Associated Decomposition of DDT to DDE in the Diffusion of DDT on Homoionic Clays

Juan de Dios López-González and Cristobal Valenzuela-Calahorro

A study has been made of the decomposition of molecules of DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] to DDE[1,1 - dichloro - 2,2 - bis(*p* - chlorophenyl)-ethylene]. Diffusion experiments were carried out at 0, 16, and 32° C. Diffusion time in all cases was 20 hr. The type of clay mineral and the exchangeable cations influence the dehydrohalogenation of DDT to DDE. This decomposition of DDT is also favored by the interaction of its molecules with the clean surface of the clay particles with which the DDT comes in contact as diffusion is taking place.

DDT [1,1,1-trichloro-2.2-bis(*p*-chlorophenyl)ethane] is considered as one of the most stable and persistent insecticides. It is accumulated by living beings which eat it in their food, and they can transmit it to their descendents (Carson, 1962). It is known that certain enzymes, both *in vivo* and *in vitro* (Kallman and Andrews, 1963; Perry *et al.*, 1963) transform it into DEE [1,1,dichloro-2,2-bis(*p*-chlorophenyl)-ethylene], which lacks insecticidal properties.

Decomposition of DDT also occurs in plant tissues (Findley and Pillmore, 1963) and in animal tissues (Nasir, 1953; Peterson and Robinson, 1964; Wasserman *et al.*, 1965). The most abundant metabolite is DDE, but several other metabolites also appear (Peterson and Robinson, 1964).

Decomposition of DDT is very important in living tissues, but its decomposition in soils is of equal importance to agriculture.

Numerous experiments have been directed towards determining the stability of DDT (Fleck and Haller, 1946; Wichmann *et al.*, 1946) and its persistence in the soil (Carne, 1948; Chisholm *et al.*, 1950; Lichtenstein *et al.*, 1960; Smith, 1948; Wheley and Hardman, 1962). The conclusion has been reached that the stability of DDT in the soil is related to the type of soil (Ginsburg, 1952) and the chemical composition of the soil (Fleck and Haller, 1944; Fleck *et al.*, 1945; Fowkes *et al.*, 1960). The stability of DDT in the soil also depends on moisture (Harris, 1964; Weidhaas *et al.*, 1961), on the temperature of the soil (Birrell, 1963; Cutkomp, 1947; Gunther and Tow, 1946; Lichtenstein and Schultz, 1959), and on the quantity of visible radiations (Chisholm and Koblitsky, 1947; Ginsburg, 1952; Nurova, 1953) and ultraviolet radiations (Mitchell, 1961; Nasir, 1953). Due to the influence of these factors, the main decomposition product of DDT is DDE, although 1,chloro-1,hydroxy-2,2,bis(*p*-chlorophenylethylene) and many others of less importance have been identified.

All the authors quoted have studied the decomposition of DDT in natural soils, where the presence of organic matter and microorganisms contributes greatly to this decomposition. Due to the simultaneous action of those factors, interpretation of the results are often difficult. In the study reported here, only homoionic clays were used and decomposition due to organic matter and microorganisms was negligible.

Possibly dehydrohalogenation of DDT to give DDE might take place on surfaces of high free energy. If this is so, a DDT molecule can undergo dehydrohalogenation on being fixed on the active surface. If fixation is not made directly on the surface, but on top a layer of DDT or DDE molecules such dehydrohalogenation ought not to take place. Then it is logical to expect that there should be a decomposition process associated with that of diffusion of the DDT molecules on active surfaces.

The authors have carried out the experiments to check whether such decomposition takes place, and here they give the results obtained on studying the decomposition process associated with that of diffusion of DDT through columns of homoionic acidic bentonite ($B-H^+$), homoionic sodium bentonite ($B-Na^+$), homoionic acidic vermiculite ($V-H^+$), and homoionic sodium vermiculite ($V-Na^+$).

