after the completion of reaction. ESCA measurements show oxygen and carbon signals due to molybdenum oxides and molybdenum carbides.
7. Sobota, P.; Pluzinski, T.; Jezowska-Trzebiatowska, B.; Rummel, S. *J. Organomet. Chem.* **1980**, *185*, 69.
8. Dobson, J. E.; Remick, R. J.; Wilburn, B. E.; Skell, P. S. *Inorg. Synth.* **1980**, *19*, 80.

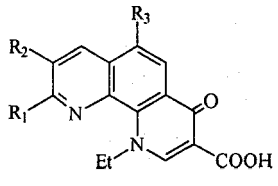
Quinolone(III) : Synthesis of Pyrido[2,3-h]quinolone and Pyrido[2,3-g]quinolone-3-carboxylic Acid Derivatives as Potential Antibacterials

Jae Keun Lee* and Sha Joung Chang

Department of Chemistry, College of Natural Sciences, Kyungpook National University, Taegu 702-701, Korea

Received October 11, 1995

In earlier paper,[1] we reported the synthesis of 1-ethyl-6-fluoro-4-oxo-pyrido[3,2-h]quinoline-3-carboxylic acid (**1**), 1-ethyl-9-(4-methylpiperazin-1-yl)-4-oxo-pyrido[3,2-h]quinoline-3-carboxylic acid (**2**) and 1-ethyl-8-fluoro-9-(4-methylpiperazin-1-yl)-4-oxo-pyrido[3,2-h]quinoline-3-carboxylic acid (**3**) as potential antibacterial compounds.

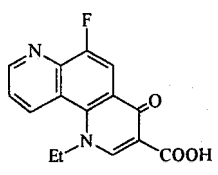


1 R_1=R_2=H, R_3=F

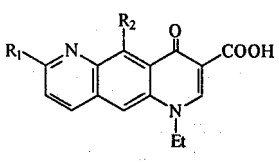
2 R_1=4-methyl-1-piperazinyl R_2=R_3=H

3 R_1=4-methyl-1-piperazinyl R_2=F, R_3=H

These potent antibacterial compounds belong to 4-quinolones, an important new class of synthetic antibacterial agents.[2~4] Among the above three compounds, **1** was found to be the most active. Considering the structure activity relationship of quinolone antibacterials,[2~4] 4-oxo-3-carboxyl group are essential.



4

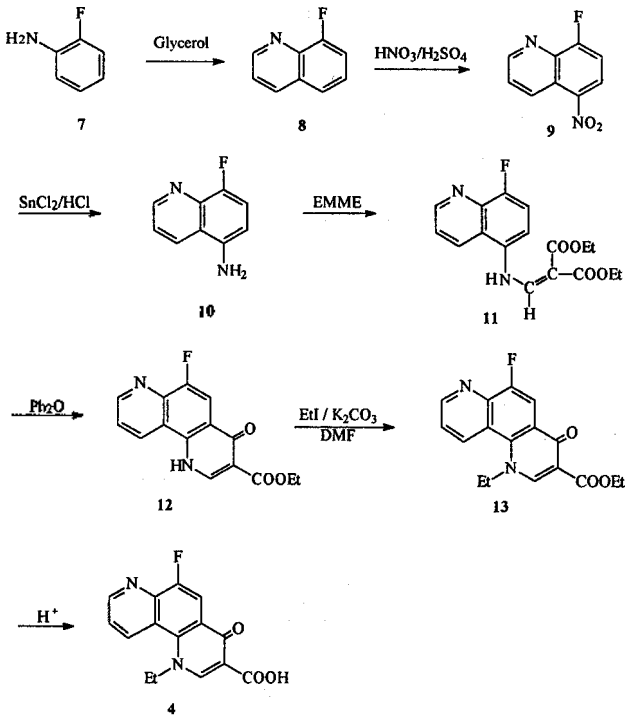


5 R_1=CH_3, R_2=H

6 R_1=H, R_2=F

The substituents on N_1 are mostly to be small alkyl groups, e.g, ethyl or cyclopropyl. Besides 6-fluoro and 7-*t*-amine are known to be the magic groups.

Comparing the structural similarity of **1** to norfloxacin, it is understandable that 6-fluoro is the main reason to make it the most active. This result prompted us to synthesize



Scheme 1.

