37. Haruo Saikachi, Zennosuke Aramaki, and Takashi Aoki: Synthesis of Furan Derivatives. XIV.* Condensation of 2-(5-Nitro)furylacrolein and 2-(5-Nitro)furaldehyde with Hydrazides.

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For about ten years, an attempt to find some bactericidal and fungicidal compounds possessing a nitro group in the 5-position of furan ring have been carried out by one (S) of the authors,[1] his co-warkers,[2] and many researchers.[3] Möller[4] also undertook the synthesis of many nitrofuran compounds and studied their bacteriological observations. Furthermore, Cramer and Dodd[5] reported in full detail the mode of antibacterial action of nitrofuran derivatives, and especially the effect of 2-(5-nitro)furaldehyde semicarbazone upon the oxidation-reduction potential of growing cultures of *Staphylococcus aureus* has been demonstrated by means of polarographic method that this nitro compound is destroyed by the bacteria in culture medium. Bender and Paul[6] concluded tentatively that the nitro group of 2-(5-nitro)furaldehyde semicarbazone *in vitro* might be first of all reduced by xanthine oxidase to hydroxyamino group. It is particularly interesting to note that the relationship between half-wave potential of the nitro group and bactericidal activity was cleared to some extent recently by one of the co-workers.[7] Consequently, these foregoing papers suggested that the lowing of the nitro group may be one of the most essential factors for the antibacterial action and the action exerted by interfering in some way with those enzyme systems which play a vital role in the metabolism of bacterial cells.

In connection with the above, Affonson and Khoana[8] announced that halogenated derivatives of cinnamic acid and *p*-nitrocinnamic acid possess a very high antibacterial activity. Subsequently, on the basis of the above work, Carrar[9] announced an interesting result related to the effect of 2-(5-nitro)thienylacrolein derivatives having a remarkable antibacterial activity. These two works more especially prompted the present workers to synthesize and screen compounds of the 2-(5-nitro)furfurylidene and 2-(5-nitro)furylacrylidene type in this laboratory.

In this present work, picolinic acid hydrazide, nicotinic acid, 6-amino-3-pyridinecarboxylic acid hydrazide, 4-hydroxyethylsemicarbazide, benzoic acid hydrazide, *p*-chlorobenzoic acid hydrazide, 2,4-dichlorobenzoic acid hydrazide, cinnamic acid hydrazide, 2,4-adipic acid dihydrazide (m.p. 177~180°), *p*-aminosalicylic acid hydrazide, and 2,5-diaminopyridin were used as the auxo-antibacterial group.[1]

The condensation of various amines and hydrazides with 2-(5-nitro)furfural and 2-(5-nitro)furylacrolein was accomplished by the usual manner.

One of the most important intermediates used in this work, 2-(5-nitro)furylacrolein (m.p. 119°),[1] was prepared by the condensation of nitrofurfural with acetaldehyde

* Part XIII: J. Pharm. Soc. Japan, **75**, 427 (1955).
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1) J. Pharm. Soc. Japan, **69**, 36 (1949); **69**, 39 (1946); **71**, 982 (1651); **72**, 30 (1952); **74**, 404 (1954).
2) T. Sasaki: This Bulletin, **2**, 95 (1954); **3**, 123 (1954).
3) U. S. P. 2,416,233; 2,416,234; 2,416,235; 2,416,236; 2,416,237; 2,416,238; 2,416,239; 2,319,482.
4) E. F. Möller: Ber., 85, 76 (1949).
5) D, L. Cramer, M. C. Dodd: J. Bacteriol., **51**, 119 (1947); **51**, 293 (1947).
6) R. C. Bender, H. E. Paul: J. Biol. Chem., **191**, 217 (1951).
7) T. Sasaki: This Bulletin, **2**, 104 (1954).
8) Affonson, Khoana: Indian. J. Pharm., **14**, 3 (1952).
9) J. Carrar: J. Am. Chem. Soc., **76**, 4391 (1954).

