Antibacterial and Antifungal Test——The antibacterial test was made by the dilution method after 24 hr. and 48 hr. The bacteria used were Bacillus subtilis, Staphyrococcus aureus and Escherichia coli B. These were incubated at 37° in the Biuillon medium by the usual method.

In the case of Aspergillus niger, the Biuillon medium containing glucose (4%) was used (pH 7.0) and after 72 hr. (at 37°) the results were observed.

The authors are grateful to Prof. H. Matsumura of Kyushu University for his encouragement throughout this work. Thanks are also due to Prof. T. Toda and Dr. K. Hisatsune, Department of Bacteriology of this University, for the antibacterial and antifungal tests. They are also indebted to Mrs. S. Matsuba, Mr. M. Shirōzu and Miss S. Indō for the microanalyses and to Messrs. H. Yano, H. Matsui and K. Hikita for infrared and ultraviolet spectral measurements.

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Summary

1) Dehydroaroylacetic acids were directly obtained by Friedel-Crafts reaction of triacetic acid lactone (TAL) and aroyl chloride in the presence of an excess of aluminum chloride. They were also derived from the corresponding 4-benzoates of TAL by Fries rearrangement using the excessive aluminum chloride.

2) The monobenzoate of TAL synthesized by the usual method as also reported in the previous reports was definitely shown to be the 4-benzoate rather than the 2-benzoate.

3) None of these new compounds was superior to DHA in the activity against Bacillus subtilis, Staphylococcus aureus, Escherichia coli B and Aspergillus niger *in vitro*.

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174. Morio Ikehara, Akihiro Yamazaki, and Toshiko Fujieda : Studies on Coenzyme Analogs. XIII.[*1] Oxidation of Methylmercaptopurine and its Nucleoside by means of N-Chloro- and N-bromosuccinimide.

(*Faculty of Pharmaceutical Sciences, School of Medicine, Hokkaido University*[*2])

Recently several investigators reported the reaction of nucleophilic reagent with thiolated purine riboside.[1,2] In these instances, methylmercapto group situated on the 6-position of purine nucleus reacted readily with nucleophiles, such as mono-and di-alkylamine or ammonia. However the latter reagent failed to react with 6-methylmercapto group when the same nucleus was substituted with additional electron-releasing group on position 2, even in the drastic conditions.[3]

In efforts to increase the susceptibility of this type of methylmercapto group against

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*1 Part XII. T. Ueda, *et al.* : This Bulletin, **10**, 788 (1962).

*2 Kita 12-jo, Nishi 5-chome, Sapporo (池原森男, 山崎晤弘, 藤枝聰子).

1) J. J. Fox, I. Wempen, A. Hampton, I. L. Doerr : J. Am. Chem. Soc., **80**, 1669 (1958).
2) M. Ikehara, T. Ueda, S. Horikawa, A. Yamazaki : This Bulletin, **10**, 665 (1962).
3) M. Ikehara, A. Yamazaki, T. Fujieda : Unpublished results.

nucleophilic replacement, authors found the same group was easily converted to a methylsulfonyl group by a moderate treatment with NCS*[3] in aqueous solution. In the present paper, the reaction of this reagent and NBS*[3] with 2- and/or 6-substituted purine and its nucleoside was reported.

The oxidation of methylmercapto group on purine nucleus to methylsulfonyl group by means of hydrogen peroxide[4] and/or chlorine gas[5,6] was reported by several investigators.

When 2,6-bis(methylmercapto)purine (Ia) was reacted with 4 equivalents of NCS in aqueous methanol-DMF*[3] solution, 2,6-bis(methylsulfonyl)purine (IIa) was obtained in 68% yield. The structure of compound (IIa) was confirmed by the direct comparison with an authentic sample synthesized according to the procedure described by Noell *et al.*[6] The compound (IIa) was further converted to 2-methylsulfonyladenine by the reaction with ammonia. The yield of bissulfonyl derivative in NCS-oxidation reaction increased along with increased amount of oxidant used up to a maximum yield of 80% for 8 moles of the reagent.*[4]

Although 6-methylmercaptopurine (Ib) afforded 6-methylsulfonylpurine (IIb) by its reaction with 2 moles of NCS in a yield of 64%, the stoichiometry of this reaction could not be ascertained. 2-Methylmercaptohypoxanthine (Ic) also gave a methylsulfonyl derivative (IIc) in a good yield by oxidation with excess NCS.