The authors have not included the data referring to the diffusion process in this paper, as these have been the object of previous publications (López-González and Valenzuela-Calahorro, 1968abc).

EXPERIMENTAL

Bentonite from Almería and vermiculite from Benahavís (Málaga) were used in the experiments. Both clay minerals were identified by chemical analysis, X-ray diffraction, differential thermal analysis, infrared spectrum, and exchange capacity.

The homoionic samples, $B-H^+$, $B-Na^+$, $V-H^+$, and $V-Na^+$, were prepared by methods described by (Lewis, 1951, 1953; Gutierrez-Rios and Cano-Ruiz, 1954; Bolt and Frissel, 1960). The homoionic sodium samples were prepared by treating the original samples with 2*N* sodium acetate solution. The homoionic acidic samples were prepared from the corresponding homoionic ammonium samples ($B-NH_4^+$ and $V-NH_4^+$). The homoionic ammonium samples were prepared by treating the original samples with a 2N ammonium acetate solution.

With bentonite, the exchange of NH_4^+ for H^+ was made in a column of Amberlite IR-120, 350 mm long and 35 mm in diameter. Aqueous suspensions of 2% homoionic ammonium bentonite were passed through the column of Amberlite. Flow was 19 ml per min. This process was repeated three times. In each case only the quantity of ammonium bentonite necessary to change half the H^+ of the resin was passed.

$V-H^+$ was prepared from $V-NH_4^+$. Sufficient Amberlite was added to a 2% suspension of $V-NH_4^+$ in water so that it contained twice the exchange mol equiv of vermiculite. The suspension was shaken for 24 hr, and then the resin was separated by a suitable sieve.

Department of Inorganic Chemistry, University of Granada, Section of Inorganic Chemistry of C.S.I.C., Granada, Spain

A Chamberlain filterstick was used to separate the water from the homoionic acidic bentonite of vermiculite. This was dried at 30° to 40° C by means of infrared radiation. Once dried, the samples were ground to a particle size equal to or less than 150 μ.

The specific surface area, S, of the natural bentonite and natural vermiculite used was determined by the method of Brunauer, Emmet, and Teller (Brunauer *et al.*, 1938). Determination of S was made at 0° C, and *n*-butane was used as the adsorbate. The conventional gas adsorption apparatus used was previously described by one of the authors (López-González, 1956). The specific surface areas were 39.5 m^2 per g for bentonite and 15.5 m^2 per g for vermiculite.

The *p,p'*-DDT isomer used (mp, 110.0°–110.5° C) was obtained from a commercial insecticide by means of successive recrystallizations in ethanol (Cook and Cook, 1946). The DDE was obtained by dehydrohalogenation of DDT with KOH in an ethanol solution (Melgarejo, 1964). The DDE obtained melted at 90.0–90.5° C.

The value of 145 A^2 was taken for the area, A, covered by one molecule of DDT or of DDE (Rodriguez, 1966).

S and A being known, the quantity of DDT necessary to cover 10 g of each homoionic clay mineral with a monomolecular layer was determined. This quantity of DDT in a benzene solution was added to 10 g of homoionic clay mineral dried at 110° C. The solvent was evaporated at 30° to 40° C, using infrared radiation. The sample so prepared was hydrated until its weight increased approximately 20%. Hydration took place at room temperature with the mentioned sample of homoionic clay mineral in an atmosphere saturated with water vapor.

Twenty grams of homoionic bentonite or 14 g of homoionic vermiculite (dried at 110° C until their weight was constant), free from pesticide, were also hydrated. Hydration was carried out in the same conditions and up to the same point as the samples containing pesticide.

Two semicolumns, one with the homoionic clay mineral containing pesticide and the other with the homoionic clay mineral without pesticide, were formed with the samples. Both semicolumns were placed in contact with each other, by means of one of their bases, for 20 hr.