in the presence of piperidinum acetate or piperidinum 2-(5-nitro)furoate as a catalyst.[10] This reaction may be shown as follows:

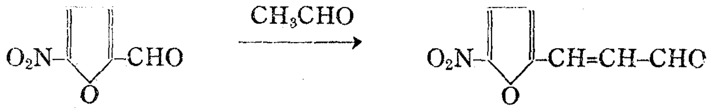
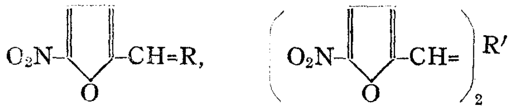
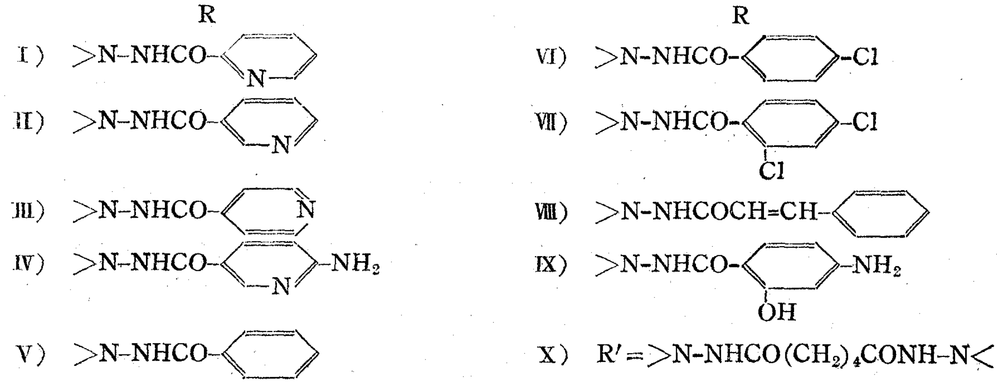


Table I gives the condensation products in the two types, 2-(5-nitro)furfurylidene and 2-(5-nitro)furylacrylidene.

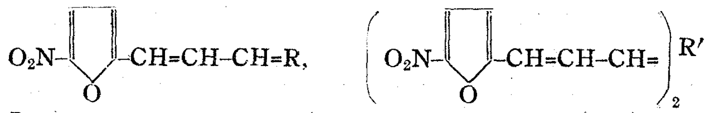
TABLE I.

