

The use of the various substituted keto alkyl quaternary ammonium salts ( $R-CO-CH_2-N^+-N$ ) should

give different substituted derivatives of pyrrocoline quinones. This should be a general reaction for preparing such compounds. Further work in synthesising these compounds is in progress.

#### Experimental

All melting points have been determined on a Kofler instrument and are uncorrected.

*N*-Acetyl pyridinium quinolinium iodide.—These compounds are prepared and purified by the known methods<sup>1</sup>.

*Benzo-dibenz (h, h')-pyrrocoline quinones*—The following general procedure was adopted:—A mixture of chloranil (1 mole), *N*-acetyl pyridinium iodide or *N*-acetyl quinolinium iodide (1 mole) and quinoline (1 mole) in 25–30 ml ethanol was heated under reflux on a water bath for 4 hours, when all the chloranil dissolved and a deep red coloured reaction mixture was obtained. The product separated on cooling was filtered and washed with ethanol, ether, hot water and then dried. The product was recrystallised twice from pyridine. Benzo-dipyrrocoline quinones. Same procedure was adopted while using *N*-acetyl pyridinium iodide, chloranil and pyridine. The *E* and *Z* products were separated through chromatography over alumina using benzene and methanol as eluants.

#### Compounds :

(1) 7:15-diacetyl-benzo (1:2-*b*, 4:5-*b'*)-dibenz (*h, h'*) pyrrocoline quinone—m.p. does not melt upto 356° (Found : C, 76.5; H, 3.8; N, 5.9;  $C_{30}H_{18}N_2O_4$  requires C, 76.5; H, 3.8, N, 5.9%).

(2) 5:11-diacetyl-benzo (1:2-*b*, 4:5-*b'*)-dipyrrocoline quinone (*E* form)—m.p. does not melt upto 356° (Found : C, 71.1; H, 3.5; N, 7.4;  $C_{22}H_{14}N_2O_4$  requires C, 71.3; H, 3.7; N, 7.5%).

(3) 5:11-diacetyl benzo (1:2-*b*, 4:5-*b'*)-dipyrrocoline quinone (*Z* form)—m.p. does not melt upto 356° (Found: C, 71.2; H, 3.4; N, 7.3;  $C_{22}H_{14}N_2O_4$  requires: C, 71.3; H, 3.7; N, 7.5%).

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### CHEMICAL EXAMINATION OF THE LEAVES OF *GUAZUMA TOMENTOSA* KUNTH

THE presence of friedelin 3 $\beta$ -ol, friedelin 3 $\alpha$ -acetate,  $\beta$ -sitosterol besides a plant alcohol is reported from the leaves of *Guazuma tomentosa* Kunth.

*Guazuma tomentosa* Kunth (N.O. Sterculiaceae) is a moderate sized deciduous tree indigenous to tropical America and introduced into India<sup>1</sup>. The presence of kaempferol, quercetin and kaempferitrin were reported earlier from the flowers of *G. tomentosa* Kunth<sup>2</sup>. Isolation and characterisation of friedelin,  $\beta$ -sitosterol and betulin have been recently reported by us from the hexane extract of its bark<sup>3</sup>. Chemical examination of the leaves is now reported.

The air dried leaves (1.2 kg) were extracted with petroleum ether. The extract after concentration left a residue which resisted crystallisation. It was chromatographed over a column of silica gel. The first three fractions (500 ml) of the hexane eluate gave only waxes. The next two fractions gave Compound A (0.08 gm). Further elution with hexane: benzene (9:1) gave Compound B (0.1 gm), with hexane: benzene (3:1) Compound C (0.5 gm), with hexane: benzene (7:3) Compound D (1.0 gm) and further elution with hexane: benzene (1:1) and benzene did not yield any crystalline compounds.

Compound A,  $C_{32}H_{54}O_2$ , crystallised from petroleum ether-chloroform as colourless shining needles, m.p. 306–8°,  $[\alpha]_D^{30} - 14^\circ$ . It gave Liebermann Burchard test positive for triterpenes. It indicated acetoxyl group (1730 and 1250  $cm^{-1}$ ) in I.R. Compound A on hydrolysis with 5% methanolic KOH furnished a compound,  $C_{30}H_{50}O$ , m.p. 300–301° which was identified as friedelin 3 $\alpha$ -ol by direct comparison (m.m.p. and I.R.) with an authentic sample. Compound A is thus friedelin 3 $\alpha$ -acetate.

Compound B,  $C_{30}H_{50}O$ , crystallised from chloroform-petroleum ether as colourless needles, m.p. 278–279°,  $[\alpha]_D^{30} + 14^\circ$ . It answered positive LB test for triterpenes and gave an acetate, m.p. 288–289°. Compound B was characterised as friedelin 3 $\beta$ -ol by direct comparison (m.m.p. and I.R.) and through its acetate with authentic samples.

Compound C, crystallised from methanol as colourless solid, m.p. 89–90° and was found to be a plant alcohol.

Compound D,  $C_{29}H_{50}O$ , crystallised from chloroform-methanol as colourless needles, m.p. 137–138°,  $[\alpha]_D^{30} - 36.5$ . It gave positive LB test for steroids

and was identified as  $\beta$ -sitosterol by comparison with an authentic sample (m.m.p. and I.R.).