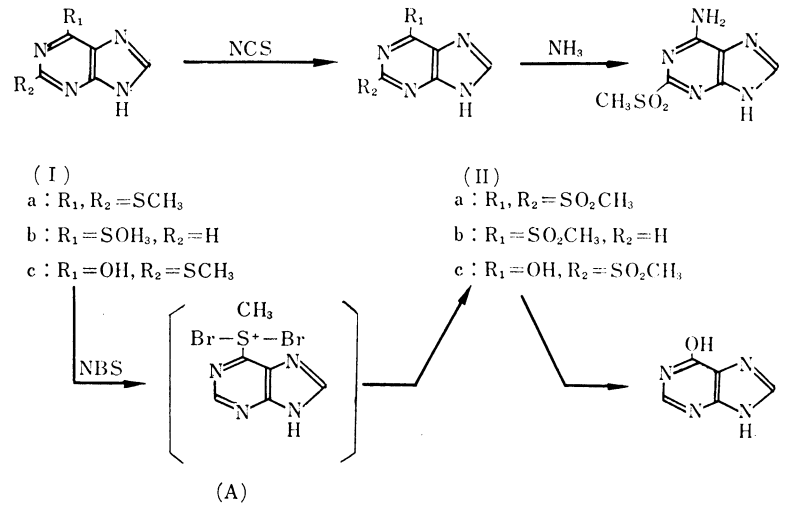

Chart 1.

The reaction of NBS with methylmercaptopurine in an aqueous solution was then studied. 6-Methylmercaptopurine (Ib) afforded a substance having an ultraviolet absorbing spectrum which closely resembled that of 6-methylsulfonypurine. Although this substance (A) could not be purified by usual recrystallization techniques, it was converted to adenine and hypoxanthine by reactions with ammonia and with water respectively. Substance (A) proved to have an halogen atom by Beilstein's test and was also

*[3] Following abbreviations were used : NCS : N-chlorosuccinimide; NBS : N-bromo-succinimide; DMF : N,N-dimethylformamide.

*[4] In the case of oxidation with limitted amount of NCS, an unidentified oxidized substance, m.p. 284~285° (decomp.) was obtained.

4) K. J. M. Andrews : J. Chem. Soc., **1949**, 2490.
5) D. J. Brown : *Ibid.*, **1957**, 683.
6) C. W. Noell, R. K. Robins : J. Am. Chem. Soc., **81**, 5998 (1959).

converted to 6-methylsulfonylpurine (IIb) by bubbling chlorine gas into an aqueous solution. From these evidences, substance (A) was assumed to possess a structure indicated in the Chart 1. The brominated methylmercapto group seemed to have comparable reactivity to nucleophiles as that of $CH_3S^+(Cl_2)$-group.[6] However the activity of sulphur-bromide bond against acidic hydrolysis appeared to be lower than that of sulphur-chloride and afforded only substance (A) intermediary.

In the reaction described above, 6-methylmercaptopurine was directly produced by NCS-oxidation to hypoxanthine when the reaction was carried out in a slightly elevated temperature and for prolonged reaction time. The ease of hydrolysis of 6-methylsulfonyl group was ascertained by the treatment with 0.1*N* hydrochloric acid and 0.1*N* sodium hydroxide. In the former case, at reflux temperature total hydrolysis occurred within 5 minutes and in the latter, the reaction required 1 hour. In contrast, 6-chloropurine required 1 hour for total hydrolysis in 0.1*N* hydrochloric acid.[7]

The reaction of NCS in anhydrous media with methylmercaptopurine also resulted in the formation of methylsulfonyl derivative in contrast to the case of chlorine gas-oxidation which afforded chloropurine exclusively.[6,8~10] Bearing these results in mind, NCS-oxidation method was then extended to several purine nucleosides having a methylmercapto-group on 2- and/or 6-position.

