
12β				
13		46.1 (s)[b]		
13′		46.0 (s)[b]		
14		48.5 (s)[c]		
14′		48.6 (s)[c]		
15α	1.18, m	36.1 (t)		
15β				
16α	1.12, m	25.8 (t)		
16β				
17	1.69, m	50.5 (d)[d]		
17′		50.2 (d)[d]		
18-CH_3	0.99, s	18.3 (q)	C-12, C-13, C-14, C-17	H-8
19a	0.72, d, J = 4.0	30.1 (t)	C-1, C-5, C-8, C-9, C-10, C-11	H-6β, H-8, 30-CH_3
19b	0.54, d, J = 4.0		C-1, C-5, C-8, C-9, C-10, C-11	H-1, H-11β
20	2.17, m	39.2 (d)		
20′		39.0 (d)		
21-CH_3	1.26, d, J = 6.8	13.1 (q)	C-17, C-20, C-22	
21′-CH_3	1.22, m	13.1 (q)	C-17′, C-20′, C-22′	
22	4.88, m	79.9 (d)		
22′	4.13, m	78.1 (d)		

	^{1}H	^{13}C	1a HMBC Correlations	NOE Correlations
23α	2.13, m	37.5 (t)		
23β		35.4 (t)		
24		85.4 (s)		
24′		81.8 (s)		
25	2.62, m	33.9 (d)	C-26, C-27	
25′	1.98, m[g]	33.8 (d)	C-26′, C-27′	H-31′
26-CH_3	1.39, d, J = 6.8	18.1 (q)[e]	C-24, C-25, C-27	
26′-CH_3	1.20, d, J = 6.8[g]	17.5 (q)f	C-24′, C-25′, C-27′	
27-CH_3	1.29, d, J = 6.8	18.5 (q)[e]	C-24, C-25, C-26	
27′-CH_3	1.20, d, J = 6.8[g]	17.9 (q)[f]	C-24′, C-25′, C-26′	
28-CH_3	0.85, s	19.7 (q)	C-8, C-13, C-14, C-15	H-11α
29		176.8 (s)		
30-CH_3	1.68, s	9.7 (q)	C-3, C-4, C-5, C-29	
31	5.78, s	103.1 (d)	C-22, C-23	26 or 27-CH_3
31′	5.47, s[g]	98.8 (d)	C-22′, C-23′, C-24′	26′ or 27′-CH_3, H-25′
G1	6.52, d, 7.6	96.5 (d)	C-29	
G2	4.16, t, 8.0	74.8 (d)	G-1, G-3	
G3	4.28, t, 8.4	78.5 (d)	G-2, G-4	
G4	4.38, m	70.9 (d)	G-3, G-6	
G5	4.02, m	79.7 (d)		
G6	4.40, m	62.0 (t)	G-5	

[a]The chemical shifts of the two sets of the proton(s) and carbon(s) were not differentiated.
[b, c, d, e, f]Assignments with the same superscript can be reversed.
[g]H-25′, 26′-CH_3, 27′-CH_3 and H-31′ were assigned to 31′-α-OH (*i.e., cis* of 24-OH and 31-OH), H-25, 26-CH_3, 27-CH_3 and H-31 were assigned to 31-β-OH (*i.e., trans* of 24-OH and 31-OH).

Cycloartanols with 1α-OH and 29-COOR functionalities are rare and relatively little NMR data has been reported for them[3–5]. The availability of ^{2}D NMR data allowed assignment of the full ^{1}H and ^{13}C resonances for both epimers of **1** to be made.

Proton and carbon chemical shifts in the cycloartanol skeleton of **1** could be assigned unambiguously from the comprehensive COSY, HMQC and HMBC data (Table-1). Thus the assignments of the skeleton were determined by HMBC according to the following two or three bond C—H correlations: H_2-19 to C-1, C-5, C-8, C-9, C-10 and C-11; 18-CH_3 to C-12, C-13, C-14 and C-17; H_3-28 to C-8, C-13, C-14 and C-15; H_3-30 to C-3, C-4, C-5 and C-29. Resonances of H_2-19 (0.54 and 0.72 ppm, br d, J = 4 Hz) were characteristic of a cyclopropyl function. From HMBC data the anomeric proton (δ 6.52) in glucose had a significant correlation to C-29 (COO). The β-D-glucose was thus located unambiguously on the 29-carboxyl group.

In the ^{1}H NMR spectrum, half-intensity signals for two singlet anomeric protons (H-31, δ 5.78 and H-31′, δ 5.47) were observed, indicating the presence of a mixture of epimers. In the ^{13}C NMR spectrum, resonances for the side chain

carbons showed two sets of signals, indicating that the epimeric carbons were associated with the side chain. In the HMBC data, H_3-26 and H_3-27 showed correlations to a methine carbon and a quaternary oxygenated carbon, indicating that the isopropyl group was connected to an oxygenated quaternary carbon (C-24). Correlations of the H-31′ anomeric proton to C-22′, C-23′ and C-24′ and of H_3-21′ to C-17′, C-20′,and C-22′, made it possible to build the side chain structure as shown in **1b.** A similar set of resonances from the other epimer could also be connected. The observation of an NOE between H-25′ and H-31′ and of no NOE between H-25 and H-31 indicated that H-31′ and the isopropyl group are in the *cis* position and that H-31 and the isopropyl group are in the *trans* position on the five-membered ring. In other words, 24-OH and 31-OH are *trans* as shown in **1a** and 24′-OH and 31′-OH are *cis* shown as in **1b.** From the correlations shown in Table-1, all the ^1H and ^{13}C resonances could be assigned. The assignments of some overlapping proton signals were achieved from HMQC data (not shown).

The NOE between H-11α and H_3-28 and between H-11β and H-19b (back side) indicates that ring C is in the boat form conformation; in this conformation H-11α is in an axial position and H-11β is in an equatorial position, allowing them to interact with H_3-28 and H-19b, respectively.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the help in recording the spectra and discussions by David G.I. Kingston, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia-24061-0212. One of the authors (YDR) is grateful to the Management and Principal, Sri Krishna College of Engineering and Technology for providing the necessary facilities. The author (NS) is grateful to the Director of the Regional Engineering College for providing the necessary facilities.

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(*Received*: 10 December 2005; *Accepted*: 2 May 2006) AJC-4848