(Fig. 1, lines D and E); (*ii*) The values of θ and ψ vary slightly as expected for various fractions; and (*iii*) the variations in the values of K (*cf.* Varadaiah's and ours) as well as θ (Kirste's and ours) must be traced to approximations in graphical extrapolations.

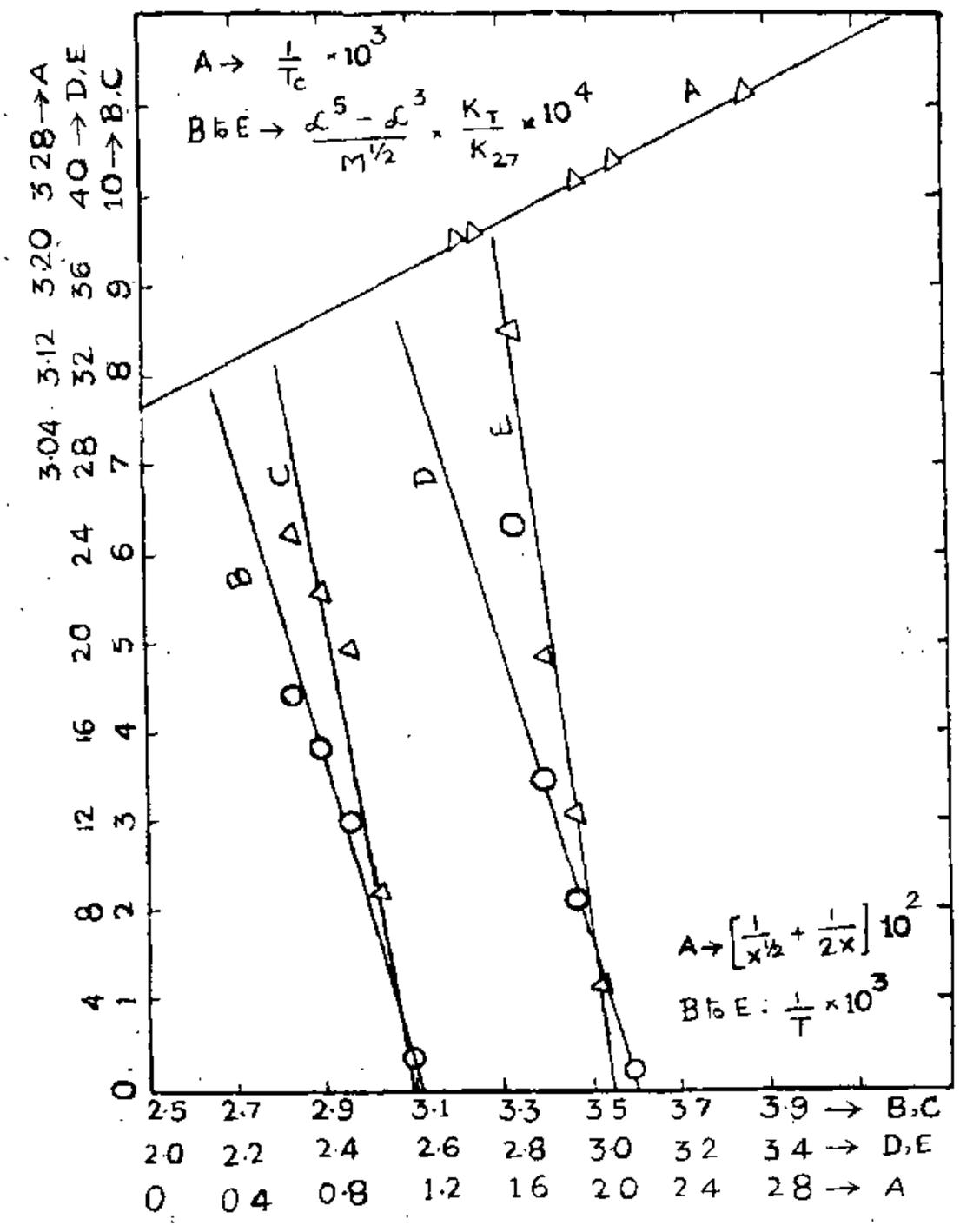

FIG. 1. Plot A. $1/T_\theta$ *vs.* $1/x^{\frac{1}{2}} + 1/2x$ for polymethyl methacrylate (Molecular weight = $2{\cdot}535 - 9{\cdot}226 \times 10^5$) in isoamyl acetate. Plots B-E. $\alpha^5 - \alpha^3/M^{\frac{1}{2}} \times K_T/K_\theta$ *vs.* $1/T$. The molecular weight of B and D = $7{\cdot}852 \times 10^5$ and that of C and E = $4{\cdot}842 \times 10^5$. Plots B and C with Fox's values of K and Plots D and E with our values of K.

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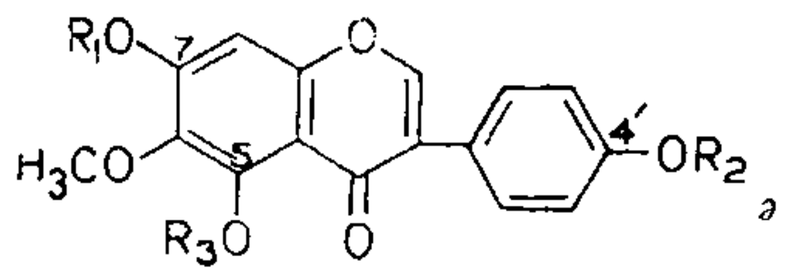
A NOTE ON TECTORIGENIN MONOMETHYL ETHERS

IN connection with other work in progress in this laboratory the different monomethyl ethers of tectorigenin (I) were required for purposes of comparison. Three isomers are possible: (*i*) 7-0-methyltectorigenin (II), (*ii*) 4'-0-methyltectorigenin (III) and (*iii*) 5-0-methyltectorigenin (IV). The first of these occurs free in the flowers[1] and the roots of *Dalbergia sissoo* and also in parts of *D. lanceolaria*[2]; recently it has been reported to be present in 'muninga' (*Pterocarpus angolensis*).[3] The 4'-0-rhamnoglucoside of (II) has been found in the green pods of *D. sissoo*.[4] We have originally synthesized (II)[1] by the partial methylation of (I); later other syntheses were also reported.[5,6]