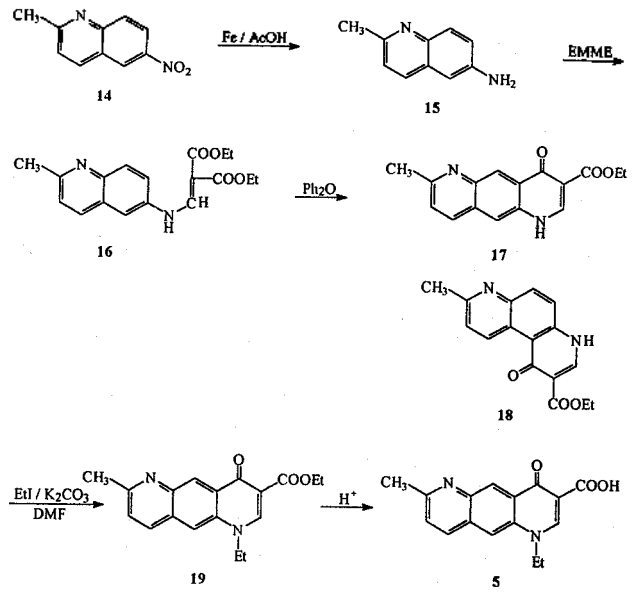
compound **4**, which has 7-*t*-amine and 6-fluoro.

Considering the proposed stacking model, the tetramer of quinolone, for the interaction of quinolone and DNA gyrase,[4] substituted 1-ethyl-4-oxo-pyrido[2,3-g]quinoline-3-carboxylic acids (**5** and **6**), which are the linear form of quinolones, are expected to form the better stacking tetramer than the previous bent quinolones (**1**, **2** and **3**). Thus we tried also to synthesize **5** and **6**, and tested their activities.

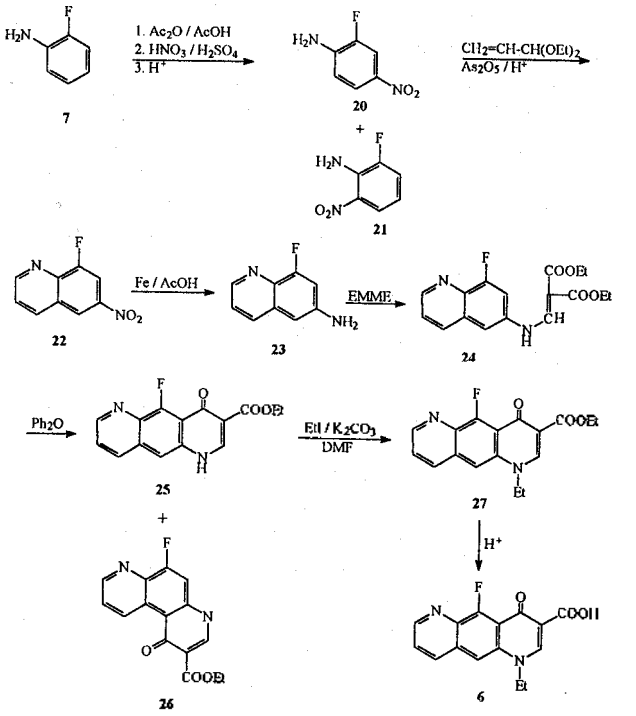
Skraup reaction with 2-fluoroaniline (**7**), glycerol and sodium m-nitrobenzenesulfonate as oxidizing agent gave high yield of 8-fluoroquinoline (**8**).[5] 8-Fluoroquinoline (**8**) was nitrated with HNO_3/H_2SO_4 to 8-fluoro-5-nitroquinoline (**9**).[6] 8-Fluoro-5-nitroquinoline (**9**) was easily reduced to 5-amino-8-fluoroquinoline (**10**) with $SnCl_2$/HCl.[7] The synthesis of 1-ethyl-6-fluoro-4-oxo-pyrido[2,3-h]quinoline-3-carboxylic acid (**4**) was achieved by reaction of 5-amino-8-fluoroquinoline (**10**) with diethyl ethoxymethylenemalonate (EMME), followed by thermal cyclization, N-ethylation and successive hydrolysis of the obtained ester **13** in mild acidic condition (Scheme 1).[8~14]

Strangely enough, we could not get the carboxylic acid **4**, through the hydrolysis in basic condition. When the last step, the hydrolysis of ethyl ester **13** to carboxylic acid **4** was carried out in basic condition, the N_1-ethyl group was also disappeared together with COO-CH_2CH_3.

