from the Beer's law data is 28.5 mg/cm² and the corresponding molar absorptivity of the complex is 4.81 × 10³ mol⁻¹ cm⁻¹.

The usual excipients like talc, starch, magnesium stearate, stearic acid, sorbic acid, glucose, lactose, gavacicia, gelatin andmannitol in amounts far in excess of their normal occurrence in pharmaceutical preparations did not interfere in the analysis of INH by the proposed method. Hence the method can be adopted for quick analytical control of INH tablets and syrup at the manufacturing stage.

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SYNTHESIS OF SULPHENAMIDE, SULPHENIMIDE AND SULPHENIMINE WITH SULPHENYL BROMIDE OF ORTHO-MERCAPTO-AZO COMPOUND

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N-sulphenylation of 2-naphthylamine, phthalimide, thioura, and alanine with 4-dimethylaminobenzene-2'-sulphenyl bromide (I) is studied. The rearranged product (II) dominates in the case of 2-naphthylamine, whereas the sulphenimine (IX) is the main product obtained from alanine. Thioura undergoes S-sulphonylation (VIII) and phthalimide gives the expected sulphenimide (VI).

To investigate the utility of o-mercaptoazo compound in the preparations of sulphenimides, we have studied the reactions of 4-dimethylaminobenzene-2-sulphenyl bromide with 2-naphthylamine phthalimide, thioura and alanine in a polar solvent in the presence of an acid scavenger triethylamine at room temperature. With 2-naphthylamine the diarylsulphide (II) is obtained as the major product. Small amounts of the sulphenamide (III), the di-N-sulphonylated product (IV) and the disulphide (V) are also obtained. N-sulphonylation of phthalimide is slow and forms the sulphenimide (VI) in a low yield, the disulphide being the other main product. Thioura undergoes S-sulphonylation instead of N-sulphonylation giving a mixture of the disulphides (VII) and (V). From the complex reaction products of alanine the sulphenimide (VIII) is obtained only as a minor product. Its IR spectra show that N-sulphonylation of alanine does not destroy its zwitter ionic nature, though the characteristic amino acid band in the range 3000-2000 cm⁻¹ disappears. The major product of the reaction is found to be the thioxime (IX). The disulphide (V) is the third product identified.

The formation of (IX) may be rationalized as per Scheme 1 or 2.

Scheme 1

```
\[
\begin{align*}
H &\quad \text{SAr} \\
\backslash & \quad \text{I} \\
H_2C - C - N - \text{SAr} & \quad \text{ArSBr} \\
\mid & \quad \text{COOH} \\
\quad & \quad \text{Br} \\
\text{H}_3C - C - N - \text{SAr} & \quad \text{B} \\
\mid & \quad \text{COOH} \\
& \quad \text{SAr}
\end{align*}
\]
```

(A)

\[
\rightarrow \quad \text{H}_3C - C - N - \text{SAr} + \text{ArSBr}
\]

\[
\rightarrow \quad \text{H}_3C - C - N - \text{SAr} + \text{COOH} + \text{SAr}
\]

(A)

\[
\text{H}_3C - C - N - \text{SAr} + \text{Br}
\]

(B)

\[
\text{H}_3C - C - N - \text{SAr} + \text{COOH} + \text{SAr}
\]

(C)

Experimental

Reaction with 2-naphthylamine

To a solution of the sulphenyl bromide (1, 1.2 g) in ethanol (100 ml) was added a solution of 2-naphthylamine (40 mg) in ethanol (100 ml) and 4-5 drops
of triethylamine. The mixture was shaken well and
kept at room temperature (2 days). The precipitate
of the diarylsulphide (II, 250 mg ~ 24%) was crystal-
lized from dilute ethanol as brown crystals, m.p.
95-97°C, IR (cm⁻¹) 1590 (υ, N=N stretch), 1650
(m, NH₃ deformation). 3450 and 3500 (υ, NH₂ stretch).
Chromatography of the mother liquor over alumina
gave on elution with benzene-light petrol the red-
disulphide (V, m.p. 222-23°C, 60 mg) IR (cm⁻¹) 1590
(υ, N=N stretch), the brown diarylsulphide (II, m.p.
95-97°C, 30 mg), the yellow sulphenamide (III, m.p.
46-48°C, 110 mg) IR (cm⁻¹) 1585 w, N=N stretch),
1640 (m, NH₃ deformation), 3210 s, SNH stretch) and
the dazzling orange crystals of the diarylsulphene-
amide (IV, m.p. 78-80°C, 120 mg) IR (cm⁻¹) 1590
(υ, N=N stretch).

