

the identification of these and other pesticides by adding to the technique the accurate measurement of the relative intensities of these exact masses, thereby providing sufficient data to distinguish the isomeric pesticides in mixtures. Application of the techniques to the identification of pesticide residues in extracts of food and soil samples is also being investigated.

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## An Empirical Relationship between Chemical Structure and the Sorption of Some Herbicides by Soils

A factor given by (parachor-45*N*), where *N* is the number of sites in a molecule which can participate in the formation of a hydrogen bond, is shown to be correlated with log Freundlich *k* value for the adsorption of 29 aromatic herbicides

by two soils. This empirical relationship may be useful for prediction of the approximate extent of adsorption of such herbicides by soils in which the organic matter is the dominant adsorbing constituent.

Lambert (1967) has proposed a relationship between the parachor of an organic molecule and its sorption by soil of the form  $\log k_{\alpha}P$ , where *k* is the adsorption equilibrium constant and *P* is the parachor. This relationship is subject to the conditions that the molecule is un-ionized and that no appreciable hydrogen bonding occurs. For compounds capable of significant hydrogen bonding an additional term is required, as such materials might be expected to show a greater interaction with water and hence be less extensively absorbed in soil-water systems than the relationship would predict. Since most soil-applied herbicides contain groups which can form hydrogen bonds, it is of interest to estimate the approximate magnitude of the additional term, so that the applicability of this relationship to these compounds may be tested.

Since the nature and energy relationships of all the possible solute-water, solute-soil, and water-soil interactions have not yet been evaluated, it is not possible to predict on theoretical grounds the contribution of hydrogen bonding to the distribution of an organic solute between water and a soil surface. It is, however, possible to ascribe an empirical value to the effect of hydrogen bonding based on experimental observations of the adsorption of organic molecules by soil. This exercise has been attempted using data previously reported (Hance, 1967) for the adsorption of 29 compounds by two soils. The compounds included ureas, 1,3,5-triazines, carbamates, and uracils. The figures were in the form of Freundlich *k* values. As Lambert has observed, this constant is not ideal on theoretical

grounds and is not strictly valid as a comparative measurement if the value of  $1/n$  in the Freundlich equation is not 1. In the present case, only six compounds gave values of  $1/n$  which were not 1 and these all gave values between 0.85 and 0.99. It was therefore decided that for the purposes of this study the Freundlich *k* value gives a useful measure of adsorption.

Simple correlation coefficients and the magnitude of the correction factor were determined for the relation between log Freundlich *k* and the figure given by parachor—(a correction factor  $\times N$ ). Parachors were calculated from the table of group and bond contributions given by Quayle (1953). The value of *N* was given by the number of proton- or electron donating sites on the molecule which could conceivably participate in hydrogen bond formation. The following groups in this category occurred in the compounds studied: primary, secondary, and tertiary amino, carbonyl, heterocyclic nitrogen, and ether oxygen. Thus *N* for diuron (*N'*-3,4-dichlorophenyl-*N,N*-dimethylurea) is 3 because of the presence of one secondary and one tertiary amino group and a carbonyl group. Similarly, *N* for simazine (2-chloro-4,6-bisethylamino-1,3,5-triazine) is 5, as it contains three heterocyclic nitrogen atoms and two secondary amino groups. Possible interactions between adjacent groups such as internal hydrogen bonding or the effects of steric hindrance were ignored.

Using this process, a value of 45 for the correction factor gave the best fit. Correlation coefficients were 0.79 for a chalky boulder clay and 0.67 for a gray sandy loam. Values of *k* were also calculated con-

sidering the organic matter of the soils to be the adsorbing medium, as proposed by Lambert. Mean values of  $k$  for each compound could thus be calculated from the figures obtained with the two soils. A correlation of 0.83 was found between the log of the mean  $k$  values and (parachor-45*N*). The equation of the line of best fit was:

$$\log k = 0.0067 (\text{parachor-45}N) - 0.65$$

The standard deviation was  $\pm 0.30$ .

It is clearly not valid to consider, as has been done here, that the contribution of every possible hydrogen-bonding site is equal and the assumption that the mechanism of adsorption is the same for each compound is questionable. In addition, Lambert's original derivation of the relationship disregarded the effects of entropy terms in comparing the free energies of partition of compounds between two phases. Recent observations of Miller and Hildebrand (1968) make this assumption debatable.

Lambert's suggestion and this modification of it apply only to situations where organic matter is the soil component primarily responsible for adsorption, as the recent results of Bailey *et al.* (1968) show that adsorption by montmorillonite follows a different pattern. All the molecules considered here contained

aromatic structures. The field observations of Upchurch *et al.* (1966) suggest that aliphatic molecules such as CDAA and CDEC behave differently.

However, the use of an empirical relationship of this sort enables some prediction of the adsorptive behavior of a molecule to be made, merely from inspection of its structural formula, and to this extent this approach may be justified until enough information becomes available to enable a more rigorous approach to be made.

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## Methionine Loss during Protein Hydrolysis of Plant Material

The high degree of methionine loss during the acid hydrolysis of protein in plant material has been demonstrated by comparing methionine recovery figures from leaf material hydrolyzed with and without prior oxidative protection treatment. The

range of methionine loss was 30 to 59%. The results indicate the necessity of prior methionine protective treatment for the accurate determination of this amino acid in hydrolyzates of plant material.

Although it is known that methionine as well as cystine is damaged during acid hydrolysis in the presence of carbohydrates (Schram *et al.*, 1953), the extent to which methionine can be damaged during the hydrolysis of plant material does not appear to be fully realized by many workers in the protein nutritional field. This is evident from the number of recently published analytical figures for methionine derived from analyses of plant material in which no adequate form of methionine preservation has been used.

To indicate the seriousness of this loss, results of methionine assays on hydrolyzates of leaf material prepared with and without prior oxidation of methionine to the sulfone are compared below.

#### MATERIALS AND METHODS

Methionine determinations were made on duplicate hydrolyzates of untreated leaf material and leaf material previously oxidized with performic acid under controlled conditions.

**Unprotected Methionine Assays.** A known quantity of lyophilized leaf powder containing approximately 10

mg. of nitrogen was hydrolyzed with 15 ml. of 6*N* glass-distilled HCl for 24 hours under nitrogen in a sealed hydrolyzate flask. The hydrolyzate was filtered, freeze-dried, and dissolved in 100 ml. of pH 2.2 buffer. Of this solution 0.2 ml. was assayed for methionine on a Beckman-Spinco Model 120C amino acid analyzer. The buffers used for chromatography contained thiodiglycol to prevent oxidation of the sulfur amino acids on the ion-exchange column (Moore and Stein, 1954).

**Protected Methionine Assays.** The same quantity of lyophilized leaf powder was oxidized with performic acid and hydrolyzed as described by Lewis (1966). The final lyophilizate was dissolved in 100 ml. of pH 2.2 buffer and the methionine content of 0.2 ml. was determined as methionine sulfone on the analyzer.

#### RESULTS AND DISCUSSION

Table I shows that up to 59% of the methionine content of a sample of leaf material can be destroyed during acid hydrolysis. The actual degree of destruction seems to be unpredictable, as evidenced by the wide range of methionine losses shown and the poor correlation be-