When 2,6-bis(methylmercapto)-9-(2′,3′,5′-tri-O-benzoyl)-β-D-xylofuranosyl- or -(2′,3′,4′,6′-tetra-O-acetyl)-β-D-glucopyranosylpurine (IIIa,b) was reacted with excess NCS, corresponding 2,6-bis(methylsulfonyl) derivative (IVa,b) was obtained in 55 and 74% yield, respectively. Unprotected nucleoside, 2,6-bis(methylmercapto)-9-β-D-glucopyranosylpurine (IIIc) readily yielded 2,6-bis(methylsulfonyl) derivative (IVc).

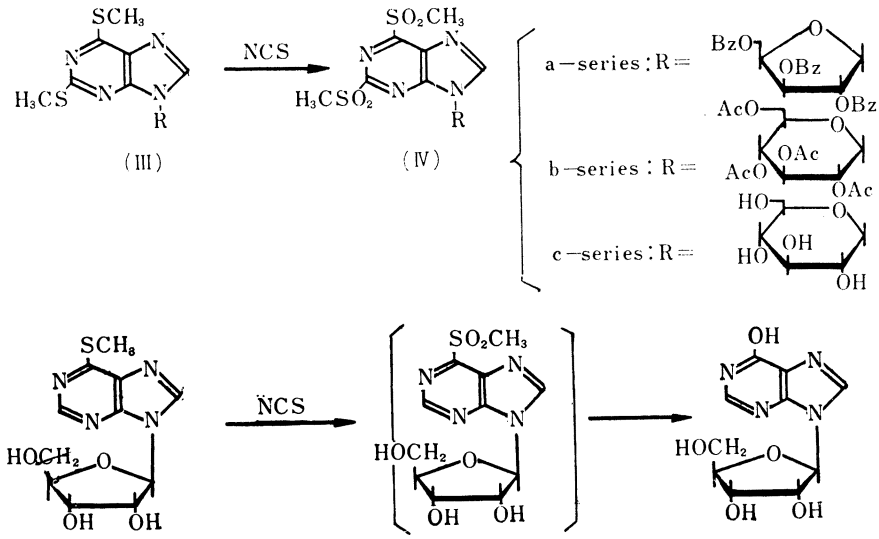

Chart 2.

7) A. Bendich, P.J. Russel, Jr., J.J. Fox : J. Am. Chem. Soc., **76**, 6073 (1954).
8) R.W. Balsiger, J. Montgomery : J. Org. Chem., **25**, 1573 (1960); R.K. Robins : J. Am. Chem. Soc., **82**, 2654 (1960).
9) G.D. Daves, C.W. Noell, R.K. Robins, H.C. Koppel, A.G. Beanan : J. Am. Chem. Soc., **82**, 2633 (1960).
10) R.K. Robins : J. Org. Chem., **26**, 447 (1961).

However, in the case of 2,6-bis(methylmercapto)-9-β-D-xylofuranosylpurine, the product obtained was solely 2,6-methylsulfonylpurine. This type of cleavage of nucleoside linkage was also observed when 2-amino-6-methylmercapto-9-β-D-ribofuranosylpurine(6-methylthioguanosine) was oxidized with NCS. Contrary to the cleavage of these furanosides, 6-methylmercapto-9-β-D-ribofuranosylpurine (V) produced only inosine using the same reaction. Although the explanation of these results could not be satisfactorily made as yet, methylsulfonyl or amino group at position 2 seemed to exert, to a certain extent, labilizing effect on nucleoside bond in unprotected furanoside and to make it susceptible to acid hydrolysis.

Further transformation and biological activity of these methylmercapto and methylsulfonyl derivatives will be reported later.

Experimental

2,6-Bis(methylsulfonyl)purine——a) 212 mg. of 2,6-bis(methylmercapto)purine[5] was dissolved in 2 cc. of DMF by slight heating and to the solution was added 15 cc. of H_2O-MeOH (20:80, v/v) cautiously to avoid precipitating the starting material. To this solution, 1.076 g. of NCS[11] was added with stirring and then, the mixture was heated at 40~50° for 1 hr. After 30 min., precipitation of bismethylsulfone was observed. At the end of the reaction, 5 cc. of Et_2O was added and the reaction mixture was further stirred at room temperature. Resulting crystal was collected on a filter and recrystallized from MeOH, m.p. 242°(decomp.). Yield 220 mg. (80%). *Anal.* Calcd. for $C_7H_8O_4N_4S_2$: C, 30.43; H, 2.89; N, 20.29. Found : C, 30.49; H, 2.80; N, 20.21. UV : $\lambda_{max}^{pH\,1}$ 280, $\lambda_{max}^{pH\,14}$ 228.5, 286 mμ. IR : ν_{max}^{Nujol} 1130~1150, 1310 cm^{-1}(sulfone). This sample was identical in every respect with an authentic sample synthesized by the Noell's procedure.*5,6)

