

by gradually raising the temperature from 100° C. to 120° C. On working up as above the starting material was obtained back in 90% yield.

*Reduction of Methyl-2-O-mesyl-6-azido 6-deoxy -  $\alpha$  - D - glucopyranoside*<sup>8</sup>.—Methyl - 2 - O - mesyl - 6 - azido - 6 - deoxy -  $\alpha$  - D - glucopyranoside (1.5 g.) was dissolved in methanol (30 c.c.) and Raney Ni Catalyst (No. 28, 5.0 gm.) was added in two instalments during 48 hours with occasional stirring. The reaction mixture was evaporated to dryness under reduced pressure (temp. 45° C.) when the entire thing smells to a white foam which could be ground to a fine powder (m.p. 63-66° C. Yield: 1.20 gm., 92%). Found: C, 35.41; H, 6.42; N, 5.38. Calculated for methyl-2-O-mesyl-6-amino-6-deoxy- $\alpha$ -D-glucoside. C<sub>8</sub>H<sub>17</sub>O<sub>7</sub>NS, C, 35.42; H, 6.27; N, 5.16.

All attempts to crystallise this product from different solvents failed because this product was readily susceptible to aerial oxidation.

*Paper chromatography*.—Paper chromatography was carried out as before in Whatman No. 1 paper using solvent system (a) and ninhydrin solution as spray reagent. The product was revealed as a single spot with R Glycin.<sup>4,21</sup>

*Acetylation of the amino glucoside*.—Methyl-2-O-mesyl-6-amino-6-deoxy- $\alpha$ -D-glucoside (1.0 gm.) was dissolved in 10 c.c. anhydrous pyridine, cooled to 4° C. and acetic anhydride (5 c.c., cooled to 4° C.) was added with stirring and the entire thing kept at 15° C. for 24 hours. The reaction mixture was evaporated to dryness under reduced pressure (temp. 60° C.), the syrup was poured over ice chips with stirring and extracted with chloroform. The chloroform extract was washed successively with 5% hydrochloric acid solution, saturated sodium bicarbonate solution and distilled water and finally dried over sodium sulphate. The chloroform extract was then concentrated to a syrup and dried under high vacuum. Attempts to crystallise the syrup from different solvent mixtures were unsuccessful. IR spectra: No stretching for free-OH group (3400-3600 cm.<sup>-1</sup>), max. (2.2% CHCl<sub>3</sub>): 3130 cm.<sup>-1</sup> (NH), 1740 cm.<sup>-1</sup> and 1230 cm.<sup>-1</sup> (O-Ac), 1720 cm.<sup>-1</sup> (N-Ac).

We are thankful to the authorities and U.S. Department of Agriculture, Foreign Agricultural Research Service, for enabling us to carry out this piece of work under a suitable grant of P.L. 480 fund.

Carbohydrate Lab.,  
Dept. of Food Tech. and  
Biochemical Engineering,  
Jadavpur University,  
Calcutta, November 20, 1967.

S. P. DUTTA,  
A. K. MITRA.

1. Baker, Reist, Spenser and Goodman, *Chem. and Ind.*, London, 1962, p. 1794.
2. — and Haines, *J. Org. Chem.*, 1963, p. 442.
3. Cramer, Otterbach and Springmann, *Chem. Ber.*, 1959, **92**, 384.
4. Frendenberg and Hixon, *Ber.*, 1923, **56**, 2119.
5. Guthrie and Murphy, *J. Chem. Soc.*, 1963, p. 5288.
6. Hanessain and Haskell, *J. Org. Chem.*, 1963, p. 2604.
7. Mitra, Long and Ball, *Ibid.*, 1962, **27**, 1960.
8. Wolfrom, Bernsmann and Horton, *Ibid.*, 1962, p. 4505.

#### SPECIFIC RATES FOR OXIDATION OF LACTATE AND OF LACTIC ACID BY PEROXYDISULPHATE CATALYSED BY SILVER IONS

OXIDATION of lactic acid by peroxydisulphate catalysed by silver ions has been investigated by Bakore and Joshi<sup>1</sup> and also by Mishra and Ghosh.<sup>2</sup> The rate is proportional to the concentration of silver ions and of peroxydisulphate but is independent of the concentration of the lactic acid.

Mishra and Ghosh<sup>2</sup> have observed that an increase of pH increases the rate of oxidation. This suggests that the specific rates of oxidation are different for the undissociated lactic acid and for lactate ions and that the observed rate is the result of two parallel reactions:

- (i) between lactic acid, peroxydisulphate and silver ions;
- (ii) between lactate, peroxydisulphate and silver ions.

An attempt has been made to evaluate the specific rates for lactate and for lactic acid.

Lactic acid and potassium peroxydisulphate of 'Analar' specifications were used. All other chemicals used were chemically pure. The rate of consumption of peroxydisulphate was followed by the procedure used earlier.<sup>1</sup>

If ' $\alpha$ ' be the fraction of the total lactic acid present as lactate, then the fraction of the undissociated lactic acid = (1 -  $\alpha$ ). The observed rate constants, K, can be written as:

$$K = \frac{k_1}{[Ag^+]} = K'(a) + K''(1-a) = (K' - K'')a + K'' \quad (1)$$

where K' and K'' represent the specific rates for lactate and undissociated lactic acid.

