

tuberculosis, *in vitro*². A large number of diaryl substituted thioureas have been prepared by various workers^{3,4,5,6} so far and a good number of them were found to be active. It is interesting to find out whether, the replacement of one of the aryl rings by a para substituted quinoline ring does increase the activity or not. Quinoline ring was of interest as 8-alkoxy quinolines and aminoquinolines are generally bacteriostatic^{7,8}.

$\begin{array}{c} \text{S} \\ \parallel \\ \text{R}-\text{NH}-\text{C}-\text{NH}-\text{C}_6\text{H}_4-(p)\text{R}^1 \end{array}$				
No.	R	R ¹	M.P.*	** Activity Micrograms per ml
1	8-ethoxy-5-quinolyl	-OCH ₃	192°	40.0
2		-OC ₂ H ₅	154°	0.5
3		-OC ₄ H ₉ (n)	164°	0.5
4		-OC ₄ H ₉ (iso)	165°	2.0
5		-OC ₆ H ₁₁ (n)	170°	0.5
6		-OC ₆ H ₁₁ (iso)	176°	5.0
7		-CH ₃	198°	10.0
8		-Cl	186°	40.0
9		-N(CH ₃) ₂	193-194°	100.0
10		-H	184°	100.0
11	8-n-butoxy-5-quinolyl	-OCH ₃	170°	5.0
12		-OC ₂ H ₅	150°	0.5
13		-OC ₄ H ₉ (n)	151°	0.2
14		-OC ₄ H ₉ (iso)	160°	1.0
15		-OC ₆ H ₁₁ (n)	184°	0.5
16		-OC ₆ H ₁₁ (iso)	152°	5.0
17		-CH ₃	172°	20.0
18		-Cl	178°	40.0
19		-N(CH ₃) ₂	188°	100.0
20		-H	175°	100.0
21	8-chloro-5-quinolyl	-OCH ₃	151°	5.0
22		-OC ₂ H ₅	158°	0.5
23		-OC ₄ H ₉ (n)	165°	2.0
24		-OC ₄ H ₉ (iso)	178°	2.0
25		-OC ₆ H ₁₁ (n)	177°	0.5
26		-OC ₆ H ₁₁ (iso)	198°	10.0
27		-CH ₃	187°	40.0
28		-Cl	179°	20.0
29		-N(CH ₃) ₂	170°	100.0
30		-H	168°	100.0
31	5-chloro-8-quinolyl	-OCH ₃	177°	10.0
32		-OC ₂ H ₅	150°	0.5
33		-OC ₄ H ₉ (n)	145-146°	2.0
34		-OC ₄ H ₉ (iso)	141°	5.0
35		-OC ₆ H ₁₁ (n)	127°	0.5
36		-OC ₆ H ₁₁ (iso)	138°	5.0
37		-CH ₃	179-180°	5.0
38		-Cl	174° d	100.0
39		-N(CH ₃) ₂	163-164° d	100.0
40		-H	174°	40.0
41	6-quinolyl	-OCH ₃	146°	5.0
42		-OC ₂ H ₅	161°	0.5
43		-OC ₄ H ₉ (n)	146°	0.2
44		-OC ₄ H ₉ (iso)	139-140°	5.0
45		-OC ₆ H ₁₁ (n)	153°	0.5
46		-OC ₆ H ₁₁ (iso)	133°	2.0
47		-CH ₃	131°	2.0
48		-Cl	158-159°	5.0
49		-N(CH ₃) ₂	168°	100.0
50		-H	163°	40.0

* All the m.p.s. are uncorrected and depend on the speed of heating.

** Micrograms/ml for (i) INH=0.04
(ii) Streptomycin=1.0.

The present communication describes diaryl substituted thioureas in which, one of the aryl ring is substituted by a substituted quinoline ring. These have been prepared by refluxing the substituted aminoquinolines with different aryl isothiocyanates in ethanol. The yields range from 60-80%. All the prepared compounds are new and gave correct elemental analysis. All the compounds were tested *in vitro*. The results of the testing are expressed in minimum inhibitory concentration in micrograms/ml. Compounds having -OC₂H₅, -OC₄H₉(n) and -OC₆H₁₁(n) in para position of the phenyl ring were found to be more active.

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Solid State Studies on Polymerization and Depolymerization of Tungstate Ion with Mn(IV) as the Hetero-atom

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A new polymeric compound, Na₄[MnW₁₂O₄₀]·32H₂O, has been prepared and characterised on the basis of analytical and molecular weight determinations. The oxidation state of the central manganese(IV) ion has been established by magnetic and e. s. r. data. The thermal depolymerization of the compound has been studied extensively in solid state.

