SYNTHESIS OF NEW METHINE CLASS OF DYES BEARING MALEIMIDE RING SYSTEM

Yoshinori Tominaga,[a]* Kaori Komiya,[a] Sachiko Itonaga,[a] Noriko Yoshioka,[a] Seigo Kataoka,[a] Kenji Sasaki,[b] and Takashi Hirota[b]

[a]Faculty of Pharmaceutical Sciences, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852, Japan, [b]Faculty of Pharmaceutical Sciences, Okayama University, Tsushima, 1-1-1, Okayama 700, Japan

Abstract······Reaction of 1-methyl-3-methylthiomaleimides (**1a-c**) with *N,N*-dialkylanilines (**2**) under refluxing in acetic acid condition gave the corresponding 3-(4-diakylamino)phenyl-1-methylmaleimides (**3a-g**). Treatment of these 1-methyl-3-phenylmaleimides (**3a, c**) with Lawesson's reagent under refluxing in toluene afforded new blue dyes, 4-(4-dialkylamino)phenyl-3-cyano-1-methyl-5-oxopyrrole-2-thiones (**5a, b**) which are brilliant blue dyes appearing at 606 and 615 nm (log ε: 4.59 and 4.50) in UV spectra. Reaction of 4-methoxycarbonyl-1-methyl-3-methylthiomaleimide (**1b**) with 3-dialkylamino-phenol under the same reaction conditions gave cyclized products, 2*H*, 4*H*-[1]-benzopyrano[3,4-*c*]pyrrole-1,3,4-triones (**6a-c**) in good yields.

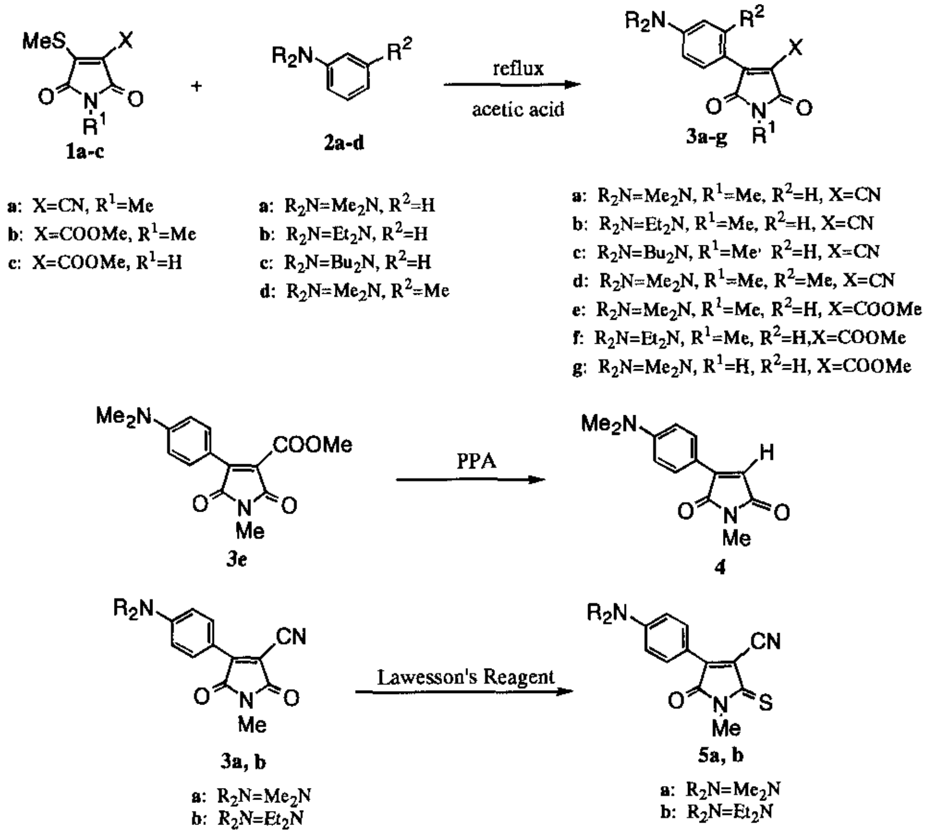
4-Cyano-1-methyl-3-methylthiomaleimide (**1a**) and 3-methylthio-4-methoxycarbonylmaleimides (**1b, c**) were previously shown to undergo displacement reactions with 2-amino heterocyclic compounds followed by nucleophilic cyclization of amino maleimides to give polycyclic pyrrolopyrazolopyridines and pyrrolopyrimidines.[1,2] These polycyclic pyrroloheterocycles have been used for the synthesis of various chemiluminescence compounds such as 4-hydroxypyrazolo[4',3':5,6]pyrido[2,3-*d*]pyridazine-5,8(*6H,7H*)-diones[2] and 12-aminopyridazino[4',5':4,5]pyrimido[1,2-*a*]benzimidazole-1,3(2*H*)-dione.[1]
This paper presents the synthesis of 3-(4-dialkylamino)phenylmaleimides and 7-dialkylamino-2*H*, 4*H*-[1]benzopyrano[3,4-*c*]pyrrole-1,3,4-triones as dyes for polyester fibers such as polymethine dyes through use of the above maleimides. The methine or arylidine class of dyes has found widespread use for the coloration of acetate and polyester textiles. Only one brilliant dispase polymethine blue dye is commercially available, but has certain disadvantages, such as limited chemical stability and is below average light fastness.[3,4]