2-Methyl-6-nitroquinoline (**14**) was reduced to 6-amino-2-methylquinoline (**15**) with H-reduced Fe/AcOH.[15] The next steps of EMME cyclization, N-ethylation and hydrolysis were carried out by the well known methods (Scheme 2). Thermal cyclization of the malonate **16** was carried out in diphenyl ether to give the mixture of ethyl 7-methyl-4-oxo-pyrido[2,3-g]quinoline-3-carboxylate (**17**) and ethyl 7-methyl-4-oxo-pyrido[3,2-f]quinoline-3-carboxylate (**18**), which was successfully separated by recrystallization. Ethylation of **17** and hy-



Scheme 2.



Scheme 3.

drolysis of **19** gave the desired product **5** in good yield.

Finally, the reaction of 2-fluoroaniline (**7**) with acetic anhydride to give 2-fluoroacetanilide, nitration of the acetanilide with HNO_3/H_2SO_4 and hydrolysis produced the mixture of two isomers, 2-fluoro-4-nitroaniline (**20**) and 2-fluoro-6-nitroaniline (**21**).[16~17] 2-Fluoro-4-nitroaniline (**20**) was separated from the mixture by silica gel column chromatography. 2-Fluoro-4-nitroaniline (**20**) was cyclized with acrolein diethylacetal by using arsenic pentoxide as oxidizing agent into 8-fluoro-6-nitroquinoline (**22**).[18] The reduction of nitro group to amino group, thermal cyclization with EMME, N-ethylation and hydrolysis were performed as the well established method. Thermal cyclization of the malonate **24** gave the mixture of ethyl 5-fluoro-4-oxo-pyrido[2,3-g]quinoline-3-carboxylate (**25**) and ethyl 9-fluoro-4-oxo-pyrido[3,2-f]quinoline-3-carboxylate (**26**), which was separated by recrystallization (Scheme 3).

Table 1. MICs (mg/mL) of Pyrido[2,3-g]quinolonecarboxylic acid Derivatives

Strains	Control. (NAL)	Control. (CIP)	Comp. 5	Comp. 6
Gram *Bacillus subtilis* (6633)	16	<0.25	256	16
(+) *Staphylococcus aureus* (6538P)	128	<0.25	256	16
Gram *Salmonella typhimurium* (14028)	16	<0.25	>256	>256
(−) *Proteus mirabilis* (25933)	8	<0.25	>256	128
Escherichia coli (25922)	8	<0.25	>256	256
Pseudomonas aeruginosa (25619)	32	<0.25	>256	>256

The solubility of compound **4** in any solvents except TFAA was so low that MIC test could not be done.

The activities of compound **5** and **6** were shown in Table 1 together with nalidixic acid and ciprofloxacin.[19~20] They were not good enough to further investigation.

Experimental

Melting points were determined on a Electrothermal melting point apparatus and uncorrected. NMR spectra were recorded on a Varian EM-360 and Bruker AM-300 spectrometer. Chemical shifts are expressed in ppm downfield from internal TMS. Significant ^1H NMR data are tabulated in the order of multiplicity, coupling constant, the number of protons and designation. Mass spectra were recorded on a GC/MS-QP 1000A spectrometer.

8-Fluoro-5-nitroquinoline (9). 8-Fluoroquinoline (**8**) (5.0 g, 34 mmol) was added gradually to a mixture of fuming nitric acid (50 mL) and sulfuric acid (10 mL) at 0 ℃. The solution became hot and was heated on steam-bath for five hours. It was poured into water, and the mixture was made alkaline with sodium hydroxide solution. The precipitate was collected and washed with water. The product was purified by silica gel column chromatography with ethyl acetate and pet. ether (1 : 2) as an eluent. (4.37 g, 67% yield, mp 131-132 ℃); ^1H NMR ($CDCl_3$) δ 9.2-7.5 (m, 5H, Ar-H); MS: m/e (relative intensity) 192 (M^+, 100), 162 (32), 146 (53), 127 (32).

