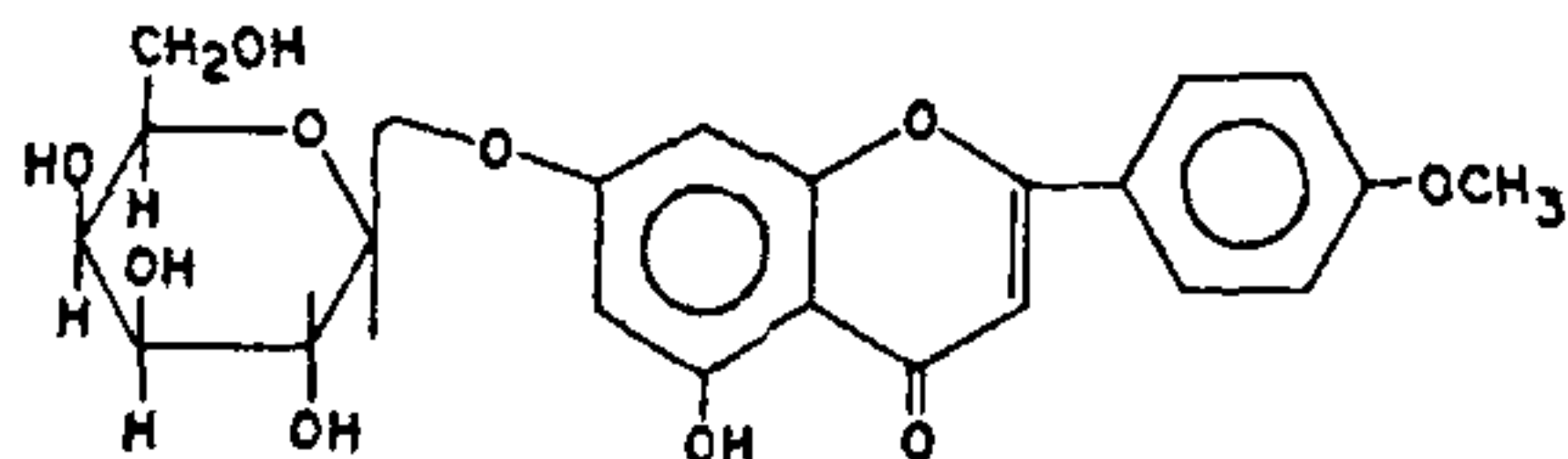


been isolated. Homogeneity and purity of both the compounds were established by paper and thin layer chromatography.

The compound A,  $C_{22}H_{22}O_{11}$ , m.p.  $310-12^\circ$  gave the characteristic colour reactions of flavone and it is glycosidic in nature. On acid hydrolysis (7% ethanolic  $H_2SO_4$ ), an aglycone  $C_{16}H_{12}O_5$ , m.p.  $180^\circ$  and a sugar D-galactose was obtained. It was confirmed by its derivatives such as phenyl osazone, m.p.  $196^\circ$  (lit.  $198^\circ$ ) and p-nitrophenyl D-galactosylamine m.p.  $218^\circ$  (lit.  $220^\circ$ ). The aglycone is found to contain one methoxyl group by Ziesel's method<sup>4</sup> (IR at  $2830\text{ cm}^{-1}$ ,  $1180\text{ cm}^{-1}$ ). The presence of -OH group at C-7 was confirmed by the bathochromic shift of 25 nm in band II on addition of NaOEt and shift of 47 in band I confirmed the substitution at C-4'. Position of OH group ethanolic at C-5 was confirmed by the bathochromic shift of 50 nm in band I on addition of 1% ethanolic  $AlCl_3$ . KOH degradation and  $KMnO_4$  oxidation gave phloroglucinol and anisic acid respectively which confirmed the positions of OH group and OCH at C5, C7 and C4'.

The sugar moiety is attached to aglycone at position C-7 because glycoside did not give positive test with the reagent vanillin hydrochloride<sup>5</sup>. This position was also confirmed by the UV spectra. On periodate oxidation it consumed 2.2 moles of periodate with the liberation of 1.2 mole of formic acid showing that one mole of sugar is present in pyranose form. It was also supported by a peak at  $822\text{ cm}^{-1}$  in the IR spectrum<sup>6</sup>.