25 grams of sodium tungstate in water (200 ml) was heated to 90° and a mixed solution of manganese(II) sulphate (5 g.) in water (50 ml) and

sodium peroxodisulphate (7 g.) in water (100 ml) was added dropwise, with vigorous stirring. To the resulting solution, acetic acid was added till pH comes just in the range of 3.7 to 4.0. The solution was boiled for an hour, left overnight and crystallised under vacuum when bright orange needle-shaped crystals of sodium 12-tungstomanganate(IV) separated which were recrystallised from hot water (Found: Na, 2.41; W, 60.99; Mn, 1.42; H, 1.85% Calcd. for $\text{Na}_4[\text{MnW}_{12}\text{O}_{40}] \cdot 32\text{H}_2\text{O}$: Na, 2.50; W, 61.14; Mn, 1.53; H, 1.85%). Hydrogen has been estimated by element estimation method and tungsten has been determined¹ by precipitating it as tungstic acid with HCl and cichonine hydrochloride, igniting it at 780° and finally weighing as WO_3 . Sodium was estimated by flame photometer and manganese was volumetrically determined by bismuthate method². From the analytical data, the molecular formula of the compound, as per Keggins' view³, comes out to be $\text{Na}_4[\text{MnW}_{12}\text{O}_{40}] \cdot 32\text{H}_2\text{O}$, which falls under the category of heteropoly compounds.

Molecular weight determinations: The cryoscopic method as has been applied successfully by Alexander⁴ and by Thilo and Kruger⁵ for molecular weight determinations of polymerised silicic acids, condensed phosphates, etc., in water and molten sodium sulphate decahydrate; has also been applied here for determination of approximate molecular weight of the compound. This determination showed the molecular weight of the polymeric compound to be 3470 as compared with the calculated value 3569.22. To know the accurate degree of polymerisation this result has been corroborated by X-ray crystal diffraction technique^{6,7} for molecular weight determination of heteropoly salts. The crystal diffraction data of the compound are $a=12.56$, $b=30.22$, $c=11.40$ and $\alpha=\beta=\gamma=90^\circ$, volume per unit cell $V=4327.02\text{\AA}^3$. The space group is established as $D_{2h}^{24}-P_{nnn}$ from the following systematic presence of reflections: $hkl=\text{no condition}$; $0kl=k+l=2n$; $h0l=1+h=2n$; $hk0=h+k=2n$; $h00=(h=2n)$; $0k0=(k=2n)$; $00l=1=2n$ and $hkl=h+k+l=2n$. The last condition gives the no. of molecules in unit cell (z) to be 2. Pycnometric measurement gives the observed density, $\rho_{\text{obs}}=2.71\text{ gml}^{-1}$. From the relation⁸, $\rho_{\text{obs}}=1.66\text{ M.Z/V}$, the molecular weight 'M' of the compound comes to 3646 against the calculated value 3569.22.

Determination of oxidation state of manganese ion: e.s.r. spectrum of heteropoly molybdomanganate and heteropoly tungstomanganate in frozen aqueous solution at 77 K have been measured. Both the compounds showed broad asymmetric signals with $g=3.8$. This is an expected value⁹ for a trigonally distorted d^5 ion. The effective magnetic moment of 12-sodium tungstomanganate(IV) was found by susceptibility measurements, the values being 3.88 B.M. at 302° and 3.89 B.M. at 77°K. Both the values are close to the spin-only for an $S=3/2$ ion, as expected⁹ for $3d^3$

system (three unpaired electrons), which definitely concludes that central heteroatom, Mn, is in +4 oxidation state.

Thermal depolymerization: The thermal depolymerization of the compound has been studied in the light of the investigations made by West and Audieth⁹ on a few heteropoly tungstic acid. Use was made of the apparatus described by Ray and Sinha¹⁰ with continuous pumping the depolymerised product, followed by successive weighing using a thermogravimetric balance and estimating at some stages. The dissociation⁹ of the compound was observed at 75° under reduced pressure when seven molecules of water was lost. At 140°, further twelve molecules of water were eliminated. The rest of water molecules remained intact in the crystal lattice till 290°, above which they were completely removed. When the temperature was raised still higher, then nearly at $480 \pm 5^\circ$, the compound was broken as a whole into the basic units of lower oxides of tungsten and manganese which have been confirmed by analysis. So the thermal stability of sodium-12-tungstomanganate(IV) is 480 ± 50 .

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Formation Constants of $\text{Ti(1)-5-Nitro Salicylates}$ and Effect of Nitro Substituent on the Formation Constants

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IN continuation to the previous work on Ti(1)-complexes of 3-Nitrosalicylic acid (3NSA)², and 3:5-Dinitrosalicylic acid (3:5 DNSA)³, the

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