SYNTHESIS OF DUTADRUPINE

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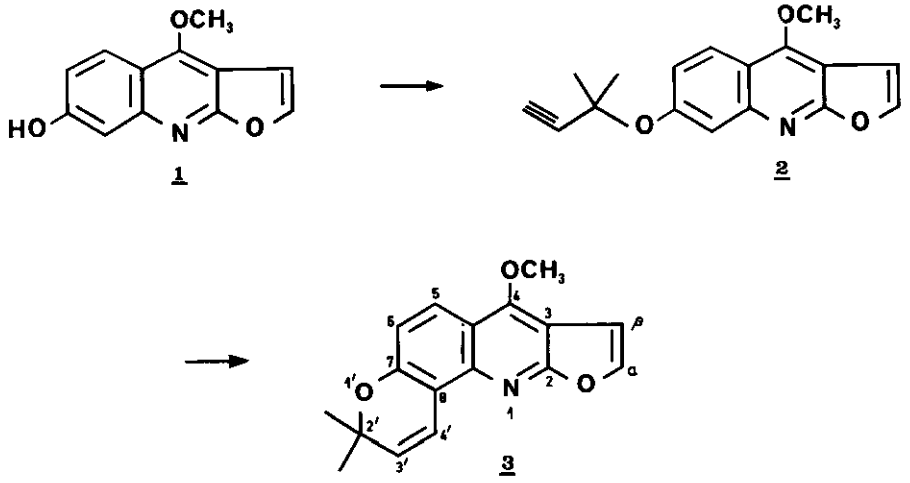
Abstract --- Dutadrupine (3) was synthetized by Claisen rearrangement of 7-(1,1-dimethylpropyn-1-oxy)-4-methoxyfuro[2,3b]quinoline (2) obtained by condensation of 7-hydroxy-4-methoxyfuro[2,3b]quinoline (1) with 3-chloro-3-methylbutyne.

In a previous paper[1], we reported the isolation from Dutaillyea drupacea (Rutaceae) and the structure determination of a novel alkaloid, dutadrupine (3). As a further contribution to the chemistry of new caledonian plants, we report here a simple synthesis of this compound by condensation of 7-hydroxy-4-methoxyfuro[2,3b]-quinoline (1)[2] with 3-chloro-3-methylbutyne[3,4] followed by Claisen rearrangement of the obtained propargyl ether (2)[5-10].



To a solution of 7-hydroxy-4-methoxyfuro[2,3b]quinoline (1)(0.86 g) in dry acetone (25 ml) containing potassium carbonate (2 g) and potassium iodide (2 g) was added 3-chloro-3-methylbutyne (5 g). The reaction mixture was refluxed for 72 h and then evaporated. The solid residue was extracted with chloroform. Concentration of the chloroform solution gave a gum, the tlc analysis of which showed two major products, easily isolated by column chromatography (silica gel, eluent : benzene - ethyl acetate 9 : 1). The first one was the expected propargyl ether (2) (0.39 g, yield : 35 %). The second was identified to dutadrupine (3)(0.31 g, yield : 28%), identical with the natural product, the Claisen rearrangement having surprisingly occurred at relatively low temperature.

7-(1,1-dimethylpropyn-1-oxy)-4-methoxyfuro[2, 3b]quinoline (2) : mp 144-145°C ; UV (EtOH) : 247, 308, 320, 332(sh)nm ; IR (KBr) : 3240, 2995, 2950, 1625, 1590, 1460, 1380, 1295, 1150, 1090, 980, 865, 755, 725 cm^{-1} ; MS m/z (%) : 281 (M^+)(18), 280(6), 266(39), 251(9), 215(100), 200(20), 172(10) ; ^{1}H-NMR ($CDCl_3$) : δ = 8.03 (1H, d, J = 9Hz, H-5), 7.62 (1H, d, J = 2.5Hz, H-α), 7.42 (1H, d, J = 2.5Hz, H-8), 7.10 (1H, dd, J = 9Hz, J'= 2.5Hz, H-6), 6.92 (1H, d, J = 2.5Hz, H-β), 4.35 (3H, s, O-Me), 2.57 (1H, s, -C≡C-H), 1.72 (6H, s, CMe_2).

Dutadrupine (3) : mp 139-140°C[11] ; UV (EtOH) : 249(sh), 257, 279(sh), 293(sh), 315, 331, 350, 359 nm ; IR (KBr) : 2980, 2870, 1635, 1595, 1375, 1280, 1130, 1100, 990, 825, 780, 750 cm^{-1} ; MS m/z (%) : 281 (M^+)(20), 267(18), 266(100), 251(28) ; ^{1}H-NMR ($CDCl_3$) : δ = 8.00 (1H, d, J = 9Hz, H-5), 7.51 (1H, d, J = 3Hz, H-α), 7.44 (1H, d, J = 10Hz, H-4'), 6.98 (1H, d, J = 3Hz, H-β), 6.93 (1H, d, J = 9Hz, H-6), 5.67 (1H, d, J = 10Hz, H-3'), 4.40 (3H, s, O-Me), 1.51 (6H, s, CMe_2).

References and Notes

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2. For synthesis and/or natural sources of this compound, see :
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