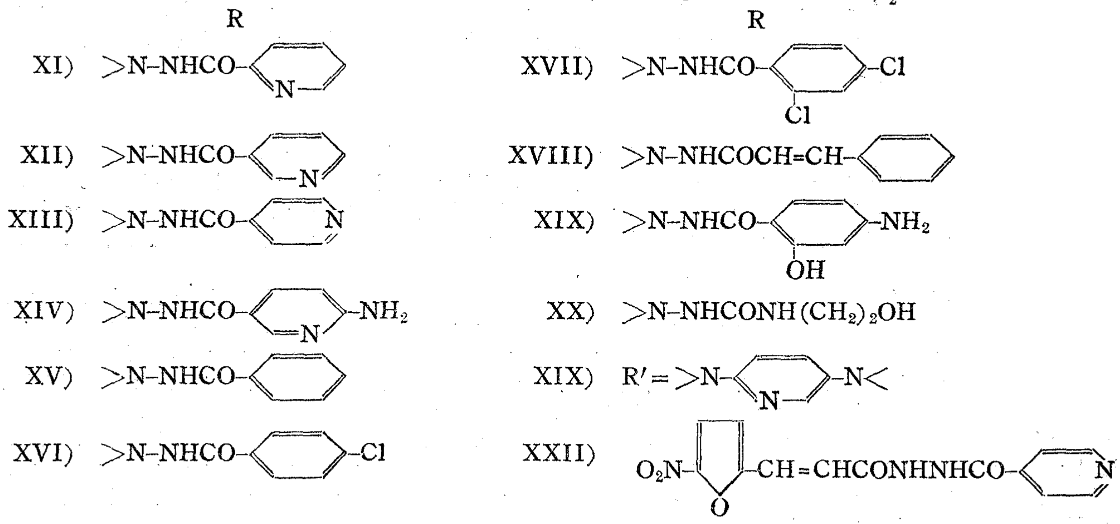
2-(5-Nitro)furfurylidene Type





2-(5-Nitro)furylacrylidene Type





The data of antibacterial activity of each compound are listed in Table II.

TABLE II. Maximum Bacteriostatic Dilution (Unit: 10,000)

Compound	*Mycobact. tuberc.**	*Staph. aureus*	*Vibrio cholerae*	*E. coli*
I	32	8	16	8
II	8	8	8	4
III	64	1	4	4
IV	< 1	2	4	2

10) H. Saikachi, R. Kimura: J. Pharm. Soc. Japan, **73**, 716(1953).

V	—	2	8	4
VI	—	1	2	< 1
VII	—	4	8	< 1
VIII	—	1	1	< 1
IX	—	4	2	2
X	—	< 1	< 1	< 1
XI	32	4	128	64
XII	2	16	64	16
XIII	128	8	32	16
XIV	8	16	64	16
XV	—	64	64	64
XVI	—	32	8	4
XVII	—	8	8	1
XVIII	—	8	8	8
XIX	—	4	8	4
XX	8	4	32	16
XXI	—	< 1	< 1	< 1
XXII	8	2	16	4
Streptomycin	—	128	8	32

* Aoyama B-strain; time of incubation, 4 weeks; culture medium, Kirchner's.

These compounds all have a broad spectrum of activities as can be seen from Table II.

The present work showed that the introduction of a double bond between the primary amines (auxo-antibacterial group) and 2-(5-nitro)furfurylidene group causes a marked increase of the bactericidal activity in this series.

As was shown previously, the hypothesis[1] proposed as being convenient in finding an excellent antibacterial compound in this field is gradually becoming likely to be true on the basis of many experimental facts obtained to date.

The authors thank Mr. M. Hirosawa, Mitsubishi Chemical Ind. Ltd., and Dr. S. Kato for contributing the many important intermediates for this research, and are indebted to Mr. T. Hattori for the microanalyses. The authors are grateful to Professor Dr. T. Toda, University of Kyushu, for the microbiological test. This study was supported by a Grant from the Ministry of Education.

Experimental

Ethyl 6-Aminonicotinate—Two g. of 6-aminonicotinic acid was refluxed with 4.5 g. of abs. EtOH and conc. H_2SO_4 for 3 hrs. After completion of this reaction, the reaction mixture was poured into ice water, the aq. solution was made carefully alkaline, and colorless crystals deposited from the solution. Recrystallization from EtOH gave colorless prisms, m.p. 155°; yield, 1.5 g. *Anal.* Calcd. for $C_8H_{10}O_2N_2$: N, 16.89. Found: N, 17.16.

6-Aminonicotinic Acid Hydrazide—The solution of 0.22 g. of ethyl 6-aminonicotinate and 0.7 g of $NH_2NH_2 \cdot H_2O$ in 10 cc. of abs. EtOH was heated under reflux for 3 hrs. On cooling the reaction mixture, colorless crystals deposited which were filtered by suction, and recrystallized from EtOH to 0.3 g. of the hydrazide, m.p. 225°. *Anal.* Calcd. for $C_6H_8ON_4$: N, 36.76. Found: N, 36.63.

