

Other organophosphorus insecticides such as malathion, parathion, methyl parathion, fenthion, fenitrothion, methyl demeton when sprayed with the above reagent failed to give this unique coloured spot. Similarly monocrotophos, extracted from biological material with ether, also responded to the above reagent. Since the above spray reagent is sensitive to detect 10 µg of monocrotophos and is specific, it can be used as a routine reagent in the laboratory.

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## MICROGRAM DETERMINATION OF QUININE WITH SOLOCHROME GREEN V 150 BY EXTRACTIVE SPECTROPHOTOMETRY

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THE trace analysis of quinine is of particular interest to toxicologists, pharmaceutical and forensic chemists. Many of the commonly employed methods are indirect and time consuming. Desirable sensitivity of determination is achieved by the use of acidic dyes which form extractable ion pair complexes with the basic alkaloid. Generally, triphenylmethane dyes are used for the determination of quinine<sup>1-3</sup>. Very few azo dyes<sup>4</sup> have been employed for its determination. During the investigations on the use of diazo dyes of solochrome series for the quantisation of various alkaloids the authors found that Solochrome Green V 150 forms extractable ion pair complex with quinine. The dye is not extracted itself into the solvents studied and thus the problem of reagent blank, which is common with most of the triphenylmethane dyes, has

been eliminated. The present report describes a very sensitive and rapid extractive spectrophotometric method for the determination of quinine applicable to 0.4 µg/ml.

### Experimental

#### Reagents

Solochrome Green V 150 (Fig. 1) was supplied by ICI, Calcutta. Absorbance measurements were carried out using a Bausch and Lomb spectronic-20 spectrophotometer. Walpole and Clarke and Lubs buffers were used. All other reagents used were of analytical grade.

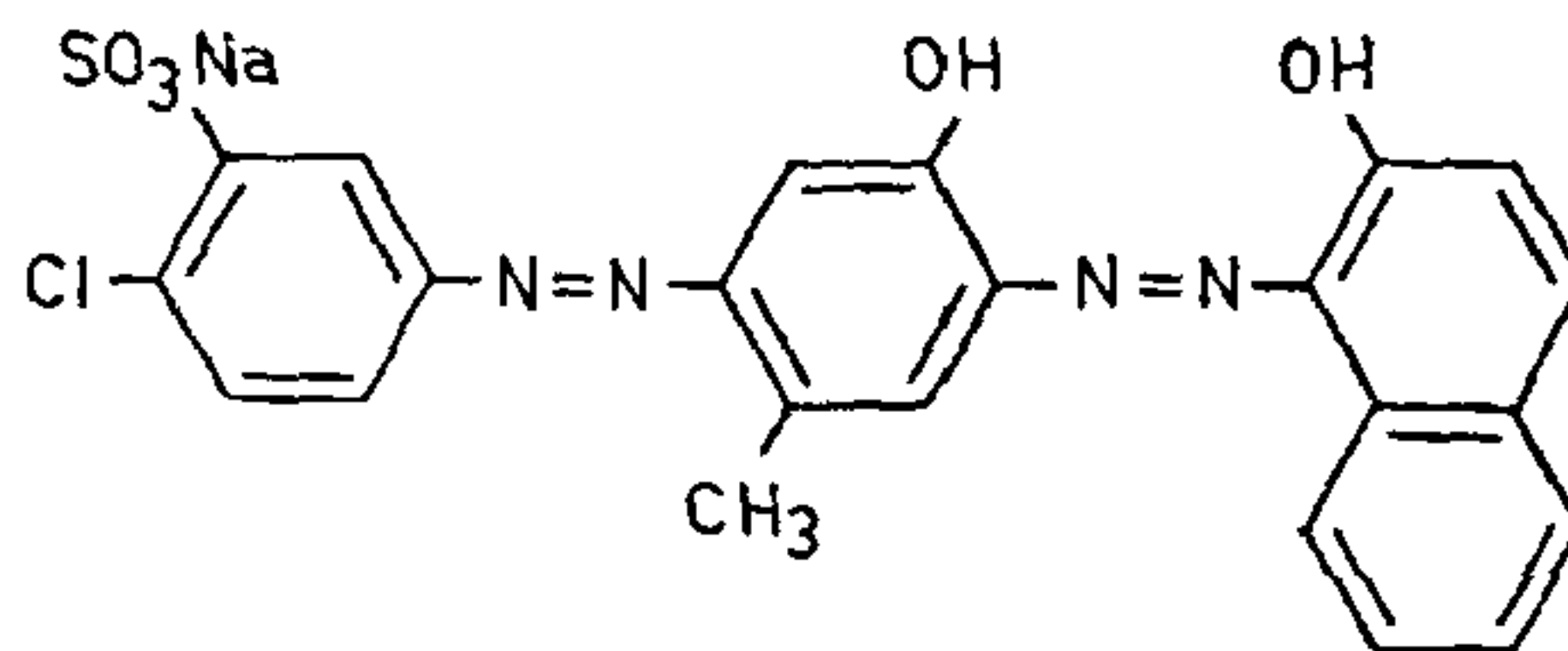


FIG NO. 1

### Results and Discussion

Aqueous solution of the dye Solochrome Green V 150 has a maximum absorbance at 490 nm. Change in pH of the solution does not affect the max of the dye. The dye as such is not extractable into chloroform, dichloromethane and dichloroethane at any pH in the range 1-11. The molar absorptivity of the dye is 7500 lit. mol<sup>-1</sup> cm<sup>-1</sup>. The alkaloid quinine forms an ion pair complex extractable as pink coloured species into chloroform, the pH of maximum extraction being 6. The ion pair has a maximum absorbance at 510 nm. Of the three halogenated solvents, chloroform, 1,2-dichloroethane and dichloromethane, chloroform has been found to be the best extractant. About one minute of shaking is sufficient for the complete extraction of ion-pair. The colour of the extract is stable for 2 hours. The Beer's law is obeyed in the range 10-310 µg with the minimum amount of determination being 0.4 µg/ml. The molar absorptivity of the ion pair complex is 16,220 lit. mol<sup>-1</sup> cm<sup>-1</sup>. Since it is the dye alone that contributes to the absorbance, the composition of the ion pair complex from molar absorptivity study is 1:2 (Alkaloid : Dye). This is confirmed by Job's continuous variation and mole ratio methods. Five-fold excess of the dye is used in the experiment. Concen-

