

## CONFIGURATION OF IMPERIALINE AND VERTICINE

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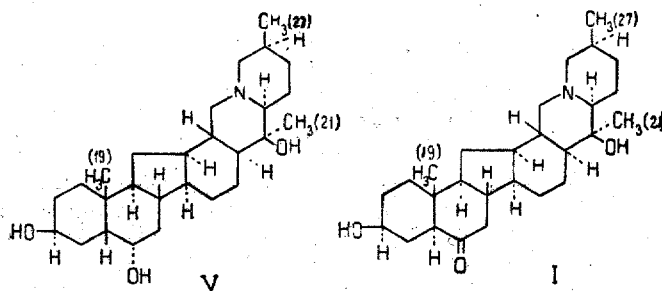
In determining the structure and the partial configuration of imperialine [1-3]\* and the configuration of verticinone [4], their structural identity was demonstrated. The properties of the same compounds differ markedly, which shows that their molecules have different configurations. A comparison of the NMR spectra of imperialine (I) and of acetyl-imperialine (II) with the corresponding NMR spectra of verticinone (III) and acetylverticinone (IV) makes it possible to elucidate the difference in the configurations of these substances.

Chemical Shifts ( $\tau$ )

Substance	Singlet, 3H, C-19 CH <sub>3</sub>	Singlet, 3H, C-21 CH <sub>3</sub>	Doublet, 3H, C-27 CH <sub>3</sub>
(I)	9.33	9.01	9.01
(II)	9.31	9.01	8.99
(III)	9.24	8.99	8.94
(IV)	9.24	9.01	8.97

The results given in the table show that, in the NMR spectra of imperialine and of acetyl-imperialine, the signals from the C-19 methyl protons are located in a stronger field than the signals from the conversion products of verticine. This convincingly shows that in imperialine the hydrogen atom at C<sub>5</sub> is in the  $\alpha$ -position. In the configuration of verticine shown by the Japanese workers Ito et al. [4], the hydrogen at C<sub>5</sub> also has the  $\alpha$ -orientation, this deduction being based on a comparison of the chemical shifts from the C-19 methyl protons of verticine and some of its conversion products with a 5 $\alpha$ -H steroid nucleus [5]. These authors did not take into account differences in the shifts in steroid compounds and in the C-nor-D-homosteroid alkaloids. The establishment of the trans-linked configuration of rings A and B of imperialine unambiguously shows that in verticine the hydrogen C<sub>5</sub> is located in the  $\beta$ -position. The configuration that we propose is confirmed by the absence of a shift in the signal from the 19-methyl group into the weak field when an acetyl group is introduced into verticine. This property is also characteristic for the 3 $\beta$ -OH-5 $\beta$ -H steroids [5]. In the NMR spectrum of imperialine and of acetyl-imperialine, the signals from the C-21 and C-27 methyl protons are, respectively, close to the values of the signals from verticinone and acetylverticinone. Consequently, the configuration of rings C, D, E, and F in imperialine and in verticinone are similar. The small shifts of the signals from the C-27 methyl group to the weak field are the result of the geometry of the molecule, i.e., the C-27 methyl group "sees" a smaller part of the molecule in the same group in imperialine.

Thus, verticine has the configuration (V) and imperialine (I).



On reconsideration of the values of the signals from the C-21 and C-27 methyl protons of korseveridinone and diacetyl-korseveridine [6], the configurations of rings D, E, and F of korseveridine have been corrected.

In korseveridine the configuration of rings D, E, and F is the same as in imperialine and the C-21 and C-27 methyl groups have the  $\alpha$ -orientation.

## REFERENCES

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\*The IR spectrum of imperialine has  $\nu_{\max}$  2780 cm<sup>-1</sup> (trans-quinolizidine); the spectrum was taken in chloroform on a UR-10 instrument.

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## STRUCTURE AND CONFIGURATION OF PETILININE

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From the methanolic mother liquor of the hydrochloride of petiline [1], after the usual treatment, we have isolated a new alkaloid petilinine with mp 277-278° C (from methanol),  $[\alpha]_D - 9.6^\circ$  [c 1.25; methanol-chloroform (1:1)] with the composition  $C_{27}H_{45}O_2N$ , mol. wt. 415 (mass spectrum). The hydrochloride has mp 296-297° C and the hydrobromide mp 281-283° C. IR spectrum of petilinine;  $\nu_{\max}$  3410, 3140, 1053 (OH), 2980-2860, 1455, 1435 ( $-\text{CH}_3$ ), 2785  $\text{cm}^{-1}$  (trans-quinolizidine). The base contains two secondary hydroxy groups, as is shown by the production of diacetylpetilinine (I) with mp 193-194° C ( $\nu_{\max}$  1730, 1250, 1025  $\text{cm}^{-1}$ ) and petilinedione (II) with mp 226-228° C ( $\nu_{\max}$  1710  $\text{cm}^{-1}$ ). The latter, on Huang-Minlon reduction, forms desdioxotetrahydropetilinedione (III) with mp 150-151° C. Petilinine is not oxidized by periodic acid.

Chemical Shifts ( $\tau$ )

Sub- stance	(S), 3H, C-19 $\text{CH}_3$	(D), 3H, C-21 $\text{CH}_3$	(D), 3H, C-27 $\text{CH}_3$	(S), 3H, 3 $\alpha$ - $\text{OCOCH}_3$	(S), 3H, 6 $\alpha$ - $\text{OCOCH}_3$	(M) $\beta\text{H}$ , at $\text{C}_3$	(M), $\beta\text{H}$ at $\text{C}_6$
(I)	9.24	9.23	9.23	8.05	8.02	4.97	5.42
(II)	9.13	9.21	9.21	—	—	—	—
(III)	9.34	9.22	9.22	—	—	—	—

Note: S—singlet, D—doublet, M—multiplet.

The NMR spectra of substances (I), (II), and (III) have signals from methyl protons (in each case two in the form of a doublet and one in the form of a singlet) and the mass spectrum of petilinine has characteristic peaks of the ions with m/e 97 (24%), 98 (10%), 111 (100%) and 112 (33%), 415 ( $\text{M}^+$ ) (32%) [2].

The information given shows that petilinine has the heterocyclic skeleton of imperialine [2]. It can be seen from the table that in petilinine rings A and B have a trans-linkage and the hydroxy groups are located at  $\text{C}_3$  and  $\text{C}_6$  [3]. The presence in the IR spectrum of petilinine of a band with  $\nu_{\max}$  1053  $\text{cm}^{-1}$  and the appearance after acetylation of one with  $\nu_{\max}$  1025  $\text{cm}^{-1}$  shows that one of the hydroxy groups in the substance is located at  $\text{C}_3$  and has the  $\alpha$ -orientation [4]. This position is confirmed by the fact that the NMR spectrum of (I) has a signal from a  $\beta\text{H}$ .

The difference in the chemical shifts from the C-19 methyl protons of (I) and (III) is characteristic for C-3 $\alpha$ - $\text{OCOCH}_3$  and C-6 $\alpha$ - $\text{OCOCH}_3$ . Consequently, the hydroxy group at  $\text{C}_6$  is in the  $\alpha$ -position. Rings A and B and the trans-quinolizidine part of the molecule in petilinine are connected in the same way as in the alkaloid cervine. The difference in the values of the signals from the C-21 and C-27 methyl protons in compounds (I), (II), and (III) shows the angular