2,4-Dichlorobenzoic Acid Hydrazide—Ethyl 2,4-dichlorobenzoate (b.p_2 108~112°) was prepared by the esterification with abs. EtOH and conc. H_2SO_4 in usual manner. The solution of 2 g. of ethyl 2,4-dichlorobenzoate and 0.8 g. of $NH_2NH_2 \cdot H_2O$ was heated at the reflux temperature for 6 hrs. on a water bath, and the colorless crystals deposited after cooling were filtered and dried in the air. Recrystallization from EtOAc yielded 1.1 g., m.p. 158~161°.[11]

4-Chlorobenzoic Acid Hydrazide—This compound was obtained by the condensation of ethyl 4-chlorobenzoate (b.$p_{2.5}$ 85~91°) with 0.5 g. of $NH_2NH_2 \cdot H_2O$ by the same procedure as above. Recrystallization from EtOAc gave colorless needles, m.p. 161~163°.[12]

Cinnamic Acid Hydrazide—A solution of 1.7 g. of ethyl cinnamate (b.p. 85~91°) and 0.25 g. of $NH_2NH_2 \cdot H_2O$ in 10 cc. of abs. EtOH, was heated by the Werger process in a sealed tube at 130~140° for 8 hrs. After pouring into ice water, an oily viscous matter separated and gardually solidified as an apparently resinous matter. Recrystallization from EtOAc gave 0.42 g. of colorless solid,

11) Ann., **227**, 77(1885).
12) Kahl: Chem. Zentr., **1904**, II, 1493.

m.p. 99~101°.[13]

Adipic Acid Hydrazide—A mixture of 3 g. of diethyl adipate (b.p. 110~120°) and 2.3 g. of NH_2-NH_2·H_2O was heated at reflux temperature in an oil bath for 4 hrs. After cooling, the crystals deposited from the dark brown reaction mixture were filtered by suction. Recrystallization of this product from EtOAc gave 3.2 g. of colorless needles, m.p. 179~180°.[14]

***p*-Aminosalicylic Acid Hydrazide**—The heating of a mixture of 4.7 g. of methyl *p*-aminosalicylate (m.p. 122°) and 3.6 g. of NH_2NH_2·H_2O at a reflux temperature for 8 hrs. gave a dark crystalline product. Recrystallized three times from EtOH to 3 g. of colorless needles, m.p. 198~200°.[15]

2-(5-Nitro)furfurylidenepicolinoylhydrazine (I)—After heating MeOH solution of 0.2 g. of picolic acid hydrazide and 0.2 g. of 2-(5-nitro)furfural on a water bath for a few mins., yellow crystalline mass deposited from the reaction mixture. The precipitate was filtered after being cooled. The crude substance was recrystallized from MeOH, yielded 0.17 g. of yellow needles, m.p. 256~267°(decomp.). *Anal.* Calcd. for $C_{11}H_8O_4N_4$: N, 21,53. Found: N, 21.64.

2-(5-Nitro)furfurylidenenicotinoylhydrazine (II)—Condensation of 0.2 g. of nicotinic acid hydrazide with 0.18 g. of 2-(5-nitro)furfural in 100 cc. of MeOH was accomplished by heating on the water bath for 20 mins. After cooling, a pale yellow crystalline fraction gradually deposited from the reaction mixture. Recrystallization from MeOH gave 0.5 g. of bright yellow needles, m.p. 226~232° (decomp.). *Anal.* Calcd. for $C_{11}H_8O_4N_4$: N, 21.53. Found: N, 21.72.

2-(5-Nitro)furfurylideneisonicotinoylhydrazine (III)—MeOH solution of 0.5 g. of isonicotinic acid hydrazide (m.p. 178°) and 0.43 g. of 2-(5-nitro)furfural was gently heated on a water bath for about 10 mins. A pale yellow crystalline precipitate separated on chilling. The analytical sample, yellow prisms, m.p. 214~225°(decomp.), was prepared by recrystallization from a mixture of MeOH and EtOAc. *Anal.* Calcd. for $C_{11}H_8O_4N_4$: N, 21.53. Found: N, 71.84.

