JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Effects of Accelerators on Mobility of ^{14}C-2,4-Dichlorophenoxy Butyric Acid in Plant Cuticles Depends on Type and Concentration of Accelerator

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Effects of diethyl suberate (DESU), diethyl sebacate (DES), dibutyl suberate (DBSU), dibutyl sebacate (DBS), and tributyl phosphate (TBP) on diffusion of ^{14}C-2,4-dichlorophenoxy butyric acid (2,4-DB) across cuticular membranes (CM) was studied. Astomatous CM were isolated enzymatically from *Stephanotis floribunda* Brongn. leaves, and diffusion was measured at 20 °C. The alkyl-substituted dicarboxylic acids constitute a homologous series with carbon numbers increasing from C_{12} to C_{18}. Molecular weights increased only moderately from 230.0 (DESU) to 314.5 (DBS), while partition coefficients varied over orders of magnitude from 92 (DESU), to 1213 (DES), to 15 988 (DBSU), to 210 762 (DBS). All the above compounds turned out to be accelerators as they increased 2,4-DB mobility by up to 40-fold with accelerator concentrations in the CM ranging from only 9.2 to 105 g kg^{-1}. Efficacy (2,4-DB mobility in the presence/mobility in the absence of accelerators) increased with increasing concentrations of accelerators in CM or in reconstituted cuticular waxes. Plotting efficacy vs accelerator concentration in the CM resulted in straight lines, and their slopes increased in the order DBS (0.14), DBSU (0.31), DES (0.51), and DESU (0.85). Hence, DESU was the most powerful accelerator in this series as it increased 2,4-DB mobility in the CM about 6 times more than DBSU. Waxes constitute the major barrier in plant cuticles, and plots of efficacy vs accelerator concentration in *Stephanotis* wax were also linear, but compared to CM slopes were steeper by factors of 3.20 (DBS), 2.97 (DBSU), 2.70 (DES), and 1.62 (DESU). TBP was similarly effective as DESU, but plots of efficacy vs concentration were not linear, and curves approached a plateau at 60−80 g kg^{-1}. These data are discussed with regard to suitability of these accelerators for formulating systemic pesticides.

KEYWORDS: Adjuvant; diffusion; foliar uptake; permeability; pesticide; plasticizer; solute mobility

INTRODUCTION

Effectiveness of systemic pesticides is often limited by the low permeability of cuticles, and adjuvants are employed to improve the performance of active ingredients. Adhesion and retention of spray liquid, wetting of leaves, dissolution or dispersion of active ingredients, partitioning between spray residues and leaf cuticles, and solute diffusion in cuticles can be modified by adjuvants (*1*−*4*). Adjuvants that increase solute mobility in cutin and waxes have been termed accelerators or accelerator adjuvants in order to distinguish them from mechanistically ill-defined "penetration enhancers" or "activator adjuvants" (*5*, *6*). Accelerators increase solute mobility in cutin and amorphous wax matrixes by increasing segmental chain mobility (*7*−*9*), that is, they are typical plasticizers (*10*). Some ethoxylated alcohols (EA's) are powerful accelerators (*11*−*13*), but accelerator activity does not depend on surface activity. Nonamphiphilic compounds have been shown to be accelerators, among them diethyl suberate, diethyl sebacate, tributyl phosphate, chlorfenvinphos, and pentafluorophenol (*14*−*16*). Thus far, it is not clear which structural features determine accelerator activity in cuticles.

Different types of accelerators are available for formulating systemic pesticides, but it is still not known if all types of accelerators are equally effective with all a.i. and cuticles from different plant species. Accelerators plasticize both cutin and waxes (*8*), but their effect on waxes is most relevant, as waxes represent the main barriers in cuticles (*16*, *17*). Diffusion across cuticles of 2,4-D and a few other model compounds was shown to be proportional to concentrations of EA's in cuticles (*15*, *16*, *18*, *19*) and reconstituted barley leaf wax (*9*, *12*). Effects of ethoxylated alcohols on diffusion of various pesticides and other model compounds in reconstituted barley leaf wax has been studied extensively, but waxes from other plant species were rarely investigated (*20*). Diffusion of 2,4-DB across *Stephanotis* leaf cuticles increased with concentrations of diethyl suberate or tributyl phosphate in cuticles, but their concentrations in waxes are not known (*15*).

