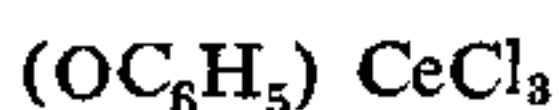


## LETTERS TO THE EDITOR

### STUDIES ON PHENOLIC DERIVATIVES OF Ce (IV)

REACTIONS of hexachlorocereric acid,  $H_2CeCl_6$  with phenol, resorcinol and pyrogallol yield  $(OC_6H_5)_3CeCl_3$ ,  $(OC_6H_4 \cdot OH)CeCl_3$  and  $[OC_6H_3(OH)_2]_2CeCl_3$ .  $H_2CeCl_6$  was prepared by passing dry HCl gas through ceric hydroxide (2.1 g) suspended in absolute alcohol for 12 hours till the colour changed to deep red. It was filtered to remove undissolved  $Ce(OH)_4$ . To hexachlorocereric acid was added phenol (0.94 g) and the mixture was refluxed till there was no evolution of HCl gas. The solution was filtered and excess of ethanol was removed by distillation under reduced pressure (20–25 mm). It gave a brown paste which on repeated crystallisations from petroleum ether (60–80° C) gave a brown crystalline compound whose analysis is given below:



%Ce found 41.0 calc. 41.26; %C found 21.34 calc. 21.22; %H found 1.62 calc. 1.47; %Cl. found 31.45 calc. 31.32.

Other phenolic derivatives of Ce (IV) were prepared by a similar method. The complexes were vacuum dried for 48 hours and analysed for metal, chlorine, carbon and hydrogen. Their analysis corresponded to  $(OC_6H_4 \cdot OH)CeCl_3$  and  $[OC_6H_3(OH)_2]_2CeCl_3$ .

#### Results and Discussion

From the analytical data, the reaction can be represented in case of phenol as:  $H_2CeCl_6 + C_6H_5OH \rightarrow (OC_6H_5)_3CeCl_3 + 3 HCl$ . A study of the infrared spectra indicates the characteristic aromatic C–H stretching frequency at  $\sim 3050 \text{ cm}^{-1}$ , out of plane C–H bend around 810 and  $759 \text{ cm}^{-1}$ , C=C frequency at  $1650 \text{ cm}^{-1}$ , out of plane C–C bend at  $690 \text{ cm}^{-1}$ , phenolic C–O stretching peak at about  $1400 \text{ cm}^{-1}$  and the disappearance of hydrogen bonded  $-OH^{1,2}$  which are relevant to the presence of phenoxy ions. In addition, a high frequency shift ( $\sim 180 \text{ cm}^{-1}$ ) of phenolic C–O stretch has been observed in these complexes. The shift in all the compounds is to a higher frequency which is indicative of M–O–C bond formation through oxygen of  $-OH$  group of phenols. Out of the three and two hydrogen atoms of the hydroxyl groups present in pyrogallol and resorcinol respectively, only one hydrogen atom has been replaced on complexation with  $H_2CeCl_6$ , as confirmed by the i.r. spectra of their derivatives which show bands at  $\sim 3620 \text{ cm}^{-1}$  due to the presence of free  $-OH$

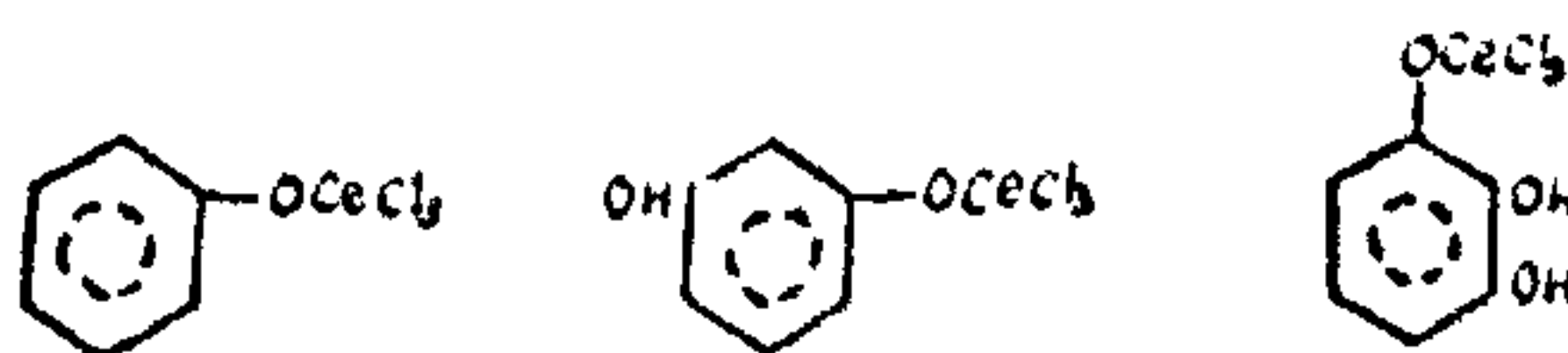
(phenolic) group and at about  $1180 \text{ cm}^{-1}$  due to  $-OH$  deformation. The bands of phenolic group at  $\sim 3620 \text{ cm}^{-1}$  result from the monomeric structure<sup>3,4</sup>. There is absence of a hydroxyl frequency in the i.r. spectrum of complex with phenol.

