LEAD TETRAACETATE OXIDATION OF PHENOLIC ISOQUINOLINE ALKALOIDS

Bunsuke Umezawa, Osamu Hoshino, Hiroshi Hara,
Masashi Ogawa, Machiko Hosaka, and Akira Tsunashima
Faculty of Pharmaceutical Sciences, Science University of Tokyo
Shinjuku-ku, Tokyo, 162, Japan

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.

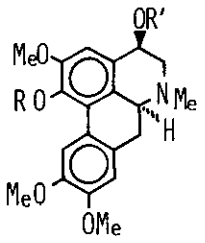
Oxidation of 1-hydroxy-aporphines and 1-hydroxy-homoaporphines gave directly and stereospecifically 4β-acetoxy derivatives, an acetate (1) of which was transformed into (±)-cataline (2).

Similar oxidation of 1-hydroxy-homoproaporphine yielded a *p*-quinol acetate, which was treated with Ac_2O-H_2SO_4 giving 1,4β-diacetoxy compound stereospecifically.

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

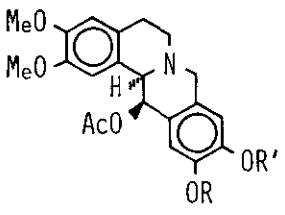
On the other hand, 3-hydroxy congener was oxidized to give 5α- or 5β-monoacetate, but in the case of 11-hydroxy congener a novel rearranged product (4) was obtained mainly, together with a minority of 13β-acetoxy derivative (5).

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



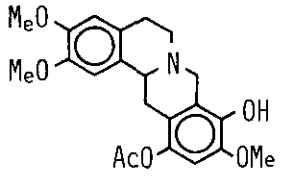
1 : R=H, R'=Ac

2 : R=Me, R'=H



3 : R=Me, R'=Ac

5 : R=H, R'=Me



4