ACACETIN-7-O- $\beta$ -D-GALACTOSIDE

On methylation, and subsequent acid hydrolysis of the compound 2, 3, 4, 6 tetra-O-methyl D-galactose was found which showed that sugar moiety is attached through C<sub>1</sub> to C<sub>7</sub> of the aglycone. Emulsion hydrolysis of the glycoside gave galactose showing  $\beta$ -linkage. Thus the compound has been identified as acacetin-7-O- $\beta$ -D-galactopyranoside.

The compound B,  $C_{31}H_{50}O_6$ , m.p.  $271^\circ$ ,  $[\alpha]_D^{26} + 114^\circ$  (in pyridine) was obtained as a residue settled in ethylacetate extract of leaves of this plant. The compound was insoluble in most of the organic solvents but highly soluble in pyridine. It gave positive Molisch's test showing it to be a glycoside. On hydrolysis with 10% methanolic HCl, an aglycone, m.p.  $137-38^\circ$ ,  $[\alpha]_D^{30} - 34.6^\circ$  (in  $CHCl_3$ ) and a sugar D-galactose was obtained. The aglycone was identified as  $\beta$ -sitosterol as it gave all characteristic tests<sup>7-10</sup>.

Methylation of the compound showed that sugar is attached at C-3 position of the aglycone. The compound was hydrolysed with enzyme taka-diaxase showing  $\alpha$ -linkage between sugar and aglycone.

The positive optical rotation of the phytosteroline suggested the  $\alpha$ -glycosidic linkage. Hence from the above discussion the phytosteroline has been represented as 24-b-ethyl cholest 5-ene-3-O- $\alpha$ -D-galactopyranoside.

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## KINETICS OF POLYMERISATION OF METHYL-METHACRYLATE IN PRESENCE OF CRYSTAL VIOLET

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THE retarding effect of 2,6-dichloro-phenol indophenol on polymerisation of methyl-methacrylate (MMA) has been studied<sup>1</sup>. In this paper we report the kinetics of polymerisation of MMA using crystal violet as a retarder.

The monomer has been polymerised under nitrogen atmosphere employing a modified dilatometric apparatus<sup>2</sup>. The monomer was purified by the method given by Overberger<sup>3</sup>. The initiator azobisisobutyronitrile (AIBN) was recrystallised twice from ethanol. The solution of the dye (BDH) was prepared in dimethyl-formamide (DMF) at  $25^\circ\text{C}$ . The

intrinsic viscosity  $[\eta]$  of polymer solution was measured in purified benzene (SDS) using an Ubbelohde viscometer. The polymer was precipitated with acidified methanol (AR.), dried and weighed to a constant weight. The time average rate of polymerisation ( $R_p$ ) was calculated (mol/l/sec.) equations (1) and (2)<sup>4</sup>

$$R_p = \frac{1000 \times S \times M}{60 \times V_s} \quad (1)$$

where  $S$  is the slope of volume contraction versus time plot,  $M$  is the mole of monomer polymerised/cm contraction and  $V_s$  is the volume of solution.  $M$  is calculated by (2):

$$M = \frac{W \times 10^{-4}}{V_c} \quad (2)$$

In (2),  $W$  is the weight of polymer formed during the polymerisation of monomer and  $V_c$  is the total volume contraction occurring in a definite polymerisation time.

A plot of  $1/R_p$  against polymerisation time is linear. The slope and intercept of the plot can be used for calculating the rate of initiation ( $R_i$ ) employing the following formula<sup>5</sup>.

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{R_i}{[\text{dye}]} \quad (3)$$

The average degree of polymerisation ( $\bar{P}_n$ ) was calculated with the following equation<sup>6</sup>.

$$\log \bar{P}_n = 3.342 + 1.13 \log[\eta] \quad (4)$$

The crystal violet retards the rate of polymerisation table I and the magnitude of retardation is a direct function of the [dye]. A plot of  $\log R_p$  versus  $\log[\text{dye}]$  is linear (figure 1), the slope of which gives the following relationship:

$$\frac{1}{R_p} \propto [\text{dye}]^{0.23} \quad (5)$$

The retarding effect of dye on  $R_p$  can be either due to (i) a decrease in  $R_i$  or  $R_p$  or (ii) an increase in rate of termination ( $R_t$ ).

