

In the subsequent stages of chlorination, methylation and other treatments the yields were good. Spectroscopic examination of the final product agreed well with an authentic sample of diploicin methyl ether.

Similarly, 3, 5, 5'-tribromolecanoric acid⁸ and 5, 5'-dichloroatranorin⁸ were also converted into the corresponding halogenated depsidones by this method.

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THE KINETICS OF THE BROMINATION OF AROMATIC COMPOUNDS

Our present knowledge about the kinetics of the bromination of the aromatic nucleus is very limited. Although the over-all reaction between bromine and an aromatic substrate is generally known to be of the third order in several organic solvents, the exact mechanism of the process has not been clearly understood.¹⁻⁴ The precise rate constants and the Arrhenius parameters for various types of aromatic compounds have also not been determined so far. We have therefore undertaken in this laboratory a systematic study of the kinetics of the reaction in various non-aqueous media.

We have measured the rates of bromination of paradimethoxybenzene and anisole in dry acetic acid, and our new results are reported in

this communication. The reaction was carried out in iodine flasks of capacity 50 c.c., under the usual thermostatic conditions ($\pm 0.05^\circ \text{C}$). The unreacted bromine present after various time intervals was estimated iodimetrically.

The experimental data for the reaction between bromine and paradimethoxybenzene in equimolar amounts were found to fit in best with the integrated form of the appropriate third-order equation

$$k_3 = \frac{1}{2t} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\}.$$

The plot of $1/(a-x)^2$ against t is a straight line with an intercept of $1/a^2$, for two different initial concentrations of the reactants (Fig. 1, plots A and B). The values of k_3 , as obtained from the slopes of the lines, are 2.17 and 2.33 litre² mole⁻² sec.⁻¹ at 30°C . Additional evidence for the correctness of these values was obtained as follows. The rate of consumption of bromine was measured in a few experiments in which the initial concentration of the substrate was several times (10 to 40) larger than that of bromine. The data obtained fitted well with the second-order rate expression

