UDC 547.944/945

STRUCTURE AND CONFIGURATION OF THE ISOIMPERIALINES

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Khimiya Prirodnykh Soedinenii, Vol. 4, No. 5, pp. 335-336, 1968

It is known that the C-nor-D-homosteroid alkaloid imperialine contains a secondary and a tertiary hydroxyl and a carbonyl group. Chu and Loh, on heating imperialine in alcoholic alkali, obtained an isoimperialine [1] with mp 226°-228° C. The IR spectrum of this substance lacked the absorption band of a carbonyl group.

We have established that isoimperialine is a mixture of two epimeric bases giving two spots with R_f 0.39 and 0.44 in a thin layer of Al_2O_3 and $CaSO_4$ (9 : 1) in the ethyl acetate—chloroform—methanol (30 : 20 : 3) system. By separating isoimperialine by a preparative method on the adsorbents and with the system of solvents mentioned, we isolated substances with mp 205°-207° C, R_f 0.44, and mp 221°-223° C (R_f 0.39), which we have called β-isoimperialine and α-isoimperialine, respectively. The mixture of epimers melts at 226°-228° C.

The action of 10% sulfuric acid at 95° C on the isoimperialines forms imperialine. Consequently, imperialine exists in three tautomeric forms, depending on the medium.

A comparative study of the IR and NMR spectra of imperialine (I), α-isoimperialine (II), and β-isoimperialine (III) enables the structures and configurations of (II) and (III) to be demonstrated (table).

The similar values of the chemical shifts from the C-21 and C-27 methyl protons shows the structural and configurational identity of rings D, E, and F in substances (I), (II), and (III), and excludes the possibility of the participation of their tertiary hydroxy groups in the chemical transformations.

Chemical Shifts, τ

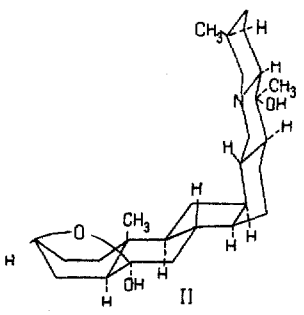
Substance	(S) 3H, C-19 CH_3	(S) 3H, C-21 CH_3	(D) 3H, C-27 CH_3
(I)	9.32	9.01	9.01
(II)	9.28	8.97	8.96
(III)	9.07	9.00	9.00

Note: S—singlet, D—doublet.

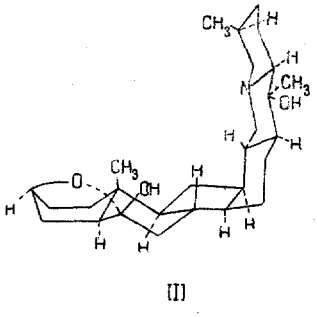
The dissimilar values of the chemical shifts from their C-19 methyl protons in these compounds can be explained by a difference in the structures and configurations of rings A and B in (I), (II), and (III). Consequently, in the structural transformations of imperialine, its secondary hydroxy group and carbonyl group form epimeric ketals.

In the NMR spectrum of α-isoimperialine, the signal from the protons of the C-19 methyl group are found in the strong field at 9.28 τ. From this value of the chemical shift in this compound, the ketal hydroxy group has has the α-orientation. The similar signal in the NMR spectrum of β-isoimperialine is observed in the weaker field at 9.07 τ and, correspondingly, in this compound the hydroxy group must have the β-orientation [2,3]. In the formation from imperialine of the epimeric ketals of the α- and β-isoimperialines, apparently, the "chair form" ring A of imperialine assumes the "boat" form.

Thus, α-isoimperialine has the structure and configuration (II) and β-isoimperialine, (III).



I



II

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12 May 1968

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