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### POTENTIOMETRIC TITRATIONS OF BENZENEDIAMINES IN NON-AQUEOUS MEDIUM

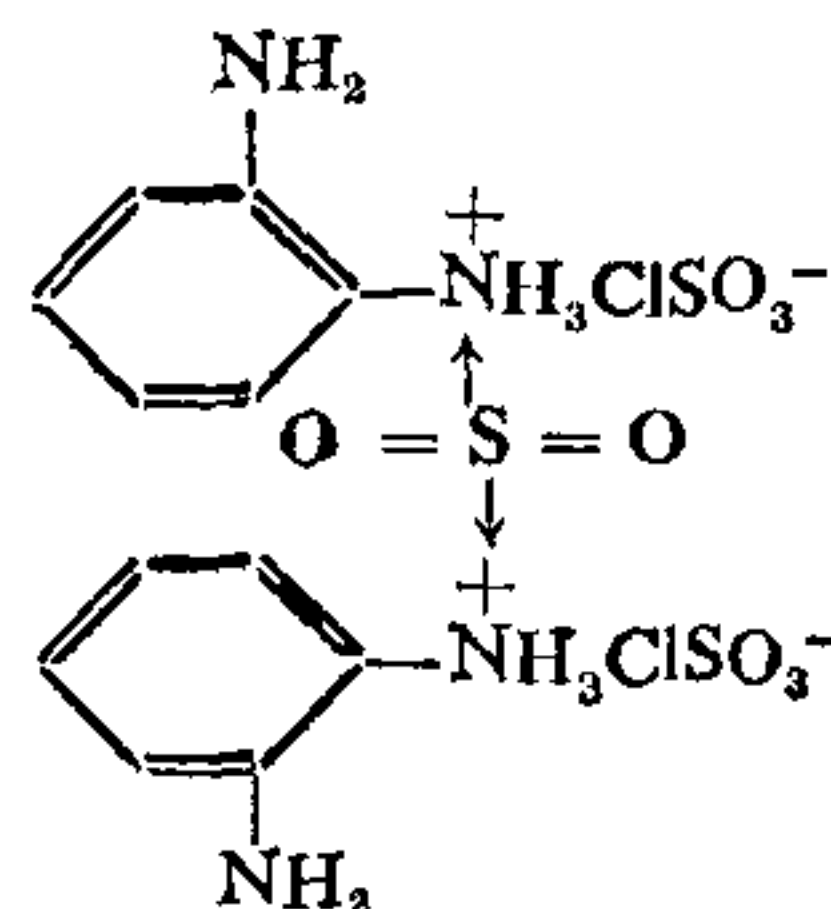
BENZENEDIAMINES were determined potentiometrically in methylethyl ketone by Kreshkov and Aldarova<sup>1</sup>. Kreshkov *et al.*<sup>2</sup> carried out differential titrations of mixtures of diamines in chloroform-methylethyl ketone medium. Both the groups employed perchloric acid as a titrant. The results reported by the former group were associated with an error of 2.6% and the error reported by the latter group was 3%. In the present investigation the isomeric benzene diamines have been determined potentiometrically in acetic acid-methylethyl ketone medium using chlorosulphonic acid as a titrant. The advantages of using chlorosulphonic acid in place of perchloric acid have been described earlier by Rao and Naidu<sup>3, 4</sup>.

Chlorosulphonic acid (BDH) was used without further purification. Acetic acid (BDH) and methylethyl ketone (BDH) were purified by the method used by Rao and Naidu<sup>3</sup>. The three benzenediamines were purified by the method recommended by Vogel<sup>5</sup>.

Approximately 1M stock solution of chlorosulphonic acid was prepared by adding 7 ml of the acid to 250 ml of chilled acetic acid. The solution was then diluted with methylethyl ketone to obtain the solution of required concentration. The acid solution was standardised potentiometrically employing anhydrous sodium carbonate as the primary standard. Weighed samples of bases were dissolved directly in the mixed solvent.

Titration of bases dissolved in 1:1 acid-ketone medium were carried out using the Elico pH meter. The exact end point was obtained by the calculation method given in the literature<sup>6</sup>. Base to acid mole ratio was found to be 1:2 in respect of 1, 3 and 1, 4 benzenediamines and the ratio was 1:1.5 in the case of 1, 2 benzenediamine. These observations

suggest that both the amino groups in 1, 3 and 1, 4 isomers react with the acid to form salt. In the 1, 2 isomer the acid base reaction appears to be restricted to only one amino group due to steric effect and the residual 0.5 mole of the acid may be ascribed to a condensation reaction as indicated below:



The experimental results are given in Table I

TABLE I

Base	Amount mg	
	taken	found
1, 2 benzenediamine	43.2	42.4
	21.6	21.2
1, 3 benzenediamine	43.2	42.4
	21.6	21.2
1, 4 benzenediamine	43.2	42.6
	21.6	21.2

The data in the table show that chlorosulphonic acid can be used successfully for the determination of semimicro quantities of the three diamines with an apparently negative bias and an error of < 2%. The method is more accurate than that reported by Kreshkov and Aldarova<sup>1</sup>.

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