For optimum performance accelerators should (i) penetrate into cuticles very rapidly, (ii) remain sorbed in the cuticles until

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10.1021/jf048364o CCC: $30.25
Published on Web 02/19/2005

Table 1. Properties and Sources of Accelerators Used

chemical name	formula	molecular weight [g mol^{-1}]	purity [%]	cuticle/receiver partition coefficient $K_{CM/REC}$
diethyl suberate (DESU)	$C_{12}H_{22}O_4$	230.01	>98	92[a]
diethyl sebacate (DES)	$C_{14}H_{26}O_4$	258.36	>95	1213[b]
dibutyl suberate (DBSU)	$C_{16}H_{30}O_4$	286.41	>99	15 988[b]
dibutyl sebacate (DBS)	$C_{18}H_{34}O_4$	314.47	>97	210 762[b]
tributyl phosphate (TBP)	$C_{12}H_{24}O_4P$	266.32	>98	343[a]

[a] Taken from Schönherr et al. (*15*). [b] Estimated using the equation log $K_{CM/REC} = 1.964 + 0.56(nCH_2)$. The constant represents log 92, nCH_2 is the number of methylene groups, and the slope 0.56 was taken from Sangster (*24*).

a.i. have reached the mesophyll, (iii) have a high intrinsic activity such that only small amounts suffice, and (iv) be biodegradable and not phytotoxic. In our search for optimum accelerators we investigated the efficacy of a homologous series of *n*-alkyl esters of dicarboxylic acids at increasing lipophilicity as well as tributyl phosphate in cuticles isolated from *Stephanotis* leaves and related activities to their concentration in cuticles or waxes.

MATERIALS AND METHODS

Plant Material. Astomatous adaxial cuticular membranes (CM) of mature leaves from greenhouse-grown Madagascar jasmine (*Stephanotis floribunda* Brongn.) were isolated enzymatically, dried, and stored at 8 °C until used. *Stephanotis* CM were selected as model CM for their availability and easy handling and because solute mobilities resemble those of CM from important crop plants such as apple, pear, and *Citrus* leaves (*7*, *21*, *22*, *23*).

Chemicals. The following chemicals (source and purity in parentheses) were used: citric acid (>99%, Merck, Darmstadt, Germany), L-(+)-lactic acid (Roth, Karlsruhe, Germany), 1,2-propanediol (>98%, Fluka, Neu-Ulm, Germany), polydisperse alkyl polyglycoside (APG) surfactants Plantacare 1200 UP and Glucopon 215 CSUP (Fluka, Neu-Ulm, Germany), and sodium azide (>99%, Merck). [U-phenyl-^{14}C]2,4-dichlorophenoxy butyric acid (International Isotopes, München, Germany) with a specific activity of 444 GBq mol^{-1} was selected as model solute. The five accelerators investigated are listed in **Table 1**.

