

the alcohol underwent dehydration above 180° C. The gas chromatograph employed in the present work was fabricated locally as described by Miller.⁶ The column was first activated by flushing with hydrogen at a flow rate of 80 ml/min for 6 hrs at 230° C. The surface area of the silica gel sample (BET, N₂, -196° C) was found to be 377. m²/g and the total pore volume was 0.534 cc/g.

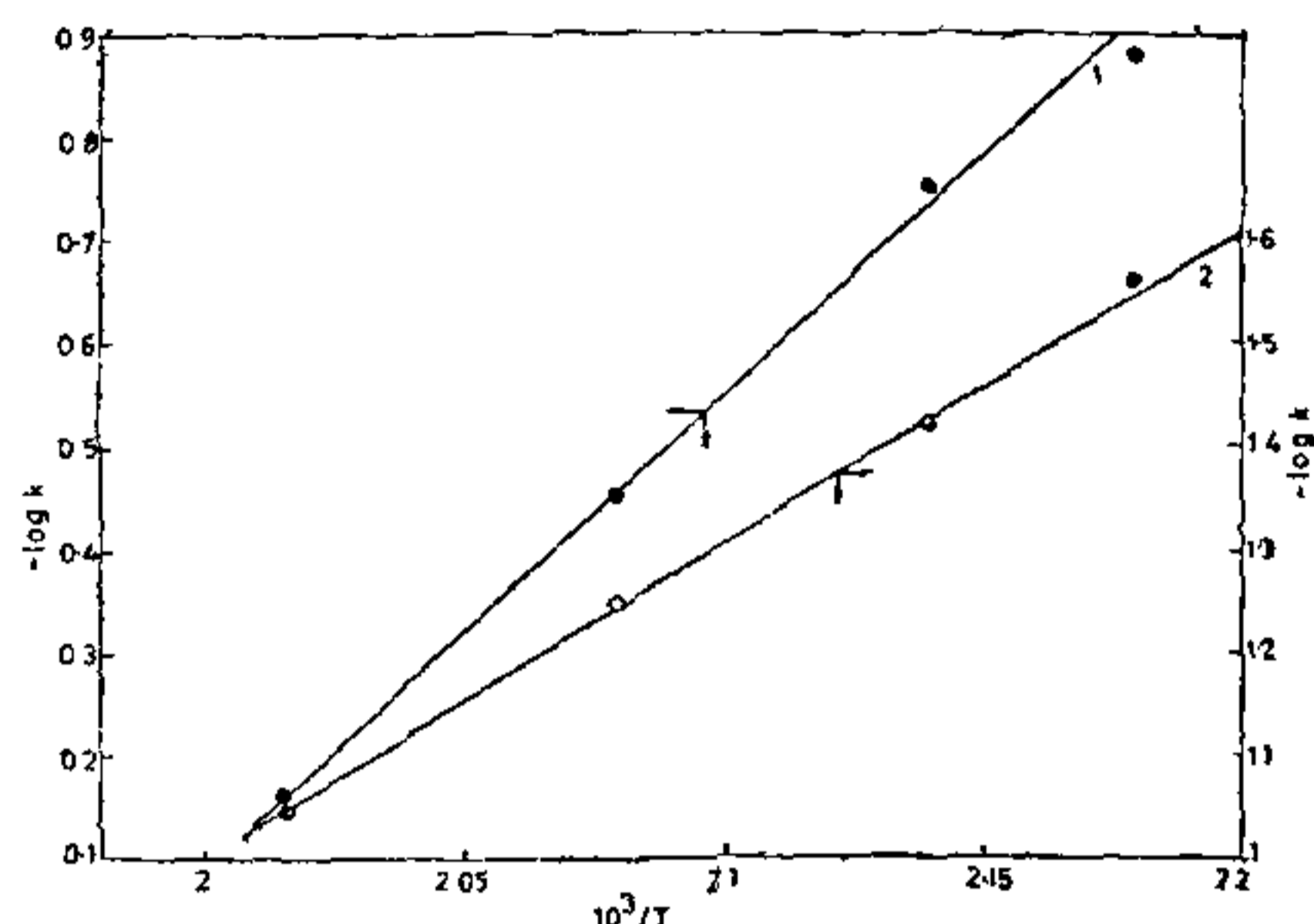


FIG. 1. Arrhenius plots for the dehydration of *t*-butanol. 1. E_{surface} —Phillips *et al.*⁵ method. 2. E_{app} —From the distortion in the elution chromatographic peaks.

The mathematical model for an irreversible first order reaction⁴ was assumed for the dehydration process. When the specific retention volumes were corrected for the pressure gradient, the plots of $\log S_x$ vs V [$= (V_x - V_b) / (V_a - V_b)$], obtained from the distorted elution peaks, were found to be straight lines indicating the correctness of the assumption. Here V_a and V_b denote the specific retention volumes of TBA and water respectively. V_x is the specific retention volume at any point x on the chromatogram between the two peak maxima and S_x is the magnitude of the signal at any point x . It has been observed that one of the products (propylene) formed during the reaction does not produce any separate signal [$A \rightarrow B + (C)$]. Hence, the model proposed by Phillips *et al.*⁵ for this type of reaction has also been made use of in the evaluation of the first order rate constants by the pulse method.

From the corresponding Arrhenius plots (Fig. 1) the energy of activation (E_a) by the two methods has been evaluated. It is observed that E_a calculated from the distortion in the peak has a value 14.11 kcal/mole and the corresponding value obtained by the method of Phillips *et al.* is 21.2 kcal/mole. This is only to be expected since in the latter method the E_a value obtained is for the sur-

face reaction (E_{surface}) whereas the E_{app} for the dehydration process is obtained by the former method. The values of E_{surface} and E_{app} would differ from each other in magnitude by the heat of adsorption of the adsorbate. Hence, to check the accuracy of the values obtained by the two methods, the heat of adsorption of TBA was calculated from the $\log V_g$ vs. $1/T$ plot and was found to be 7.4 kcal/mole. This agrees well with the difference (7.09 kcal/mole) in the E_a values obtained in the present instance, thus indicating the advantage of using solid-gas chromatography for the rapid and accurate evaluation of kinetic parameters of heterogeneous reactions.

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STUDIES IN THE RELATIONSHIP BETWEEN BETAFITE AND PYROCHLORE

LITERATURE survey revealed that the relationship between betafite and pyrochlore has not been clearly established.¹⁻⁴ Hogarth⁴ has not classified betafite as a mineral with pyrochlore structure containing 15% or more, uranium.

In the present studies synthetic betafite has been prepared by introducing 15% uranium in $Y_2Ti_2O_7$ (pyrochlore). The procedure adopted in the preparation of the samples is the same as in the previous communication,⁵ except that the samples were quenched. The diffractometer patterns were taken by using $CuK\alpha$ radiation filtered through nickel.

The results are given in Table I.

It is seen from Table I that in the composition A, synthetic betafite consists of two phases pyrochlore as major phase and brannerite as minor phase. This agrees well with the mineral betafite reported by Gasperin.³

TABLE I

	Composition (wt. %)				Phases present
	Y ₂ O ₃	CaO	U ₃ O ₈	TiO ₂	
A	43.56	..	15	41.44	Betafite (pyrochlore + brannerite) ($a=10.02 \text{ \AA}$)
B	40.56	3	15	41.44	Betafite (pyrochlore + brannerite trace) ($a=10.03 \text{ \AA}$)
C	34.56	9	15	41.44	Pyrochlore ($a=10.05 \text{ \AA}$)
D	28.56	15	15	41.44	Pyrochlore ($a=10.09 \text{ \AA}$) + perovskite

On introducing 3% of Ca²⁺ ions in the betafite (composition B) the intensity of the brannerite phase decreased and the lattice constant of the pyrochlore phase increased to 10.03 Å. This is due to the higher ionic radius of Ca²⁺ ion (0.99 Å). On further increasing the percentage of Ca²⁺ ions (composition C) a single pyrochlore phase with increased lattice constant (10.05 Å) was observed, which indicates that the brannerite phase has formed a solid solution with pyrochlore phase. In composition B with increased percentage of Ca²⁺ ions perovskite phase along with pyrochlore was obtained.

In the above pyrochlore structure Ca²⁺ (0.99 Å), Y³⁺ (0.92 Å) and U⁴⁺ (0.97 Å) are in the A sites while Ti⁴⁺ (0.68 Å) ions are in the B sites.

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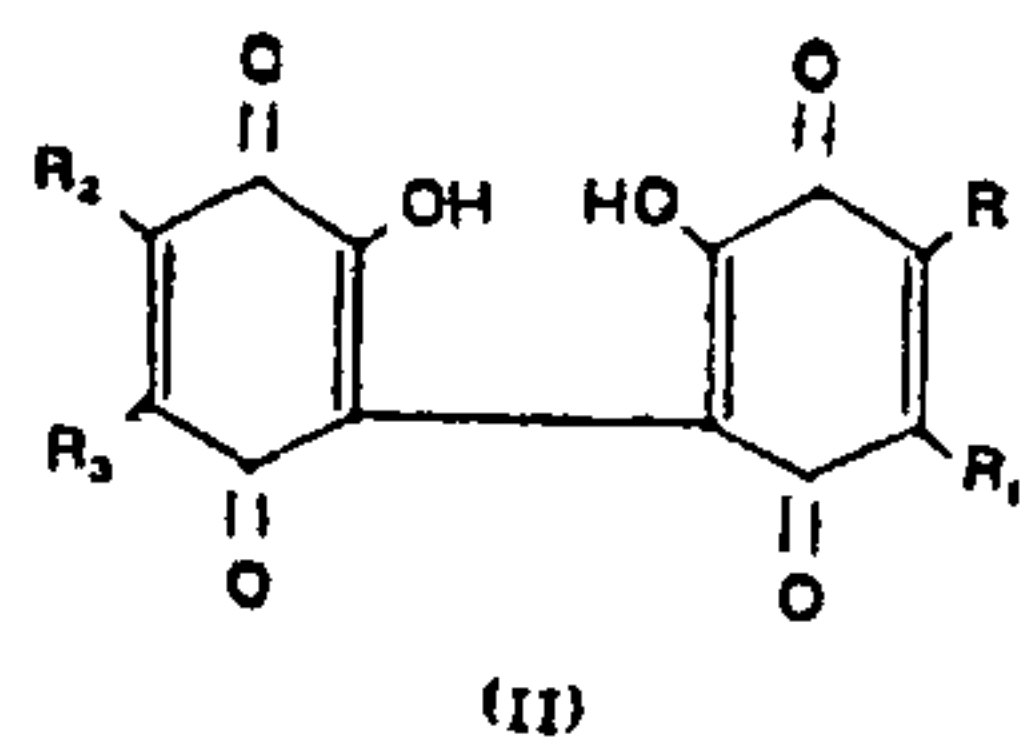
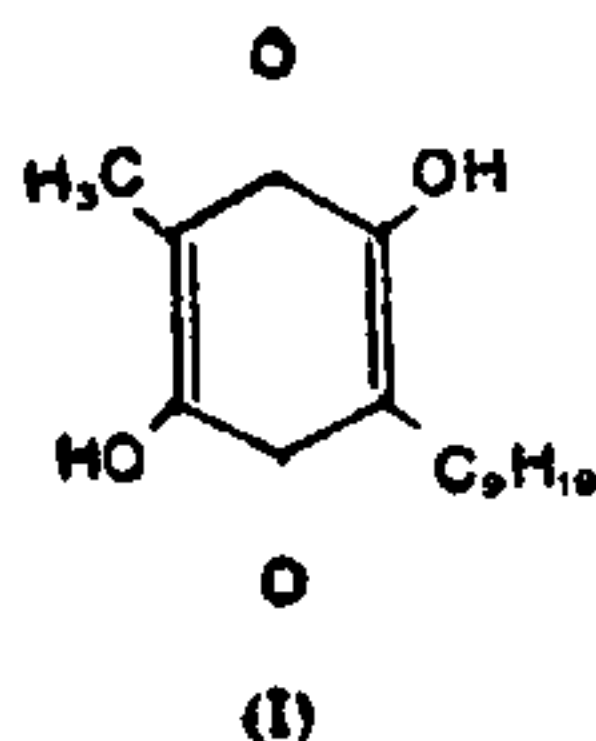
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CHEMICAL EXAMINATION OF THE LEAVES OF MAESA MACROPHYLLA WALL A. DC

An earlier publication¹ reports the isolation of bhogatin, its constitution and synthesis. We now report further studies on the chemical components of the leaves of *M. macrophylla*,

Extraction of the dry leaves with normal hexane gave (1) an alkali-soluble fraction from which bhogatin (I) has been isolated (Yield: 2.5%), besides a new quinone (II), m.p. 55–57° (Yield: 0.1%), u.v. λ_{\max} (CHCl₃) 275 m μ (log ϵ , 4.51), 400–405 m μ (log ϵ , 2.98); i.r. (CHCl₃), 3420 cm⁻¹ (OH) 1665–50, 1630 (>C:O) cm⁻¹. Mass spectrum M⁺ 526, molecular formula, C₃₂H₄₆O₆. It gives violet solutions with alkalis and a purple colouration with ferric chloride. It shows the properties of a p-quinone since it underwent ready reduction and reoxidation. It formed a diacetate, molecular formula, C₃₆H₅₀O₈, as a liquid and an acetate of its reduction product also as a colourless liquid. N.M.R. spectral studies of (II) indicated the following data: (CDCl₃) 2.8 τ (broad, 2H, hydroxyls), 7.5–7.97 τ (benzylic methylenes, 4H), 8.12 τ (ring methyls, 6H singlet), 8.5–8.97 τ (centered at 8.82 τ , side-chain methylenes, 28–34H), 9.2 τ (side-chain end methyls, 6H, triplet, J = 5–6 cps). These results indicated that it is a dibenzoquinone having possibly the structure (II), which is named by us, macrophyllin. The occurrence of macrophyllin in plant products, a dibenzoquinone, is the first isolated so far, while phoenicin² and oosperin³ are mould products. Oxidation of macrophyllin (1 mol.) with neutral permanganate gave two molecules of decoic acid, indicating thereby, that the side-chain in both the rings is -C₉H₁₉. Further, macrophyllin undergoes dehydration with concentrated sulphuric acid in dioxan to give anhydro-macrophyllin, the infrared spectrum showing clearly the absence of -OH frequencies. These reactions support the structure assigned to macrophyllin.



(a) R = R₂ = CH₃; R₁ = R₃ = C₉H₁₉

(b) R = R₂ = C₉H₁₉; R₁ = R₃ = CH₃

(c) R = R₃ = CH₃; R₁ = R₂ = C₉H₁₉

The neutral fraction of the *n*-hexane extract gave β -amyrene, identified by comparison with an authentic sample of β -amyrene.

Subsequent extraction of the dry leaves with benzene to remove completely chlorophyll,