Reaction with phthalimide

To a solution of (I, 1·0 g) in ethanol (100 ml) was
added a solution of phthalimide (400 mg in ethanol
(200 ml) and 4-5 drops of triethylamine. The mixture
was swirled well and kept at room-temperature (5 days).
Chromatography of the concentrated mixture over
alumina gave on elution with benzene-light petrol,
the disulphide (V, 70 mg) and the sulphenimide (VI,
m.p. 153-55°C), 200 mg IR (cm⁻¹) 1600 (υ, N=N
stretch) 1720 (υ, C=O stretch).

Reaction with thiourea

A mixture of I (1·0 g) in ethanol (100 ml) thiourea
(220 mg) in ethanol (50 ml) and 4-5 drops of triethyl-
amine was swirled well and kept at room temperature
(5 hr). The yellow crystals of S-sulphenylated iso-
thiourea was crystallized from ethanol (VII, m.p.
68-7°C, 300 mg) IR (cm⁻¹) 1590 (υ, N=N stretch),
1650 (υ, NH₃ deformation and C=O stretch overlapped),
3220 (υ, =NH stretch), 3450 and 3500 (υ, NH₂ stretch).
The mother liquor gave the disulphide (V, 20 mg).

Reaction with alanine

To a solution of I (1·0 g) in methylene chloride
(200 ml) was added a solution of alanine (260 mg)
in methylene chloride (50 ml) and 4-5 drops of triethyl-
amine. The mixture was shaken well and kept at
room temperature (3 days). On removing the solvent
the residue was dissolved in minimum volume of
benzene. The chromatography of the resulting solution
over silica gave on elution with benzene-light petrol
the disulphide (V, 50 mg), the yellow crystals of the
sulphenamide (VIII, m.p. 109-11°C, 90 mg) IR
(cm⁻¹) 1590 (υ, N=N stretch) 1600 and 1620
(υ, partially overlapped bands due to C=O and NH₃),
3050-3100 (υ, single broad band due to SNH stretch)
and the dazzling blue violet crystals of the thiooxime

IX, m.p. 147-49°C, 260 mg) IR (cm⁻¹) 1590 (υ, N=N
stretch), 1690 (υ, C=N stretch).

The analytical results for C, H and N of the com-
pounds (II-IX) agreed with the calculated values.

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A NEW SPRAY REAGENT FOR THE
IDENTIFICATION OF MONOCROTOPHOS
BY THIN LAYER CHROMATOGRAPHY

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It is observed that even though monocrotophos is an
organophosphorus insecticide, it does not respond to
different spray reagents such as mercuric nitrate
followed by diphenyl carbazone¹, mercutus nitrate²,
mercuric nitrate followed by potassium ferricyanide³
and silver nitrate in phenoxyethanol followed by UV
radiation⁴. Since poisoning cases of monocrotophos
are increasing, it has become necessary in Forensic
Toxicology to find specific color test for mono-
crotophos (marketed as "Nuvacron") having struc-
tural formula as follows :

\[
\text{CH}_2\text{O} \quad \parallel \\
\text{P} = \text{OC} = \text{CHCONHCH}_3
\]

Dimethyl 2-methylcarbamoyl-1-methylvinyl phosph-
ate

In this paper a new spray reagent (potassium tri-
iodide) has been described for the detection of mono-
crotophos on thin layer chromatographic plates.

Glass plates of the size 10 cm x 15 cm were coated
with a slurry of silica gel G (Acme) with water in
proportion 1 : 2. The plates were activated at 110°C
for about 1 hour and used for T.L.C. monocrotophos
solution (1 mg/l ml) in ethanol was spotted on thin
layer plates and the plates were developed in the
solvent hexane and acetone (4 : 1) up to a height of
10 cm in a chamber saturated with the same solvent.
The plates were taken out, dried in air and sprayed
with potassium tri-iodide (2 g of iodine) and 4 g of
potassium iodide dissolved in 50% ethanol and conc.
HCl (1 : 1). The monocrotophos gave a distinct
violet pink coloured spot at (RF = 0·6).