5-Amino-8-fluoroquinoline (10). 8-Fluoro-5-nitroquinoline (**9**) (2.0 g, 10.4 mmol) was added gradually to a well-stirred solution of stannous chloride dihydrate (9.6 g) in 18 ml of conc-hydrochloric acid cooled to below 10 ℃ in an ice-bath. After the addition was completed, the solution was heated on a water bath for three hours. It was poured into water (25 mL), and the orange red solution was made strongly alkaline by careful addition of concentrated sodium hydroxide solution while cooling. The tin salt was precipitated first, then redissolved in the excess alkali addition. After a couple of minutes later 5-amino-8-fluoroquinoline (**10**) was

precipitated, collected on a filter and washed with water. The product was purified by silica gel column chromatography using ethyl acetate and pet. ether (1 : 2) as an eluent. (1.40 g, 83% yield, mp 111-113 ℃); ^{1}H NMR ($CDCl_3$) δ 8.9-6.7 (m, 5H, Ar-H), 3.4 (broad, 2H, NH_2); MS: m/e (relative intensity) 162 (M^+, 100), 135 (28).

Diethyl N-(8-fluoro-5-quinolinyl)aminoethylenemalonate (11). A mixture of 8-amino-5-fluoroquinoline (**10**) (1.2 g, 7.4 mmol) and diethyl ethoxymethylenemalonate (EMME) (1.6 ml, 7.4 mmol) was heated at 100 ℃ for three hours, while stirring, to yield yellow solid. This product was recrystallized from ethanol to give 2.06 g (6.2 mmol) of pure product **11**. (84% yield, mp 110-112 ℃); ^{1}H NMR ($CDCl_3$) δ 11.7 (d, J=12.8 Hz, 1H, NH), 9.1-7.3 (m, 5H, Ar-H), 8.6 (d, J=12.8 Hz, 1H, N-CH), 4.4-4.2 (m, 4H, $2CH_2$), 1.5-1.3 (m, 6H, $2CH_3$); MS: m/e (relative intensity) 332 (M^+, 40), 286 (100), 225 (28), 213 (36), 186 (27), 162 (26).

Ethyl 6-fluoro-4-oxo-pyrido[2,3-h]quinoline-3-carboxylate (12). Compound **11** (1.0 g, 3.0 mmol) was suspended in 10 mL of diphenyl ether and refluxed for two hours at 250 ℃. Then the reaction mixture was cooled to room temperature, the resulting solid was filtered and washed with pet. ether (low boiling) and recrystallization from DMF to give 0.75 g (2.6 mmol) of pure product **12**. (87% yield, mp 289-291 ℃); ^{1}H NMR (DMSO-d_6) δ 12.8 (broad, 1H, NH), 9.2-8.0 (m, 3H, Ar-H), 8.6 (s, 1H, C_2-H), 7.9 (q, J=4.4 Hz, 1H, C_5-H), 4.3 (q, J=7.1 Hz, 2H, CH_2), 1.3 (t, J=7.1 Hz, 3H, CH_3); MS: m/e (relative intensity) 286 (M^+, 28), 240 (100), 212 (23), 184 (32).

Ethyl 1-ethyl-6-fluoro-4-oxo-pyrido[2,3-h]quinoline-3-carboxylate (13). The mixture of compound **12** (0.65 g, 2.3 mmol), ethyl iodide (1.7 g, 10.9 mmol) and anhydrous K_2CO_3 (0.95 g, 6.9 mmol) in 20 mL DMF was heated at 80 ℃ for three hours. After finishing the reaction, DMF was evaporated under reduced pressure. The residue was dissolved in water and extracted with $CHCl_3$. The $CHCl_3$ solution was dried with anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure after filtering the $MgSO_4$. The product was purified by silica gel column chromatography using ethyl acetate and pet. ether (4 : 1) as an eluent. (0.56 g, 78% yield, mp 112-113 ℃); ^{1}H NMR ($CDCl_3$) δ 9.5-8.0 (m, 3H, Ar-H), 9.2 (s, 1H, C_2-H), 7.7 (q, J=4.2 Hz, 1H, C_5-H), 4.5 (q, J=7.1 Hz, 2H, N-CH_2), 4.3 (q, J=7 Hz, 2H, $COOCH_2$), 1.6-1.5 (m, 6H, $2CH_3$); MS: m/e (relative intensity) 314 (M^+, 28), 268 (13), 240 (100), 212 (10).