The semicolumns were formed in a transparent lucite cylinder, closed at one end. This cylinder was composed of 100 plates, 40 mm square and 2.5 mm thick, arranged as shown in Figure 1. The diameter of the column of homoionic clay mineral was 15.5 mm, equal to the internal diameter of the lucite cylinder.

Once the clay column was formed, it was put into a suitable zinc container (Figure 1). By means of the weight L, the column of homoionic clay mineral is maintained at a constant pressure of 0.48 kg per cm^2, in all the diffusion experiments.

After the 20 hr of contact between the two semicolumns, the diffusion column was divided into slices 5 mm thick. Each of the slices was put into a Soxhlet and extracted continuously for 7 hr with spectroscopically pure cyclohexane.

The liquids extracted were brought to a suitable volume in each case. Measurements of the absorption of ultraviolet radiation at 238 mμ and 247 mμ on a Beckman DU-2 spectrophotometer enabled us to determine the concentration of DDT and DDE in the extracts. This analytical method enables mixtures of DDT and DDE to be determined to concentrations of between 0.4 and 20.0 ppm. The margin of error of this method is ±0.1 ppm within these limits (López-González *et al.*, 1969).

As only DDT had been added initially, the DDE must be the result of the decomposition of the DDT in contact with the surface of the homoionic clay minerals.

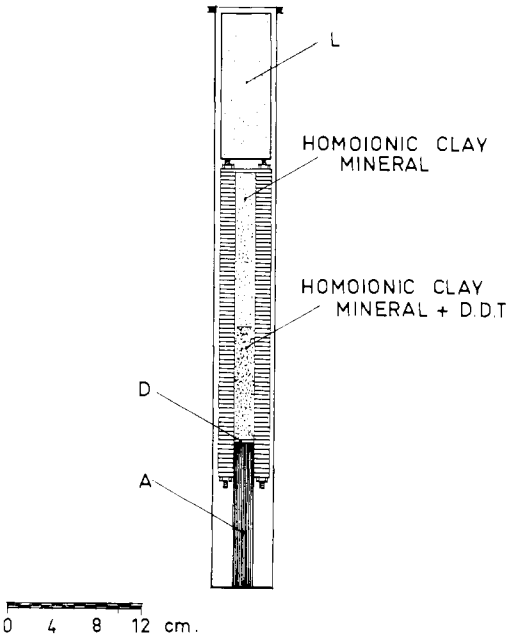


Figure 1. Cross section of the diffusion system

A—stainless steel rod, 15.5 mm diameter; D—lucite disk, 15.5 mm diameter and 2.5 mm thick; and L—lead weight, 970 g

RESULTS AND DISCUSSION

The initial concentrations of DDT in the clays were 4.523 × 10^{-5} mole DDT/g dried bentonite and 1.775 × 10^{-5} mole DDT/g dried vermiculite.

During the time of hydration of the samples (about 10 days), approximately 5 to 10% of the DDT was transformed into DDE.

The quantities of DDT and DDE contained in each slice were determined from the analytical data of the extracts of the slices of the clay columns.

Diffusion curves of DDT were obtained on representing the quantity of DDT contained in each slice as a function of its distance from the interphase (the contacting surface between the two semicolumns). Diffusion curves of DDE were obtained in the same way.

Although the diffusion curves were published in previous papers by the authors (López-González and Valenzuela-Calahorro, 1968abc), one of them is included in this paper (Figure 2, which corresponds to diffusion at 0° C of DDT in homoionic sodium bentonite), so that the reader can see the diffusion curves corresponding to DDT, DDE, and to the apparent overall diffusion process (DDT + DDE).

The diffusion coefficients, which were of the order of 10^{-7} cm^2 per sec, as well as the activation energies and the "average" net diffusion rates, were determined from the diffusion curves. These data appear in the previously mentioned papers.