A plot of  $1/\bar{P}_n$  against  $R_p$  is linear, the slope of which gave the value<sup>7</sup> of  $K_p^2/K_t$  (where  $K_p$  and  $K_t$  are the propagation and the termination rate constants, respectively). It has been found that the value of  $K_p^2/K_t$  is constant with [dye], hence it could be concluded that the dye does not effect either  $R_p$  or  $R_t$ .

TABLE I

Effect of crystal violet on the rate of polymerisation of methyl-methacrylate.

Concentration of crystal violet (mol/l) $\times 10^5$	Rate of polymerisation (mol/l/sec) $\times 10^4$
Zero	30.33
1	24.76
3	21.44
5	18.45
7	15.78
10	13.64

[MMA] =  $7.05 \times 10^{-2}$  mol/l

[AIBN] =  $2 \times 10^{-4}$  mol/l

Polymerisation time = 60 min

Polymerisation temperature = 60°C

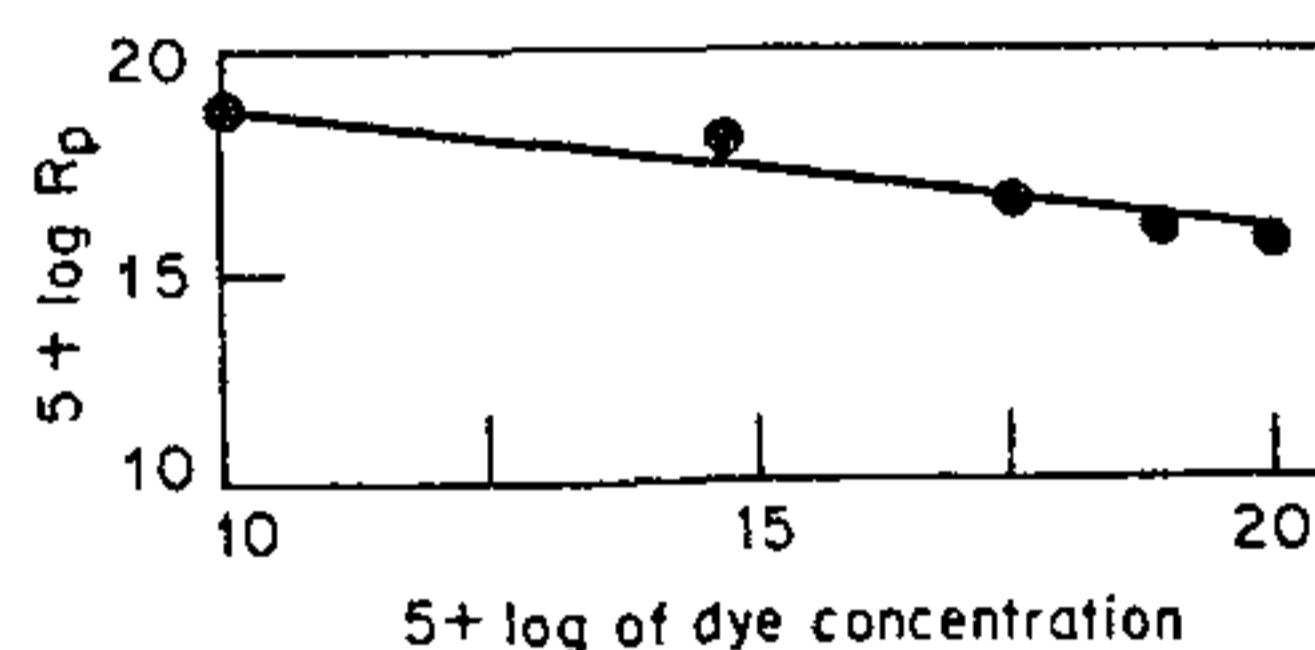


Figure 1. Relationship between log rate of polymerisation and log concentration of dye (crystal violet) on the polymerisation of MMA.

