



being shifted so far to the right even at maximal sodium hydroxide concentration that practically all the mandelic acid is in the form of ion II. Thus the molar absorption of II cannot be calculated directly and hence we calculated it by Stearns and Wheland's method<sup>3</sup>. The molar absorption of I at 244 m $\mu$  is 120.5, while that of II is 719 at the same wave-length. Using these values the concentrations of I and II in the dissociation constant:

$$K = \frac{[\text{II}][\text{H}^+]}{[\text{I}]}$$

can be calculated. The values of  $K$  are given in the fourth column of Table 1, its average being  $7.19 \times 10^{-16}$ .

Table 1

[NaOH]	pH	$A_{244}$	$K \times 10^{16}$
—	4	0.250	—
—	10	0.238	—
0.279	13.3	0.250	6.75
1.395	14.1	0.344	8.24
2.79	14.5	0.477	8.29
5.58	15.2	0.747	4.45
10.16	16.2	1.315	7.96
Average			7.19

Details of this research will be published in full elsewhere. Thanks are due to Dr. J. Császár for the measurements of absorption.

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<sup>1</sup> Warner, R. C., and Weber, I., *J. Amer. Chem. Soc.*, **75**, 5086 (1953).

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## BIOCHEMISTRY

### Structure of Bhilawanol

BHILAWANOL is the golden yellow liquid found in the pericarp of the marking nut *Semecarpus anacardium*. It forms a di-naphthylurethane and a dimethyl ether and on catalytic reduction it absorbs one mole of hydrogen to give hydrourushiol (3-pentadecylcatechol)<sup>1,2</sup>.

Ozonolysis of the diphenylmethylen ether gave heptaldehyde<sup>2</sup> (in low yield), suggesting that at least a portion of the bhilawanol is 3-(pentadecenyl-8')-catechol (thus corresponding to the urushenol of poison ivy and Japanese lac<sup>3</sup>).

Although distillation of dimethyl bhilawanol<sup>1</sup> and chromatography of the diphenylmethylen ether<sup>2</sup> pointed to bhilawanol as being a single substance, chromatography of the dimethyl bhilawanol using the procedure described by Symes and Dawson<sup>4</sup> showed that it was not homogeneous (Symes, W. F., unpublished work). Furthermore, the glycol, m.p. 56–60°, prepared by performic acid hydroxylation of distilled dimethyl bhilawanol, on chromatographing, separated into two glycols, one melting at 66.8°, the other at 93–4° (Symes, W. F., unpublished work).

The low-melting isomer is identical to the glycol prepared by performic acid (*trans*) hydroxylation of

the dimethyl ether of the stereochemically pure *cis* poison ivy urushenol<sup>4</sup>. The high-melting isomer is identical to the glycol prepared by osmium tetroxide (*cis*) hydroxylation of this same material<sup>3</sup>. It therefore becomes clear that the bhilawanol is a mixture of the *cis* and *trans* isomers of urushenol.

These conclusions are evident from Table I.

Table 1

Compound	$n_D^{25}$	m.p.	Dimethyl ether		Di-naphthyl-urethan, m.p.
			$n_D^{25}$	Glycol, m.p.	
Bhilawanol*	1.5032 (ref. 1)	15°	1.5000	67 and 93†	138–40° (ref. 1)
Urushenol ( <i>cis</i> )‡	1.5081	33°	1.4945	95†	139–41° (ref. 3)
Urushenol ( <i>cis-trans</i> ) (ref. 3)	1.4970	10–15°		67‡ and lower melting solid†	137–39° (ref. 3)

\* Distilled but not chromatographed; † performic acid hydroxylation; ‡ synthetic (ref. 3); § osmium tetroxide hydroxylation.

The melting ranges of the solid derivative, the dinaphthyl urethane, is evidently a poor criterion of homogeneity in this series.

Bhilawanol and the *cis-trans* urushenol prepared by acid catalysed isomerization of *cis* urushenol<sup>3</sup> are very similar, and there can be little doubt that bhilawanol contains a component identical to the monolefinic component of poison ivy urushenol.

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### Age Difference in Nicotinamide Mononucleotide Synthesis by Human Erythrocytes

It is well known that human erythrocytes contain an active enzyme system capable of synthesizing considerable amounts of nicotinamide mononucleotide from nicotinamide added *in vitro*<sup>1</sup>. The nicotinamide mononucleotide synthetase is very specific for human erythrocytes as the only other mammal in the blood cells of which it could be detected is the guinea pig<sup>2</sup>. It was found here, however, that the activity of the given synthetase in human erythrocytes can be shown at the beginning of the fifth month of life when its activity rapidly reaches almost a maximum level, remaining then practically without change. Whereas mammalian erythrocytes not synthesizing nicotinamide mononucleotide are characterized by a high content of pyridine nucleotides, their amount being several times higher than in human and guinea pig erythrocytes<sup>2</sup>, the non-synthesizing child erythrocytes contain even somewhat less pyridine nucleotides than those of adult humans.

The amount of pyridine nucleotides and the nicotinamide mononucleotide synthetase activity were determined fluorometrically by a slightly modified method of Leder and Handler<sup>1</sup>. The nicotinamide mononucleotide synthetase activity was expressed as: