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BIOGENETIC-TYPE SYNTHESIS OF (±)-OXOMARITIDINE BY THE CATALYTIC OXIDATION WITH $[Fe(DMF)_3Cl_2][FeCl_4]$

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In the proceeding communication[1], a iron complex $[Fe(DMF)_3Cl_2][FeCl_4]$ prepared from ferric chloride and dimethyl formamide (DMF) is a usuful oxidizing agent for the intramolecular and intermolecular oxidative coupling reaction of phenols. The present report deals with the biogenetic-type synthesis of (±)-oxomaritidine (1a), a representative alakaloid of Amaryllidaceae, using the iron-DMF complex at the oxidative coupling step.

N-trifluoroacetyl derivative of O-methylnorbelladine (2), m.p. 74-75°, was prepared from the treatment of O-methylnorbelladine with trifluoroacetic anhydride in pyridine followed by aqueous work-up[2]. Oxidation of (2) with 10 mol equiv of the complex in two phase ether and water under refluxing with stirring for 12 hours gave rise, after silica gel chromatography[3], to the para-para coupled dienone (3) in yield 35 %: oily: ir (nujol) 5.92 and 6.01 μ: nmr ($CDCl_3$) (τ) olefinic proton at 6.35 (2H, d, J=9.5 Hz), 7.03 and 7.13 (each 1H, d, J=9.5 Hz), aromatic proton at 6.59 (1H, s), 6.85 and 6.96 (each 0.5 H, s). Alkaline hydrolysis by potassium carbonate in aqueous ethanol resulted in spontaneous hydrolysis and cyclization to give the phenolic enone (1b) in 95 % yield: m.p. 250-252° dec: ir (nujol) 5.98 μ: nmr (DMSO-d_6) (τ) olefinic proton at 5.98 (1H, d, J=10 Hz) and 8.05 (1H, d, J=10 Hz), aromatic proton at 6.49 and 7.10 (each 1H, s). The ir and nmr spectra of (1b) were superimposable upon that of an authentic sample, kindly donated by Professor M. A. Schwartz.

Thus, we accomplished the biogenetic-type synthesis of (±)-oxomaritidine, since (1b) to (±)-oxomaritidine (1a) is readily able to transform by methylation with phenyltrimethylammonium hydroxide[2].

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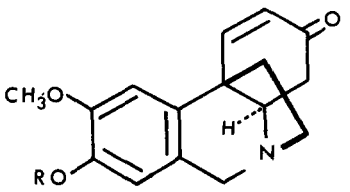
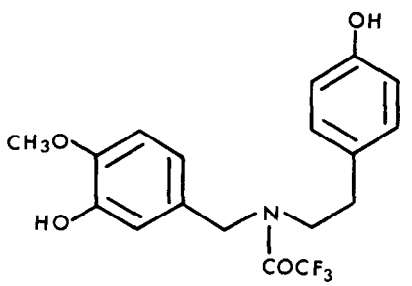
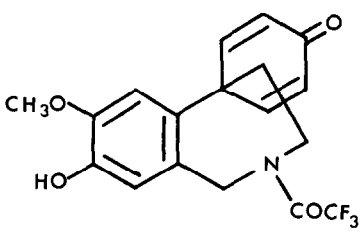


(1a) R=CH_3

(1b) R=H



(2)



(3)

References

1. S. Tobinaga and E. Kotani, J. Amer. Chem. Soc., 1972, 94, 309.
2. M. A. Schwartz and R. A. Holton, J. Amer. Chem. Soc., 1970, 92, 1090.
3. The remaining substance except the dienone (3) consisted with mainly starting material.