1-(2-(5-Nitro)furfurylidene)-2-(6-amino-3-pyridoyl)hydrazine (IV)—A mixture of 0.11 g. of 6-aminopyridine-3-carboxylic acid hydrazide (m.p. 225°) and 0.2 g. of 2-(5-nitro)furfural was dissolved in 10 cc. of MeOH and gently heated to 60° on a water bath and kept at that temperature for about 10 mins. After cooling to the room temperature, canary yellow mass was collected by filtration. For analysis, the product was recrystallized from MeOH, yielding 0.24 g. of canary yellow prisms, m.p. 268~269°(decomp.). *Anal.* Calcd. for $C_{11}H_9O_4N_5$: N, 25.41. Found: N, 25.78.

2-(5-Nitro)furfurylidenebenzoylhydrazine (V)—A solution of 2.8 g. of benzoic acid hydrazide (m.p. 114°) and 2.8 g. of 2-(5-nitro)furfural in 15 cc. of MeOH was heated at 60° for a few mins. After cooling, a pale yellow crystalline mass deposited from the reaction mixture and filterered off. After removal of EtOAc in a vacuum desiccator, this compound was recrystallized from a mixture (1:3) of pyridine and water, washed with ether again until free from pyridine, and yielded 2.1 g. of pale yellow prisms, m.p. 218~220°(decomp.). *Anal.* Calcd. for $C_{12}H_9O_4N_3$: N, 16.22. Found: N, 16.04.

2-(5-Nitro)furfurylidene-*p*-chlorobenzoylhydrazine (VI)—A solution of 3.4 g. of *p*-chlorobenzoic acid hydrazide (m.p. 161~165°) and 2.8 g. of 2-(5-nitro)furfural in 100 cc. of MeOH was heated under reflux for a few mins. and then a yellow mass precipitated from the solution. Recrystallization of the crude mass from a mixture of H_2O and EtOH (1:3) gave 2.2 g. of yellow needles, m.p. 216~219° (decomp.). *Anal.* Calcd. for $C_{12}H_8O_4N_3Cl$: N, 14.31. Found: N, 14.10.

2-(5-Nitro)furfurylidene-2,4-dichlorobenzoylhydrazine (VII)—To 2.0 g. of 2,4-dichlorobenzoic acid hydrazide (m.p. 158~162°) in 10 cc. of EtOAc, a solution of 1.4 g. of 2-(5-nitro)furfural in 10 cc. of EtOH was added, the mixture was refluxed for 15 mins, and filtered. Recrystallization from EtOAc produced 1.7 g. of yellow prisms, m.p. 206°(decomp.). *Anal.* Calcd. for $C_{12}H_7O_4N_3Cl_2$: N, 12.80. Found: N, 12.63.

2-(5-Nitro)furfurylidenecinnamoylhydrazine (VIII)—A solution of 1.6 g. of cinnamic acid hydrazide (m.p. 101°) in 10 cc. of EtOAc was added to 2.0 g. of 2-(5-nitro)furfural in 5 cc. of MeOH and the mixture was heated on a water bath for 20 mins. The crystalline mass separating from the reaction mixture was collected by suction, recrystallized from a mixture of pyridine and water, and then carefully washed with ether until free from pyridine. Yield, 1.0 g. of yellow prisms, m.p. 217°. *Anal.* Calcd. for $C_{14}H_{11}O_4N_3$: N, 14.74. Found: N, 14.37.

2-(5-Nitro)furfurylidene-*p*-aminosalicyloylhydrazine (IX)—A solution of 3.4 g. of *p*-aminosalycylic acid hydrazide (m.p. 198~200°) and 2.8 g. of 2-(5-nitro)furfural in 15 cc. of EtOH was warmed moderately on a water bath for 20 mins. The reaction mixture was allowed to stand at 10° for 1 hr., when a pale yellow crystalline mass gradually deposited. The mass was collected by suction and recrystallized from a mixture of pyridine and H_2O in the presence of activated charcoal. Yield, 0.7 g. of orange needles, m.p. 237°(decomp.). *Anal.* Calcd. for $C_{12}H_{10}O_5N_4$: N, 19.31. Found: N, 18.89.