As explained in the first part of this paper, the authors had foreseen the possibility that there would be a dehydrohalogenation process associated with that of diffusion of the molecules of DDT on the surface of homoionic clay minerals. The analytical results were expressed in percentage of DDT and DDE found as a function of the distance to the interphase of the clay column, with the object of checking whether this decomposition process takes place. The percentage of

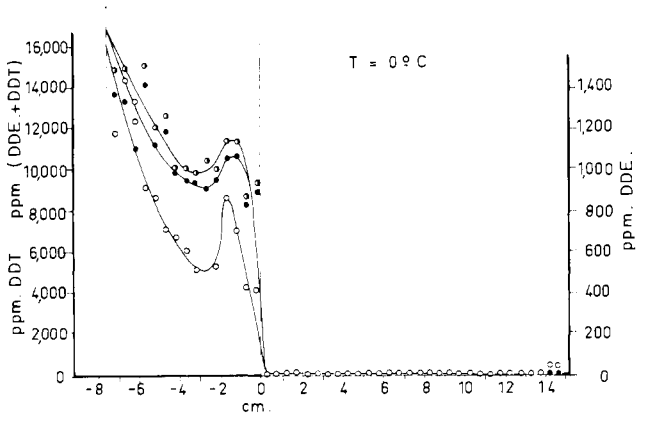


Figure 2. Diffusion curves of DDT (●), DDE (○), and DDT + DDE (◑) on homoionic sodium bentonite. Temperature of diffusion: 0° C; time of diffusion: 20 hr

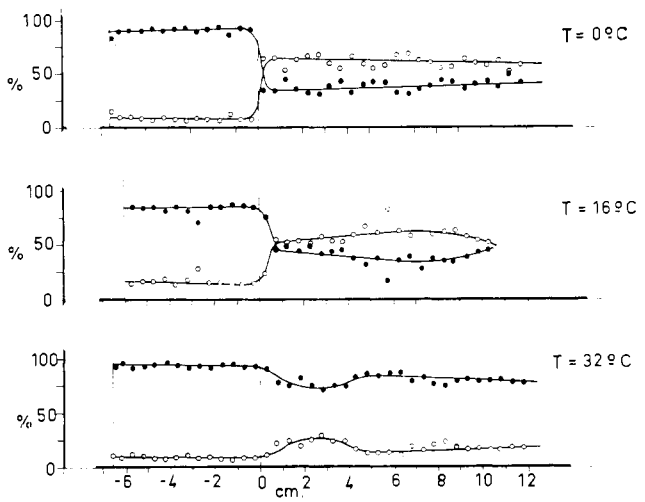


Figure 3. Relative distribution of DDT and DDE in the diffusion process of DDT through the B-H column at different temperatures: 0° C, 16° C, 32° C

DDT is called "relative DDE content" and that of DDE "relative DDE content" of each slice.

The representation of the relative content of DDT and of DDE in each slice, as a function of the distance to the interphase, enabled us to obtain the curves which we call "curves of relative distribution." These are shown in Figures 3 to 6, from which it can be seen that there is greater dispersion of the experimental data in the $x > 0$ than in the $x < 0$ zone; $x > 0$ corresponds to the semicolumn initially pesticide-free; and $x < 0$ corresponds to the semicolumn initially containing pesticide.

It is possible to think that the greater dispersion of experimental data in the $x > 0$ zone is due to the high relative error on determining very low concentrations (0.5 ppm) of DDT and of DDE. Besides this effect, it is necessary to take into account the possible existence of heterogeneities in the columns of homoionic clay minerals. These give rise to a different degree of decomposition of the DDT.

These differences increase in general with temperature, and the dispersion in the experimental points in the $x > 0$ zone of the curves also increases with temperature (Figures 3–6), probably due to a greater effect of "cold distillation" (López-González and Valenzuela-Calahorro, 1968 abc).