I $R_1 = R_2 = R_3 = H$.
II $R_1 = CH_3$; $R_2 = R_3 = H$
III. $R_2 = CH_3$; $R_1 = R_3 = H$.
IV $R_3 = CH_3$, $R_1 = R_2 = H$.

The 4'-0-methyltectorigenin (III) (irisolidone) occurs in *Iris nepalensis*.[7] It was earlier obtained[8] by the base-catalysed isomerisation of 7-benzyloxy-8, 4'-dimethoxy-5-hydroxy isoflavone to 7-benzyloxy-6, 4'-dimethoxy-5-hydroxy isoflavone followed by debenzylation; a new synthesis has also been reported recently.[9] This compound has now been prepared as follows: tectorigenin was partially benzylated by refluxing with benzyl chloride, sodium bicarbonate and potassium iodide in acetone solution for 24 hours to yield the 7-0-benzyl ether (m.p. 195–96° from methanol; green ferric reaction); the latter was converted (methyl sulphate and potassium carbonate in acetone solution for 4 hours) into 7-benzyloxy-6, 4'-dimethoxy 5-hydroxy isoflavone (m.p. 153–54° from methanol). Subsequent catalytic debenzylation in ethyl acetate solution furnished the required 4'-0-methyltectorigenin (III). Its properties agreed with those described by the previous workers. For the synthesis of 5-0-methyltectorigenin, (I) was converted into the 7, 4'-di-0-benzyl ether (m.p. 148°) which was then methylated to obtain the 7, 4'-dibenzyloxy-5, 6-dimethoxy isoflavone (m.p. 150°). Catalytic debenzylation of the latter gave (IV), whose properties agreed

with those described for the material by Farkas *et al.*[6]