1-Ethyl-6-fluoro-4-oxo-pyrido[2,3-h]quinoline-3-carboxylic acid (4). Compound **13** (0.5 g, 1.6 mmol) was dissolved in 30 mL of 15% HCl solution and stirred at room temperature for one hour. When the reaction mixture was neutralized with 10% NaOH solution, white crystal was obtained. The product was recrystallized from DMF, yielding 0.38 g (1.3 mmol) of pure product **4**. (84% yield, mp 289-290 ℃); ^{1}H NMR (TFA-D+$CDCl_3$) δ 10.1-8.6 (m, 3H, Ar-H), 9.6 (s, 1H, C_2-H), 8.5 (q, J=4.7 Hz, 1H, C_5-H), 4.7 (q, J=7.1 Hz, 2H, CH_2), 1.6 (t, J=7.1 Hz, 3H, CH_3); MS: m/e (relative intensity) 286 (M^+, 30), 240 (100), 212 (11), 184 (21).

6-Amino-2-methylquinoline (15). The nitro group was reduced to amino group with H-reduced Fe/AcOH. 83% yield, mp 185-186 ℃; ^{1}H NMR ($CDCl_3$) δ 7.8-6.6 (m, 5H, Ar-H), 2.6 (s, 3H, CH_3); MS: m/e (relative intensity) 158 (M^+, 100), 142 (4), 130 (11).

Diethyl N-(2-methyl-6-quinolinyl)aminomethylenemalonate (16). The reaction was carried out as described in the preparation of compound **11**. 92% yield, mp 136-138 ℃; ^{1}H NMR ($CDCl_3$) δ 11.2 (d, J=13.8 Hz, 1H, NH), 8.6 (d, J=13.8 Hz, 1H, N-CH), 8.0-7.3 (m, 5H, Ar-H), 4.4-4.2 (m, 4H, $2CH_2$), 2.7 (s, 3H, C_2-CH_3), 1.4-1.3 (m, 6H, $2CH_3$); MS: m/e (relative intensity) 328 (M^+, 60), 283 (100), 255 (6), 227 (38), 210 (40), 182 (47), 158 (21).

Ethyl 7-methyl-4-oxo-pyrido[2,3-g]quinoline-3-carboxylate (17). The reaction was carried out as described in the preparation of compound **12**. 48% yield, mp 288-290 ℃; ^{1}H NMR (DMSO-d_6) δ 12.7 (broad, 1H, NH), 10.4 (d, J=9 Hz, 1H, C_{10}-H), 8.6 (s, 1H, C_2-H), 8.2-7.6 (m, 3H, Ar-H), 4.2 (q, J=7.1 Hz, 2H, CH_2), 2.7 (s, 3H, C_7-CH_3), 1.3 (t, J=7.1 Hz, 3H, CH_3); MS: m/e (relative intensity) 282 (M^+, 32), 237 (100), 208 (11).

Ethyl 1-ethyl-7-methyl-4-oxo-pyrido[2,3-g]quinoline-3-carboxylate (19). The reaction was carried out by the same method described in the preparation of compound **13**. 42% yield, mp 223-224 ℃; ^{1}H NMR ($CDCl_3$) δ 10.7 (d, J=9 Hz, 1H, C_{10}-H), 8.5 (s, 1H, C_2-H), 8.3-7.5 (m, 3H, Ar-H), 4.5-4.4 (m, 4H, $2CH_2$), 2.8 (s, 3H, C_7-CH_3), 1.6-1.4 (m, 6H, $2CH_3$); MS: m/e (relative intensity) 310 (M^+, 15), 265 (10), 239 (100), 224 (15).

1-Ethyl-7-methyl-4-oxo-pyrido[2,3-g]quinoline-3-carboxylic acid (5). Compound **18** (0.2 g, 0.65 mmol) was dissolved in 10 mL of 30% HCl solution and heated under steam bath for two hours. When the reaction mixture was cooled to room temperature and neutralized with 10% NaOH solution, white crystal was obtained. The product was recrystallized from DMF, yielding 0.16 g (0.57 mmol) of pure product **5**. (87% yield, mp 280-282 ℃); ^{1}H NMR (DMSO-d_6) δ 10.6 (d, J=9.3 Hz, 1H, C_{10}-H), 9.2 (s, 1H, C_2-H), 8.6-7.9 (m, 3H, Ar-H), 4.8 (q, J=7.2 Hz, 2H, CH_2), 2.6 (s, 3H, C_7-CH_3), 1.5 (t, J=7.2 Hz, 3H, CH_3); MS: m/e (relative intensity) 282 (M^+, 15), 239 (100), 211 (30).