b) 100 mg. of 2,6-bis(methylmercapto)purine was dissolved in hot dehyd. MeOH (10 cc.), to which was added 280 mg. of NCS and the mixture was stirred for 2 hr. at 40~50°. After standing overnight in a refrigerator, resulting precipitates were collected and recrystallized. 50 mg. of 2,6-bis(methylsulfonyl)purine was obtained.

2-Methylsulfonyladenine——100 mg. of 2,6-bis(methylsulfonyl)purine was dissolved in 10 cc. of MeOH, which was previously saturated with dry ammonia at 0°, and reacted for 9 hr. at 150~160° in a sealed tube. Crystalline ammonium succinate was removed and filtrate was evaporated *in vacuo*. Residue was recrystallized from DMF-H_2O, m.p. >300°. Yield, 40 mg. (55%). UV : $\lambda_{max}^{pH\,1}$ 267, $\lambda_{max}^{pH\,14}$ 270 mμ. *Anal.* Calcd. for $C_6H_7O_2N_5S$: C, 33.80; H, 3.29; N, 32.86. Found : C, 34.29; H, 3.52; N, 32.39.

6-Methylsulfonylpurine——0.5 g. of 6-methylmercaptopurine[12] was dissolved in 3 cc. of DMF by warming and 20 cc. of H_2O-MeOH (20:80, v/v) was added. Into this mixture was added 1.21 g. of NCS and stirred for 2 hr. at 40~50°. Crystal was collected by filtration and recrystallized from MeOH. Yield, 380 mg. (64%), m.p. 205°. UV : $\lambda_{max}^{pH\,1}$ 278, $\lambda_{max}^{pH\,14}$ 282 mμ. *Anal.* Calcd. for $C_6H_6O_2N_4S$: C, 36.36; H, 3.03; N, 28.28. Found : C, 36.21; H, 3.05; N, 28.23.

Hydrolysis of 6-methylsulfonylpurine——50 mg. of 6-methylsulfonylpurine was refluxed in 5 cc. of 0.1*N* HCl for 5 min. After it was concentrated to a small amount and neutralized with $NaHCO_3$, the amorphous substance was collected and recrystallized from H_2O. UV : $\lambda_{max}^{pH\,1}$ 247, $\lambda_{max}^{pH\,14}$ 261 mμ. *Anal.* Calcd. for $C_5H_4ON_4$: C, 44.11; H, 2.94. Found : C, 44.12; H, 3.06. Paperchromatography with authentic hypoxanthine as a standard showed that both possessed the same Rf-values, 0.15 (BuOH saturated with H_2O).

2-Methylsulfonylhypoxanthine——200 mg. of 2-methylmercaptohypoxanthine[13] was dissolved in a small amout of DMF and to which was added 30 cc. of MeOH-H_2O (80:20, v/v). After the addition of 400 mg. of NCS (or NBS), the mixture was kept for 2 hr. at 40~50° under stirring. Resulting crystals were collected by filtration, recrystallization from DMF gave 130 mg. of crystal, m.p. >300° (56%). *Anal.* Calcd. for $C_6H_6O_3N_4S$: C, 33.65; H, 2.82; N, 26.10. Found : C, 34.57; H, 3.21; N, 26.18. UV : $\lambda_{max}^{pH\,1}$ 255, $\lambda_{max}^{pH\,14}$ 266 mμ.

Reaction of 6-methylmercaptopurine with NBS——i) Synthesis of adenine : 83 mg. of 6-methylmercaptopurine was dissolved in 15 cc. of MeOH-H_2O (80:20, v/v) and to the mixture was added 178 mg. of NBS. This solution was stirred for 1.5 hr. at room temperature, neutralized with $NaHCO_3$

*5 In this paper Noell reported that the m.p. of 2,6-bis(methylsulfonyl)purine was 258°, but authors obtained a crystal, m.p. of 242°(decomp.) and utilized as such for identification.

