

A REVISED STRUCTURE FOR THE ISOFLAVONE LANCEOLARIN

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(Received 4 December 1986)

Key Word Index—*Dalbergia lanceolaria*; Leguminosae; root bark; isoflavone; biochanin A 7-(β -apiofuranosyl(1 \rightarrow 6)- β -D-glucopyranoside).

Abstract—The structure of lanceolarin has been revised as biochanin A 7-(apiosyl(1 \rightarrow 6)glucoside).

Lanceolarin, an apiose containing isoflavone glycoside from the root bark of *Dalbergia lanceolaria* was given the structure; biochanin A 7-(β -apiofuranosyl(1 \rightarrow 2)- β -D-glucopyranoside on the basis of chemical studies [1, 2]. It was used as a reference compound in the structural studies of adicardin, an umbelliferone based apioglucoside from the root bark of *Adina cordifolia*. A detailed spectral study coupled with periodic acid consumption and enzymic hydrolysis were consistent with the structure umbelliferone 7-(β -apiofuranosyl(1 \rightarrow 6)- β -D-glucopyranoside for adicardin [3]. Adicardin and lanceolarin on exhaustive methylation followed by hydrolysis gave identical partial methyl ethers of apiose and glucose. Thus, the structure of lanceolarin needed revision.

The FT NMR of the acetate of lanceolarin in CDCl_3 indicated that the sugars were attached at the 7-hydroxyl of biochanin A. The two doublets ($J=2.5$ Hz) at δ 6.52 (H-6) and 6.65 (H-8) are characteristic of a 5,7-dihydroxy-isoflavone moiety. The attachment of the disaccharide unit at C-7 is indicated by the downfield shift of these signals. The H-2 signal at δ 7.96 is characteristic of isoflavones. A typical four peak A_2B_2 pattern of two doublets ($J=8$ Hz) in the range 6.9 to 7.44 suggested a C-4' oxygenated B-ring. The low field doublets at δ 7.44 and 7.14 are for H-2' and H-6', respectively. The 4'-methoxyl appeared at δ 3.83 as a singlet. The phenolic acetoxyl (s, 3H) appeared at δ 2.40 while the sugar acetoxyls (18 H) occurred in the range δ 2.00 to 2.10. The sugar protons (12 H) were found between δ 4.2 and 5.4, a range typical of a disaccharide.

The structure of lanceolarin was further revealed by its ^{13}C NMR spectrum in $\text{DMSO}-d_6$ (See Table 1). The chemical shift values (computed from those of formononetin and genistein) [4] agreed well with those for biochanin A. The sugar carbons were typically consistent with those corresponding to the ones in adicardin [3]. Of particular interest are the signals due to C-2 and C-6 of the glucose moiety. The C-2 of glucose appeared at δ 72.9 while the C-6 at δ 67.6 suggested that the inter sugar linkage in lanceolarin is apiosyl(1 \rightarrow 6)glucose. If the linkage were to be apiosyl(1 \rightarrow 2)glucose as suggested by the earlier workers, the value for the C-2 and C-6 should be δ 60.9 and 77.2 respectively [7].

Periodic acid oxidation [5] of lanceolarin consumed 3.80 mol indicating four glycol units. Therefore, lanceolarin is biochanin A 7-(β -apiofuranosyl(1 \rightarrow 6)- β -D-glucopyranoside).

EXPERIMENTAL

Mps are uncorr. ^1H NMR spectra were recorded using the FT technique and ^{13}C NMR spectra carried out in $\text{DMSO}-d_6$. The ^1H NMR of lanceolarin acetate was recorded in CDCl_3 .

Isolation of lanceolarin was carried out as reported in [1, 2]. It cryst. from MeOH as colourless needles, mp 168–170°, which sintered earlier and collected at 190–193°; $[\alpha]_D^{30} -97^\circ$ (80% MeOH; c 1.0). The ^{13}C NMR spectral data is given in Table 1.

