Chatterjee method at different R.H. varied from ~33 to ~109 kJ. mol^{-1} for nitrated *m*-XF resin and from ~82 to ~114 kJ. mol^{-1} for chlorinated *m*-XF (Tables 1b and 1c). The stability as revealed from the TG has the order *m*-XF > nitrated *m*-XF > chlorinated *m*-XF.

The kinetic data calculated according to Reich[6] method from differential thermal analysis (DTA) showed that the order of degradation for all the resin samples was different at different R.H. (Table 2). The DTA thermogram for all the three resin samples at different R.H. were exothermic in nature. The DTA curves for nitrated *m*-XF resin showed a hump before the exothermic peak.

Summarising the kinetic parameters obtained from DTA and TG it is found that the E_A increased as the R.H. decreased. This might be ascribed to the relaxation time, τ, and regrouping of the molecules as explained before[3]. In absence of the detailed analysis of the volatile product and the residues to be collected at various temperatures, it is difficult to explain the detailed mode of decomposition of the resin sample studied.

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Studies on Some Thiosemicarbazones and 1,3,4-Thiadiazolines as Potential Antitubercular and Antibacterial Agents

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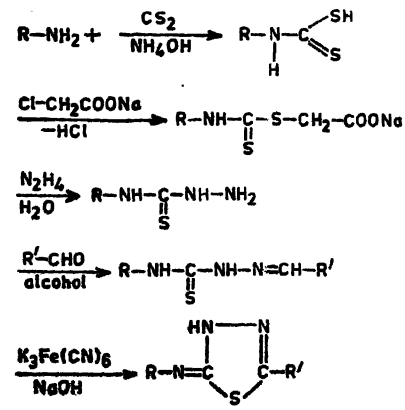
THE discovery of tibione [*p*-acetamino benzaldehyde thiosemicarbazone][1] as a reputed clinically active tuberculostat brought to fore-front thiosemicarbazones[2] as a group of antitubercular agents.

Thiosemicarbazide has been prepared by following the method of Kozokov and Vostovskii[3]. The initial amine was treated successively with carbon disulfide, sodium chloroacetate and hydrazine hydrate to get the thiosemicarbazide on cooling. This thiosemicarbazide was then condensed with different aromatic aldehydes to furnish thiosemicarbazones which have been cyclised by alkaline $K_3[Fe(CN)_6]$ in alcohol.



1,3,4-thiadiazolines

Experimental

2,6-Xylidene (0.1 mole) was dissolved in ethanol (95% ; 50 ml) and NH_4OH (20 ml) was added to it. The reaction mixture cooled below 30° and carbon disulfide (8 ml) added slowly during 15 min with shaking. After complete addition of CS_2 the solution was allowed to stand for 1 hr. Sodium chloroacetate (0.1 mole) was added to it. During this addition the reaction mixture usually got warm and changed colour from red to yellowish green. To it 50% of hydrazine hydrate (20 ml) was added. The mixture was warmed gently, filtered and boiled to half of its volume and kept overnight. Next day, the product thiosemicarbazide is filtered, recrystallised from ethanol (95%) ; m.p. 205° (m.p. reported 204°)[4].

(a) *Thiosemicarbazones :* To a boiling solution of an aromatic aldehyde (0.01 mole) in ethanol (95% ; 50 ml), the thiosemicarbazide (0.01 mole) in ethanol was added and the mixture refluxed for 2 hr on a water bath. It was cooled and recrystallised from ethanol (95%).

(b) *1,3,4-Thiadiazolines :* Thiosemicarbazone in ethanol (95% ; 50 ml) and NaOH with a little water (solution) was warmed on a water bath and a solution of potassium ferricyanide (5%) was added dropwise until precipitation took place. The contents were warmed for 5 min, cooled and filtered. The product so obtained was washed with hot water to remove excess $K_3[Fe(CN)_6]$, crystallised from ethanol or methanol. The data of these compounds (a) and (b) are recorded in Tables 1 and 2.

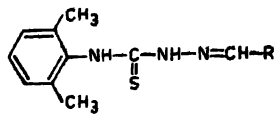
Pharmacological screening :

These thiosemicarbazones and 1,3,4-thiadiazolines were screened for antitubercular and antibacterial activity.

