

LEAD TETRAACETATE OXIDATION OF
PHENOLIC ISOQUINOLINE ALKALOIDS

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In order to introduce an oxygen functional group to the 4-position on 6- or 7-hydroxy-tetrahydroisoquinoline moiety in several isoquinoline alkaloids, lead tetraacetate oxidation in acetic acid was applied.

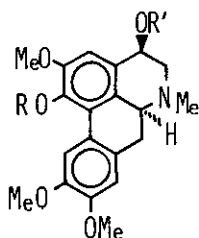
Oxidation of 1-hydroxy-aporphines and 1-hydroxy-homoaporphines gave directly and stereospecifically 4 β -acetoxy derivatives, an acetate (1) of which was transformed into ($\pm$)-cataline (2).

Similar oxidation of 1-hydroxy-homoproaporphine yielded a *p*-quinol acetate, which was treated with $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ giving 1,4 β -diacetoxy compound stereospecifically.

Similarly, 2- or 10-hydroxy-tetrahydroprotoberberine was oxidized to afford a *p*-quinol acetate, acid treatment of which gave the corresponding 2,5 β -diacetate stereospecifically or 10,13 α - and 10,13 β - (3) diacetates.

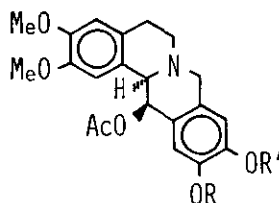
On the other hand, 3-hydroxy congener was oxidized to give 5 α - or 5 β -monoacetate, but in the case of 11-hydroxy congener a novel rearranged product (4) was obtained mainly, together with a minority of 13 β -acetoxy derivative (5).

Among others, the reaction leading to 13 β -acetoxy compounds (3 and 5) could be referred as biomimetic.



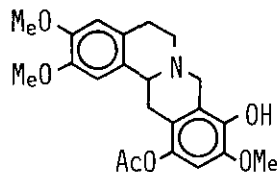
1 : R=H, R'=Ac

2 : R=Me, R'=H



3 : R=Me, R'=Ac

5 : R=H, R'=Me



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