

absorption system I, the band at 30590 cm^{-1} was identified as due to the pure electronic transition and 30904 cm^{-1} was understood as due to the non-totally symmetric excited state frequency of 314 cm^{-1} corresponding to the ground state value 350 cm^{-1} reported in Raman spectrum of the compound.³ The assignment was supported by the non-appearance of 314 cm^{-1} ground state value in Raman and also 313 cm^{-1} excited state value reported from the mixed crystal study by Shpak and Sheka.⁴ However, the emission study shows that 350 cm^{-1} ground state vibration is not found superposed over 30590 cm^{-1} band, which itself appears very weakly. All the other bands of the emission spectrum could be understood in terms of the Raman frequencies or their overtones and combinations. Further, if a non-totally symmetric vibration appears so prominently in the absorption system I of β -naphthol, similar feature is also expected in other β -substituted naphthalenes. But β -fluoro-, and β -methyl-naphthalenes studied during the present investigation do not show such frequency; even if the same substituent -OH is taken in α -position, this feature is not retained. Therefore, in the light of these observations the band at 30904 cm^{-1} is taken as the (O-O) band and the band at 30590 cm^{-1} is identified as due to the ground state frequency of 314 cm^{-1} , not reported in the Raman spectrum.

Other bands of the emission spectrum have been understood in terms of the totally symmetric frequencies. The possible modes of vibrations for all the ground state frequencies obtained during the present studies along with the corresponding Raman values are presented in Table I.

TABLE I

Ground state frequencies of β -naphthol obtained from the emission spectrum

Emission spectrum	Raman spectrum	Probable assignments
314	..	Skeletal bending (I) or C-OH bending (II)
530	527	Skeletal distortion (II)
781	769	Ring breathing
1035	1015	C-H bending (II)
1400	1386	C-C stretching

In conclusion, the vibrational analysis of the emission spectrum of β -naphthol shows that the most prominent vibrations of mono-substituted naphthalenes are related to a_g -motions of naphthalene. This can be explained on the basis of the reduction of b_{1g} -type vibrations of

naphthalene (D_{2h}) to a (totally symmetric)-type vibrations in mono-substituted naphthalenes (C_s).

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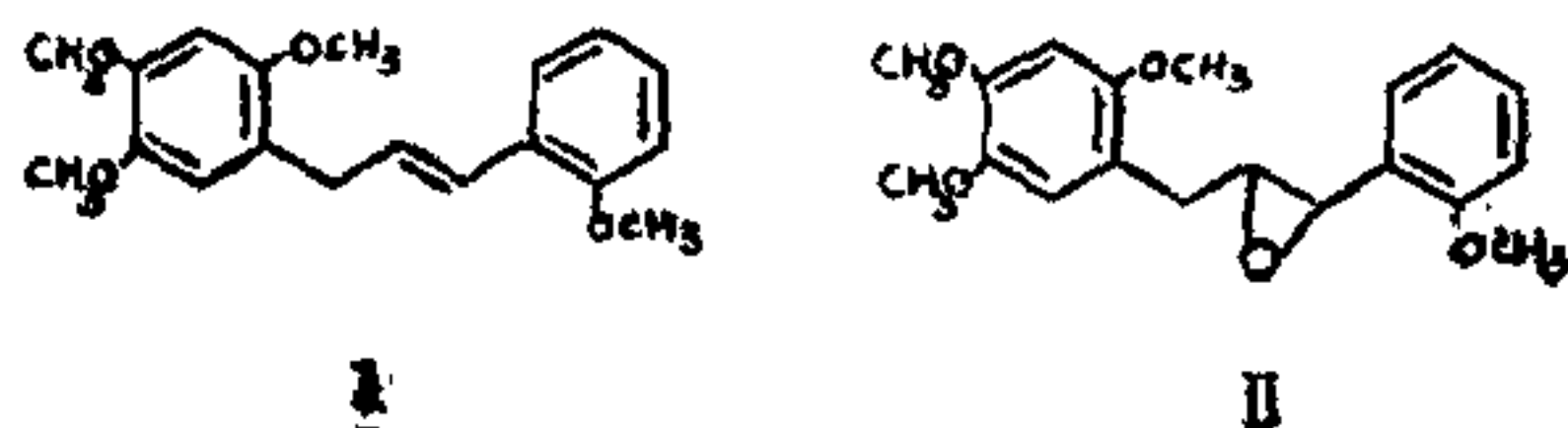
EPOXIDE FORMATION AS A SIDE REACTION ON SILVER NITRATE-ALUMINA COLUMN

