

Fig. 2. Experimental difference curve and theoretical curves calculated on the assumption of free rotation.

represent three different choices for the half-width, *i. e.*, 0.314 Å, 0.418 Å, and 0.530 Å. The theoretical curves were normalized to the experimental curve.

The agreement between the theoretical and experimental curves is good. The discrepancies are easily understood: 1) The choice of the subtracted envelope<sup>7</sup> is somewhat arbitrary, 2) the subtraction of the invariable distances leaves some uncertainty, and 3) the  $\text{Br}_1-\text{H}_4$  distances are expected to give rise to a detectable effect. The  $\text{Br}_1-\text{H}_4$  distances should have a probability curve similar to that for  $\text{Br}_1-\text{Br}_4$ , but with peaks at about 5.37 Å and 5.87 Å and a total area about 15 % of the  $\text{Br}_1-\text{Br}_4$  area. The maximum and minimum  $\text{Br}_1-\text{H}_4$  distances are marked by dashed arrows in Fig. 2. The maximum and minimum  $\text{Br}_1-\text{Br}_4$  distances are marked by solid arrows.

There remains one unexplained point in the radial distribution curve, namely the comparatively large area located at 4.67 Å. The  $\text{C}_1-\text{H}_4$  distance at 4.58 Å should not give rise to such a large area. Even though we are not able to interpret this point, we feel it has no essential effect on our conclusion that there is internal rotation in the gaseous  $\text{CBrH}_2-\text{C}\equiv\text{C}-\text{CBrH}_2$  molecule.

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## Phenol Dehydrogenations

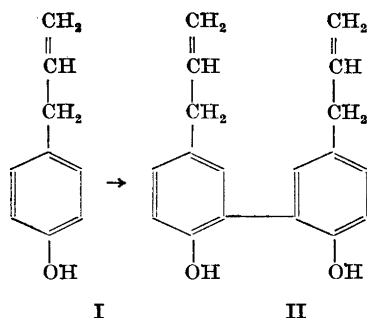
### VII. \*. Dehydrogenation of Chavicol to Magnolol

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The biosynthetic importance of dehydrogenative coupling of phenols with the formation of diphenyl or diphenyl-oxide derivatives has been discussed by Erdtman and Wachtmeister<sup>1</sup>. Magnolol (II) is a particularly simple example with a structure indicating that it has been formed by the coupling of two molecules of chavicol (I) or an aromatic precursor.

\* Part VI: *Svensk Kem. Tidskr.* **47** (1935) 223.



Magnolol occurs in the bark of a number of *Magnolia* species. The compound was isolated and its structure elucidated by Sugi<sup>2</sup> who also synthesised tetrahydro-magnolol.

We have now obtained magnolol in a yield of about 25 % by dehydrogenation of chavicol with ferric chloride. During this work Ohta and Mori<sup>3</sup> reported the formation of tetrahydro-magnolol from *p*-(*n*-propyl)-phenol by dehydrogenation with a mixture of hydrogen peroxide and aqueous ferrous sulphate. Tetrahydro-magnolol was also obtained recently by Haynes, Turner and Waters<sup>4</sup> during their studies on the dehydrogenation of various phenols with potassium ferricyanide.

**Experimental \*.** *Dehydrogenation of 1-allyl-4-hydroxy-benzene (chavicol)*: Ferric chloride (28 g) was dissolved in distilled water (2 500 ml) in a three-neck flask. 1-Allyl-4-hydroxy-benzene (10 g) in 95 % ethanol (40 ml) was added dropwise during 4 h with stirring while a stream of air was bubbled through. The solution turned first green and then black. Stirring and aeration was continued for 48 h more. When the stirring was stopped at the end of this period, a viscous red oil collected at the bottom of the flask. The reaction mixture was acidified and extracted with ether, the ether solution extracted with 2 N sodium hydroxide and the alkaline solution acidified and extracted with ether. After washing and drying the ether extract was evaporated and the remaining oil distilled yielding first, unchanged starting material (5.9 g), then a liquid fraction (0.79 g) boiling at 120–130°/0.8 mm which

was not further investigated and finally a crystalline fraction (1.02 g) consisting of magnolol boiling at 175–177°/0.8 mm. Allowing for recovered starting material the yield of crude magnolol was 25 %.

*Magnolol phenylurethan*: The above crude magnolol (1.0 g) was heated with phenyl isocyanate (1.2 g) at 110° for one hour in a sealed tube. Excess reagent was evaporated under vacuum on a waterbath. A benzene solution of the crystalline residue was filtered through a 20 cm column of aluminum oxide soaked with ligroin. The first product leaving the column was the phenylurethan. The impurities moved at a slower rate. Evaporation of the solvent gave the phenylurethan (1.3 g) which after recrystallisation from 95 % ethanol melted at 143.5–144.5° undepressed by magnolol phenylurethan obtained synthetically from 2,2-dihydroxydiphenyl<sup>5</sup>.

*Magnolol from magnolol phenylurethan*: Magnolol phenylurethan (2.0 g) was heated overnight in a high vacuum at 200° in a tube sealed at one end and surrounded by a coil providing a decreasing thermogradient towards the open end of the tube where the magnolol formed was deposited. Yield 0.87 g. The product was resublimed twice; m. p. 101.0–101.5° (lit. 103°), undepressed by magnolol obtained synthetically from 2,2'-dihydroxydiphenyl<sup>5</sup>.

*Isomagnolol*: In a nickel crucible, powdered potassium hydroxide (0.25 g) was dissolved in hot amyl alcohol (0.36 g). Magnolol (0.1 g) was added and the melt heated at 140° for 20 h. After cooling, water (10 ml) was added and the amyl alcohol removed by steam distillation. The remaining solution was filtered and acidified. The crystalline precipitate formed was collected, washed with water, dried and recrystallised from ligroin, m. p. 142–143° (lit. 143.5°).

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\* Melting points are uncorrected.

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