

# Partition Ratios of Some Wood Smoke Phenols in Two Oil:Water Systems

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The partition ratios ( $K_p$ ) of 12 phenols found in wood smoke were determined by gas-liquid chromatography in two oil:water systems. All the compounds partitioned into neatsoot oil to a greater extent than into water. In a mineral oil:water system, however, phenol, the cresols, and syringol

avored distribution into the water phase. All the  $K_p$  values in neatsoot oil:water exceed those in the mineral oil:water system by factors ranging from 3 to 60. A semilogarithmic plot of partition ratio vs. carbon number was linear for two homologous series.

Gas-liquid chromatography is being used more frequently to determine physical characteristics of chemical compounds. Partition studies have been performed in this manner. Bowman and Beroza (1966) listed the  $p$ -values of a wide variety of aliphatic and aromatic compounds in seven binary solvent systems. Nelson and Hoff (1968) utilized a differential headspace analysis technique to determine the partition coefficients ( $K_p$ ) of some volatile food components in a water:paraffin oil system. Buttery *et al.* (1965) used gas chromatography to analyze the liquid and vapor phases in a study of the volatilities of some aldehydes, ketones, and esters in dilute water solutions. From this information the air-water partition coefficients were calculated.

During the smoking of meat products, which may be considered in part as an oil (or fat):water system, the components of the smoke distribute themselves between the two phases of the system. Since Wasserman (1966) has shown that the sensory thresholds of three phenols present in smoke are not the same when dissolved in oil as in water, the implication of partition ratios of smoke components becomes of interest.

The  $K_p$  values of a number of phenols present in wood smoke, but not available in the literature, are reported here for two oil:water systems, as well as a simple gas chromatographic procedure for their determination.

## EXPERIMENTAL

**Materials.** The phenolic compounds were obtained from commercial sources except for the 4-propylguaiaicol (2-methoxy-4-propylphenol) and 4-methylsyringol (2,6-dimethoxy-4-methylphenol) (Cliffs Dow Chemical Co., Marquette, Mich.). When necessary the samples were purified by vacuum distillation or preparative glc.

Neatsoot oil, 30 C.T., was obtained from Reilly-Whiteman-Walton Co., Conshohocken, Pa., and paraffin oil, N.F., white, light, domestic, with a viscosity of 125/135, from Fisher Chemical Co., King of Prussia, Pa. The oils were used as obtained and were stored under nitrogen to retard air oxidation.

**Gas-Liquid Chromatography.** An F&M 810 gas chromatograph was used with a 6-ft by 1/8-in. o.d. stainless steel column containing 15% Carbowax 20M-TPA on 60- to 80-mesh Gas-Chrom P. The flame detector temperature was 230° C, injector temperature 250° C, and helium carrier flow 115 cc per min. Hydrogen flow was adjusted to give the

maximum detector response, and the air flow to yield a stable flame. Analyses were performed isothermally at 160° C, for all the compounds except the two syringols which were chromatographed at 190° C.

**Sample Preparation.** Test solutions of the various phenols were prepared with distilled water, in concentrations ranging from 480 ppm to 1120 ppm, depending on the relative solubility and chromatographic detectability of each compound. The concentration range was similar to that found in commercial smoke solutions. Four ml of test solution was mixed with 4 ml of oil in a centrifuge tube graduated in 0.1-ml divisions and the mixture agitated for 20 min at approximately 240 rpm on a New Brunswick Gyrotory shaker. Preliminary tests indicated that this was sufficient time to ensure equilibration of the extraction system. The samples were centrifuged in a Sorvall SS4 Superspeed Centrifuge at an RCF of 5900  $\times$  g for 10 min, then placed in a constant temperature water bath at 28° C. Glc analyses were performed on 5- $\mu$ l samples of the aqueous layer obtained by inserting the needle of a 10- $\mu$ l Hamilton syringe through the oil and into the water layer. Contamination of the sample with oil was prevented by wiping the needle after withdrawal. Peak heights were determined in triplicate and variation was less than  $\pm 5\%$ . In order to obtain quantitatively reproducible injections, it was necessary to change the injection port septum after every 10 injections. Occasionally more frequent replacement was required.

**Partition Ratio Determination.** Since the instrumental parameters including the column temperature were kept constant, peak heights instead of peak areas were used in the calculation of partition ratios.

The partition ratio is defined as:

$$K_p = C_{oil}/C_{water} \quad (1)$$

where  $C_{oil}$  is the concentration in oil and  $C_{water}$  is the concentration in water.

