

thiouracil (3.9  $\mu$  moles) and the biological effect was almost the same at both the doses. Table 1 summarizes the results of screening observations.

All compounds have antithyroid effects upto some extent and appear to inhibit incorporation of  $I_2$  in a manner similar to thiouracil. Compounds nos. 2-5, 7-10 and 17-19 appear to be slightly more potent than thiouracil.

**Mode of action and effect of substituents on anti-thyroid activity:** The thioureylene linkage in these compounds is capable of forming an -SH grouping by enolisation. The suggestion has been made that the interference with thyroxine synthesis was by a direct reaction between iodine and sulphhydryl grouping to form a disulphide<sup>1,2</sup>. Since this reaction proceeded at a rate considerably faster than the iodination of tyrosyl group, the competition could be quite favourable for diversion of iodine away from organic binding.

These data suggest that a disulphide bond in thyroid tissue is cleaved by antithyroid compounds containing thioureylene linkage to form a new disulphide bond. This formulation is supported by chemical studies in which thiourea was found to cleave the disulphide bond of cystine to yield the mixed disulphide S-guanylthio-l-cysteine<sup>1,3</sup>.

It is evident from the results of pharmacological studies that the introduction of chloro group in benzene ring enhances the activity to some extent.

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### Chemical Investigation of *Wrightia mollissima*

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**WRIGHTIA** (fam. Apocyanaceae) is a genus of shrubs and small trees distributed in tropical Africa, Asia and Australia<sup>1</sup>. The genus owe its importance both from its economic and medicinal points of view. The medicinal properties of *W. mollissima* are similar to *W. tinctoria* and *Holarrhena antidysenterica*, whose bark is used medicinally as a drug in amoebic dysentery. Survey of literature reveals that no work has been done previously on this plant. Hence a chemical investigation of its stem and leaves was undertaken. We have isolated  $\alpha$ -amyrin acetate, taraxerol acetate, lupenone, taraxerol and  $\beta$ -sitosterol from petroleum ether extract while no crystalline compound could be isolated from ethanolic extract.

Finely powdered stem and leaves were extracted with petroleum ether (60°-80°) in Soxhlet apparatus followed by extraction with ethanol.

**Petroleum ether extract:** It was concentrated under reduced pressure to a semi solid mass, which was chromatographed over silica gel.

**$\alpha$ -Amyrin acetate:** Elution of column with hexane and benzene (3:1) yield  $\alpha$ -amyrin acetate as white crystalline compound (chloroform-methanol), m.p. 225°-6°. Alkaline hydrolysis yielded  $\alpha$ -amyrin, m.p. 194°-5°. Identical (m.m.p., tlc and ir) with authentic sample.

**Taraxerol acetate:** Elution of the column with hexane-benzene (1:1) furnished white needles (chloroform) of taraxerol acetate, m.p. 295°-7°. Alkaline hydrolysis gave taraxerol, m.p. 282°-3°. Identity confirmed by comparison (m.m.p., tlc and ir) with authentic sample.

**Lupenone:** Further elution of the column with benzene gave lupenone as white crystals (ether), m.p. 170°-1°, NaBH<sub>4</sub> reduction gave lupeol, m.p. 215°. Identical (m.m.p., tlc and ir) with authentic sample.

**Taraxerol:** Elution of the column with benzene also yielded taraxerol as fine needles (chloroform-methanol), m.p. 282°-3°, acetate (Ac<sub>2</sub>O/Py), m.p. 295°. Finally confirmed by comparison (m.m.p., tlc and ir) with authentic sample.

**$\beta$ -Sitosterol:** Elution of the column with benzene-ethylacetate (98:2) furnished white crystals (chloroform-methanol) of  $\beta$ -sitosterol, m.p. 135°-7°, acetate (Ac<sub>2</sub>O/pyr), m.p. 128°. Identical (m.m.p., tlc and ir) with authentic sample.

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*Alcoholic extract*: Column chromatography of ethanolic extract over silica gel did not yield any crystalline compound.