trated solution of the dye results in emulsion formation. The accuracy of the method has been found to be  $\pm 1.5\%$ , based on quadruplicate measurements.

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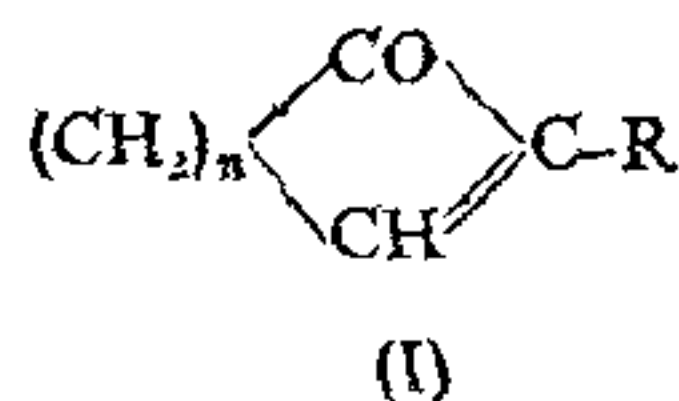
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## SYNTHESIS OF SOME 2-ALKYL CYCLOALK-2-EN-1-ONES

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CYCLOALKANONES like cycloheptanone<sup>1</sup> have been used as insect-attractants and their alkyl derivatives as flavouring agents<sup>2</sup>. With this aim in view, a number of 2-alkyl cycloalk-2-en-1-ones have been synthesised starting from simple cycloalkanones by the action of sodamide, followed by an alkyl halide in benzene by refluxing. The 2-alkyl cycloalkanones, so obtained, were acted upon by sulphuryl chloride<sup>3</sup>, when chlorine entered the 2-position. The 2-alkyl-2-chloro-cycloalkanones, during preparation of their 2,4-dinitrophenylhydrazones, in dilute sulphuric acid gave rise to 2:4-dinitrophenylhydrazones of the corresponding 2-alkyl cycloalk-2-en-1-ones (I), obviously by dehydrohalogenation. The characterisation of latter as well as those of 2-alkyl-2-chloro cycloalkanones could be possible, as the 2-methyl or 2-*n*-butyl cyclohex-2-en-1-ones are already known<sup>3</sup>.

The following 2-alkyl cycloalk-2-en-1-ones were synthesised, and characterised by elemental analysis and infrared spectra of their 2:4-dinitrophenylhydrazones.



### EXPERIMENTAL

#### (i) Synthesis of 2-Alkyl Cycloalkanones

These were prepared by refluxing either cyclohexanone or cycloheptanone (1 mol) with sodamide (1 mol) in

benzene for 8 hr, followed by addition of corresponding alkyl halide (1 mol) for 10 h. The reaction mixture was poured into cold water and upper benzene layer separated, washed with water and dried over anhydrous sodium sulphate. Removal of benzene gave a liquid, which was distilled under vacuum. The 2-alkyl cyclo-alkanones were obtained in 60-70% yield. They were characterised by the preparation of 2:4-dinitrophenylhydrazones or semicarbazones.

#### (ii) Synthesis of 2-Alkyl-2-Chloro Cycloalkanones

They were obtained by reacting 2-alkyl cyclo-alkanones, (1 mol) with sulphuryl chloride (1 mol) in carbontetrachloride at room temperature and stirring for 3 hr. Removal of the solvent, followed by distillation under vacuum, afforded 2-alkyl-2-chloro cycloalkanones.

#### (iii) Synthesis of 2-Alkyl Cycloalk-2-en-1-ones

On treatment of 2-alkyl-2-chloro cycloalkanones, with 2:4-dinitrophenylhydrazine in dilute sulphuric acid, the corresponding 2:4-dinitrophenylhydrazones free from chlorine were obtained. The m.p.s of the DNP (I)  $n=3$ ,  $R=CH_3$ ,  $n-C_4H_9$  (after crystallisation from alcohol) were  $206^\circ$  (lit.  $206^\circ$ );  $134^\circ$  (lit.  $134^\circ$ ), which confirmed that chlorination occurred in 2-position and the DNPs formed were those of the corresponding 2-methyl and 2-*n*-butyl cyclohex-2-en-1-ones. The rest of the 2-alkyl cycloalk-2-en-1-ones were characterised by satisfactory nitrogen estimation and infrared spectra (for I,  $n=3$  or 4,  $C=N$ ,  $C=C$  and R) of their DNPs (I,  $n=3$ ,  $R=C_2H_5$ , m.p.  $150^\circ$ ;  $R=n-C_4H_9$ , m.p.  $98^\circ$ ;  $R=n-C_5H_{11}$ , m.p.  $208^\circ$ ;  $R=iso-C_5H_{11}$ , m.p.  $147^\circ$ ;  $n=4$ ,  $R=CH_3$ , m.p.  $177^\circ$ ;  $R=n-C_3H_7$ , m.p.  $250^\circ$ ).

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