Measurement of ^{14}C-2,4-DB Mobility in *Stephanotis* CM. Effects of accelerators on mobility in CM were studied using unilateral desorption from the outer surface (UDOS). The apparatus and procedures have been described elsewhere in detail (*16*, *18*). Briefly, CM were inserted into the desorption chambers with the morphological inner surface facing outward. A 10 μL droplet of radioactive donor solution (500 Bq ^{14}C-2,4-DB) dissolved in lactic acid (2 g L^{-1}) buffer of pH 3.8 containing 400 g L^{-1} ethanol was placed on the center of the CM (inner surface). The solvents (water and ethanol) were allowed to evaporate at room temperature, and the surface was sealed using the sticky plastic Tesafilm. This was done to maintain high humidity on the donor side of the CM and prevent radioactive contamination of the apparatus in case a CM should break. Next, the chambers were positioned in the wells of a thermostated aluminum block (20 ± 1 °C) where they were left overnight. In the morning 0.6 mL of desorption medium (aqueous citric acid buffer at 2 g L^{-1} adjusted with KOH to pH 6.0 containing 100 g L^{-1} 1,2-propanediol, and 1 mmol L^{-1} NaN_3) was pipetted into the receiver chambers. With the CM facing down, the desorption units were returned to the thermostated aluminum block, which was rocked at 80 cycles min^{-1} to keep the desorption medium well mixed. Propanediol was employed because the accelerators were not sufficiently soluble in the citric acid buffer. Effects of accelerators on 2,4-DB mobility were studied by adding various concentrations of these accelerators to the desorption medium. Desorption media were withdrawn quantitatively in predetermined intervals and replaced by fresh media. After four successive samples had been taken the CM was cut out and residual radioactivity was extracted with scintillation cocktail. Scintillation cocktail was also added to the desorption media, and radioactivity was determined at a 2σ error of 3% using a Wallac 1409 Liquid Scintillation Counter (Wallac Oy, Turku, Finland).

To obtain the desired concentrations of accelerators in CM (C_{CM}) as shown in **Table 2** the receiver concentrations (C_{REC}) were selected based on their cuticle/water partition coefficient ($C_{CM/REC}$), which are tabulated in **Table 1**

$$C_{CM} = C_{REC}K_{CM/REC} \quad (1)$$

For DESU and TBP partition coefficients were taken from the literature (*15*). Partition coefficients (*K*) for DES, DBSU, and DBS were estimated assuming that in a homologous series log *K* increases by a factor of 0.56 for an increment of one methylene group (*19*, *24*). DBSU and DBS are very lipophilic, and accelerator concentration in the first receiver decreased rapidly due to sorption in the CM and the small volume of the receiver. Using a higher accelerator concentration in the first receiver compensated for this effect (see **Table 2**, first receiver). The necessary concentration of the first receiver was calculated from the partition coefficient, the mass of the CM exposed to the receiver (0.257 mg), and the volume of the receiver (600 mg)

$$C_{CM} = \frac{\text{mass}_{ACC}}{\text{mass}_{CM} + \text{mass}_{REC}/K_{CM/REC}} \quad (2)$$

For instance, for a desired accelerator concentration of DBSU in the CM (C_{CM}) of 50 g kg^{-1} the first receiver concentration must be 28.8 mg kg^{-1}. Due to sorption in the CM the DBS concentration decreases during the first 4 h to 3.13 mg kg^{-1}. This is the equilibrium accelerator concentration of the receiver as calculated from eq 1, and this DBSU concentration was used in all succeeding desorption steps (marked receptor in **Table 2**). This maintains the desired accelerator concentration throughout the experiment.

Data analysis consisted of plotting $-\ln(1 - M_t/M_0)$ versus *t*, where M_0 is the total amount of radioactivity applied to the sorption compartment of the CM ($t = 0$) and M_t is the amount of radiolabel desorbed from the outer surface at time *t*. These plots are linear, and the slopes of the plots are the first-order rate constants of desorption (k^*), which are proportional to the diffusion coefficient in the limiting skin of CM (*5*, *16*, *25*). Slopes were calculated for each CM separately, and 40 replicates were used. As distribution of rate constants is often not normal (*26*), average rate constants were calculated from log-transformed data. Geometric means with 95% confidence intervals will be reported.

RESULTS

Desorption plots for 2,4-DB were linear with all desorption media tested (**Figure 1**). Slopes of the lines as obtained with UDOS experiments are the first-order rate constants (k^*), and for the control they amounted to 26.1×10^{-3} h^{-1} for the control (citric acid buffer). Adding propane-1,2-diol, Glucopon 215 CSUP, or Plantacare 1200 UP to the desorption media did not significantly affect slopes.