$$k_2 = \frac{1}{t} \left\{ \frac{1}{(a-x)} - \frac{1}{a} \right\}$$

(Fig. 1 plots C, D, E). The values of k_3

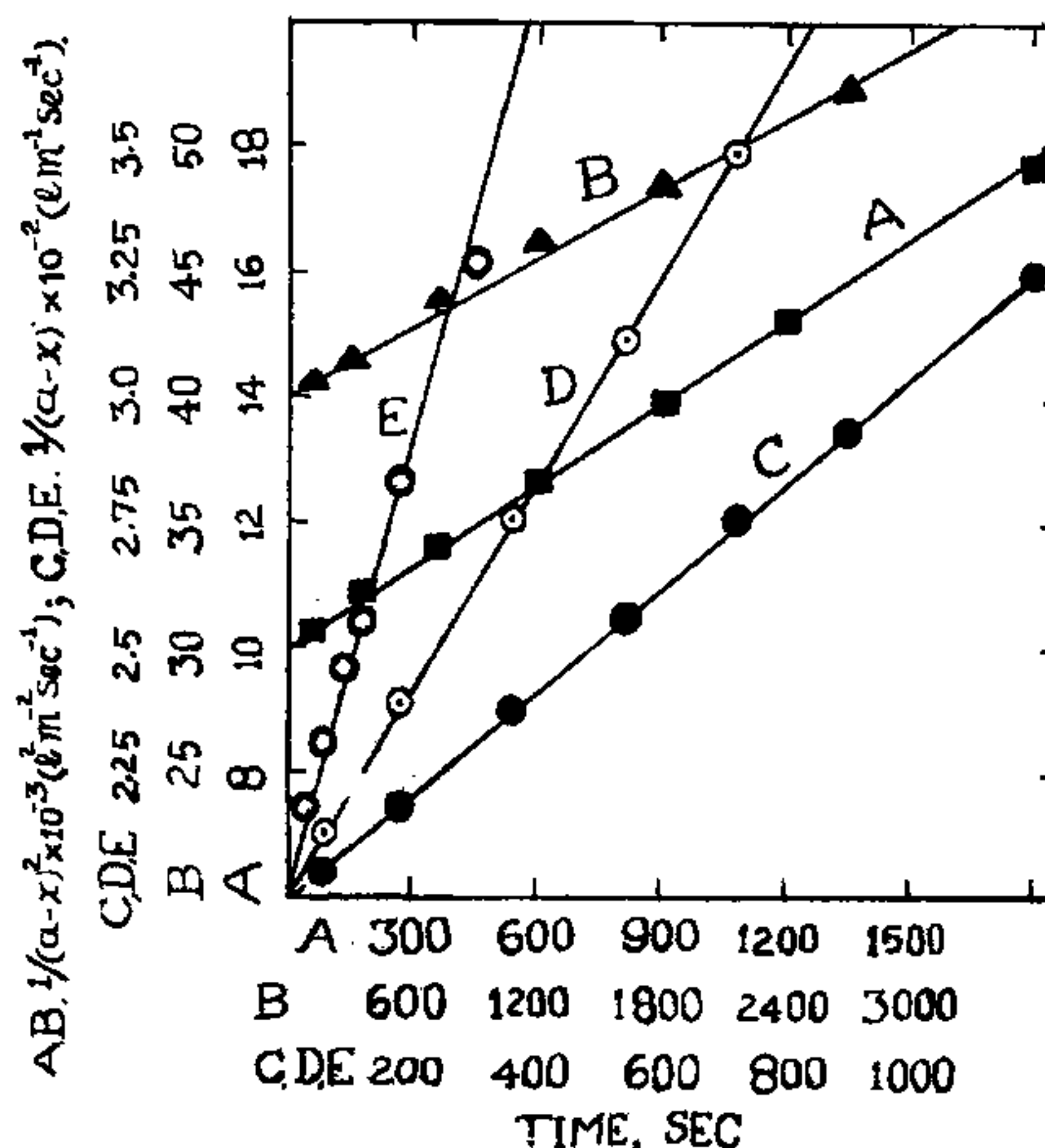


FIG. 1. A-B, Plot of $1/(a-x)^2$ vs. time for equimolar initial concentration of reactants (bromine and paradimethoxybenzene). A, 0.01 M; B, 0.005 M. C-E, Plot of $1/(a-x)$ vs. time; Initial Concentration of bromine is 0.005 M in each case; Initial concentrations of paradimethoxybenzene. C, 0.65 M; D, 0.10 M; E, 0.19 M. Temp. 30°C .

obtained from the slopes of these lines are 2.08, 2.08 and 2.40 litre² mole.⁻² sec.⁻¹. These are in very good agreement with the values obtained from straight lines A and B. These results clearly show that the over-all reaction is of the third order and the order with respect to bromine is two. In the kinetic studies on aromatic bromination published so far,²⁻⁵ the experimental data have not been treated as we have done here. In most cases, only the total order of the reaction has been evaluated (and found to be three) by adopting the less rigorous "fractional-life method".⁶

The bromination of anisole was also investigated on similar lines. The value of k_3 was found to be 32.5 litre² mole.⁻² sec.⁻¹. Using these rate constants for anisole and paradimethoxybenzene along with the product analysis data reported by Stock and Brown,⁵ and applying Holleman's product rule,⁷ we deduced that the partial rate factor for the meta position for the methoxy group is 2.

The effect of temperature on the reaction was also studied and good Arrhenius plots were obtained. In the temperature range 20-40°C., the expressions for k_3 were: $k_3 = 1.86 \times 10^5 \exp. (-6900/RT)$ for paradimethoxybenzene; and $k_3 = 1.94 \times 10^5 \exp. (-5200/RT)$ for anisole.

Work is being continued with more compounds such as orthodimethoxybenzene, paratolylmethyl ether, etc., and full details will be published elsewhere.