The ultraviolet spectra of phenolic derivatives with resorcinol and pyrogallol display two absorption peaks in 200–350 nm region, viz., around 215 nm ( $\log \epsilon_{\text{max}} = 4.26-4.29$ ) and 280 nm ( $\log \epsilon_{\text{max}} = 3.78-3.79$ ). In the u.v. spectrum of  $(OC_6H_5)_3CeCl_3$ , these two peaks are observed at 212 nm ( $\log \epsilon_{\text{max}} = 4.21$ ) and 270 nm ( $\log \epsilon_{\text{max}} = 3.6$ ). The bands around 215 nm are E bands and arise due to  ${}^1L_a \leftarrow {}^1A$  transitions and the bands at 270 nm and 280 nm are B-bands and can be assigned to  ${}^1L_b \leftarrow {}^1A$  transitions<sup>5</sup> though in phenolic derivatives with resorcinol and pyrogallol, the two bands are bathochromically shifted with hyperchromic effect by the electron donating substituent  $-OH$  group.

Ebullioscopic molecular weight determination of these complexes carried out in boiling benzene showed them to be monomeric. The molar conductance of these complexes in methanol are very low being of the order of 2–4 mhos/cm<sup>2</sup> indicating non-electrolytic nature of the complexes.

All the complexes are found to be diamagnetic. This indicates the absence of free phenoxy radicals which show paramagnetic behaviour. The above studies confirm that in these complexes the covalently bonded chlorine atoms of  $H_2CeCl_6$  have been replaced by the corresponding phenols and these compounds undergo displacement reactions similar to the phenolic derivatives<sup>6</sup> of tricyclopentadienyl and bisindenyl derivatives of Ce (IV).

On the basis of analytical data agreeing with the molecular formulae written above, molecular weight indicating absence of polymeric character, molar conductance showing the presence of non-ionic species and i.r. data giving evidence for the bonding of cerium to oxygen of the phenoxy ions, the diamagnetic behaviour indicating the absence of free phenoxy radicals, the proposed structures of these complexes are:



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1. Bellamy, L. J., *The i.r. Spectra of Complex Molecules*, Methuen, 1964, p. 105.
2. Ueno, K. and Martell, A. E., *J. Phys. Chem.*, 1956, 60, 1270.
3. Silverstein, R. M., Bassler, G. Clayton, and Morrill, T. C., *Spectrometric Identification of Organic Compounds*, Third Edition, John Wiley and Sons, 1974, p. 92.
4. Morrison, R.T. and Boyd, R.N., *Organic Chemistry*, Second Edition, 1969, p. 416.
5. Jaffe, H. H. and Orchin Milton, *Theory and Applications of Ultraviolet Spectroscopy*. John Wiley and Sons, Inc., 1966, p. 481.
6. Kapur, S., Kalsotra, B. L. and Multani, R. K., *J. Chinese Chem. Soc.*, 1972, 19, 197.

#### 1-NITROSO 2 NAPHTHOL AS A SPRAY REAGENT FOR THE DETECTION OF CANNABIS ON THIN LAYER PLATES

A NUMBER of thin layer chromatographic procedures are described for the separation and detection of the active phenolic constituents of cannabis. Chromogenic reagents like fast blue salt B<sup>1</sup>, Beam's reagent<sup>2</sup>, diazotised *p*-nitroaniline-sodium hydroxide spray<sup>2</sup>, blue tetrazolium<sup>3</sup> and Folin-Ciocalteu phenol reagent are generally used to detect the separated phenolic constituents from cannabis. The Folin-Ciocalteu reagent gives blue spots with easily oxidisable substances in addition to phenols. Further, the diazo reagents<sup>1</sup> are found to react with many non-aromatic oxygen compounds to give red colour. Though fast blue salt B is widely used for the detection of cannabis, it was stated in earlier works<sup>5</sup>, that this reagent reacts with many compounds other than phenols and can hold no claim to specificity.

In the present work, therefore, a specific reagent for phenols has been used to detect the phenolic constituents cannabis. Many phenols are known to react with nitroso phenols in its isomeric oxime form in the presence of concentrated sulfuric acid, to give coloured indophenols<sup>6</sup>. Hence 1-nitroso 2 naphthol has been used as a spray reagent for the detection of cannabis and presented in this communication. The reagent is specific for phenols and non-phenolic compounds do not interfere.

#### Experimental

The cannabis sample has been extracted with three aliquots of benzene<sup>2</sup>, which are decanted

through a short column of florasil (60-100 mesh). The extract was evaporated to a small volume, and spotted on thin layer plates of silica gel G. The plate is developed in a solvent mixture of benzene : chloroform (3 : 7). After the development the chromatograms are air dried and sprayed with 1% solution of 1-nitroso 2 naphthol, in concentrated sulfuric acid. On brief heating of the plates at 100° C, the colours are intensified. The results are given in Table I. The colours of the spots

TABLE I

Detection of the separated phenolic constituents of cannabis by spraying with 1-nitroso 2 naphthol reagent

Spot No.	R <sub>f</sub> value	Colour with the spray reagent
1.	0.24	Blue
2.	0.51	Blue
3.	0.67	Blue
4.	0.91	Greyish blue
5.	0.94	Greyish blue

1, 2, 3 change to violet on standing for 2 hours. The reagent has been found to be effective in detecting cannabis samples extracted from admixtures and diluents (like starch, jaggery, etc).

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1. De Faubert Maunder, M. J., *J. Assoc. Public. Analyst*, 1964, 7, 24.
2. Clarke, E. G. C., *Isolation and Identification of Drugs*, The Pharmaceutical Press, London, 1969 Edition, p. 235.
3. Korte, F. and Sieper, U. H., *J. Chromatogr.*, 1964, 14, 178.
4. Vegh, A., Szasz, Gy., Brantue, A. and Grazea, M., *Chem. Abstr.*, 1964, 60, 13097 a.
5. Thornton, J. I. and Nakamura, G. R., *J. Forens. Sci. Soc.*, 1972, 12, 461.
6. Feigl, F., *Spot Tests in Organic Analysis*, Elsevier, Amsterdam, 1966, p. 251.