Typical desorption plots obtained with various concentrations in CM of DES and DBSU are shown in **Figure 2**. Plots of $-\ln(1 - M_t/M_0)$ vs time were always linear, which shows that 2,4-DB concentration in the CM decreased exponentially with time. Good linearity was also observed with DBSU for which the first receiver concentration in the interval 0−4 h was much higher than the equilibrium concentration (**Table 2**). Thus, sorption equilibrium was obtained in less than 4 h. The slopes of the lines are the first-order rate constants of desorption (k^*).

Table 2. Effects of Accelerators at Various Concentrations on Rate Constants of Desorption of 2,4-DB (Means and 95% confidence intervals are given)

accelerator	$K_{WAX/REC}$[a]	concentration in first receiver (mg kg^{-1})	concentration in receiver (mg kg^{-1})	concentration in CM (g kg^{-1})	concentration in wax[a] (g kg^{-1})	rate constant (h^{-1}) $\times 10^3$
control			0	0	0	8.3 ± 1.2
DESU	56 ± 5	100	100	9.2	5.6 ± 0.6	66.1 ± 23.5
		200	200	18.4	11.2 ± 1.2	121.4 ± 36.5
		300	300	27.6	16.8 ± 1.8	207.0 ± 46.0
		400	400	36.8	22.4 ± 2.4	252.6 ± 26.3
		500	500	46.0	28.0 ± 3.0	325.7 ± 19.5
DES	447 ± 166	10	10	12.1	4.5 ± 1.7	56.7 ± 13.7
		20	20	24.3	8.9 ± 3.3	95.3 ± 20.6
		30	30	36.4	13.4 ± 5.0	149.9 ± 25.7
		40	40	48.5	17.9 ± 6.6	228.5 ± 31.0
		50	50	60.7	22.4 ± 8.3	245.2 ± 26.5
DBSU	5319 ± 1266	5.7	0.63	10.1	3.4 ± 0.8	39,4 ± 10.7
		11.5	1.25	20.0	6.6 ± 1.6	70.1 ± 22.5
		17.3	1.88	30.1	10.0 ± 2.4	86.6 ± 23.2
		23.0	2.50	40.0	13.3 ± 3.2	116.9 ± 26.3
		28.8	3.13	50.0	16.6 ± 4.0	143.2 ± 36.7
DBS	28 590 ± 1297	5	0.1	21.1	2.9 ± 0.1	30.0 ± 10.5
		10	0.2	42.2	5.7 ± 0.3	32.5 ± 9.0
		16	0.3	63.2	8.6 ± 0.4	52.4 ± 16.3
		21	0.4	84.3	11.4 ± 0.5	70.1 ± 20.8
		26	0.5	105.38	14.3 ± 0.7	49.9 ± 16.1
TBP	244 ± 35	60	60	20.6	14.6 ± 2.1	67.0 ± 21.2
		120	120	41.2	29.3 ± 4.2	131.8 ± 32.2
		180	180	61.7	43.9 ± 6.3	284.8 ± 30.1
		240	240	82.3	58.6 ± 8.4	331.5 ± 22.2
		300	300	102.9	73.2 ± 10.5	337.4 ± 12.0

[a] Taken from Simanova et al. (*28*).

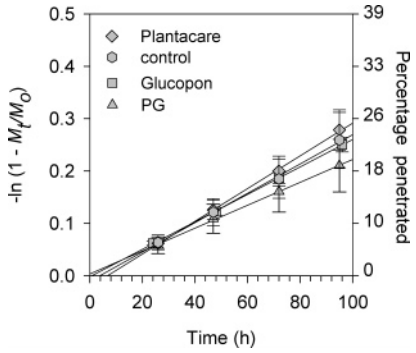

Figure 1. UDOS first-order plots showing the time course of desorption of ^{14}C-2,4-dichlorophenoxybutyric acid (2,4-DB) from *Stephanotis* CM as affected by propane-1,2-diol (100 g L^{-1}), Glucopon 215 CSUP (0.2 g L^{-1}) and Plantacare 1200 UP (0.2 g L^{-1}). Means and 95% confidence intervals were plotted.