The rate constants K at different values of ' $\alpha$ ' are summarised in Table I. From the data

in Table I and equation (1) the values of ( $K' - K''$ ) and  $K''$  can be obtained by the method of least squares.

TABLE I

$[S_2O_8] = 1.0 \times 10^{-2} M$      $[Ag^+] = 7.70 \times 10^{-4} M$   
Temp. = 35° C.

pH	[L <sup>-</sup> ]	[HL]	$\alpha$	$k_1 \times 10^2$ min. <sup>-1</sup>	$K = k_1 / [Ag^+]$
3.98	0.04	0.03	0.572	1.49	19.35
3.73	0.03	0.04	0.429	1.35	17.53
3.46	0.02	0.05	0.286	1.28	16.49
3.03	0.01	0.06	0.143	1.07	13.90

Calculations, show that the value of ( $K' - K''$ ) = 12.29 and  $K'' = 12.48$  litre mole<sup>-1</sup> min.<sup>-1</sup>. This gives  $K' = 24.77$  litre mole<sup>-1</sup> min.<sup>-1</sup>

This shows that the specific rate constant of lactate is nearly twice that of undissociated lactic acid.

Dept. of Chemistry,  
University of Udaipur,  
Udaipur, December 30, 1967.

S. N. JOSHI.  
G. V. BAKORE.

1. Bakore, G. V. and Joshi, S. N. *Z. Physik. Chemie.*, Leipzig, 1965, **229**, 250.
2. Mishra, D. D. and Ghosh, S., *J. Ind. Chem. Soc.*, 1964, **41**, 6.

### SOME NEW POTENTIAL ANTITUBERCULARS: BENZOTHIAZOLYL GUANIDINES

THE antimalarial activity exhibited by some substituted diguanides<sup>1</sup> stimulated the search for other therapeutically useful members of this series and in due course led to the discovery of high antibacterial activity<sup>2</sup> and antitubercular activity,<sup>3</sup> especially among a series of bis-diguanides. Biguanido derivatives<sup>3,4</sup> of diaryl sulphones and sulphides have been found to exhibit antitubercular activity against *Myco. tuberculosis* in *in vitro* tests. In order to determine the degree of molecular complexity necessary for high antimicrobial potency, the stepwise synthesis of polyguanidines was undertaken and it was seen that antitubercular activity was highest in bis-diguanides in which the terminal groups were aryl, alkyl or heterocyclic nucleus.

Recently, Bhargava *et al.*<sup>5,6</sup> have synthesised several N-aryl-N'-2-(substituted)benzothiazolyl guanidines and have shown that the hydrochlorides of these bases are more active against gram-positive bacteria as compared with the gram-negative ones. The above findings led the authors to synthesise some new

N - m - tolyl- N' - 2 - (substituted)benzothiazolyl-N''-alkyl guanidines as potential anti-tuberculars.

In the present communication, 2-amino-(substituted)benzothiazoles<sup>7,8</sup> were condensed with *m*-tolylisothiocyanate. The resulting benzothiazolylthiocarbamides<sup>9</sup> were desulphurised with yellow lead oxide and various ethanolic alkylamines to give corresponding guanidines.

#### EXPERIMENTAL

*N - m - tolyl - N' - 2 - (6-chloro)benzothiazolyl-N''-methyl guanidine.*—*N - m - tolyl - N' - 2 - (6-chloro)benzothiazolyl thiocarbamide* (3.3 g.), yellow lead oxide (4 g.), ethanolic methyl amine (20 ml.) were heated in a glass autoclave on a water-bath for 3 hours. After cooling, the autoclave was opened carefully, and the product was boiled with ethanol (60 ml.) and filtered hot. The filtrate on cooling gave beautiful crystals. It was recrystallised from ethanol.

Similarly, other *N - m - tolyl - N' - 2 - (substituted)benzothiazolyl-N''-alkyl guanidines* have been prepared using different alkylamines. The yields, melting point and analytical data of *N - m - tolyl - N' - 2 - (substituted)benzothiazolyl-N''-methyl guanidines* and *N - m - tolyl - N' - 2 - (substituted)benzothiazolyl-N''-ethyl guanidines* are listed in Tables I and II.

Besides these, the yields, melting points and analytical data of *N - m - tolyl - N' - 2 - (substituted)benzothiazolyl-N''-n-butyl guanidines* are as follows :

Substituent -X-	Yield %	M.P. °C.	Elemental analysis, %	
			Found	Calcd.
5-Chloro-	.. 85	202 N, S,	14.98	15.03
			8.44	8.59
4-Ethoxy-	.. 80	79 N, S,	14.50	14.66
			8.22	8.37

*Pharmacological screening.*—Pharmacological screening of these compounds has shown that *N - m - tolyl - N' - 2 - (6 - chloro)benzothiazolyl-N''-methyl guanidine*, *N - m - tolyl - N' - 2 - (6-chloro)benzothiazolyl-N''-ethyl guanidine* and *N - m - tolyl - N' - 2 - (5-chloro)benzothiazolyl-N''-n-butyl guanidine* are active at 100  $\mu$ g./ml. against *Myco. tuberculosis* (H<sub>37</sub>R). The antibacterial activity of the compound No. 1-12 (Table III) has also been tested against *S. typhi*, *Staph. aureus* and *comma* but the compounds were found to be inactive at 200  $\mu$ g./ml.

Thanks are due to the authorities of the Banaras Hindu University for providing necessary facilities, the authorities of Central Drug