During our earlier work on the characterisation of (II) isolated from the *D. sissoo* flowers the alternative structure of 7, 4′-dimethoxy-5, 6-dihydroxy isoflavone was also considered.[10] In order to arrive at the correct structure the natural compound was first partially ethylated (m.p. 163° from methanol) and the ethyl ether methylated (m.p. 186° from methanol); the final product would be either 5, 6, 7-trimethoxy-4′-ethoxy isoflavone or 5, 7, 4′-trimethoxy-6-ethoxy isoflavone. An authentic sample of the former was prepared as follows: condensation of antiarol and *p*-ethoxyphenylacetyl chloride under Friedel-Crafts' conditions employing excess of aluminium chloride gave 2-hydroxy-4, 5, 6-trimethoxy-4′-ethoxy phenylbenzyl ketone (m.p 50° from methanol; purple ferric reaction). This deoxybenzoin was cyclised (ethyl formate method) to 5, 6, 7-trimethoxy-4′-ethoxy isoflavone which was identical with the substance prepared from the natural isoflavone thus confirming the structure of the latter as (II).

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STUDIES ON THALLOUS-SALICYLATE COMPLEX

THE salicylate complexes of aluminium,[1] beryllium,[2] iron,[3] manganese,[4] uranium,[5] palladium[6] and many other metals have been investigated by physico-chemical methods. No salicylate complex of thallium (I) has been reported so far, which encouraged the present investigation.

E. Merck sample of thallous nitrate and potassium-salicylate of B.D.H. make were used for the investigation. All solutions were prepared in double distilled water. For electrical conductivity measurements Doran's conductivity bridge and 'WTW' oscillator were used. All readings were taken at a temperature of $28 \pm 1°$ C.

The stoichiometry of the complex was first studied by monovariation[7] method. M/30 and M/40 equimolar solutions of thallous nitrate and potassium-salicylate were mixed by keeping the volume of thallous nitrate constant (5 ml.) and varying the volume of potassium-salicylate, conductance measurements were done after a gap of 6 to 8 hours when the equilibrium is established. A graph of conductance against the volume of ligand added shows a clear break at the ratio of 1 : 2 (metal : ligand) indicating that thallium (I) and salicylate ion combine in 1 : 2 ratio.

The composition was further confirmed by Job's[8] method of continuous variation. M/40, M/60 and M/80 equimolar solutions were mixed, with blank sets for metal and ligand solutions. Graphs of Δ-conductance against the percent volume of potassium-salicylate shows maxima at 66% of the ligand. This result is in accord with the previous observation.

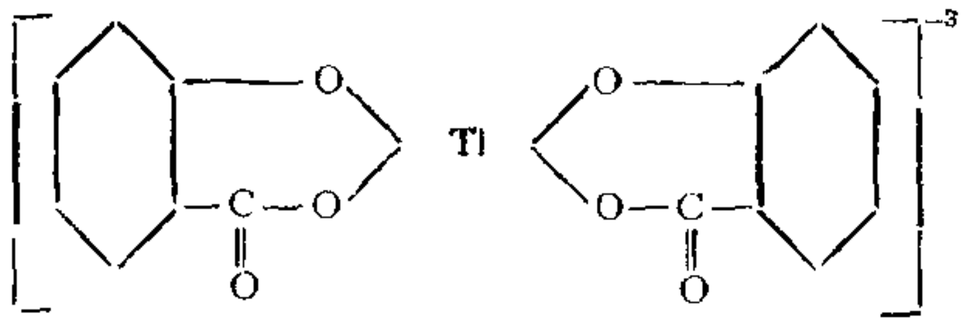
The instability constant (K) of the complex was determined in the same way as for composition by Job's method but with non-equimolar solutions. M/100 thallous nitrate and M/20, M/25 and M/40 potassium-salicylate solutions were used. The value of K was calculated by the formula:

$$K = \frac{C\,[(p-1)\,x-1]^2}{(p-1)\,(1-2x)}$$

where c = concentration of metal ion; p = ratio of concentration of ligand and metal ions and x = maxima in the curve.

The average value of instability constant is calculated to be $4{\cdot}75 \times 10^{-6}$.

Considering co-ordination number of thallium (I) to be four and the bidented nature of the ligand, the probable structure for thallous-salicylate complex is proposed to be:



Both the carboxylic and phenolic hydrogen ions are replaced by thallous ion.