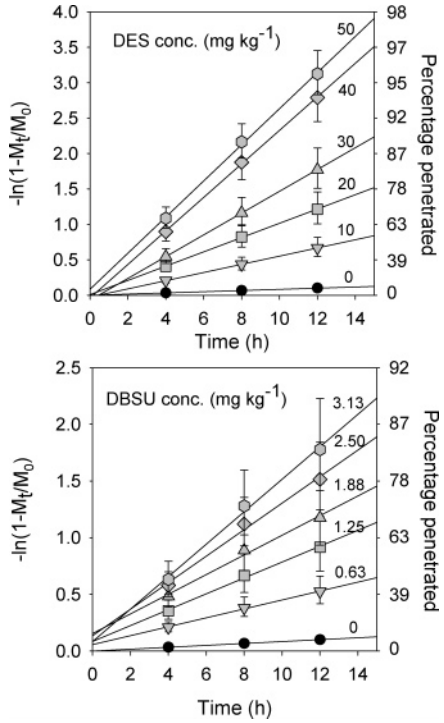

Figure 2. First-order plots showing the time course of penetration of ^{14}C-2,4-dichlorophenoxy butyric acid (2,4-DB) as affected by the accelerators DES and DBSU. Accelerator concentrations in receiver solutions are given in the graphs. Means and 95% confidence intervals were plotted. Slopes of the plots represent the first-order rate constant of penetration.

They increased with increasing concentration of accelerators. Comparable plots were obtained with all other accelerators tested, and results are summarized in **Table 2**.

When rate constants were plotted against accelerator concentration in *Stephanotis* CM, linear graphs were obtained for DESU, DES, DBSU, and DBS (**Figure 3**, top). However, with increasing carbon numbers the slopes decreased. Results obtained with TBP (**Figure 3**, bottom) differ as graphs were not linear and rate constants approached a maximum at high TBP concentrations. The maximum rate constant measured with TBP was around 0.35×10^{-3} h^{-1} when TBP concentration in the CM was 80 g kg^{-1} or higher. A similarly high k^* was obtained only with DESU (**Figure 3**, top), albeit at a much lower internal accelerator concentration of about 45 g kg^{-1}.

DISCUSSION

Cuticles are asymmetrical barriers, and a thin layer located at the morphological outer side of the CM is responsible for barrier properties (*17*, *18*). This layer is called the limiting skin. Cuticular waxes associated with cutin constitute this rate-limiting barrier in plant cuticles. Removal of these waxes by extraction increases permeability and solute mobility by several orders of magnitude (*17*, *18*). Reconstituted wax barriers devoid of cutin

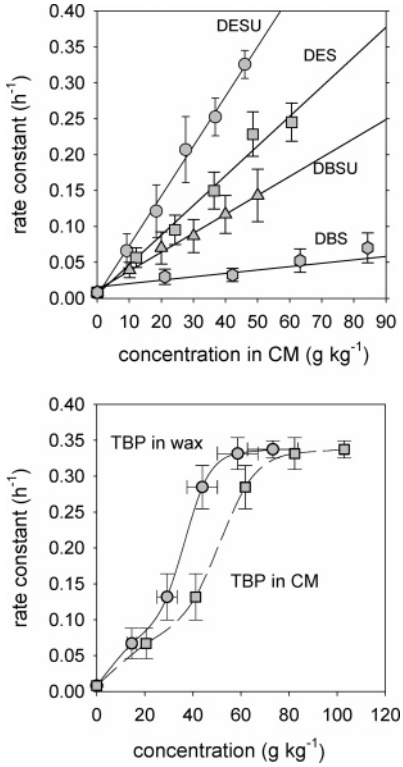

Figure 3. Effects of concentrations in cuticular membranes of accelerators on rate constants (mobility) of 2,4-DB in *Stephanotis* CM.

exhibit barrier properties and accelerator effects comparable to those of isolated cuticles (*9*, *12*, *17*).