13) Muckermann: Ber., **42**, 3452(1909).
14) Bouveault, Locquin: Bull. soc. chim. France, **3**, 439.
15) D. T. Drain: J. Chem. Soc., **1949**, 1498; C. A., **42**, 573(1950).

Bis[2-(5-Nitro)furfurylidene]adipoylhydrazine (X)—A solution of 1.74 g. of adipoylhydrazine and 3.5 g. of 2-(5-nitro)furfural in 200 cc. of EtOH was refluxed on a water bath for 20 mins. and a brown precipitate deposited. Recrystallization from a mixture of pyridine and water yielded 1.5 g. of yellowish brown needles, m.p. 216~218°(decomp.). *Anal.* Calcd. for $C_{16}H_{16}O_8N_6$: N, 20.00. Found: N, 19.89.

2-(5-Nitro)furylacrylidenepicolinoylhydrazine (XI)—To a warm solution of 0.24 g. of picolinic acid hydrazide in 10 cc. of MeOH, solution of 0.24 g. of 2-(5-nitro)furylacrolein was added. On heating this solution at 40° on a water bath for 30 mins., a yellow colored crystalline mass deposited from the reaction mixture. The crude mass obtained was collected by suction and recrystallization from MeOH yielded 0.17 g. of yellowish orange prisms, m.p. 246~260° (decomp.). *Anal.* Calcd. for $C_{13}H_{10}O_4N_4$: N, 19.85. Found: N, 19.58.

2-(5-Nitro)furylacrylidenenicotinic Acid Hydrazide (XII)—A solution of 0.6 g. of nicotinic acid hydrazide and 0.2 g. of 2-(5-nitro)furylacrolein in 20 cc. of MeOH was gently heated at 70° on a water bath for 20 mins. The resultant dark brown solution was cooled in an ice box for 30 mins. A yellowish brown crystalline mass obtained was collected by suction and recrystallization from MeOH gave 0.12 g. of yellow needles, m.p. 213°(decomp.). *Anal.* Calcd. for $C_{13}H_{10}O_4N_4$: N, 19.85. Found: N, 19.92.

1-[2-(5-Nitro)furylacrylidene]-2-isonicotinoylhydrazine (XIII)—A solution of 0.4 g. of 2-(5-nitro)furylacrolein in 20 cc. of MeOH was added to 1.2 g. of isonicotinic acid hydrazide in 10 cc. of MeOH and a yellow precipitate formed gradually. The reaction mixture was heated further on a water bath, cooled, and filtered. Recrystallization of the crude mass from MeOH yielded 1.7 g. yellow (or canary) prisms, m.p. 235~240°(decomp.). *Anal.* Calcd. for $C_{13}H_{10}O_4N_4$: N, 19.85. Found: N, 20.01.

1-[2-(5-Nitro)furylacrylidene]-2-(6-amino-3-pyridoyl)hydrazine (XIV)—A solution of 0.2 g. 6-aminopyridine-3-carboxylic acid hydrazide and 0.23 g. of 2-(5-nitro)furylacrolein in 30 cc. of MeOH was heated moderately at 50° on a water bath for 20 mins. After cooling to the room temperature, a yellow precipitate collected by suction was recrystallized from EtOAc, giving 0.28 g. of yellowish brown prisms, m.p. 250~255°(decomp.). *Aual.* Calcd. for $C_{13}H_{11}O_4N_5$: N, 23.25. Found: N, 23.57.