Assuming detector linearity over the concentration range used and since peak height is proportional to the concentration and only the water phase is analyzed by glc, then at equilibrium:

$$C_{water} = k PH_A \quad (2)$$

$$C_{oil} = k(PH_B - PH_A) \quad (3)$$

where  $PH_A$  = peak height after extraction,  $PH_B$  = peak height before extraction.

Substituting (2) and (3) in (1) we obtain:

$$K_p = \frac{k(PH_B - PH_A)}{k PH_A} = \frac{PH_B - PH_A}{PH_A} \quad (4)$$

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**Table I. Partition Ratios of Some Phenolic Smoke Components at 28° C**

Compound	Mineral Oil		Neatsfoot Oil	
	$\bar{K}_p^a$	$\sigma_s^b$	$\bar{K}_p^a$	$\sigma_s^b$
Phenol	0.14	±0.083	5.6	±0.18
<i>o</i> -Cresol	0.73	±0.035	22	±0.59
<i>m</i> -Cresol	0.31	±0.095	16	±0.59
<i>p</i> -Cresol	0.26	±0.077	16	±1.2
<i>p</i> -Ethylphenol	1.1	±0.12	42	±2.4
Guaiacol	2.0	±0.41	9.2	±0.71
4-Methylguaiacol	5.1	±0.71	23	±1.8
4-Ethylguaiacol	16	±0.59	60	±7.7
4-Propylguaiacol	60	±6.5	143	±5.9
Eugenol	22	±3.5	97	±4.7
Syringol	0.44	±0.15	3.7	±0.059
4-Methylsyringol	1.4	±0.35	11	±2.9

<sup>a</sup>  $\bar{K}_p$  = average partition ratio. <sup>b</sup>  $\sigma_s$  = instant standard deviation.

Equal volumes of oil and water were used for partitioning and no subsequent volume change occurred after mixing. Therefore, the partition ratios were calculated directly from equation 4. It was only necessary to measure the peak heights of the compound in the water layer before and after extraction with oil. For systems in which unequal volumes were used or in which partial miscibility of the two phases existed, equation 4 would have to be modified by appropriate factors to permit calculation of partition ratios.

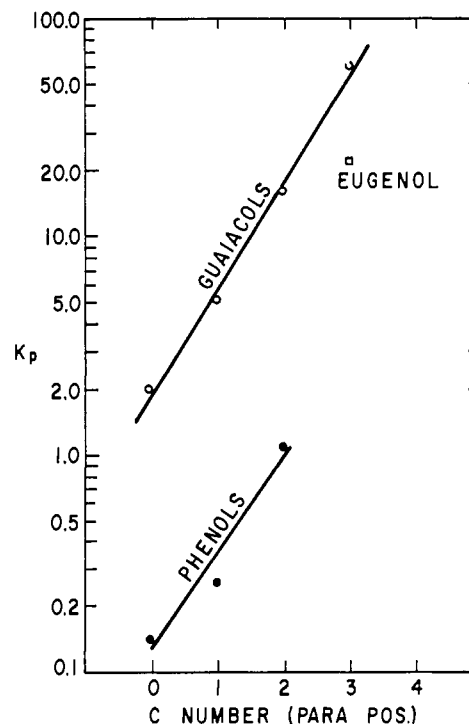
Each partition ratio was determined three times and the instant standard deviation,  $\sigma_s$ , (Aerograph Res. Notes, 1965) calculated by multiplying the range of values by 0.591, a factor specific for triplicate determinations. The resulting  $\sigma_s$  agrees with the conventional  $\sigma$  with a 99% reliability (Aerograph Res. Notes, 1965).

## RESULTS

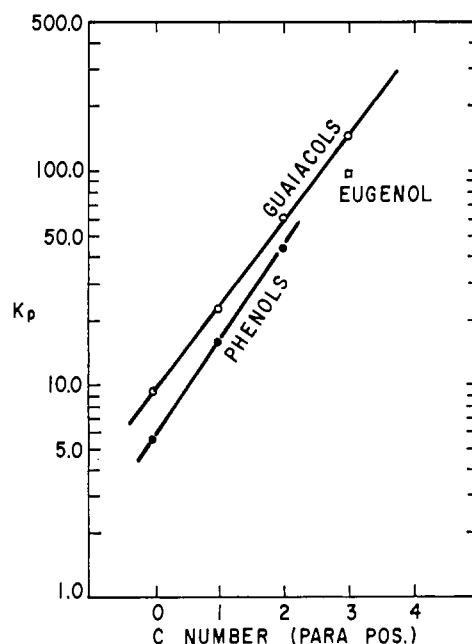
The partition ratios of several phenols present in wood smoke in paraffin oil:water and neatsfoot oil:water systems are listed in Table I. The data indicate that all the compounds partition into the neatsfoot oil to a greater extent than into the water. In the mineral oil:water system, however, phenol, the cresols, and syringol have  $K_p$  values less than unity, indicating they are present in greater concentration in the water phase.