The sorption compartment is located underneath the limiting skin and makes up the bulk of the mass of the CM (*27*). In the UDOS method radiolabeled solutes initially contained in the sorption compartment diffuse across the limiting skin into the desorption medium, and this is a first-order process as slopes of desorption plots were linear (**Figures 1** and **2**). These slopes (k^*) characterize mobility of 2,4-DB in the limiting skin, and they are proportional to the diffusion coefficient (*18*, *25*). Propylene glycol and the wetting agents Glucopon 215 CSUP and Plantacare 1200 UP did not increase slopes of the desorption plots, that is they have no accelerator properties. These two alkylpolyglycosides were included as they will be used as adjuvants in a subsequent experiment.

All accelerators used are lipophilic liquids. DESU is 92 times more soluble in the CM than in the desorption medium (receiver). With increasing carbon numbers partition coefficients increased and reached a value of 210 762 for DBS (**Table 1**). TBP is 343 times more soluble in *Stephanotis* CM than in the desorption medium. The concentrations of accelerators sorbed in the CM at equilibrium (C_{CM}) depend on partition coefficient ($K_{CM/REC}$) and accelerator concentration in the desorption media (C_{REC}) (eq 1).

Mobility of 2,4-DB in CM increased with increasing accelerator concentration in the CM. This dependence was linear, and slopes of the plots shown in **Figure 3** are 6.9 ± 10^{-3} (DESU, $r^2 = 0.99$), 5.33 ± 10^{-3} (DES, $r^2 = 0.98$), 2.6 ± 10^{-3} (DBSU, $r^2 = 0.99$), and 0.5 ± 10^{-3} (DBS, $r^2 = 0.75$). These slopes are the intrinsic activities of the accelerators based on average accelerator concentration in the CM. Relative to DBS, the intrinsic activity of DBSU was 5.2 times more effective than DES. Efficacies of DES and DESU were even 10.7 and 13.8 times higher, respectively.

Extraction of waxes from CM generally increases permeability to water and organic nonelectrolytes by several orders

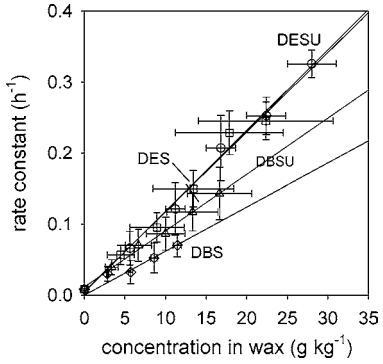

Figure 4. Effects of accelerators at various concentrations in reconstituted *Stephanotis* cuticular waxes on mobility (rate constants) of 2,4-DB in *Stephanotis* CM. Partition coefficients $K_{WAX/REC}$ were taken from Simanova et al. (*28*), and accelerator concentration was calculated using eq 1.

of magnitude. This shows that cuticular waxes constitute the major barrier in plant cuticles. In **Figure 4** rate constants were plotted against accelerator concentrations in reconstituted *Stephanotis* wax extracted from isolated adaxial leaf CM. Linear plots were obtained with slopes of 11.4 ± 10^{-3} (DESU, $r^2 = 0.99$, 11.2 ± 10^{-3} (DES, $r^2 = 0.98$), 7.4 ± 10^{-3} (DBSU, $r^2 = 0.99$), and 6.3 ± 10^{-3} (DBS, $r^2 = 0.96$). Hence, on the basis of the concentration in wax, the intrinsic activity of accelerators is higher and differences are smaller.