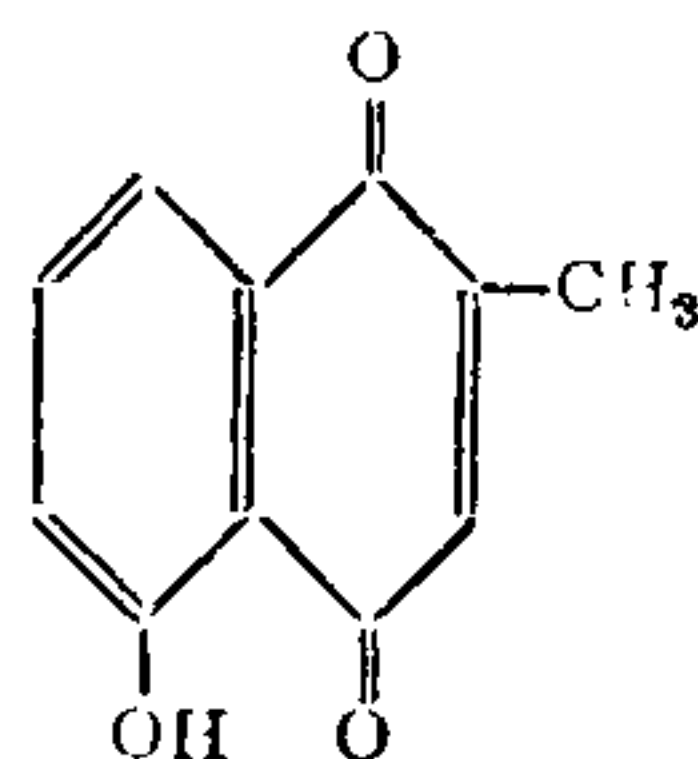
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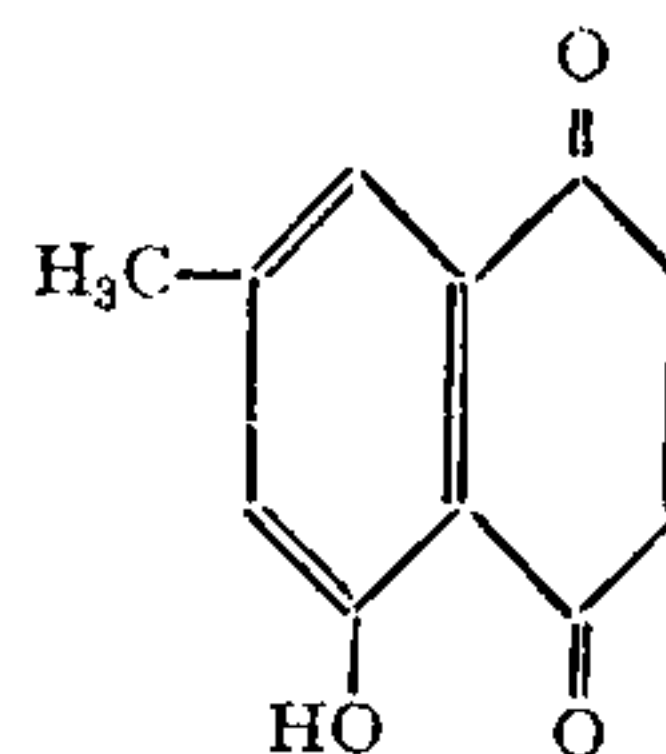
THE OCCURRENCE OF LUPEOL GROUP OF TRITERPENOIDS IN DIOSPYROS SPECIES

PLUMBAGIN (I) and 7-methyl juglone (II) have been isolated from a number of *Diospyros* species.¹⁻⁴ It has also been recorded that these are responsible for the poisonous and vesicant properties of *D. hebecarpa*⁵ and other species.