11) J. Tscherniac : Ber., **34**, 4214 (1901).

12) G. E. Elion, E. Burgi, G. H. Hitchings : J. Am. Chem. Soc., **74**, 411 (1952).

13) G. E. Elion, G. H. Hitchings, W. H. Lange : *Ibid.*, **78**, 217 (1956).

and evaporated *in vacuo*. The UV absorption spectrum of this residue was $\lambda_{max}^{pH\,11}$ 282, $\lambda_{max}^{pH\,1}$ 273 mμ. Paper chromatographic comparison showed that this material was different from 6-methylsulfonylpurine. When a small amount of this material was dissolved in MeOH and bubbled with chlorine gas for a short period, UV absorption spectrum changed to that of 6-methylsulfonyl derivative. The residue described above was taken up in 5 cc. of MeOH, saturated with ammonia at 0°, and heated at 140° for 3 hr. in a sealed tube. After cool, ammonium succinate was filtered off, and the filtrate was evaporated *in vacuo*. The residue was recrystallized from H_2O, yield, 30 mg. (44%). This was compared with an authentic sample. Paper chromatography (solvent, BuOH : H_2O=86:14) Rf 0.41. UV : $\lambda_{max}^{pH\,11}$ 267, $\lambda_{max}^{pH\,1}$ 260 mμ.

ii) Synthesis of hypoxanthine : 166 mg. of 6-methylmercaptopurine was dissolved in 20 cc. of MeOH-H_2O (80:20, v/v) and to which was added 500 mg. of NBS. This mixture was heated under stirring for 3 hr. at 40~50°. The yellow reaction mixture was concentrated *in vacuo*, added a small amount of water and the precipitate thus formed, was recrystallized from H_2O. 20 mg. (17.6%) of hypoxanthine was obtained. UV : $\lambda_{max}^{pH\,11}$ 261, $\lambda_{max}^{pH\,1}$ 247 mμ. Paper chromatography with an authentic sample showed the same Rf, 0.15.

2,6-Bis(methylmercapto)-9-(2',3',4',6'-tetra-O-acetyl)-β-D-glucopyrnosylpurine——4.8 g. of 2,6-bis-(methylmercapto)purine chloromercury salt was suspended under stirring in 250 cc. of xylene. The solution was azeotropically dried by the removal of 20 cc. of xylene by distillation and then to it, 7.0 g. of acetobromoglucose[14] was added. Reaction was completed after 4 hours' reflux under stirring and the solvent was evaporated *in vacuo*. The residue was extracted with $CHCl_3$ (3×50 cc.), and the extract was washed with 30% KI solution, twice with water, and dried over Na_2SO_4. Evaporation of $CHCl_3$ *in vacuo* and recrystallization from Et_2O (100 cc.) gave an amorphous substance, m.p. 104~110°, yield, 4.1 g. (80%).

2,6-Bis(methylsulfonyl)-9-(2',3',4',6'-tetra-O-acetyl)-β-D-glucopyranosylpurine——300 mg. of 2,6-bis (methylmercapto)-9-(2',3',4',6'-tetra-O-acetyl)-β-D-glucopyranosylpurine was dissolved in 15 cc. of MeOH-H_2O (80:20, v/v) by slight warming and to the solution was added 320 mg. of NCS. Two hr. of stirring at 40~50° gave a clear reaction mixture. Evaporation of solvent *in vacuo* gave colorless crystals, which were collected by filtration and recrystallized from MeOH. Yield, 250 mg. (74%), m.p. 178~180°. UV : λ_{max}^{EtOH} 277 mμ. *Anal.* Calcd. for $C_{21}H_{26}O_{13}N_4S_2$: C, 41.58; H, 4.32; N, 9.24. Found: C, 41.83; H, 4.40; N, 9.45.

