From a detailed study of the properties of 7-hydroxy-chromones and coumarins with particular reference to the possibility of the fixation of the aromatic double bonds it was concluded that no rigid fixation exists.\(^1\)\(^2\) It is true that the eighth position is predominantly reactive indicating a possible fixation of the aromatic double bonds as in (I) and (II) but the other alternatives (III) and (IV) promoting reactivity of position six do not seem to be altogether prohibited. It was noticed that when a fresh pyrone ring was sought to be introduced umbelliferone gave rise to two isomeric (7:8-) and (7:6-) compounds, the former being produced in a predominant proportion.\(^3\) In regard to Fries migration, allyl transformation and azo-dye formation, though position 8 is the one to react first, when it is protected by alkyl or allyl groups position six also exhibits reactivity.

\begin{align*}
\text{(I)} & \quad \begin{array}{c}
\text{HO} \\
\end{array} \\
\text{CO} \\
\end{align*}

\begin{align*}
\text{(II)} & \quad \begin{array}{c}
\text{HO} \\
\end{array} \\
\text{CO} \\
\end{align*}

\begin{align*}
\text{(III)} & \quad \begin{array}{c}
\text{HO} \\
\end{array} \\
\text{CO} \\
\end{align*}

\begin{align*}
\text{(IV)} & \quad \begin{array}{c}
\text{HO} \\
\end{array} \\
\text{CO} \\
\end{align*}

Coupling with diazonium salts to form azo-dyes is a very facile reaction taking place energetically even at low temperatures. As a consequence of the results summed up in the above paragraph it was expected that when 7-hydroxy-chromones and coumarins were treated with diazonium salts bis-azo dyes would be produced due to reaction at the eighth and sixth positions in quick succession (V). As a matter of fact our early experiments carried out two years ago supported this expectation. In the meantime a paper
by Mahal and Venkataraman recorded that 6-hydroxyflavone forms only a mono-azo dye and the authors comparing this result with the observations of Perkin who obtained bis-azo dyes from chrysin, apigenin, etc., expressed the opinion that this difference should be attributed to the existence of the fixation of the aromatic double bonds in the hydroxyflavones as in (I). The effect of this fixation should be the same whether the hydroxyl group is in the sixth or the seventh position so that 6-hydroxy-and 7-hydroxyflavones should behave alike. It was therefore felt necessary to examine in detail the behaviour of 7-hydroxy-chromones and coumarins in regard to the formation of azo-dyes. The following hydroxy-benzopyrones have been studied: (i) 2-methyl-3-methoxy-7-hydroxychromone, (2) 7-hydroxy-flavone, (3) 7-hydroxycoumarin (umbelliferone) and (4) 4-methyl-7-hydroxycoumarin. In one series of experiments one molecular proportion of diazotised \( p \)-nitraniline has been employed and in another more than two molecular proportions. The products have been characterised by the melting point and nitrogen content and the results are presented in the form of a table.

In the case of (I) there is considerable formation of the bis-azo dye even when one molecular proportion of the diazonium salt is employed. With more than two molecular proportions the formation of the bis-azo dye is complete. On the other hand in the case of the hydroxyflavone (II) the mono-azo dye is obtained pure when one molecular proportion is employed and with a large excess of the diazonium salt only a small quantity of the bis-azo dye is produced along with a large amount of the mono-azo compound which is still the main component.

In the case of the coumarins when caustic soda is employed the formation of the bis-azo dye takes place very easily even with one molecular proportion of the diazonium salt obviously due to the fact that the \( \alpha \)-pyrone ring has been opened out by the caustic alkali. When this is prevented by using aqueous sodium carbonate mono-azo dyes alone are produced with one