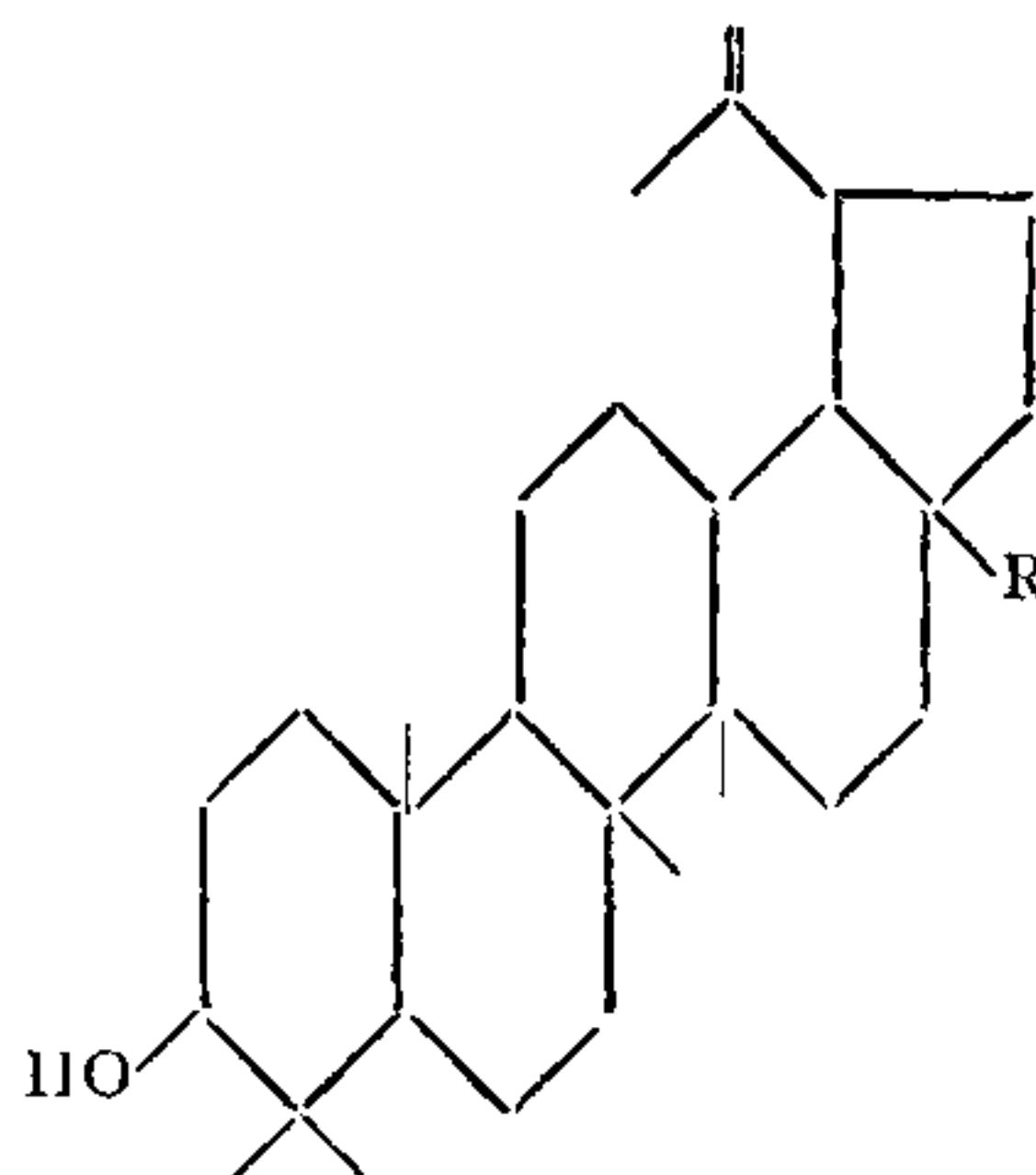
Recent investigations on *D. montana*⁶ and *D. mollis*⁷ revealed the presence of 2,2'-binaphthaquinones. The former contains all the three variants of the lupeol group of triterpenoids (III, IV and V) also.



I



II



III R = CH₃

IV R = CH₂OH

V R = COOH

During the course of our investigation of local heartwoods, five *Diospyros* species have been examined for their chemical constituents. Except *D. melanoxylon*,* the rest did not contain any naphthaquinones; but triterpenoids of the lupeol group have been encountered in good yield. Table I gives their occurrence.

TABLE I

<i>Diospyros</i> species	Lupeol (III) (%)	Betulin (IV) (%)	Betulinic acid (V) (%)	Other constituents
1. <i>D. melanoxylon</i>				
(a) bark	0.50	0.50
(b) sap wood	0.02	0.02
(c) ebony	0.02	0.02	0.01	..
2. <i>D. discolor</i>				
(a) fruit	..	0.05	0.05	β -Sitosterol
(b) wood	..	0.08	0.08	..
3. <i>D. Perigrina</i>				
(a) bark	2.5	..
(b) leaves	..	1.00
4. <i>D. kaki</i>				
wood	β -Sitosterol
5. <i>D. chloroxylon</i>				
fruits

* Under publication: *Chemistry of Diospyros Species* in N.I.S. Symposium on Natural Quinones.