1-[2-(5-Nitro)furylacrylidene]-2-benzoylhydrazine (XV)—To a solution of 1.4 g. of benzoyl hydrazine in 15 cc. of EtOAc, 1.8 g. of 2-(5-nitro)furylacrolein in 10 cc. of hot EtOH was added. The solution was carefully heated at 40° on a water bath for 20 mins., cooled, and the acrystalline mass obtained was filtered by suction. Recrystallization from MeOH gave 0.9 g. of reddish brown prisms, m.p. 224~245°(decomp.). *Anal.* Calcd. for $C_{14}H_{11}O_4N_3$: N, 14.80. Found: N, 14.75.

1-[2-(5-Nitro)furfurylidene]-2-(*p*-chlorobenzoyl)hydrazine (XVI)—To a solution of 1.4 g. of *p*-chlorobenzoic acid hydrazide in 20 cc. of EtOAc, 1.8 g. of 2-(5-nitro)furylacrolein was added. The mixture was gently heated at 60° on a water bath for 30 mins., cooled to the room temperature, and the crystalline mass was collected. Recrystallization from hydrated MeOH gave 0.8 g. of canary yellow prisms, m.p. 232°(decomp.). *Anal.* Calcd. for $C_{14}H_{10}O_4N_3Cl$: N, 13.04. Found: N, 14.75.

1-[2-(5-Nitro)furylacrylidene]-2-(2,4-dichlorobenzoyl)hydrazine (XVII)—A solution of 20 cc. of EtOAc containing 2.1 g. of 2,4-dichlorobenzoic acid hydrazide and 1.8 g. of 2-(5-nitro)furylacrolein was treated under reflux on the water bath for 30 mins. A yellow crystalline deposit was collected and recrystallized from a solution of pyridine and water. This procedure resulted in yield of 1.2 g. of pale yellow prisms, m.p. 203°(decomp.). *Anal.* Calcd. for $C_{14}H_9O_4N_3Cl_2$: N, 12,10. Found: N, 11.86.

1-[2-(5-Nitro)furylacrylidene]-2-cinnamoylhydrazine (XVIII)—A solution of 1.7 g. of cinnamoylhydrazine and 1.8 g. of 2-(5-nitro)furylacrolein in 20 cc. of MeOH was warmed at 40° on a water bath for 20 mins. A yellow precipitate gradually formed in the brown reaction mixture and this was collected by suction. Recrystallization of the crude precipitate from EtOAc gave 1.3 g. of glossy red prisms, m.p. 176~178°(decomp.). *Anal.* Calcd. for $C_{16}H_{13}O_4N_3$: N, 13.50. Found: N, 13.38.

1-[2-(5-Nitro)furylacrylidene]-2-(*p*-aminosalicyloyl)hydrazine (XIX)—A solution of 30 cc. of MeOH containing 1.7 g. of *p*-aminosalicylic acid hydrazide and 1.8 g. of 2-(5-nitro)furylacrolein was heated at 50° on a water bath for 30 mins. After cooling at the room temperature, a precipitate obtained was filtered by suction and recrystallized from hydrous pyridine (1:3). This procedure gave 1 g. of reddish prisms, m.p. 300°(decomp.). *Anal.* Calcd. for $C_{14}H_{12}O_5N_4$: N, 17.72. Found: N, 18.16.

1-[2-(5-Nitro)furylacrylidene]-4-(β-hydroxyethyl)semicarbazide (XX)—A solution of 0.1 g. of 4-(β-hydroxyethyl)acetone semicarbazone (m.p. 95°) and 0.1 g. of 2-(5-nitro)furylacrolein in 20 cc. of EtOH was heated under reflux on a water bath for 30 mins. Ethanol was distilled off from the reaction mixture under a reduced pressure to some extent, the residue cooled in ice water, and the crystlline mass obtained was filtered by suction. Recrystallization of the crude mass from MeOH gave 0.05 g. of brown prisms, m.p. 115°. This compound was fairly soluble in water at a room temperature. *Anal.* Calcd. for $C_{10}H_{12}O_5N_4$: N, 20.89. Found: N, 21.01.