The form of the curves corresponding to $x > 0$ leads one to think that, in most cases, there is an appreciable molecular reflection in the closed end of the supporting cylinder of the

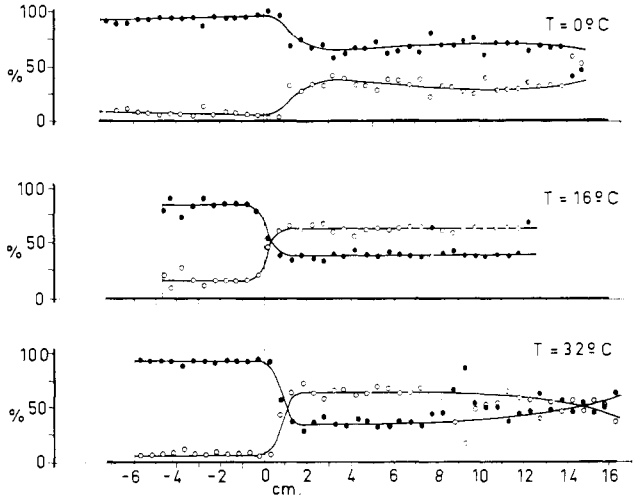


Figure 4. Relative distribution of DDT and DDE in the diffusion process of DDT through the B-Na column at different temperatures: 0° C, 16° C, 32° C

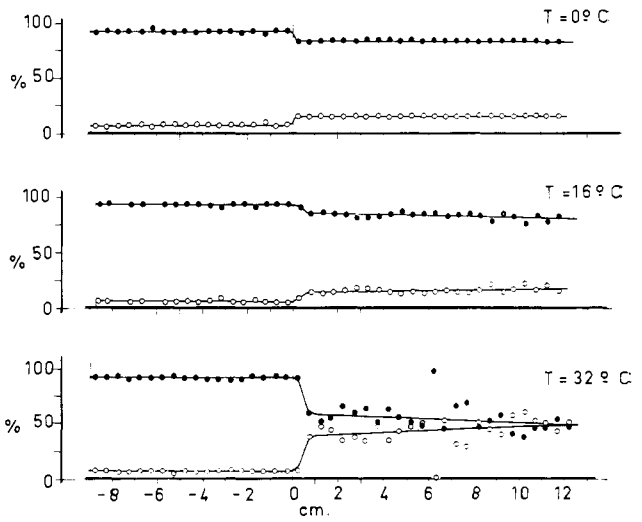


Figure 5. Relative distribution of DDT and DDE in the diffusion process of DDT through the V-H column at different temperatures: 0° C, 16° C, 32° C

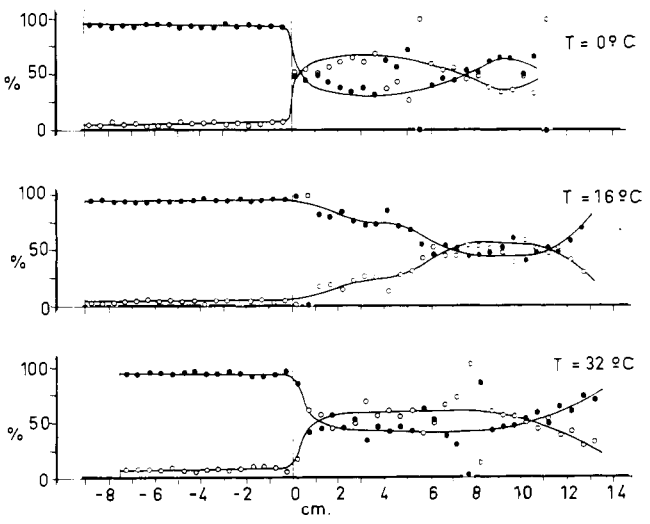
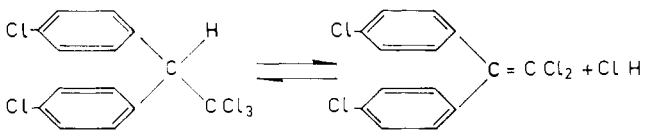


Figure 6. Relative distribution of DDT and DDE in the diffusion process of DDT through the V-Na column at different temperatures: 0° C, 16° C, 32° C

column of homoionic clay minerals. This effect is shown more clearly in the diffusion curves of DDT and DDE obtained in identical conditions in which the decomposition process was studied with that of diffusion and the existence of a "cold distillation" or diffusion effect due the volatilization of DDT or DDE was shown (López-González and Valenzuela-Calahorro, 1968abc). As a consequence of this effect, the $x < 0$ zone of the diffusion curves shows an anomalous shape (Figure 2).