The aryl group is generally introduced into aromatic or heteroaromatic compounds by displacement reactions of Grignard or lithium reagent with ketene dithioacetals.[5,6] Maleimides (**1a** and **b**) were found to be very high active electrophilic reagents from previous results.[1,2] Compound **1a** reacted with *N,N*-dimethylaniline (**2a**) under refluxing in acetic acid for 9 h to give dark violet needles, **3a**[7], mp 222-226°C in 86% yield. The color of a DMSO solution of **3a** is very brilliant violet. The UV spectrum of

3a appeared at 543 nm(log ε 4.85). Reaction of **1a** with other *N,N*-dialkylanilines (**2b-d**) under the same reaction conditions gave the corresponding 3-(4-dialkylamino)phneylmaleimides (**3b-d**) in moderate yields. Similarly, methyl ester (**3e**) was also readily obtained by reaction of **1b** with **2a** in 64% yield. This compound was treated with PPA to give demethoxycarbonylated compound (**4**)[8] as yellow needles, mp 218-220°C. The absorption of **4** in UV spectrum appeared at 459 nm (log ε 4.24). Compounds (**3e-g**) were synthesized by reactions of **1b** and **c** with *N,N*-dialkylanilines under similar reaction conditions.

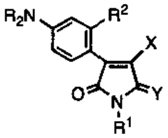
Thioimidization reactions of maleimides (**3a** and **b**) with Lawesson's reagent under refluxing in toluene gave thioamides (**5a**[9] and **b**) as the only products, possibly owing to steric effects, in moderate yields, respectively. Interestingly, the absorptions of these thioimides (**5a, b**) showed bathochromic shift of 63 nm. Essentially the same was observed on converting the corresponding carbonyl group to dicyanomethylene group.[10]

7-Dimethylaminocoumarin is an important laser dye.[11,12] In this study, pyrrolocoumarin dyes were obtained using 3-(4-dialkylamino)phenylmaleimide derivatives synthesized above. Reaction of 3-dimethylaminophenol (**2e**) with **1b** under refluxing in acetic acid gave the desired product, 7-dimethyl-



Scheme 1

Table . 1 Yields, UV and IR Spectra of 3-(4-Dialkylamino)phenylmaleimides (3a-g, 4, and 5a, b)

