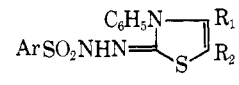
TABLE II



Compd	Ar	R_1	R_2	Mp, °C[a]	Yield, %[b]	Formula	Analysis
IIa	p-$CH_3OC_6H_4$	C_6H_5	H	180–182 dec	75	$C_{22}H_{19}N_3O_3S_2$	C, H, N, S
IIb	p-$C_2H_5OC_6H_4$	C_6H_5	H	172–173 dec	77	$C_{23}H_{21}N_3O_3S_2$	C, H, N, S
IIc	p-n-$C_3H_7OC_6H_4$	C_6H_5	H	163–164 dec	88	$C_{24}H_{23}N_3O_3S_2$	C, H, N, S
IId	p-$CH_3OC_6H_4$	Me	COOEt	181–182	72	$C_{20}H_{21}N_3O_3S_2$	N, S
IIe	p-$C_2H_5OC_6H_4$	Me	COOEt	187–188	84	$C_{21}H_{23}N_3O_3S_2$	C, H, N
IIf	p-n-$C_3H_7OC_6H_4$	Me	COOEt	194–195 dec	73	$C_{22}H_{25}N_3O_3S_2$	C, H, N, S

[a–c] See footnotes in Table I.

reported as antituberculous[5,6] and antibacterial[7] agents. Compounds Ia, Ib, Ic, and Id all gave 100% control of *Meloidogne* spp at an application rate corresponding to 29.18 kg/acre.[8] Compound Ib gave 90% control of *Puccinia sorghi* when applied sumultaneously to foliage at 500 ppm and to soil at 14.6 kg/acre.[8]

Experimental Section

1-Arylsulfonyl-4-phenylthiosemicarbazides (I).—The appropriate 1-arylsulfonylhydrazide (4 mmol) was dissolved in 95% EtOH (20 ml), followed by addition of phenyl isocyanate (5.4 g, 4 mmol). Refluxing for 30 min followed by cooling of the solution gave a white, crystalline solid that was recrystallized from MeOH or EtOH.

2-Arylsulfonylhydrazone-3-phenyl-4-thiazolines (II).—The appropriate I (5 mmol) was dissolved in DMF (25 ml), and 5 mmol of α-bromoacetophenone (1 g) or ethyl α-chloroacetoacetate (0.82 g) was added. The solution was heated 30 min on a steam bath, the dark red liquid was chilled, and 3 N NH_4OH was added to bring it to pH 8. Addition of H_2O (100 ml) gave the product as a greenish powder which was washed several times with H_2O and recrystallized from EtOH.

Acknowledgment.—We thank Dr. Juan Estevan of the University of Barcelona for elemental analyses and also the Diamond Shamrock Corp. for generous supplies of several reagents.

(5) P. C. Eisman, E. A. Konopka, T. Gisi, R. H. Mizzoni, and R. L. Meyer, *Ann. Rev. Tuberc. Pulmonary Dis.*, **77**, 703 (1958); *Chem. Abstr.*, **53**, 5494*i* (1959).

(6) R. H. Mizzoni and P. C. Eisman, *J. Amer. Chem. Soc.*, **80**, 3471 (1958).

(7) I. Ishii, M. Katagiri, M. Sakazume, and T. Misato, *Nippon Nogei Kagaku Kaishi*, **40**, 437 (1966); *Chem. Abstr.*, **66**, 9270w (1967).

(8) Personal communication from Mr. Norman M. Pollack, Diamond Shamrock Corp.

An Aminopyrimidine Steroid[1]

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Thus far, only two steroids where ring A is a pyrimidine ring capable of tautomeric forms have been reported.[3] This work describes the first amino analog of this type.

Experimental Section[4]

17β-Acetoxy-2,4-diaza-1-hydroxy-3-methylamino-1,3,5(10)-estratriene.—A solution of 50 mg of methyl 17β-acetoxy-1,5-seco-2,3,4-trisnorestran-5-on-1-oate,[3,5] 100 mg of methylguanidine sulfate, and 150 mg of anhydrous NaOAc in 5 ml of anhydrous EtOH was refluxed 96 hr. The steroids were recovered from the H_2O-diluted mixture with $CHCl_3$, then dissolved in 2 ml of glacial HOAc and refluxed for 16 hr. The material was again recovered with $CHCl_3$ after H_2O dilution of the reaction. Chromatography of the resultant mixture of starting material and product on a silica tlc plate (50% EtOAc–$CHCl_3$) gave 16 mg of product. Recrystallization from EtOAc gave pure material, mp 290 dec; ν_{max} 3460, 3340, 3230, 1720, 1635, 1610, 1570, 1515 cm^{-1}; λ_{max} 234, 290 mμ; λ_{max} (acid) 230, 261 mμ. *Anal.* ($C_{19}H_{27}N_3O_3$) N.