Concentrations of accelerators in wax were always smaller than concentration in the CM (**Table 2**), but this ratio was not constant. When concentration in wax was plotted against concentration in CM, straight lines were obtained (data not shown). For TBP and DESU the slopes amounted to 0.71 and 0.61, respectively. For these two accelerators experimental partition coefficients ($K_{CM/REC}$) are available. Slopes for DES (0.37), DBSU (0.33), and DBS (0.14) are much smaller, suggesting that with increasing molecular weight (e.g., increasing numbers of CH_2 groups) sorption of plasticizers in reconstituted wax was hindered (*28*). Wax contents of *Stephanotis* CM amounts to only 5−10%, and cutin/water partition coefficients have been shown to be much higher than wax/water partition coefficients. Thus, sorption of plasticizers in cutin might have significantly contributed to the higher $K_{CM/REC}$ values (*12*, *17*, *19*).

Effectiveness or efficacy of an accelerator is the ratio of the rate constants measured with and without accelerator. Plotting efficacy vs accelerator concentration resulted in linear plots (**Figure 5**). The accelerators investigated increased 2,4-DB mobility in CM and waxes between 10- and 40-fold. Rates of penetration are proportional to solute mobility, that is the diffusion coefficient, and a comparable effect on cuticular penetration rates is anticipated. Efficacy increased with accelerator concentration, and slopes are steeper when efficacy is referred to accelerator concentration in wax rather than in CM. The ratio of the slopes DESU/wax over DESU/CM was 1.62. For the other accelerators the ratio amounts to 2.70 (DES), 2.97 (DBSU), and 3.20 (DBS). With TBP nonlinear plots were obtained, and the plots converge at low and high concentrations. The largest difference was observed at about 40 g kg^{-1}, and it amounted to a factor of 2.2. These data are consistent with the fact that waxes represent the major barrier to diffusion of organic nonelectrolytes (*17*). Accelerators sorbed in the amorphous wax fraction increase solute mobility more than in cutin (*8*).

Efficacy of DESU and TBP had been studied previously,[15] and comparing these data with those of the present study shows large differences (**Figure 6**). The efficacy in our present study

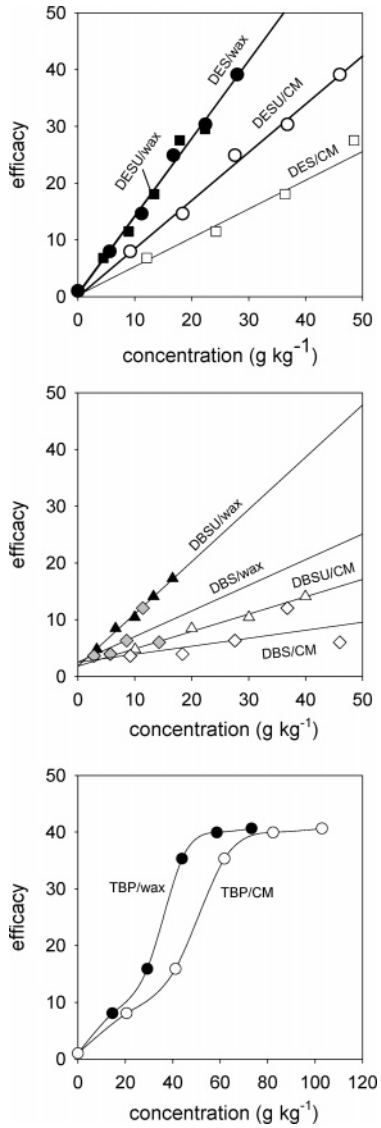

Figure 5. Efficacy of accelerators at increasing mobility of 2,4-DB in *Stephanotis* CM. Efficacy is the ratio of rate constants measured in the presence and absence of accelerators in CM or cuticular waxes.

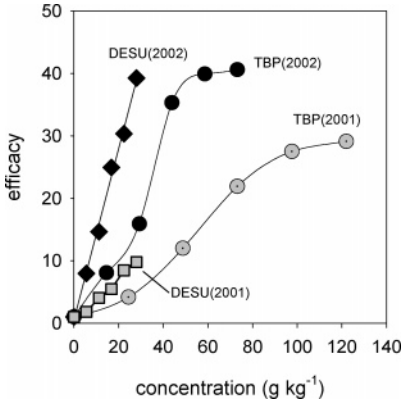

Figure 6. Efficacy of DESU and TBP as affected by year of isolation of *Stephanotis* CM. Data for DESU (2001) and TBP (2001) were taken from Schönherr et al. (*15*).