The  $K_p$  values of each of the phenols in neatsfoot oil exceed those in the paraffin oil system by a factor ranging from approximately 3 to 60. The greater affinity of the phenols for neatsfoot oil as compared to paraffin oil may be due to the fact that all the compounds tested are relatively polar and neatsfoot is the more polar of the two oils. It consists primarily of a mixture of the triglycerides of oleic, palmitic, and hexadecenoic acids, while paraffin oil is a mixture of saturated hydrocarbons.

The data shown in Table I indicate the effect of ring substitution, ring position, and chain length of the substituent group on the partition ratio in both systems. Introduction of a methyl group in a position *para* to the hydroxyl in phenol, guaiacol, and syringol results in an increase in the concentration of the compound in the oil phase with respect to the water. When the methyl group is introduced into the *ortho*, *meta*, and *para* positions of phenol, the resulting cresols show an increase in partition ratio with the effect of the methyl group diminishing from the *ortho* to *para* positions. Introducing the methoxyl ( $-\text{OCH}_3$ ) group *ortho* to the hydroxyl of phenol to form guaiacol increases the  $K_p$  value, similar to the effect observed on substituting the methyl



**Figure 1. Semilogarithmic plots of paraffin oil:water partition ratios for several *para* substituted phenols against carbon number**



**Figure 2. Semilogarithmic plots of neatsfoot oil:water partition ratios for several *para* substituted phenols against carbon number**

group in the *ortho* position. However, it appears that addition of another methoxyl group in the 6-position (syringol) results in a decrease in the partition ratio compared to guaiacol.

A semilogarithmic plot of the partition ratios *vs.* number of carbon atoms is shown in Figures 1 and 2. The effect of chain length of the *para* substituted compounds can be seen with both the phenols and guaiacols. The  $K_p$  of ethylphenol exceeds that of the methyl in both oil:water systems, while increasing the chain length of the *p*-substituent on guaiacol from  $C_1$  to  $C_3$  also results in increasing partition ratio values.

Eugenol (4-allylguaiacol), however, has a lower  $K_p$  value than the corresponding saturated 4-propylguaiacol, showing the effect of introducing a double bond into the side chain.

The effect of the substituents was the same in both oil:water systems but the magnitude of the changes was somewhat greater in paraffin oil:water than in neatsfoot oil:water.

#### DISCUSSION

The partitioning of a compound between two solvents depends upon a number of factors such as steric effects, electronic characteristics which influence the relative polarity of the solute and thus its association with the solvent, and London forces operative in all solutions. Lipid:water systems are present in most foods and the effect of this type system on flavor should be an important consideration in food processing. Mackey (1958) found that the taste of caffeine, quinine, or saccharin was more easily detected in water than in mineral oil. Lea and Swoboda (1958) demonstrated that the flavor thresholds for *n*-alkanals were much lower in water than in vegetable or paraffin oil. Wasserman (1966) also reported on the difference in threshold values for three phenols in a paraffin (mineral) oil:water system. In addition, Bratzler (1969) has shown that the smoky flavor in bologna correlates well with depth of phenol penetration. Therefore, information on the partition ratios in oil:water systems of the phenolic smoke components found in smoked foods together with appropriate sensory studies may permit prediction of their effect on smoke flavor.

Selecting the proper solvent system is important in order to obtain meaningful information. Neatsfoot oil was chosen because we are interested in the smoking of meat products and it represents an animal fat in relatively pure form. In addition, it is a liquid at room temperature, thus facilitating sample handling. Paraffin oil was selected because it is a bland medium and thus has been used extensively as a vehicle in sensory evaluation. The results of this study indicate that information obtained with paraffin oil as a partitioning agent may not be completely comparable to a situation involving an animal fat. Preliminary determinations of the  $K_p$  values of some of the compounds reported in this paper in an olive oil:water system indicate that the trends and magnitude of the partitioning effect in vegetable oils are similar to those in the neatsfoot oil.

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