This fact is further confirmed by plotting a graph between  $R_p/R_p^0$  (where  $R_p$  and  $R_p^0$  are the rates of polymerisation in presence and in absence of the crystal violet, respectively and  $\sqrt{\eta}$  of the polymers, prepared in the presence of  $1 \times 10^{-5}$ ,  $3 \times 10^{-5}$ ,  $5 \times 10^{-5}$  and  $1 \times 10^{-4}$  mol/l of the dye (the conversions were 8.3%, 7.8%, 7% and 6%). The plot showed no linearity, which confirms that the rate of termination is constant<sup>8</sup> with the [dye].

The data presented in table 2 show the effect of [dye] on  $R_i$ . It is clear that  $R_i$  decreases with increase of the [dye] due to interaction of the dye with the primary radicals. Thus on the basis of the above facts and assuming the initiator efficiency constant, the following equation for the retarded rate of initiation ( $R_i'$ ) can be written for polymerisation of MMA in the presence of crystal violet:

$$R_i' = K_i [I] / \text{dye}$$

where  $K_i$  is rate constant for initiation and  $[I]$  is the concentration of initiator. A plot of  $R_i'$  against [dye] at constant  $[I]$  gives a straight line, the slope

TABLE 2

Effect of crystal violet on the rate of initiation ( $R_i$ ) of MMA

Concentration of crystal violet (mol/l $\times 10^5$ )	$R_i$ (mol/l/sec.) $\times 10^7$
1	4.52
3	3.64
5	3.20
7	2.41
10	2.12

[MMA] =  $7.05 \times 10^{-2}$  mol/l

[AIBN] =  $2 \times 10^{-4}$  mol/l

Polymerisation temperature = 60°C.

of which gives the value of  $K_i$  as 1.4 litre mol<sup>-1</sup> sec<sup>-1</sup> at 60°C. This study therefore shows that the crystal violet reduces the primary radical in the initiation step.

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## OCCURRENCE OF NEPHELINE SYENITE WITHIN QUARTZ SYENITE OF SETTUPALLE, PRAKASAM DISTRICT, ANDHRA PRADESH

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IN the recently recognised alkaline province of Andhra Pradesh<sup>1,2</sup> minor occurrences of nepheline

syenite are reported from Kotappa Konda<sup>3</sup> and Podili<sup>4</sup>. The present note reports the occurrence of a minor nepheline syenite body within the silica-saturated alkaline pluton near Settupalle (16°01' N; 79°52' E) in the Prakasam District of Andhra Pradesh.

The nepheline syenite body, measuring (100  $\times$  10 m), is oval in outline and is exposed amidst quartz syenites; the actual contact between these two rock types is covered by soil. The body does not contain xenoliths of country rocks.

The nepheline syenites are grey in colour, coarse grained and generally gneissic in appearance; however, those occurring at the central portions of the body are massive. The mafic minerals in the massive nepheline syenites are uniformly distributed, while they are aligned into well-defined bands in the gneissic types. These bands trend NE-SW and dip SE; the width of mafic bands (which are defined by the prisms of amphibole and flakes of biotite) is always less than that of felsic bands (which are chiefly composed of K-feldspar and nepheline).

The approximate modal compositions of both massive and gneissic rocks, and the approximate crystallisation sequences of the minerals in the two varieties are given in figure 1A and 1B respectively.

A			B	
APPROXIMATE MODAL COMPOSITION			APPROXIMATE X'LLISATION SEQUENCE OF MINERALS	
Minerals	Massive	Gneissic	Massive	Gneissic
Microcline	64	48	—	—
Plagioclase	8	17	---	---
Nepheline	15	20	—	—
Amphibole	9	7	—	—
Biotite	3	2	—	—
Sphene	1	2	---	---
Apatite	tr	1	---	---
Zircon	—	1	---	---
Calcite	—	2	---	---
Colour Index	13	11	Liquid → Rock	Liquid → Rock

Under the microscope, the rocks exhibit hypidiomorphic texture, and contain K-feldspar (microcline/microcline perthite), plagioclase and nepheline, with subordinate amounts of amphibole and biotite; apatite, calcite and sphene occur in trace amounts. The rocks are characterised by the total absence of clinopyroxene.

Microcline is subhedral, equidimensional in character and is generally associated with plagioclase and nepheline. Plagioclase occurs either as granular or tabular crystals. Nepheline is subhedral in outline, equidimensional and usually carries minor inclusions of amphibole and biotite especially along the *c*-axis. It also contains inclusions of other minerals like