(3) D. M. Piatak and E. Caspi, *Steroids*, **3**, 631 (1964); E. Caspi and D. M. Piatak, *Experientia*, **19**, 465 (1963).

(4) Melting points are corrected. When analyses are indicated by the symbol for the element, analytical results obtained for those elements were within ±0.4% of the theoretical values. Uv spectra were taken in MeOH or MeOH with 2 N HCl added (0.1 ml/5 ml).

(5) E. Caspi, P. K. Grover, D. M. Piatak, and Y. Shimizu, *J. Chem. Soc.*, 3052 (1965).

Antituberculous Schiff Bases

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Schiff's bases formed by the condensation of isoniazide [I] with various benzaldehydes are reported to possess antituberculous activity.[1] We have prepared additional Schiff's bases (benzylideneisonicotinoyl hydrazones) which were tested for antituberculous activity by the technique of Doub and Youmans.[2]

Experimental Section

Preparation of Schiff's bases.—Isoniazide (1 g) was dissolved in EtOH (30 ml) and to it was added aldehyde[3] (1.3 g) in 20 ml of EtOH. The mixture was refluxed on a steam bath. In some cases, the compound separated while hot, in others on cooling or on dilution with H_2O. Most of the compounds were pale yellow and crystallized from EtOH.

(1) This work was supported by Public Health Service Grants A-5326 and CA-07137 and Niv Deans Fund.

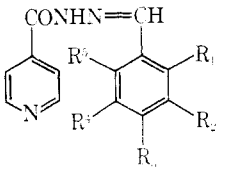
(2) Recipient of Career Program Award CA-K3-16614 from the National Cancer Institute.

(1) M. Negwer, "Organisch-Chemische, Arzneimittel und ihre Synonyma," Akademie Verlag, Berlin, 1959, pp 199–200.

(2) L. Doub and G. P. Youmans, *Amer. Rev. Tuberc.*, **61**, 407 (1950).

(3) S. R. Agrawal, V. B. Desai, H. C. Kaushik, M. S. Khan, and J. R. Merchant, *J. Indian Chem. Soc.*, **39**, 759 (1962).

