

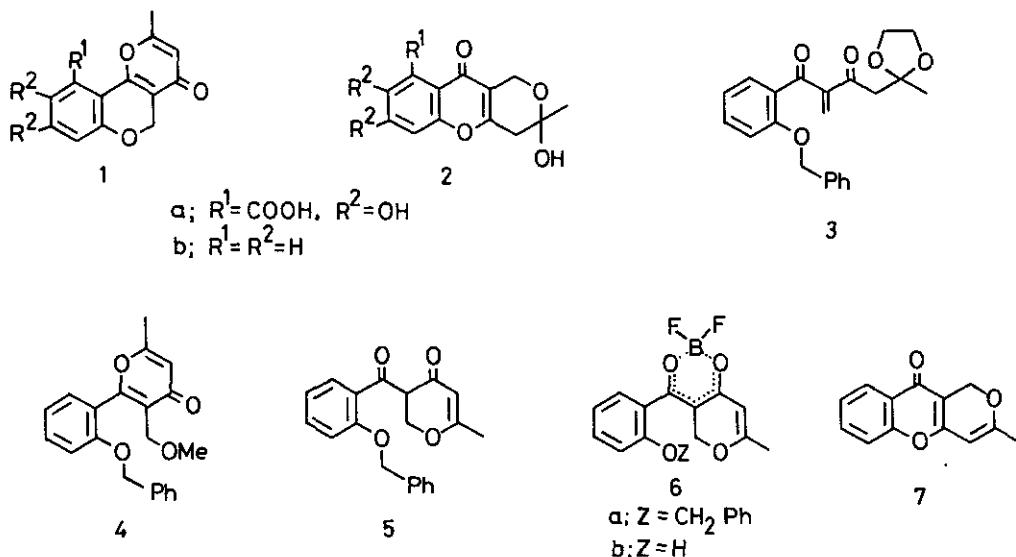
REGIOSELECTIVE SYNTHESIS OF 2-METHYL-4H,5H-PYRANO[3,2-c][1]-
BENZOPYRAN-4-ONE AND 4,10-DIHYDRO-3-HYDROXY-3-METHYL-1H,3H-
PYRANO[4,3-b][1]BENZOPYRAN-10-ONE

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 citromyctin (1a), by hydrogenolysis followed by treatment with aq. NaHCO₃.¹⁾

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 method²⁾ gave the phenol (6b) which was converted into the pyranobenzo-pyrane (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) 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.