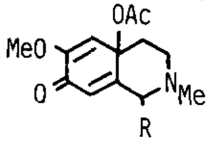
A SYNTHESIS OF MIXED TETRAHYDROISOQUINOLINE DIMERS via p-QUINOL ACETATE

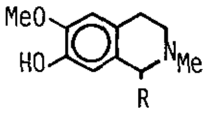
Hiroshi HARA, Masatoshi MURAKATA, Osamu HOSHINO,
and Bunsuke UMEZAWA
Faculty of Pharmaceutical Sciences, Science·University of Tokyo,
12, Funagawara-machi, Ichigaya, Shinjuku-ku, Tokyo, 162, JAPAN

A mixture of p-quinol acetate (1), obtained from corypalline (2) by lead tetraacetate oxidation, and isocorypalline (3)(1 eq.) was treated with trifluoroacetic acid in methylene chloride at room temperature for 1 hr to give mixed tetrahydroisoquinoline dimer (4) (54 %). Similarly, the reaction of 1 with 5 yielded a pair of diastereomers (6a and 6b), formation of which was attributable to the presence of axial dissymmetry and asymmetric carbon at 1'-position, and stereostructure of the former (6a) was determined by X-ray analysis. On the other hand, 6- or 7-hydroxytetrahydroisoquinoline (7 or 8) reacted with 1 to afford two regioisomers (9 and 10, or 11 and 12), respectively. However, the reaction of 1-phenyl p-quinol acetate (13) with 2 gave corypalline dimer (14) (17 %) and 1-phenyl corypalline (15). In this case such a bulky phenol as 2 could not attack on 8-position owing to the severe hindrance caused by the 1-phenyl group in 13. Therefore, 13 acted as an oxidant to change corypalline (2) into its dimer (14).

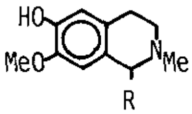
[Compound (9-12 and 14) were isolated as diacetates.]



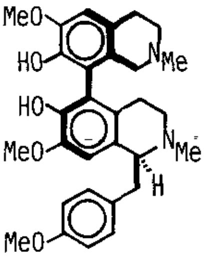
1: R=H
13: R=Ph



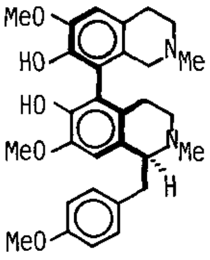
2: R=H
15: R=Ph



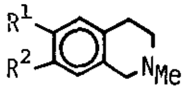
3: R=H
5: R=$CH_2C_6H_4OCH_3$-p



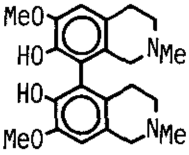
6a



6b



7 : R^1=OH, R^2=H
8 : R^1=H, R^2=OH



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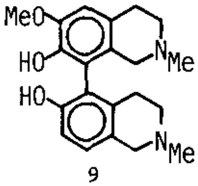

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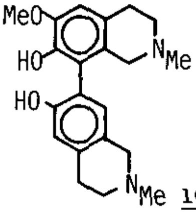

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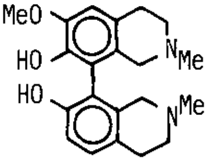

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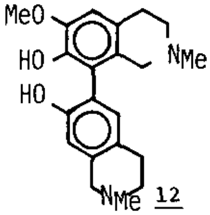

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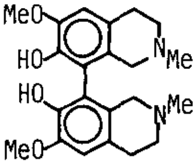

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