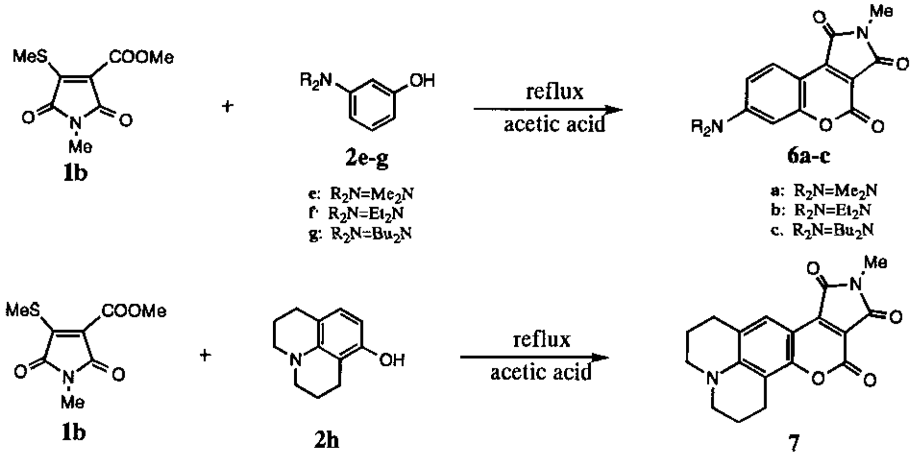


No.	NR_2	R^1	R^2	X	Y	Yield(%)	mp(℃)	UV λ max EtOH (log ε)	IRν max cm^{-1}(C=O)
3a	NMe_2	Me	H	CN	O	87	222-226	543 (4.85)*	1685
b	NEt_2	Me	H	CN	O	53	184-187	544 (4.51)	1710
c	NMe_2	Me	Me	CN	O	38	206-210	534 (4.24)	1702
d	NBu_2	Me	H	CN	O	35	121-124	547 (4.35)	1705
e	NMe_2	Me	H	COOMe	O	64	87-91	495 (3.65)	1705
f	NEt_2	Me	H	COOMe	O	36	caramel oil	508 (4.24)	1720, 1705, 1690
g	NMe_2	H	H	COOMe	O	14	180-183	478 (4.08)	1720, 1710
4	NMe_2	Me	H	H	O	13	218-220	459 (4.24)	1685
5a	NMe_2	Me	H	CN	S	72	231-235	606 (4.59)	1710
b	NEt_2	Me	H	CN	S	50	189-190	615 (4.50)	1715

*solvent(DMSO)

amino-2-methyl-2*H*,4*H*-[1]benzopyrano[3,4-*c*]pyrrole-1,3,4-trione (**6a**)[13] in 86% yield. This compound also had the form violet needles, mp 326-329 ℃[UV λ max 517 nm (log ε 4.41)]. Diethylamino and dibutylamino compounds (**6b, c**) were readily derived from **1b** and dialkylaminophenols (**2f, g**) in a manner similar to that for the preparation of **6a**. Reaction of **1b** with 8-hydroxyjulolidine (**2h**) occurred under similar reaction conditions to give 1,2,5,6,7-pentahydro-10-methyl-3*H*,10*H*,12*H*-pyrrolo-[3',4':3,4][1]benzopyrano[6,7,8-*ij*]quinolizine-9,11,12-trione (7)[14] in 96% yield and for which a slight bathochromic shift was observed.

1-Methyl-3-methylthiomaleimides (**1a-c**) were found in this study to be usefull for obtaining new methine dyes,[4] 3-(4-dialkylamino)phenylmaleimides and 7-dialkylamino[1]benzopyrano[3,4-*c*]pyrrole derivatives.



Scheme 2

Table . 2 Yields, UV and IR Spectra of 7-Dialkylamino-2*H*,4*H*-[1]benzopyrano[3,4-*c*]pyrrole-1,3,4-triones (6a-c and 7)

No.	NR_2	Yield(%)	mp(℃)	UV λ_{max}^{EtOH} (log ε)	IRν max cm^{-1}(C=O)
6a	NMe_2	86	326-329	517 (4.41)	1720, 1700, 1630
b	NEt_2	91	258-261	525 (4.47)	1720, 1700, 1600
c	NBu_2	97	213-216	526 (4.40)	1730, 1695, 1600
7	-----	96	316-319	552 (4.41)	1722, 1695, 1600