(marked 2002) is much higher. For instance, the slopes for $DESU^{2001}$ and $DESU^{2002}$ are 1.37 and 0.35, respectively, showing that in our present study efficacy of DESU was 3.9 times higher. 2,4-DB mobility in the absence of accelerators differed as well and was 2.3×10^{-3} (2001) and 8.3×10^{-3} h^{-1} (2002). In the two studies the same chemicals and procedures were used, but CM were isolated from different plants. They had been purchased at the local market and were grown in a greenhouse. CM were isolated from newly grown leaves. However, the varieties of the plants purchased were not specified, and differences in efficacy and 2,4-DB mobility are likely due to variety. With pear leaf CM large differences in solute mobilities among varieties have been reported (*23*).

The intrinsic activity of accelerators is important, but it is not the sole property to be considered in formulating active ingredients. In the present experiments the accelerator concentration was kept constant and velocity of penetration of accelerators was not limiting. In the field, active ingredients and accelerators are applied simultaneously. Accelerators can be regarded as pace makers and must penetrate rapidly, especially at low temperatures. This velocity depends on the size of the accelerator and its intrinsic activity. Rates of penetration of the accelerators tested were not measured, but even with the largest accelerators equilibration took less than 4 h. After 4 h of equilibration plots $-\ln(1 - M_t/M_0)$ vs time were linear at all accelerator concentrations and *y*-intercepts were close to zero. If equilibration between receiver and CM had taken more than 4 h, slopes would have increased with time. This suggests that rates of penetration of accelerators will not be rate limiting when applied simultaneously with active ingredients. The accelerators are needed in only small amounts of up to 5 wt % of CM or wax. These low concentrations are not expected to be phytotoxic, especially not when partition coefficients are very high. Furthermore, the ester bonds are likely to be cleaved rapidly by nonspecific esterases present in all plants.

Though rapid penetration of accelerators in the wax and cuticle is desirable, it is just as important that accelerators remain in the limiting barrier of the CM until the bulk of the solute has penetrated. The only feasible way of increasing the residence time of accelerators in the wax is by making the wax/water partition coefficient very large. This decreases the rate of transfer of accelerator from the CM into the water of the epidermal wall due to the low water solubility of highly lipophilic compounds. For pesticides to enter and move in the xylem their octanol/water partition coefficients should not be much larger than 1000, and this can be expected to apply also to accelerators. Among the accelerators tested DBSU and DBS meet these criteria, and they are not expected to be systemic.

These considerations suggest that the accelerators should be useful tools for formulating systemic nonionic active ingredients. Ionic active ingredients are always hydrated and penetrate cuticles by diffusing across aqueous pores rather than in wax (*29*, *30*). Since ionic species are excluded from the lipophilic pathway, accelerators do not affect their rates of penetration. This was recently demonstrated with inorganic foliar nutrients (*29*) and glyphosate salts (*30*). In the present study the rather lipophilic model substance 2,4-DB was used. The dependence on polarity of active ingredients on accelerator efficacy will be reported separately.

ABBREVIATIONS USED

a.i., active ingredient; CM, cuticular membrane(s); 2,4-DB, dichlorophenoxy butyric acid; DESU, diethyl suberate; DES, diethyl sebacate; DBSU, dibutyl suberate; DBS, dibutyl sebacate; TBP, tributyl phosphate.

ACKNOWLEDGMENT

This study was supported in part by a grant (SCHO 197/13) from the Deutsche Forschungsgemeinschaft.

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Received for review October 1, 2004. Revised manuscript received January 14, 2005. Accepted January 18, 2005.

JF048364O