With respect to the "curves of relative distribution" of DDT and of DDE (Figures 3 to 6), from an examination of the $x > 0$ zone, it is deduced that there is a decomposition process of the DDT associated with that of diffusion of the molecules of DDT on homoionic clay minerals. Apparently, this process in produced as a result of the interaction of the molecules of DDT with the active zones of the surface of the homoionic clay minerals previously free of DDT. DDE, a harmless product, is formed principally as a result of this decomposition.

The decomposition of DDT into DDE is notably greater in the homoionic sodium samples than in the acidic ones. This can be deduced by comparing Figures 3 and 5 with Figures 4 and 6, respectively. This is easily understood if it is borne in mind that the decomposition of DDT into DDE is a result of a dehydrohalogenation process of DDT. The dehydrohalogenation reaction of DDT can be expressed as follows:



Logically, this process will be towards the left in an acid medium. In a basic medium, the equilibrium will be towards the formation of DDE.

From a comparison of Figures 3 and 5 it could be deduced that the decomposition of DDT is greater in B–H^+ than in V–H^+ especially at 0° C, and 16° C. This is possibly due to the smaller concentration of H^+ on the surface of B–H^+, since the net charges per unit-cell-layer are 1.3 for vermiculite and 0.7 for bentonite (Brown, 1961).

The exchange capacities of the clay minerals used in this work were 91 meq per 100 g of bentonite and 144 meq per 100 g of vermiculite.

On comparing Figures 4 and 6, it is easily seen that the decomposition of DDT is greater in V–Na^+ than in B–Na^+. This is justified by the fact that the surface concentration of Na^+ ions is greater in vermiculite than in bentonite.

Consequently, in this paper it is shown that there exists a decomposition process associated with that of diffusion of the molecules of DDT on homoionic clay minerals. The results obtained are a contribution to the "dynamic degradation" process of the molecules of the DDT retained in clay minerals and which are diffused through them. Exact knowledge of the factors which influence the "dynamic decomposition" of DDT would provide sufficient data in order to know the stability of DDT in agricultural soils and determine the quantities of DDT necessary to be applied in each case.