REFERENCES AND NOTES

1. Y. Tominaga, N. Yoshioka, and S. Kataoka, *Heterocycles*, 1996, 43, 1597.
2. Y. Tominaga, N. Yoshioka, H. Minematsu, and S. Kataoka, *Heterocycles*, 1997, 44, 85.
3. R. Egli, 'Colour Chemistry: The Chemistry of Blue Disperse Dyes, Past and Present,' ed. by A. T. Peters and H. S. Freeman, Elsvier applied Science, New York, 1991, Chap. 1, pp 1-27.
4. L. Shuttleworth and M. A. Weaver, 'The Chemistry and Application of Dyes: Dyes for Polyester Fibers,' ed. by D. R. Waring and G. Hallas, Plenum Press, New York, 1991, Chap. 4, pp 107-163.
5. a) Y. Tominaga, *Trend in Heterocyclic Chemistry*, 1991, 2, 43; *b*) R. K. Dieter, *Tetrahedron*, *1986*, 42, 3029.
6. a) G. Kobayashi, S. Furukawa, Y. Matsuda, and Y. Washida, *Yakugaku Zasshi*, 1967, **87**, 857; *b*) S. Fukuda, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Heterocycles*, 1983, 20, 1793.
7. 3a: ^{1}H-NMR($CDCl_3$) δ: 3.10(3H, s, N-Me), 3.17(6H, s, NMe_2), 6.75(2H, d, *J*=9.4 Hz, 3',5'-H), 8.50(2H, d, *J*=9.4 Hz, 2',6'-H). MS *m/z* 256(M^++1, 16), 255(M^+, 100), 254(M^+-1, 72), 85(16), 32(20).
8. 4: ^{1}H-NMR($CDCl_3$) δ: 3.05(3H, s, N-Me), 3.06(6H, s, NMe_2), 6.44(1H, s, =CH), 6.70(2H, d, *J*=9.2 Hz, 3',5'-H), 8.50(2H, d, *J*=9.2 Hz, 2',6'-H). MS *m/z* 230(M^+, 100), 229(M^+-1, 72), 145(16), 144(15).
9. 5a: ^{1}H-NMR($CDCl_3$) δ: 3.17(6H, s, NMe_2), 3.37(3H, s, N-Me), 6.78(2H, d, *J*=9.2 Hz, 3',5'-H), 8.49(2H, d, *J*=9.2 Hz, 2',6'-H). MS *m/z* 272(M^++1, 16), 271(M^+, 100), 270(M^+-1, 72), 242(6), 91(15).
10. Y. Matsuda, K. Katou, H. Matsumoto, S. Ide, K. Takahashi, K. Torisu, K. Furuno, and S. Maeda, *Yakugaku Zasshi*, 1992, 42, 112, and references cited therein.
11. a) K. H. Drexhage, 'Topics in Applied Physics: Dye Lasers,' Vol. 1, ed. by F. P. Schaffer, Springer-Verlag, Berlin, 1973, Chap. 4, pp 144-193; *b*) 7-Dimethylamino-1-methylcoumarin is commercially available as a suitable laser dye (Aldlich Catalog 1996-1997).
12. N. F. Haley, *J. Heterocycl. Chem.*, 1977, 14, 683 .
13. 6a: ^{1}H-NMR($CDCl_3$+CF_3COOH) δ: 3.15(3H, s, N-Me), 3.15(3H, s, N-Me), 3.27(3H, s, N-Me), 6.60(1H, br s, aromatic-H), 6.91(1H, br s, aromatic-H), 8.27(1H, m, 9-H).
14 7: ^{1}H-NMR($CDCl_3$) δ: 2.00(4H, m, -CH_2-), 2.81(2H, t, *J*=6.2 Hz, CH_2-C=), 2.86(2H, t, *J*=6.5 Hz, CH_2-C=), 3.12(3H, s, N-Me), 3.42(4H, m, N-CH_2-), 7.84(1H, s, 8-H). MS *m/z* 325(M^++1, 21), 324(M^+, 100), 323(M^+-1, 41), 295(4), 162(4), 119(3), 44(6).

Received, 3rd February, 1997