THE π -complexing property of Ag^+ ions with ethylenic bonds is well known and has been utilised for separation of compounds containing double bonds. Thus aqueous solutions of silver nitrate have been used for counter-current separations¹ of unsaturated fatty esters and more widely on inert support for low temperature G.L.C.² and also for partition chromatography on silica gel.³ Silver ions retain their complexing property even in the dry state and this idea has been recently applied in adsorption chromatography on silica gel impregnated with silver nitrate both by column^{4,5} and thin layer techniques.⁶⁻⁸ The use of alumina impregnated with silver nitrate is rather recent⁹ in this field. So far no side reactions have been observed and recorded on these impregnated columns.

Recently in connection with other work¹⁰ we had to use a silver nitrate-alumina column for the separation of 2:4:5-trimethoxy benzyl-2'-methoxy styrene (I) from latifolin dimethyl ether (the isomeric allyl compound). It was observed that if the process is carried out slowly then a considerable amount of the benzyl styrene is retained by the column and cannot be eluted out easily. Using stronger eluants (benzene : acetone, 9 : 1 or ether) a new substance, not present in the original mixture (T.L.C.), could be isolated. It crystallised from methanol as colourless plates, m.p. $91-92^\circ\text{C}$. (Found: C, 69.4; H, 6.8. $\text{C}_{10}\text{H}_{22}\text{O}_5$ requires C, 69.1; H, 6.6%).

Its U.V. spectrum ($\lambda_{\text{max}}^{\text{EtOH}}$ 288 m μ) showed absence of styrene double bond and its I.R. spectrum showed the absence of -OH group and gave bands at 1240 cm^{-1} and 833 cm^{-1} indicative

of epoxy group. That the compound is 2:4:5-trimethoxybenzyl-2'-methoxy styrene epoxide (II) was shown by deoxygenation with triphenyl phosphine at 200° for 10 mt. to the corresponding benzyl styrene identical on T.L.C. with an authentic sample.



Clearly the epoxide is formed from the benzyl styrene during its passage through the column. The oxidising agent should be silver oxide formed on the column by interaction with alumina but the latter has also a role to play as simple silver oxide is not effective. The alternative possibility is aerial oxidation catalysed by Ag^+ ions under the basic conditions of the column. In view of the wide use of silver nitrate column there is need to be cautious about this side reaction.

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THORIUM-MELANOXETIN COMPLEX, A SPECTROPHOTOMETRIC STUDY

It is established¹ that flavonoids containing 3-hydroxy or 5-hydroxy group or both combine with thorium ions in equimolar ratio to form yellow-coloured complexes. In the present communication the complex formation between thorium and melanoxetin (7, 8, 3', 4'-tetrahydroxy flavonol) has been described. The ligand has been earlier used in spectrophotometric determination of zirconium.²

Melanoxetin was isolated from the ether extract of the heartwood of *Albizia lebbeck*.³ Its standard solution was prepared in alcohol. Thorium nitrate (A.R., B.D.H.) was used for preparing standard solutions after standardising

by oxine method. Absorbance readings were taken with a Unicam SP-600 spectrophotometer and for pH measurements a metrohm pH-meter type E-350 was used.