8-Fluoro-6-nitroquinoline (22). A mixture of 2-fluoro-4-nitroaniline (**7**) (5.0 g, 32 mmol), arsenic pentoxide (4.2 g, 18 mmol), 18 mL of concentrated sulfuric acid and 9 mL of water was heated to 80 ℃. The mixture was added dropwise to acrolein diethylacetal (5.4 mL, 36 mmol) during three hours, maintaining the temperature at 80 ℃. After the addition was completed, the mixture was heated to 120 ℃ for additional one hour, cooled, diluted to 160 mL of water. The reaction mixture was neutralized with 28% ammonia water and the precipitated 8-fluoro-6-nitroquinoline (**21**) was collected on a filter. The product was purified by silica gel column chromatography using ethyl acetate and pet. ether (1 : 3) as an eluent. (4.79 g, 78% yield, mp 158-159 ℃); ^{1}H NMR ($CDCl_3$) δ 9.2-8.2 (m, 4H, Ar-H), 7.7 (q, J=4.3 Hz, 1H, C $_7$-H); MS: m/e (relative intensity) 192 (M^+, 78), 162 (5), 146 (45), 134 (100).

Diethyl N-(8-fluoro-6-quinolinyl)aminomethylenemalonate (24). The reaction was carried out as described in the preparation of compound **11**. 94% yield, mp 127-129 ℃; ^{1}H NMR ($CDCl_3$) δ 11.2 (d, J=13.2 Hz, 1H, NH), 9.0-7.3 (m, 5H, Ar-H), 8.6 (d, J=13.2 Hz, 1H, N-CH), 4.4-4.3 (m, 4H, $2CH_2$), 1.4-1.3 (m, 6H, $2CH_3$); MS: m/e (relative intensity) 332 (M^+, 55), 287 (100), 213 (47), 186 (53), 162 (26).

Ethyl 5-fluoro-4-oxo-pyrido[2,3-g]quinoline-3-carboxylate (25). The reaction was carried out as described

in the preparation of compound **12**. 51% yield, mp 295-297 ℃; ^{1}H NMR (DMSO-d_6) δ 12.7 (broad, 1H, NH), 10.5 (d, J=9 Hz, 1H, C_{10}-H), 9.0-7.7 (m, 3H, Ar-H), 8.6 (s, 1H, C_2-H), 4.3 (q, J=7.1 Hz, 2H, CH_2), 1.3 (t, J=7.1 Hz, 3H, CH_3); MS: m/e (relative intensity) 286 (M^+, 47), 241 (100), 213 (12).

Ethyl 1-ethyl-5-fluoro-4-oxo-pyrido[2,3-g]quinoline-3-carboxylate (27). The reaction was carried out by the same method described in the preparation of compound **13**. 58% yield, mp 179-180 ℃; ^{1}H NMR ($CDCl_3$) δ 10.8 (d, J=8.7 Hz, 1H, C_{10}-H), 9.0-7.5 (m, 3H, Ar-H), 8.5 (s, 1H, C_2-H), 4.5-4.3 (m, 4H, $2CH_2$), 1.6-1.4 (m, 6H, $2CH_3$); MS: m/e (relative intensity) 314 (M^+, 9), 270 (11), 243 (100), 214 (15), 186 (4).

1-Ethyl-5-fluoro-4-oxo-pyrido[2,3-g]quinoline-3-carboxylic acid (6). The reaction was carried out by the same method described in the preparation of compound **5**. 83% yield, mp 291-294 ℃; ^{1}H NMR (DMSO-d_6) δ 10.5 (d, J=8.7 Hz, 1H, C_{10}-H), 9.2 (s, 1H, C_2-H), 9.1-7.9 (m, 3H, Ar-H), 4.7 (q, J=7 Hz, 2H, CH_2), 1.5 (t, J=7 Hz, 3H, CH_3); MS: m/e (relative intensity) 286 (M^+, 7), 243 (100), 214 (32), 186 (16).

Acknowledgment. We are grateful to the Korea Science and Engineering Foundation(931-0300-029-2) for the financial support for this research and also Miss Hong, S. H. in Department of Genetic Engineering, Kyungpook National University for the MIC test.