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### Mercurimetric Determination of Organotrithiocarbonates and A Method for the Analysis of Mercaptans

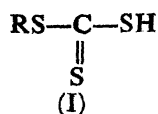
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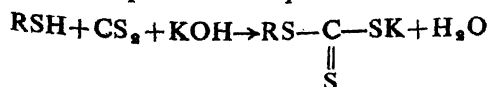
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**ORGANOTRITHIOCARBONATES** are the salts of the corresponding trithiocarbonic acids (I) and



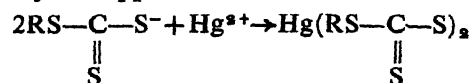
are prepared through the reaction of mercaptans with carbon disulphide in the presence of an alkali:



They find applications<sup>1</sup> as flotation agents, vulcanisation accelerators, pesticides, plant defoliants, rust inhibitors, lubricating oil additives and modifiers in bulk styrene polymerisation. Some trithiocarbonates have recently been reported to possess activity as anti radiation drugs. In spite of their numerous applications in industry, agriculture and medicine, their determination has not received much attention. Verma and Kumar<sup>2-3</sup> recently described some oxidimetric methods for the determination of these compounds in aqueous and non-aqueous media.

The fact that organotrithiocarbonates react with mercury and other heavy metals to form salts, is already known<sup>1,8,9</sup>. The present communication reports a method for the determination of organotrithiocarbonates based on their tendency to react with metals to form salts. The use of mercury(II) is described for the first time for the determination of these compounds. Diphenylcarbazine has been

found a suitable indicator. The end-point is marked by the appearance of blue colour.



The simplicity and reliability of the above method prompted us to apply this method to the determination of mercaptans after their transformation to the corresponding organotrithiocarbonates through reaction with carbon disulphide in presence of alkali. The transformation has been found to be extremely fast and quantitative<sup>8,7</sup>. Though mercury(II) salts have been used for the direct determination of mercaptans, doubts have frequently been expressed over the uniform stoichiometry of the reaction, that is, one or two molecules of mercaptans could react forming both  $\text{RSHgX}$  and  $(\text{RS})_2\text{Hg}$  compounds<sup>10,11</sup>. These observations in fact lead to the use of organo-mercury compounds (containing only one available mercury valency) in place of mercury(II) salts. The proposed method involving the transformation of mercaptans to organotrithiocarbonates is free from such ambiguity since the stoichiometry of the reaction of mercury(II) with organotrithiocarbonates is clear.

The proposed methods for the determination of organotrithiocarbonates and mercaptans are simple, rapid, accurate and reliable. They possess wide applicability.

#### Experimental

*Mercury(II) acetate, 0.0125 M in water*: The solution was standardised as described by Vogel<sup>12</sup>.

*Organotrithiocarbonates*: The compounds were prepared and purified as described earlier<sup>1,2</sup>. The purity of the compounds was checked by iodimetric titrations<sup>8</sup>.

*Mercaptans*: Isopropyl-, isobutyl-, benzyl- and dodecyl mercaptans as well as  $\beta$ -mercaptoethanol and thiophenol were distilled before use. 2-Mercaptobenzothiazol was used as received.

*Diphenylcarbazine*: 0.1% solution in ethanol.

#### Procedure:

(a) *Determination of organotrithiocarbonates*: Aliquots of the solution in water of each trithiocarbonate were taken in titration flasks and diluted with 40 ml of water. Each solution was mixed with 0.5 ml of diphenylcarbazine indicator and titrated at room temperature (24°) with standard (0.0125 M) mercury(II) acetate solution. The end-point was marked by the appearance of blue colour. From the volume of standard mercury(II) acetate solution used corresponding to the end-point in each titration, the amount of each trithiocarbonate was calculated. Results are given in Table 1.

(b) *Determination of mercaptans*: To aliquots (1-5 ml) of solutions in acetonitrile of each mercaptan were added another 5 ml of acetonitrile,