2,6-Bis(methylmercapto)-9-β-D-glucopyranosylpurine——500 mg. of 2,6-bis(methylmercapto)-9-(2',3',4',6'-tetra-O-acetyl)-β-D-glucopyranosylpurine was dissolved in 37 cc. of dehyd. MeOH. Into this, a solution of 18 mg. of Na in 2 cc. of MeOH was added and refluxed for 4.5 hr. Bared nucleoside precipitated during the reaction was collected on a filter after standing overnight. Recrystallization from DMF-MeOH gave 300 mg. of needles, m.p. 276~277° (decomp.), yield, 86%. UV λ_{max}^{EtOH} mμ (ε): 225 (12600), 259 (22600), 305 (12900). *Anal.* Calcd. for $C_{13}H_{18}O_5N_4S_2$: C, 41.71; H, 4.85; N, 14.97. Found: C, 41.46; H, 5.17; N, 15.14.

2,6-Bis(methylsulfonyl)-9-β-D-glucopyranosylpurine——1.0 g. of 2,6-bis(methylmercapto)-9-β-D-glucopyranosylpurine was dissolved in 50 cc. of hot DMF, to which was added 5 cc. of H_2O and 1.7 g. of NCS. After stirring for 2.5 hr. at 50°, the solution was neutralized with $NaHCO_3$ and concentrated *in vacno*. Separation of residual NaCl and syrup was accomplished by suspending them in 50 cc. of Me_2CO-EtOH (1:1, v/v) and filtrating the mixture. The filtrate was concentrated and to which was added 20 cc. of EtOH. After storage in a refrigerator for a while, crystals formed were collected by filtration. Recrystallization from H_2O gave 650 mg. of pure substance, m.p. 213~214° (by rapid heating). Yield, 55%. UV : $\lambda_{max}^{H_2O}$ 277 (ε 16400) mμ. *Anal.* Calcd. for $C_{13}H_{18}O_9N_4S_2$: N, 12.78. Found : N, 12.84.

2,6-Bis(methylmercapto)-9-(2',3',5'-tri-*O*-benzoyl)-β-D-xylofuranosylpurine——3.0 g. of D-xylofuranose-1,2,3,5-tetra-O-benzoate[15] was dissolved in 6 cc. of CH_2Cl_2 by warming. Then the solution was cooled rapidly to 30° and added with 30% HBr in AcOH (15 cc.). After standing for 30 min. at room temperature under exclusion of moisture, solvent was removed at 60~70° *in vacuo*. Resulting syrup was dried by codistillation with xylene (2×9 cc.), and the residue was collected in 30 cc. of xylene. 3.0 g. of 2,6-bis(methylmercapto)purine chloromercury salt was suspended in 180 cc. of xylene, dried azeotropically by distillation of 20 cc. of solvent, and added to above bromoxylose solution. The resulting mixture was dried again by distilling of 20 cc. of the solvent and it was refluxed for 2 hr. under stirring. The reaction mixture was filtered while hot and the precipitate was washed with $CHCl_3$. $CHCl_3$-layer was washed with 30% KI solution, saturated $NaHCO_3$ solution, and finally H_2O, respectively. After drying over Na_2SO_4, the solvent was removed under reduced pressure. Residual glassy substance weighed 3.1 g. (70%). UV λ_{max}^{EtOH} mμ : 230, 259, 307.

14) M. Barczai-Martos : Nature, **165**, 369 (1950).
15) B. R. Baker, R. E. Shaub : J. Am. Chem. Soc., **77**, 5900 (1955); B. R. Baker : J. org. Chem., **22**, 959 (1957).

2,6-Bis(methylsulfonyl)-9-(2′,3′,5′-tri-O-benzoyl)-β-D-xylofuranosylpurine——300 mg. of 2,6-bis-(methylmercapto)-9-(2′,3′,5′-tri-O-benzoyl)-β-D-xylofuranosylpurine was added in 20 cc. of MeOH-H_2O (80:20, v/v) and in order to obtain clear solution a small amount of Me_2CO was added. Into this solution 400 mg. of NCS was added and stirred for 3 hr. at 40~50°. After the reaction, the entire mixture was neutralized with $NaHCO_3$, evaporated *in vacuo*, and residue was taken up in 20 cc. of H_2O-$CHCl_3$ (1:1, v/v). $CHCl_3$-layer was separated, dried over Na_2SO_4, and evaporated *in vacuo*. Glassy residue (250 mg.) was recrystallized from EtOH-Me_2CO, m.p. 121~123°, yield, 180 mg. (55%). UV λ_{max}^{EtOH} mμ: 229, 274. *Anal.* Calcd. for $C_{33}H_{28}O_{11}N_4S_2$: C, 54.99; H, 3.92; N, 7.77. Found: C, 55.12; H, 4.10; N, 7.66.

