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On the structure and spectroscopic properties of two 13-hydroxysparteine epimers

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Abstract

The ^{13}C and ^{1}H NMR spectra of 13α-hydroxysparteine and 13β-hydroxysparteine in $CDCl_3$ have permitted identification of their conformation with ring C a boat, the same as that of sparteine. Very weak hydrogen bond involving hydroxy group does not shift a possible conformation equilibrium as it occurs in 13α-hydroxy-2-oxosparteine and 13β-hydroxy-2-oxosparteine.

Keywords: Quinolizidine alkaloids; Sparteine; Lupanine; NMR; IR; Conformation; Hydroxy group

1. Introduction

Sparteine (**1**), the main tetracyclic bis-quinolizidine alkaloid, is built of two quinolizidine systems: a relatively resistant to configurational – conformational changes double-chair *trans*-quinolizidine system A/B and a much more flexible *cis*-quinolizidine system C/D, susceptible to inversion at the N16 atom connected with a conformational–configurational change. The DFT calculations derived by Galasso et al. [1] have conclusively proved that **1** has a strong preference (3.4 kcal/mol, 99.95%) to conformation **1a** (with ring C a boat) over **1b** (with ring C a chair). Most other bis-quinolizidine alkaloids with the sparteine skeleton adopt the same configuration and conformation of the C/D part of the molecule in the solid but many of them exist in a conformational equilibrium in solution [2]. Some chemical modifications of the sparteine skeleton or the presence of some groups attached to it can influence the proportion of conformers in this equilibrium. For instance, 2-oxosparteine (lupanine, **2**) which has the conformation with ring C a boat in the solid [3] occurs in the equilibrium with 90% dominance of the boat form [2,4] in chloroform solution. We have recently published our X-ray, NMR and IR investigation on the conformation of two epimers of 13-hydroxy-2-oxosparteine (13-hydroxylupanine, **3** and **4**) [5]. Surprisingly, in the solid state, **3** and **4** adopt the conformation with a chair ring C but they prefer the conformation with ring C a boat in solution. However, the fraction of the chair conformer is a little larger in **3** and **4** than in lupanine (**2**) [5].

In the present paper, we report our investigation on the conformation of epimeric 13-hydroxysparteines (**5** and **6**) in solution. We are particularly interested in finding out the influence of the axial and equatorial hydroxy group attached to the carbon atom in position 13 of sparteine (**1**) on the conformational equilibrium of the compounds.

2. Experimental

2.1. General techniques

Melting points were determined on a Boetius apparatus (PHMK 05 VEB Wagetechnik Rapido, Radebeul). IR spectra were recorded on a FT-IR Bruker IFS 113v spectrometer (KBr pellets technique). ^{13}C NMR spectra were obtained on a Varian 300 Mercury spectrometer at 75.462 MHz number of transients 10,000, acquisition time

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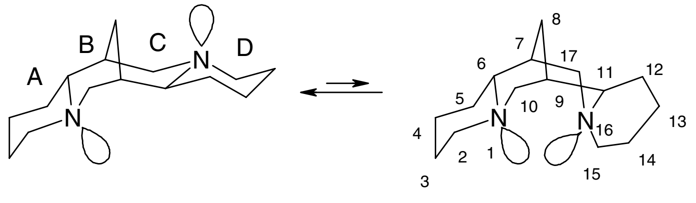
1.5 s, spectral width 13,718 Hz, number of points 27,372, digital resolution 0.50 Hz. ^{1}H NMR spectra: number of transients 64, acquisition time 3.0 s, the 90° pulse width 8 μs, the 45° pulse width 4 μs, spectral width 9000 Hz, number of points 54,016, digital resolution 0.167 Hz per point The ^{1}H and all 2D correlation spectra were recorded on a Bruker AVANCE 600 (600.31 MHz for ^{1}H and 150.052 MHz for ^{13}C) spectrometer, with a 5 mm triple – resonance inverse probe head (^{1}H/^{31}P/BB) with actively shielded *z* gradient coil (90° ^{1}H pulse width 90 μs, ^{13}C pulse width 13.3 μs). All 2D spectra were acquired and processed using standard Bruker software. Spectral width of 6313.13 and 25,000 Hz were used for ^{1}H and ^{13}C, respectively. Relaxation delays of 2.0 s were used for all 2D experiments and mixing time 0.8 s for ^{1}H–^{1}H NOESY spectrum was applied. All 2D spectra were collected with 2K points in F2 and 256 increments (F1) with 4 (g-COSY) and 64 (NOESY and g-HSQC) transients each and zero filling in F2 to 2048 × 1024 data matrix.

2.2. Substances

13α-Hydroxylupanine was extracted from seeds of *Lupinus angustifolius* according to the method described previously [6] and characterized like in Ref. [5].

2.2.1. 13α-Hydroxysparteine

0.100 g PtO_2 were suspended in 25 ml of 2 N HCl in a two-necked 100 ml round bottom flask equipped with a hydrogen supplying pipe dipped into the liquid, with another pipe used to carry away the air, replaced by a stopper after some minutes and a magnetic stirrer. Gas hydrogen was bubbled into the suspension. After 20 min, brown PtO_2 was converted into black Pt catalyst. 13α-Hydroxylupanine (0.800 g) suspended in 10 ml of 2 N HCl was added to the suspension of the catalyst and hydrogen was bubbled in. The progress of the reaction was controlled by TLC (silca gel, acetone–methanol–aqueous 25% NH_3 10:1:1 mixed immediately before use). The reduction was



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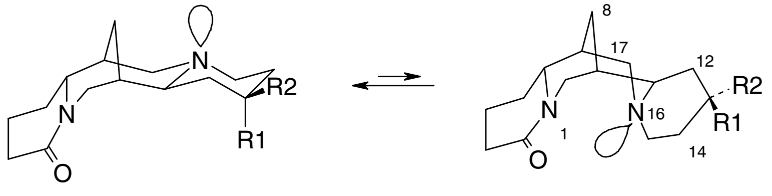
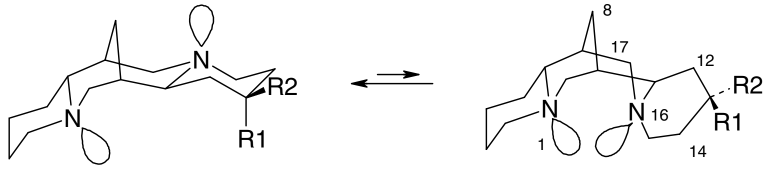


2 R_1 = H, R_2 = H

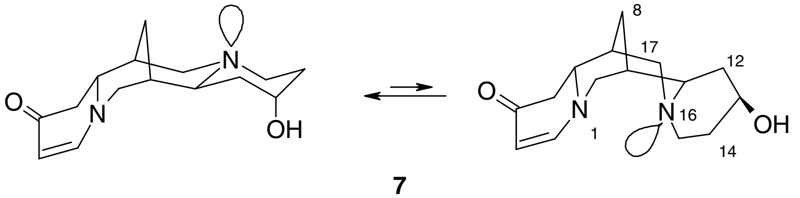
3 R_1 = OH, R_2 = H

4 R_1 = H, R_2 = OH



5 R_1 = OH, R_2 = H

6 R_1 = H, R_2 = OH



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