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LITERATURE CITED

Birrell, K. S., *N. Z. J. Sci.* **11,** 65–8 (1963).
Bolt, G. H., Frissel, M. J., *Soil Sci. Soc. Amer. Proc.* **24,** 172–77 (1960).
Brown, G. (Ed.), "The X-ray Identification and Crystal Structures of Clay Minerals," Mineralogical Society, London (1961).
Brunauer, S., Emmet, P. H., Teller, E., *J. Amer. Chem. Soc.* **60,** 309 (1938).
Carne, P. B., *Nature* **162,** 743 (1948).
Carson, R., "Silent Spring," Houghton Mifflin Company, Boston, The Riverside Press, Cambridge, Mass., 1962.
Chisholm, R. D., Koblitsky, L., *Agr. Chem.* **2** (9), 35–7 (1947).
Chisholm, R. D., Koblitsky, L., Fahey, J. E., Westlake, W. E., *J. Econ. Entomol.* **43,** 941–42 (1950).
Cook, K. H., Cook, W. A., *J. Amer. Chem. Soc.* **60,** 1163 (1946).
Cutkomp, L. K., *J. Econ. Entomol.* **40,** 444–5 (1947).
Findley, R. B., Jr., Pillmore, R. E., Amer. Inst. Biol. Sci. Publ., Bull. **13,** 41–2 (1963).
Fleck, E. E., Haller, H. L., *J. Amer. Chem. Soc.* **66,** 2095 (1944).
Fleck, E. E., Haller, H. L., *J. Amer. Chem. Soc.* **68,** 142–3 (1946).
Fleck, E. E., Preston, H. K., Haller, H. L., *J. Amer. Chem. Soc.* **67,** 1419 (1945).
Fowkes, F. M., Benesi, H. A., Ryland, L. B., Sawyer, W. M., Detling, K. D., Loeffler, E. S., Folckemer, F. B., Johnson, M. R., Sun, V. P., J. AGR. FOOD CHEM. **8,** 203–10 (1960).
Ginsburg, J. M., *Proc. N. J. Mosq. Exterm. Ass.* **39,** 162–7 (1952).
Gunther, F. A., Tow, L. R., *Science*, **104,** (2926), 203 (1946).
Gutierrez-Rios, E., Cano-Ruiz, J., *An. Edafol. Agrobiol.* **13,** 797 (1954).
Harris, C. R., *Nature* **202,** 724 (1946).
Kallman, B. J., Andrews, A. K., *Science* **141,** (3585), 1050–51 (1963).
Lewis, D. R., *Ind. Eng. Chem.* **45,** 1782–83 (1953).
Lewis, D. R., A. P. I. Research Project, 49 Sect., 3, Rep. No. 77, New York, Columbia University Press (1951).
Lichtenstein, E. P., De Pew, L. J., Eshbaugh, E. L., Sleesman, J. P., *J. Econ. Entomol.* **53,** 136–42 (1960).
Lichtenstein, E. P., Schultz, K. R., *J. Econ. Entomol.* **52,** 124–31 (1959).
López-González, J. D., Memoria XXVIII Congreso Internacional de Química Industrial (Vol. I, pp. 637–41). Madrid (1956).
López-González, J. D., Valenzuela-Calahorro, C., *An. Quím.* **64** (2), 139–46 (1968a).
López-González, J. D., Valenzuela-Calahorro, C., *An. Quím.* **64** (4), 359–64 (1968b).
López-González, J. D., Valenzuela-Calahorro, C., *An. Quím.* **64** (7–8), 713–21 (1968c).
López-González, J. D., Valenzuela-Calahorro, C., Bañares-Muñoz, M. A., Martinez-Becerra, M. A., J. AGR. FOOD CHEM. **17** (5), 1045–6 (1969).
Melgarejo, M., University of Granada, private communication, 1964.
Mitchell, L. C., *J. Ass. Offic. Agr. Chem.* **44,** 643–712 (1961).
Nasir, M. M., *J. Sci. Food Agr.* **4,** 374–8 (1953).
Nurova, V. P., *Med. Parazitol. Parazit. Bolez.* 246–8 (1953).
Perry, A. S., Miller, S., Buckner, A. J., J. AGR. FOOD CHEM. **11,** 457–62 (1963).
Peterson, J. E., Robinson, W. H., *Toxicol. Appl. Pharmacol.* **6** (3), 321–27 (1964).
Rodriguez, A., University of Madrid, private communication, 1966.
Smith, M. S., *Ann. Appl. Biol.* **35,** 496–504 (1948).
Wasserman, M., Wasserman, D., Zellermayer, L., *Arch. Environ. Health* **11** (3), 357–9 (1965).
Weidhaas, D. E., Bowman, M. C., Schmidt, C. H., *J. Econ. Entomol.* **54,** 175 (1961).
Wheley, G. A., Hardman, J. A., *Plant Pathol.* **11,** 81–90 (1962).
Wichmann, H. J., Patterson, W. I., Clifford, P. A., Klein, A. K., Claborn, H. V., *J. Ass. Offic. Agr. Chem.* **29,** 218–33 (1946).

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