The reagent has been found to exhibit λ_{max} at 254 and 310 m μ . Solutions were prepared containing thorium and the ligand in different molar ratios (1.0:0.33 to 1:10) and at different pH's (1.5 to 4.0). They were diluted to 10.0 or 12.5 ml. maintaining 40% alcoholic medium to avoid possible precipitation of the reagent. Absorption spectra of the solutions taken against corresponding reagent blanks show λ_{max} at 420 m μ (Fig. 1) in all cases. Also, absorption

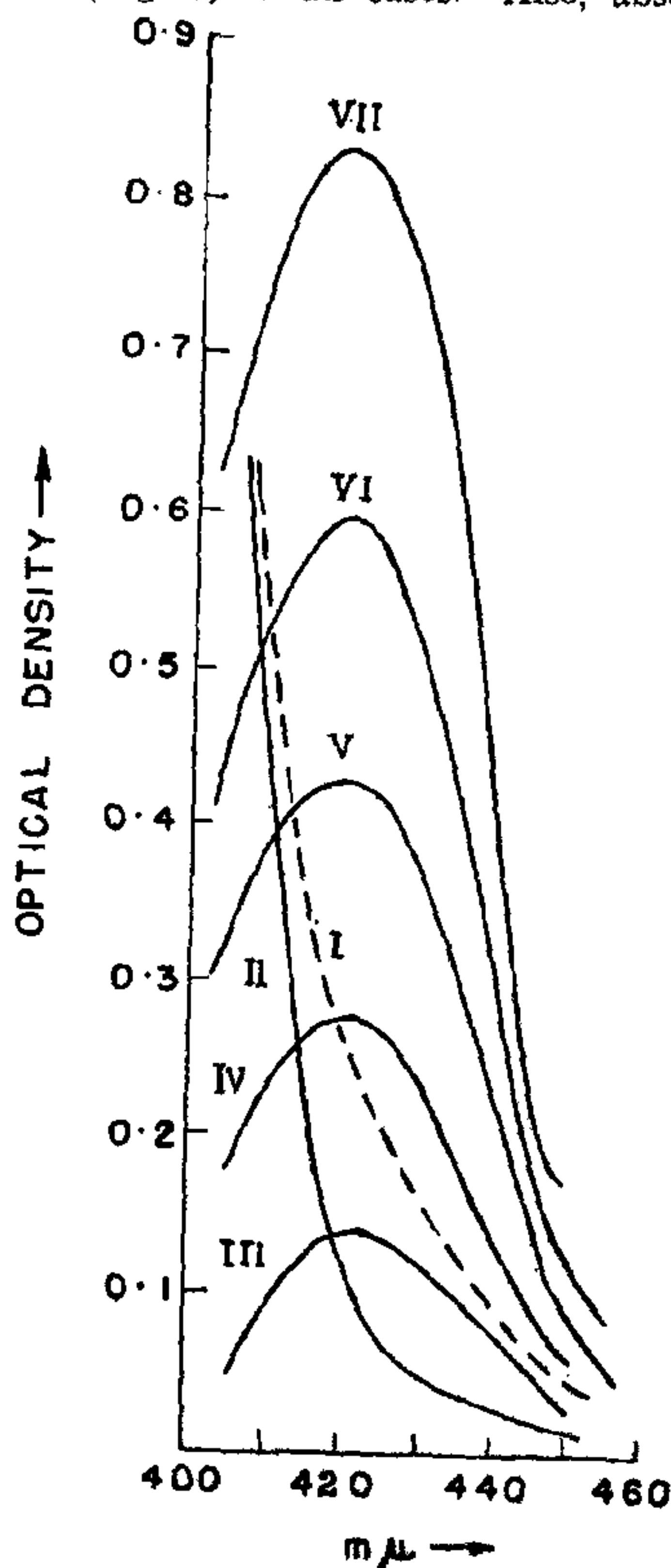


FIG. 1. Absorption spectra. I. 0.4 ml. Th (M/2500) + 4.0 ml. R (M/2500); pH 2.0; TV 10.0 ml. II. 4.0 ml. R (M/2500); pH 2.0; TV 10.0 ml. III. I-IV. 0.4 ml. Th (M/2500) + 4.0 ml. R (M/2500); pH 3.0; TV 10.0 Reagent blank. V. 1.5 ml. Th (M/2500) + 1.0 ml. R (M/2500); pH 2.0; TV 12.5 ml.; Reagent blank. VI. 1.5 ml. Th (M/2500) + 1.5 ml. R (M/2500); pH 2.0; TV 12.5 ml. Reagent blank. VII. 1.5 ml. Th (M/2500) + 2.0 ml. R (M/2500); pH 2.0; TV 12.5 ml.; Reagent blank.