Bis[2-(5-Nitro)furylacrylidene]-2,5-diaminopyridine (XXI)—To a solution of 0.2 g. of 2,5-diaminopyridine in 20 cc. of EtOH, 0.3 g. of 2-(5-nitro)furylacrolein was added and this solution was boiled on a water bath for 40 mins. After cooling the resulting solution, the red precipitate that

formed in the reaction mixture was filtered by suction. Recrystallization from MeOH gave 0.3 g. of deep red needles, m.p. >320°. *Anal.* Calcd. for $C_{19}H_{13}O_6N_5$: N, 17.80. Found: N, 17.90.

1-[2-(5-Nitro)furylacryloyl]-2-isonicotinoylhydrazine (XXII)—A solution of 0.55 g. of isonicotinic acid hydrazide (m.p. 178°) and 0.75 g. of 2-(5-nitro)furylacryloyl chloride (m.p. 92~94°) in 5 cc. of pyridine was gently heated on a water bath for 30 mins. After cooling to the room temperature, the reaction mixture was poured into ice water, the pale yellow mass that formed from the reaction mixture was filtered by suction, and washed with cold water. Recrystallization from hydrous pyridine or dilution of MeOH solution with some water gave 0.4 g. of light yellow crystals, m.p. 218°(decomp.). *Anal.* Calcd. for $C_{13}H_{10}O_5N_4$: N, 17.98. Found: 17.46.

Summary

Twenty-two new nitrofuran derivatives were prepared by the condensation of 2-(5-nitro)furfural and 1-(5-nitro)furylacrolein with hydrazides. Among these compounds, 1-[2-(5-nitro)furylacrylidene]-2-isonicotinoylhydrazine (XIII) showed an excellent bacteriostatic activity for *Mycobacterium tuberculosis*.

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38. Tyunosin Ukita, Makoto Miyazaki, and Hiroshi Watanabe: Studies on Azulenes. II.[1] Synthesis of Polybromoazulenes.

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Besides the various alkylazulenes obtainable by dehydrogenation of naturally occurring or synthetic azulenogenes, the recent progress on electrophilic substitution reactions of azulene ring offered a great possibility for synthesizing new azulenes substituted with different kinds of radicals such as acetyl, halogen, nitro, and amino groups.[2,5] However, the electrophilic substitution of the azulene ring is limited to its 1- or 3-position, and 1,3-derivatives are the only disubstituted azulenes synthesized by this procedure.

This paper describes the synthesis and properties of three new polybromoazulenes which were obtained by a new synthetic route involving no dehydrogenation reaction in the stages.

Some years before, the occurrence of one oily and three crystalline bromoazulenes was reported by Anderson, *et al.*[3] These products were separated from a mixture obtained by the dehydrobromination of reaction product from 1,2,3,4,5,6-hexahydroazulene and N-bromosuccinimide, but because of insufficient amounts of the yield, they failed to give properties of these new derivatives.

Independent of the above authors, the present writers attempted the preparation of some bromoazulenes by the bromination of 1,2,3,4,5,6,7,8-octahydroazulene with N-bromosuccinimide and by subsequent dehydrobromination with pyridine.

The starting material 1,2,3,4,5,6,7,8-octahydroazulene (I) was prepared by the Wolff-Kishner or the Clemmensen-Martin reduction of 4-oxo-1,2,3,4,5,6,7,8-octahydroazulene which is obtainable by Hückel and Schnitzspahn's method.[4] (I) was treated

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1) Part I: T. Ukita, H. Watanabe, M. Miyazaki: J. Am. Chem. Soc., **76**, 4584(1954).
2) A. G. Anderson, Jr., J. A. Nelson: *Ibid.*, **72**, 3824(1950).
3) *Ibid.*, **73**, 232 (1951).
4) W. Hückel, L. Schnitzspahn: Ann., **505**, 274(1933); see also Footnote 3.