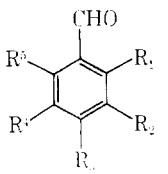
TABLE I



Compd	Aldehyde R1	R2	R3	R4	R5	Time of reflux, hr	Mp, °C	% yield	Formula[d]	Antituberculous[e] act., μg/ml. lowest inhibiting concn
1	CH_3	H	OH	H	CH_3	2	265	55[a]	$C_{15}H_{15}N_3O_2$	0.1
2	CH_3	CH_3	OH	H	H	0.5	262	73[b]	$C_{15}H_{15}N_3O_2 \cdot H_2O$	0.2
3	OH	CH_3	CH_3	H	H	5	187–188	42[c]	$C_{15}H_{15}N_3O_2 \cdot H_2O$	0.1
4	CH_3	H	CH_3	H	OH	5	233–234	42[c]	$C_{15}H_{15}N_3O_2$	0.2
5	OH	CH_3	H	H	CH_3	5	240–242	55[c]	$C_{15}H_{15}N_3O_2$	0.1
6	CH_3	H	OH	CH_3	H	2	249–250	70[c]	$C_{15}H_{15}N_3O_2$	0.2
7	CH_3	OH	CH_3	H	H	2	278–280	69[c]	$C_{15}H_{15}N_3O_2$	0.1
8	H	CH_3	OH	CH_3	H	2	286–288	42[c]	$C_{15}H_{15}N_3O_2$	10
9	OH	H	H	CH_3	CH_3	17	209–210	33[c]	$C_{15}H_{15}N_3O_2 \cdot H_2O$	0.2
10	OH	CH_3	H	CH_3	H	16	180–181	30[c]	$C_{15}H_{15}N_3O_2 \cdot H_2O$	0.2
11	CH_3	CH_3	OCH_3	H	H	6	221–222	85[c]	$C_{16}H_{17}N_3O_2 \cdot H_2O$	Not tested
12	CH_3	CH_3	OC_2H_5	H	H	6	258–259	38[c]	$C_{17}H_{19}N_3O_2$	Not tested
13	OCH_3	H	CH_3	CH_3	H	18	218–219	50[b]	$C_{16}H_{17}N_3O_2$	0.1
14	OC_2H_5	H	CH_3	CH_3	H	14	215–216	75[b]	$C_{17}H_{19}N_3O_2$	0.2
15	CH_3	H	OCH_3	H	CH_3	10	195–196	85[b]	$C_{16}H_{17}N_3O_2 \cdot H_2O$	0.2
16	CH_3	H	OC_2H_5	H	CH_3	2	195–196	98[a]	$C_{17}H_{19}N_3O_2$	0.2
17	CH_3	H	OCH_3	CH_3	H	7	203–204	65[b]	$C_{16}H_{17}N_3O_2$	0.4
18	CH_3	H	OC_2H_5	CH_3	H	7	196–197	56[b]	$C_{17}H_{19}N_3O_2 \cdot H_2O$	0.1
19	CH_3	OCH_3	CH_3	H	H	17	211–212	21[c]	$C_{16}H_{17}N_3O_2$	Not tested
20	H	CH_3	OCH_3	CH_3	H	10	219–220	26[b]	$C_{16}H_{17}N_3O_2 \cdot H_2O$	0.1
21	H	CH_3	OC_2H_5	CH_3	H	7	178–179	62[b]	$C_{17}H_{19}N_3O_2 \cdot H_2O$	0.1

[a] The compound separated from the hot solution. [b] The compound separated on cooling. [c] The compound separated on diluting (H_2O). [d] All compounds were analyzed for C, H, and N. [e] *M. tuberculosis in vitro*.[2]

TABLE II[a]



Sr. No.	Aldehyde R1	R2	R3	R4	R5	% yield	Mp of 2,4-DNP, °C[b]	Formula[c]
1	CH_3	H	CH_3	H	OCH_3	47.5	178–179	$C_{16}H_{16}N_4O_5$
2	CH_3	H	CH_3	H	OC_2H_5	45.5	219–220	$C_{17}H_{18}N_4O_5$
3	CH_3	H	OCH_3	CH_3	H	80	268–269	$C_{16}H_{16}N_4O_5$
4	CH_3	H	OC_2H_5	CH_3	H	82	246–247	$C_{17}H_{18}N_4O_5$
5	CH_3	OCH_3	CH_3	H	H	70	201–202	$C_{16}H_{16}N_4O_5$
6	CH_3	OC_2H_5	CH_3	H	H	65	230–231	$C_{17}H_{18}N_4O_5$
7	OCH_3	CH_3	H	CH_3	H	70	194–195	$C_{16}H_{16}N_4O_5$
8	OC_2H_5	CH_3	H	CH_3	H	73	162–163	$C_{17}H_{18}N_4O_5$
9	OCH_3	H	H	CH_3	CH_3	55	222–223	$C_{16}H_{16}N_4O_5$
10	OC_2H_5	H	H	CH_3	CH_3	50	225–226	$C_{17}H_{18}N_4O_5$
11	OCH_3	CH_3	H	H	CH_3	60	255–256	$C_{16}H_{16}N_4O_5$
12	OC_2H_5	CH_3	H	H	CH_3	45	236–237	$C_{17}H_{18}N_4O_5$
13	H	CH_3	OCH_3	CH_3	H	80	225–226	$C_{16}H_{16}N_4O_5$
14	H	CH_3	OC_2H_5	CH_3	H	85	241–242	$C_{17}H_{18}N_4O_5$

[a] New compounds prepared by alkylation of the hydroxyaldehydes with alkyl halides–K_2CO_3 in acetone. [b] All compounds crystallized from AcOH except **1** (from EtOH). [c] All compounds were analyzed for C, H, and N.

Acknowledgment.—We are thankful to Dr. C. V. Deliwalla for carrying out the pharmacological testing of our compounds at the Haffkine Institute, Bombay, India, and to the Maharashtra State Industrial Research Committee for a research grant to one of us (D. S. C.). Thanks are also due to Miss J. S. Pradhan for carrying out microanalyses of the compounds.