Rise in temperature increased the rate, while increase in $[H^+]$ decreased the rate of polymerization.

The rate of ascorbic acid disappearance was found to be independent of [M], while it increased with increase in [Cu(II)], [AA] and $[O_2]$.

Direct dependence of chain length on [M] and inverse dependence on [Cu(II)] and $[O_2]$ were observed. 'n' values were found to be unaffected by [AA].

These observations may be accounted by the following tentative scheme for the polymerization of methyl methacrylate. The HO_2^0 and ascorbate anion radicals produced by the decomposition of the metal ascorbate oxygen complex may initiate the polymerization. The termination of the growing chains is by mutual combination at lower [Cu(II)] and by linear termination by Cu(II) ions at higher [Cu(II)]. Termination of the vinyl monomers by metal ions has been very well established[3, 12–18] both in aqueous and non-aqueous media. These two different modes of termination may result in the transient orders with respect to monomer at two different Cu[II] concentration ranges. The overall rate of polymerization may be expressed by the following relationships:

$$R_p \propto [M]^{3/2}[Cu^{2+}]^{0.5}[O_2][AA]^0$$

at lower copper concentration range.

$$R_p \propto [M]^2[O_2][AA]^0/[Cu^{2+}]$$

at higher copper concentration range

The rate of AA disappearance

$$-d[AA]/dt \propto [Cu^{2+}][O_2][AA]$$

and chain length 'n'

$$n \propto [M]/[O_2][Cu^{2+}].$$

Further details with reaction mechanism will be published elsewhere. Studes with other metal ions are being carried out to arrive at the efficiency of these initiating systems.

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PHYTOCHEMICAL STUDIES ON *CASSIA SIAMEA* LEAVES

In view of the popular use of *Cassia siamea* leaves to cure skin diseases and to reduce swellings[1] a detailed chemical examination was taken up. There was only one report of chemical investigation of *Cassia siamea* leaves in which Hussaniali-Walji *et al.*[2] reported only barakol, a novel dioxaphenalene derivative.

The powdered leaves were completely extracted with alcohol and the total alcoholic extract was concentrated to a small bulk and fractionated with petroleum ether, ether and ethyl acetate.

The petroleum ether extract was saponified and chromatographed over alumina when two crystalline substances were obtained. Of the two, one was wax m.p. 84–86°. The second crystalline component was obtained as shining plates from acetone m.p. 139°, $[\alpha]_D^{29}$ −35·7° $C_{29}H_{50}O$; acetate, m.p. 126° $(\alpha)_D^{29}$ −40·7° $C_{31}H_{52}O_2$. The identity of the compound was established by m.m.p. and TLC comparison and identical I.R. spectra with authentic *β*-sitosterol.

The residue from the ether extract gave positive colour reactions for flavonoids. This residue was macerated with 5% dilute hydrochloric acid. The acid solution was neutralised and the residue was extracted with chloroform and crystallised from methanol when lemon yellow refracting needles were obtained, m.p. 165°; $C_{15}H_{12}O_4$. Survey of literature indicated this compound could be barakol and hence the derivatives reported for barakol were attempted.

Hydrochloride of anhydroderivative was obtained by treating concentrated solution in methanol with conc. HCl, yellow needles, m.p. 205–206 , $C_{13}H_{11}ClO_3$. Hydrobromide was prepared similarly, m.p. 246–48° $C_{13}H_{11}BrO_3$. Treatment with 2N sodium bicarbonate at 50° for 20 minutes gave colourless needles, m.p. 216–18 ; $C_{13}H_{12}O_4$ presumably a chromone. The compound was identified as barakol by m.m.p., T.L.C. and I.R. comparison with authentic barakol.

The remaining ether residue gave positive colour reaction for flavonoids. This residue when chromatographed over silica gel gave yellow needles, m.p. 348°, $C_{15}H_{10}O_5$; acetate, m.p. 185–87°; $C_{21}H_{16}O_8$; methyl ether, m.p. 155–57°, $C_{18}H_{16}O_5$. The properties of the compound and its derivatives compared well with those reported for apigenin and its derivatives. The identity was confirmed by m.m.p., I.R., U.V. and T.L.C. comparison with authentic apigenin.

The residue obtained from ethyl acetate also gave positive colour reaction for flavonoids and was subjected to chromatography over silica gel when two amorphous and identical fractions from ethyl acetate: benzene (1:1) and (3:1) eluates gave strongly positive flavonoid colour reactions. The residues were mixed and hydrolysed. The aqueous portion after hydrolysis did not show the presence of sugars. The aglycone portion after chromatography gave a crystalline component, m.p. 275°, $C_{15}H_{10}O_6$, acetate m.p. 184–86°; $C_{23}H_{18}O_{10}$, methyl ether m.p. 165–67°, $C_{19}H_{18}O_6$. The aglycone was found to be identical with kaempferol. This suggests that kaemferol occurs as ester probably with tannins. Since the biological properties of some of the flavonoid compounds are known, the only unknown compound reported, barakol possibly possesses medicinal properties alleged to the leaves.

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2-METHYLBENZOTHIAZOLE COMPLEXES WITH SOME URANYL SALTS

SEVERAL studies appear to have been made on the coordination compounds formed by 2-methylbenzothiazole (Mbt) with transition and non-transition metal salts[1]. However, there is no report on the complexes of uranyl salts with this potentially bidentate ligand. The present study on the preparation and i.r. spectra down to 200 cm^{-1} on the coordination compounds formed by the interaction of Mbt with uranyl chloride, sulphate and nitrate was, therefore, undertaken to elucidate the mode of bonding of Mbt and of the anionic groups and the tentative stereochemistry of the complexes in the solid state.

2-Methylbenzothiazole (Mbt) was obtained from Koch-Light Laboratories Ltd., and used as such. The uranyl chloride and nitrate complexes with Mbt were obtained by adding an excess of the ligand to a hot solution of the respective uranyl salt in ethanol. The complexes which crystallized out were filtered, washed with ethanol and dried.

$UO_2(Mbt)_2Cl_2$:

Found U, 37·7; Cl, 11·5 Cal. U, 37·2; Cl., 11·1%.

$UO_2(Mbt)_2(NO_3)_2$:

Found U, 34·4; NO_3, 18·3 Calc. U, 34·4; NO_3; 17·9%.

The uranyl sulphate complex was obtained by adding an excess of the ligand to a methanol solution of uranyl sulphate. The complex which precipitated immediately was filtered, washed with methanol and dried.

$UO_2(Mbt)SO_4$: Found U, 46·4; SO_4, 18·3 Calc. U, 46·2; SO_4, 18·6%.

I.r. spectra were recorded as nujol mulls supported between sodium chloride plates (rock salt region) and thin polythene sheets (15–50 μ) on a Perkin-Elmer 621 spectrophotometer equipped with caesium idodide optics.

2-Methylbenzothiazole formed 1:1 complex with uranyl sulphate and 2:1 with uranyl chloride and nitrate. Absorption bands in the range 1600–200 cm^{-1} in uncoordinated Mbt and in the uranyl complexes are given in Table I. Contributions due to coordinated Mbt were selected by comparing the i.r. spectra of the uranyl complexes with those of the uncoordinated ligand and the residual features were assigned to uranyl group and coordinated anionic groups.