References

1. Lee, J. K.; Chang, S. J. *Korean J. of Med. Chem.* **1994**, *4*, 92.
2. Albrecht, R. *Pro. Drug Res.* **1977**, *21*, 9.
3. Siporin, C.; Heifetz, C. L.; Domagala, J. M. *The New Generation of Quinolones.* Marcel Dekker, Inc. 1990.
4. Hooper, D. C.; Wolfson, J. S. *Quinolone Antibacterial Agents.* American Society for Microbiology, Washington, D. C. 1993.
5. Mirek, J. *Rooz. Chem.* **1960**, *34*, 1599.
6. Burger, A.; Modlin, L. R. *J. Amer. Chem. Soc.* **1940**, *62*, 1079.
7. Elderfield, R. C.; Gensler, W. J.; Williamson, T. A.; Griffing, J. M.; Morris Kupchan, S.; Maynard, J. T.; Kreysa, F. J.; Wright, J. B. *J. Amer. Chem. Soc.* **1946**, *68*, 1584.
8. Lesher, G. Y.; Froelich, E. J.; M. D. Gruett, M. D.; Bouley, J. H.; Brundage, R. P. *J. Med. Chem.* **1962**, *5*, 1063.
9. Kamimsky, D.; Meltzer, R. I. *J. Med. Chem.* **1968**, *11*, 160.
10. Burnie, J. B.; Brunie, R. *Drugs of the Future.* **1984**, *9*, 179.
11. Koga, H.; Itoh, A.; Murayama, S.; Suzue, S.; Irikura, T. *J. Med. Chem.* **1980**, *23*, 1358.
12. Matsumoto, J.; Minami, S. *J. Med. Chem.* **1975**, *18*, 74.
13. Minami, S.; Shono, T.; Matsumoto, J. *Chem. Pharm. Bull.* **1971**, *19*, 1426.
14. Minami, S.; Shono, T.; Matsumoto, J. *Chem. Pharm. Bull.* **1971**, *19*, 1482.
15. Janina, K. R. *Acta Polon. Pharm.* **1966**, *23*, 97.
16. Hodgson, H. H.; Nicholson, D. E. *J. Chem. Soc.* **1941**, 766.
17. Ishikawa, N.; Tanabe, T. *Kogyo Kagashi Zasshi.* **1967**, *70*, 1530.
18. Yale, H. L. *J. Amer. Chem. Soc.* **1947**, *69*, 1230.
19. Hewitt, W.; Vincent, S. *Theory and Application of Microbiological Assay*; Academic Press., pp 19-21, 1989.
20. Koneman, E. W.; Allen, S. D.; Winn. Jr, W. C. *Diagnostic Microbiology*; Lippicott, J. B. Co., 3rd. Ed. p 485, 1988.

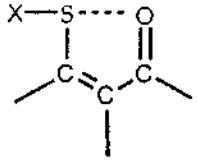
Intramolecular Sulfur-Oxygen Interaction. Structure of Dimethyl 1,3-dithiolan-2-ylidenemalonate

Kwan Mook Kim, Young-A Lee, Ok-Sang Jung, and Youn Soo Sohn*

Inorganic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea

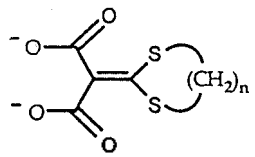
Received October 11, 1995

Intramolecular interactions between sulfur and oxygen often occur in organic and inorganic compounds.[1,2] This type of interaction (shorter than the sum of the van der Waals radii) plays an important role in controlling physicochemical properties such as structural conformation and reactivity.[3,4] Such a strong sulfur-oxygen interaction is particularly favorable in the conjugated system of X-S-C=C-C=O with the following configuration and conformation.[2,5] For the conjugat-



ed system, the planar conformation can be stabilized by the S···O interaction. The intramolecular interaction can be also affected by properties of the X group.[5]

Recently the authors are involved in a synthetic and structural works on platinum(II) complexes using sulfur-containing dicarboxylate ligands of the following structure and have shown that a variety of coodination modes (O,O'-, O,S-, and



S,S'-chelates) were formed depending on their dithioether ring size.[6~8] In particular, 1,3-dithiolan-2-ylidene malonic acid (n=2) alkyl esters of the above system are commerciallized compounds as horticultural fungicides or therapeutic agents for treating hepatic diseases.[9] The platinum complex of 1,3-dithiolan-2-ylidenemalonate ligand exhibits exclusively O,O'-chelation probably due to remarkable decrease of sulfur basicity, which, in addition to the ring size effect, may be at