Reaction of 2,6-Bis(methylmercapto)-9-β-D-xylofuranosylpurine with NCS——300 mg. of 2,6-bis-(methylmercapto)-9-β-D-xylofuranosylpurine was dissolved in 15 cc. of MeOH-H_2O (80:20, v/v). After the addition of 200 mg. of NCS, the resulting mixture was stirred for 3 hr. Neutralization with $NaHCO_3$ and evaporation of solvent *in vacuo* gave a syrupy residue which was recrystallized from H_2O. 105 mg. of 2,6-bis(methylsulfonyl)purine was obtained. This sample melted at 242° (decomp.) and was identical with an authentic sample when tested by mixed m.p. analysis.

Reaction of 6-methylmercapto-9-β-D-ribofuranosylpurine (6-methylthioinosine) with NCS——130 mg. of 6-methylthioinosine[1] was dissolved in 10 cc. of MeOH-H_2O (80:20, v/v), followed by the addition of 120 mg. of NCS. Stirring was maintained for 3 hr. at 40~50°, then reaction mixture was neutralized with $NaHCO_3$ and concentrated *in vacuo*. Residue was added with a small amount of EtOH-Me_2CO and stored in a refrigerator. Recrystallization from Me_2CO-EtOH gave m.p. 215~216°. Direct comparison with authentic inosine by mixed m.p. test showed no depression. UV: λ_{max}^{EtOH} 249 mμ. Paper chromatography: Rf 0.10 (Solvent, ButOH sat. with water).

2-Amino-6-methylmercapto-9-β-D-ribofuranosylpurine (6-methylthioguanosine)——1.2 g. (4 mmole) of thioguanosine[1] was suspended in 10 cc. of 0.4*N* NaOH and insoluble material was solubilized by further addition of 0.4*N* NaOH. Into this solution was added 505 mg. (4 mmole) of dimethyl sulfate dropwise under vigorous stirring at room temperature. After 2 hr. of reaction pH of the solution was dropped to 8.4. When the mixture was kept overnight in an refrigerator a white substance precipitated. This was collected by filtration, washed with EtOH-Et_2O, and recrystallized from anhyd. EtOH. White needles, m.p. 195~198° (softened at 141~142° and decomposed) was obtained after drying for 3 hr. at 50° under reduced pressure. Yield, 250 mg. (19.7%). UV: λ_{max}^{pH1} 319, 247; λ_{max}^{pH11} 307, 244 mμ. *Anal.* Calcd. for $C_{11}H_{15}O_4N_5S$: C, 42.18; H, 4.83; N, 22.68. Found: C, 42.55; H, 4.71; N, 22.28.

Reaction of 2-Amino-6-methylmercapto-9-β-D-ribofuranosylpurine with NCS——100 mg. (0.41 mmole) of 6-methylthioguanosine was dissolved in 10 cc. of MeOH-H_2O (80:20, v/v) and to which was added 150 mg. of NCS. After stirring for 2 hr. at 30~40°, UV absorption spectra changed to λ_{max} 225, 326 mμ. Neutralization with $NaHCO_3$ and evaporation of solvent under reduced pressure gave a syrup. Work-up of this residue gave 10 mg. of crystalline material, which contained N and no S. Paper chromatography of above syrup showed a fluorescent material at Rf 0.3, which did not decolorlize in metaperiodate-benzidine reagent This indicated the absence of sugar moiety attached to the base of this compound.

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Summary

The methylmercapto group situated on the 2- or 6-position of purine and purine nucleoside was readily oxidized to methylsulfonyl group by treatment with N-chlorosuccinimide. In this reaction unprotected nucleoside occasionally caused the cleavage of nucleoside linkage. N-Bromosuccinimide could also be used for replacement of methylmercapto to amino or hydroxy group by successive treatment of the intermediate with water or ammonia.

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