Tuberculostatic activity :

In vitro antitubercular activity of the synthesised compounds were studied against $H_{37}R_v$ strain of

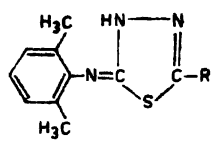
TABLE 1—THIOSEMICARBAZONES OF TYPE



Sl. No.	R	m.p. °C	Antitubercular activity at 25.0 μg/ml
1.	$-C_6H_5$	175	—
2.	$-2-OH-C_6H_4$	165	—
3.	$-5-Br-2-OH-C_6H_3$	158	—
4.	$3,5-diBr-2-OH-C_6H_3$	180	—
5.	$-2-Cl-C_6H_4$	219	—
6.	$-4-OCH_3-C_6H_7$	146	—
7.	$-3-NO_2-C_6H_4$	161	—
8.	$-4-NO_2-C_6H_4$	220	—
9.	$-C_4H_3O$	216	—
10.	$-4-N(CH_3)_2-C_6H_4$	179	—

All the compounds gave satisfactory C, H, N, S analysis.

TABLE 2—1,3,4-THIADIAZOLINES OF TYPE



Sl. No.	R	m.p. °C
1.	$-C_6H_5$	218
2.	$-2-OH-C_6H_4$	200
3.	$-5-Br-2-OH-C_6H_3$	178
4.	$-3,5-diBr-2-OH-C_6H_3$	above 360
5.	$-2-Cl-C_6H_4$	238
6.	$-4-OCH_3-C_6H_4$	195
7.	$-3-NO_2-C_6H_4$	208
8.	$-4-NO_2-C_6H_4$	242
9.	$-C_4H_3O$	200
10.	$-4-N-(CH_3)_2-C_6H_4$	210

All the compounds gave satisfactory C, H, N, S analysis. The above compounds show some antibacterial activity against *E. coli* and *S. aureus*.

Mycobacterium tuberculosis in Lowenstein-Jensen egg media (4 ml) at 5.00 μg/ml and 25.00 μg/ml concentrations of the test substances (solvent-acetone). The retardation of growth has been studied upto six weeks at 37°.

(c) *Antibacterial activity :*

The antibacterial activity have been tested by nutrient agar pour plate method in DMF and the compounds are found active against *E. coli* and *S. aureus* in various concentrations.

Acknowledgement

The authors are thankful to Bhavnagar University for Junior Research Fellows to two of them (H. K. S. and N. C. D.) and to Dr. S. B. Trivedi, Director and Shri S. B. Andharia of Tuberculosis Research Centre, Amargadh, for preliminary antibacterial screening.

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Preparation and Antimicrobial Activity of Some Substituted 4-Thiazolidinones and Their Benzoyl Derivatives

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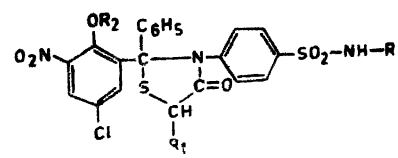
4-THIAZOLIDINONE derivatives have been found to possess wide variety of physiological properties[1-7]. With a view to prepare better therapeutic agents, we have synthesised 4-thiazolidinones of type (I) containing nitrophenol residue, by the action of thioglycollic acid, thiolactic acid or thiomalic acid on Schiff bases which were obtained by condensing 5-chloro-2-hydroxy-3-nitro-benzophenone[8] with different sulpha drugs. The structure was supported by ir spectra[9-12].



I

R=H, pyrimidyl, 4'-methylpyrimidyl-4',6'-dimethyl pyrimidyl, 2'-thiazolyl or 3,4'-dimethyl oxazolyl.
R_1=H, CH_3-CH_2COOH
R_2=H, COC_6H_5

IR spectra :

The ir spectra of 4-thiazolidinones of type (I) were taken on KBr pellets and characterised. The ν (−C=O) group frequency was obtained at 1635 cm^{-1}, ν (N−CO) at 1585 cm^{-1} ν(phenolic OH) at 341 cm^{-1} and ν ($NHSO_2$) at 1155 cm^{-1}. The reported frequencies are ν (−C=O) at 1655-1760 cm^{-1}, ν (N−CO) at 1580 cm^{-1}, ν ($NHSO_2$) at 1140-1160 cm^{-1} and ν (phenolic OH) at 300-340 cm^{-1}).

Experimental

(1) *Preparation of α-phenyl-5-chloro-2-hydroxy-3-nitro benzalanil/2-benzoate :* 5-Chloro-2-hydroxy-3-nitro benzophenone (0.01 mole) dissolved in ethanol was added to sulphanilamide (0.01 mole in ethanol) and refluxed on water bath for 6 hr. The