The acetate (Ac_2O -pyridine; 100°; 2 hr) cryst. from EtOAc-petrol, mp 181–182°; $[\alpha]_D^{30} -48^\circ$ (DMF; c 1.2). The

Table 1. ^{13}C chemical shifts of lanceolarin (1)*

C	Biochanin—A	C	D-Glucose	C	Apiose
	Chemical shift		Chemical shift		Chemical shift
2	154.8	1	99.7	1	109.3
3	122.7	2	72.9	2	75.9
4	180.3	3	78.6	3	75.5
5	162.1	4	69.8	4	73.3
6	99.6	5	76.3	5	63.24
7	161.5	6	67.6		
8	94.6				
9	157.2 ^a				
10	106.1				
1'	122.1				
2'	130.1				
3'	113.7				
4'	159.2 ^a				
5'	113.7				
6'	130.1				
-OMe	55.1				

^a Values interchangeable.

* Off resonance spectrum.

^1H NMR spectrum was recorded in CDCl_3 and the data presented in the text. Periodic acid consumption of lanceolarin alongside adicardin and followed by the spectrophotometric method of Aspinall and Ferrier [5] revealed the uptake of 3.80 and 3.98 mol, respectively of periodic acid. Details of permethylation of lanceolarin and adicardin and their hydrolytic studies are already reported in connection with the structural studies on adicardin [3].

Acknowledgements—The authors thank Dr R. D. H. Murray (Glasgow) for running the ^{13}C NMR spectrum of lanceolarin, Professor E. V. Sundaram (Head of the Dept. of Chemistry, Kakatiya University, Warangal) and Professor K. Ramaiah (JNTU, Hyderabad) for providing facilities. One of us (Y.A.) thanks the CSIR for the award of a Research Fellowship.

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Phytochemistry, Vol. 28, No. 3, pp. 958–959, 1989.
Printed in Great Britain.

0031 9422/89 \$3.00+0.00
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ABSOLUTE CONFIGURATION OF (+)-5,6-DEHYDROLUPANINE, A KEY INTERMEDIATE IN BIOSYNTHESIS OF LUPIN ALKALOIDS

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(Received in revised form 30 August 1988)

Key Word Index—*Thermopsis chinensis*; Leguminosae; aerial parts; lupin alkaloid; quinolizidine alkaloid; (+)-5,6-dehydrolupanine; lupanine; absolute configuration; biosynthesis.

Abstract—(+)-5,6-Dehydrolupanine, a key intermediate in biosynthesis of lupin alkaloids, was isolated from *Thermopsis chinensis*. The absolute configuration of the compound was determined to be 7R,9R,11R by chemical transformation to (–)-lupanine.

INTRODUCTION

(+)-5,6-Dehydrolupanine (**1**) is rather widely distributed in the Leguminosae, although usually as a minor alkaloid [1]. Compound **1** has been postulated as a key biosynthetic intermediate between the sparteine-type alkaloids, e.g. lupanine, and the α -pyridone-type bases, e.g. anagyrine [2–4]. However, the absolute configuration of **1** has not been clarified. In the present investigation, we have determined the absolute configuration of (+)-5,6-dehydrolupanine (**1**) from *Thermopsis chinensis* as 7R,9R,11R by chemical transformation of **1** to (–)-lupanine (6S,7R,9R,11R) (**2**).

RESULTS AND DISCUSSION

From the 75%-EtOH extract of the aerial parts of *T. chinensis*, **1** was isolated in a yield of 0.002% of the fresh weight by repeated chromatography. We also isolated seven known lupin alkaloids, (–)-anagyrine (main base), (–)-N-methylcytisine, (–)-baptifoline, (–)-cytisine, (+)-lupanine, (–)-N-formylcytisine and rhombifoline [5].

The relative stereostructure of **1** was identified by the analysis of ^{13}C and ^1H NMR, mass spectrometry, IR and UV data and comparison with those reported previously [3–22]. In its CD spectrum, **1** showed a negative Cotton