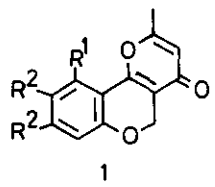
# REGIOSELECTIVE SYNTHESES OF 2-METHYL-4H,5H-PYRANO[3,2-c][1]-BENZOPYRAN-4-ONE AND 4,10-DIHYDRO-3-HYDROXY-3-METHYL-1H,3H-PYRANO[4,3-b][1]BENZOPYRAN-10-ONE

Masashige YAMAUCHI, Sadamu KATAYAMA, Yoshihiko NAKASHITA, and Toshio WATANABE

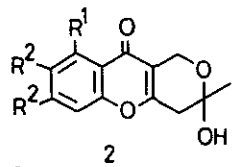
Faculty of Pharmaceutical Sciences, Josai University, Keyakidai, Sakado, Saitama 350-02

Regioselective synthesis of titled compounds will be described. The acetal (3) was treated with HCl in methanol to afford the pyrone (4) which was converted into 2-methyl-5H-pyrano[3,2-c][1]benzopyran-4-one (1b), the basic skeleton in citromycetin (1a), by hydrogenolysis followed by treatment with aq. $NaHCO_3$.[1)]

On the other hand treatment of 3 with HCl in tetrahydrofuran gave the another pyrone (5) which gave the boron complex (6a) on treatment with boron trifluoride-diethyl ether in dichloromethane. Debenzylation of the boron complex (6a) with Fujita's method[2)] gave the phenol (6b) which was converted into the pyranobenzopyrane (7) by HCl-acetic acid. Hydration of 7 with 5% HCl-acetone (1:1) afforded 4,10-dihydro-3-hydroxy-3-methyl-1H,3H-pyrano[4,3-b][1]benzopyran-10-one (2b), the basic skeleton in fulvic acid (2a).[3)]

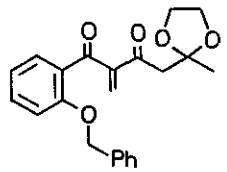


1

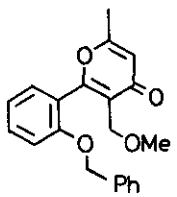


2

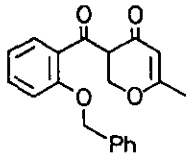
a; $R^1$=COOH, $R^2$=OH
b; $R^1$=$R^2$=H



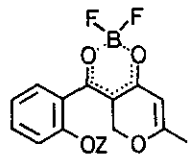
3



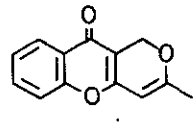
4



5



6
a; Z = $CH_2$Ph
b; Z = H



7

1) T. Watanabe, S. Katayama, Y. Nakashita, and M. Yamauchi, J. Chem. Soc. Chem. Commun., 1981, 761.

2) K. Fuji, T. Kawabata, and E. Fujita, Chem. Pharm. Bull., 1980, 28, 3662.

3) M. Yamauchi, S. Katayama, Y. Nakashita, and T. Watanabe, J. Chem. Soc. Chem. Commun., 1983, in press.