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Reference Data

Complete Assignment of ^{1}H and ^{13}C NMR Spectra of Ikarisoside A and Epimedoside C

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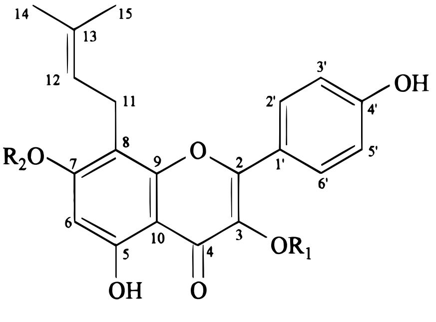
ABSTRACT: The complete assignment of the proton and carbon NMR spectra for ikarisoside A and epimedoside C from the aerial parts of *Epimedium koreanum* were achieved using the concerted application of one- and two-dimensional NMR techniques including COSY and HMBC spectroscopy. The parameters previously reported in the literature were found to be incorrect or incomplete. © 1997 John Wiley & Sons, Ltd.

KEYWORDS: ikarisoside A; epimedoside C; NMR; ^{1}H NMR; ^{13}C NMR

INTRODUCTION

During the course of our investigations on the chemical composition of the aerial parts of *Epimedium koreanum*,[1,2] a herb native to northeast China, we isolated from the EtOAc fraction some desmethylanhydroicaritin glycosides. Their structural elucidation was mainly based on the comparison with literature reported previously.[3,4] Recently, within the context of further NMR studies on these glycosides, the complete ^{1}H and ^{13}C chemical shift assignments were derived for ikarisoside A (**1**) and epimedoside C (**2**). Although ^{1}H and ^{13}C NMR spectra of these compounds have been reported previously, the proposed assignments[1–4] are incorrect or incomplete. The use of two-dimensional NMR techniques permitted us to obtain unambiguous assignments of chemical shifts for these molecules.



	R$_1$	R$_2$
1	Rha	H
2	H	Glc

RESULTS AND DISCUSSION

The ^{13}C NMR spectra of **1** and **2** present well resolved resonances. Assignments of carbons in sugar moieties was trivial on the basis of comparison with the data previously reported.[3,4] However, it is difficult to assign precisely the chemical shifts of C-5, C-7, C-4′ and CH$_3$ in the prenyl groups, owing to their similar chemical environments. Therefore, assignment of their ^{13}C resonances was achieved by concerted application of two-dimensional chemical shift correlation experiments. The starting points of the assignments were the unique ^{1}H resonance of the hydroxy groups at C-5, C-7, C-4′, and methyl groups at C-14, C-15. One-bond proton–carbon chemical shift correlations were established using a standard 2D sequence (HETCOR)[5], providing the identifications of the responces and giving assignments of C-14 and C-15. By utilizing the contour plots of the long-range heteronuclear multiple bond connectivity (HMBC)[6] experiments, the umbiguous assignment of C-5, C-7 and C-4′ was made. ^{13}C NMR chemical shifts data for the aglycone moieties of **1** and **2** are given in Table 1 and ^{1}H NMR chemical shifts of the aglycone moieties obtained from heteronuclear correlation diagrams are presented in Table 2. Our assignments are largely in agreement with those previously reported,[1–4] however,

Table 1. ^{13}C NMR data (δ, ppm) for aglycone moieties of compounds 1 and 2

Position	1	2
2	157.2	147.5
3	134.1	135.8
4	178.0	176.4
5	158.9	158.6
6	98.3	97.4
7	161.4	160.1
8	105.9	108.1
9	153.7	152.7
10	104.2	104.5
11	21.2	21.5
12	122.4	122.5
13	131.0	131.0
14	25.4	25.5
15	17.5	17.9
1′	120.7	121.9
2′, 6′	130.5	129.6
3′, 5′	115.4	115.5
4′	160.0	159.4

Table 2. ^{1}H NMR data (δ, ppm) for aglycone moieties of compounds 1 and 2

Position	1	2
6	6.61	6.59
2′, 6′	7.76	8.06
3′, 5′	6.94	6.94
11	3.33, 3.45	3.21, 3.56
12	5.14	5.20
14	1.61	1.62
15	1.66	1.76
3-OH		9.52
5-OH	12.55	12.47
7-OH	10.83	
4′-OH	10.23	10.19

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the ^{13}C NMR signals for C-5, C-7, C-4′, C-14 and C-15 in both **1** and **2** have to be reversed.

EXPERIMENTAL

Compounds **1** and **2** were obtained from *Epimedium koreanum*. Their isolation and purification have been reported.[1,2]

All NMR spectra were recorded on a Bruker ARX-400 spectrometer in DMSO-d_6 solutions; tetramethylsilane (TMS) was used as an internal standard. The heteronuclear two-dimensional ^{1}H–^{13}C chemical shift correlation spectra were obtained with ^{13}C detection using proton decoupling in the F_1 dimension.[5] The spectra were acquired with 4 K × 256 data points. Spectral widths of 20 000.00 and 3921.28 Hz were employed in the F_2 (^{13}C) and F_1 (^{1}H) domains, respectively. Data were processed using shifted sine-bell functions for weighting in both dimensions. The refocusing delay was 3.45 ms, the mixing delay 2.3 ms and the relaxation delay 2 s.

The long-range heteronuclear multiple quatum bond connectivity (HMBC) spectra were obtained using the standard pulse sequence (INV4PLRND) in the Bruker software.[6] The spectral widths were F_2 5813.95 Hz and F_1 21 130.62 Hz. The delays D_1, D_2 and D_6 were set to 2.0, 3.45 and 70 ms, respectively.

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