Release of Trifluralin from Starch Xanthide Encapsulated Formulations

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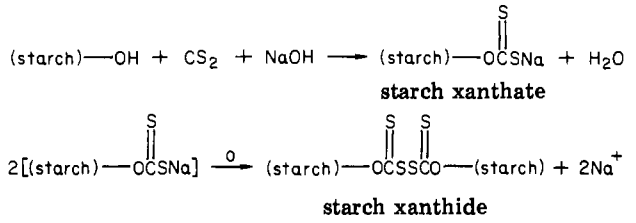
The release of trifluralin from various starch xanthide encapsulated and adsorbed formulations was determined both in the dry state and in the presence of water. Volatilization of the herbicide into filter paper suggested slower release from encapsulated than from adsorptive formulations. More consistent results were obtained by measuring the release through desorption with hexane. In air-dried formulations, 8–94% of trifluralin was desorbed within the first 3–5 min, and there was 0–19% subsequent desorption over the following week. When water was added to the formulations, the desorption within the first few minutes was less than with dry formulations, but there was a continuous desorption in the following days. Release over a 7-day interval became greater as particle size decreased.

Trifluralin [2,6-dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)benzenamine] is a preplant-incorporated herbicide used for control of annual grasses and broadleaf weeds (Alder et al., 1960). The recommended application rate of 0.5–1.0 lb/acre as a 4 lb/gal emulsifiable concentrate gives control usually for 4–6 months. It is subject to loss by volatilization and decomposition by sunlight when applied to the surface of soils and to loss from soil microorganisms when mixed into the soil at the time of planting.

Water has an important influence upon the loss of trifluralin from the soil. The volatility is low in the daytime under conditions of low soil moisture and higher at night when moisture has condensed in the soil (Harper et al., 1976). The diffusion of trifluralin in silt loam soil reaches a maximum near 18% (w/w) soil moisture and decreases at higher moisture levels (Bode et al., 1973).

It is possible to encapsulate trifluralin in a starch matrix by first forming starch xanthate, followed by dispersing the trifluralin in the xanthate and coagulating the dispersion by oxidation to starch xanthide (Shasha et al., 1976):



The coagulated dispersion containing trifluralin is dried to provide a granular product that temporarily protects the herbicide from loss by volatilization and photodecomposition (Foley and Wax, 1978) and controls weeds more efficiently. Also, side effects of phytotoxicity to desirable plants are minimized (Devisetty and Hanson, 1978).

Moisture may have a different influence upon the rate of release of trifluralin from a starch matrix than from the unencapsulated material in the soil (Foley and Wax, 1978). Further control of release in starch-encapsulated formulations might then be achieved by varying the ratio of adsorbed to encapsulated trifluralin. Retention of trifluralin in starch is achieved by means of tiny cells trapped within an amorphous starch matrix. The matrix is softened in the presence of moisture to allow release of trifluralin.

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Formulations designed to contain about 40% of the trifluralin adsorbed and 60% encapsulated may be useful for providing good initial control, followed by a slower sustained control. We have prepared such formulations by mixing encapsulated trifluralin and trifluralin adsorbed onto a carrier surface and by adsorbing trifluralin onto the surface of starch xanthide encapsulated trifluralin. In initial experiments, the release of trifluralin was determined after allowing the herbicide to volatilize onto Whatman No. 2 filter papers for a given interval. Qualitative differences were found among various formulations in the absence or presence of water, but results were erratic.

More reliable data were obtained by suspending the samples in a suitable solvent (Shasha, 1978) such as hexane, either along or mixed with various ratios of water. The hexane dissolved the trifluralin immediately available and the amount subsequently diffusing out over a longer interval. From such results it was possible to observe differences among formulations that might ultimately be related to the rate of release of active ingredient under field conditions.

EXPERIMENTAL SECTION

Trifluralin was technical grade, 95% active ingredient, and was obtained from Eli Lilly and Co. Starch was modified pearl no. 3005, CPC International, 12% moisture.

Starch xanthate with a degree of substitution (DS) of 0.17 was prepared by suspending 90 g of starch in 500 mL of water, followed by adding 10 mL of carbon disulfide and 10 g of sodium hydroxide dissolved in 190 mL of water. The mixture was kept at room temperature for at least 2 h before use.

Encapsulation of Trifluralin. A solution of 5.0 g of trifluralin in 12.5 g of acetone was mixed with 200 g of starch xanthate. For formation of starch xanthide, a solution of 2.5 mL of 30% hydrogen peroxide and 3.1 g of sulfuric acid in 10 mL of ice water was added portionwise with stirring until solidification was complete. After 5 min, the product was filtered through cheesecloth by using suction and a rubber dam to remove most of the solvent. The moist particles were ground in a Waring Blendor to pass 12 mesh and air-dried overnight. The dried particles were separated into fractions of 20–30, 30–40, 40–60, and 60–120 mesh.

Alternatively, the trifluralin was melted at 80 °C and poured quickly into a rapidly agitated starch xanthate dispersion in the Blendor. When emulsification was complete, the peroxide–sulfuric acid mixture was added and stirring continued until the mass solidified and became dispersed into small particles. After filtration, the particles

were again broken up in the Blendor and then simultaneously sieved and dried in a current of air to obtain fractions in the 12–120-mesh range.

Although trifluralin is considered to be very soluble in organic solvents such as acetone and hexane, dispersion of encapsulated products in these solvents dissolves usually <20% of the total herbicide present. The part which does not dissolve is therefore entrapped within the starch matrix and considered to be encapsulated.

Adsorptive Formulations of Trifluralin. Starch xanthide (SX) was prepared as above but in the absence of trifluralin. A solution of 5.0 g of trifluralin in 12.5 g of acetone was mixed with 24.6 g of the dried xanthide, and the acetone was allowed to evaporate. Trifluralin (1.5 g) was adsorbed onto pearl starch (8.5 g) by mixing the starch and trifluralin in 5 mL of acetone and evaporating the acetone.

Analysis of Total Trifluralin. Samples of 0.1–0.2 g containing 10–15% active ingredient (a.i.) were pulverized repeatedly with methanol or hexane by using a mortar and pestle until no more color was extracted and then filtered by suction through a medium glass fritted filter. Filtrates were diluted to 100 mL with the extracting solvent, and the visible maxima at 380–385 nm were used to determine trifluralin content [λ 385 nm, ϵ 2446 (methanol); λ 380 nm, ϵ 2642 (hexane)].

Volatilization of Trifluralin. Solid formulations of trifluralin (0.1–0.5 g) containing various amounts of water were spread evenly over 9-cm Petri dishes and covered with circles of Whatman No. 2 filter paper. After 24 h at 25 °C, the papers containing volatilized trifluralin were wrapped in a 3.5 × 28 cm glass tube, and the papers were washed with methanol to desorb the trifluralin. After dilution to 10 mL with methanol, the trifluralin was determined by visible spectroscopy.

Desorption of Trifluralin. Solid formulations of trifluralin were placed in 10–100-mL volumetric flasks and treated with various amounts of water to give water:formulation ratios of 0:1, 1:1, 2:1, and 3:1 (w/w). Hexane was added to the volumetric mark and the flasks were stoppered. Desorbed trifluralin was measured periodically by visible spectroscopy after shaking prior to each measurement. Trifluralin release was recorded during measurements over several days.

Formulations Prepared by Physical Mixing. Trifluralin encapsulated from acetone solution and passing 12 mesh contained 12.1% a.i. Desorption experiments in hexane indicated that ~19% of this amount was available at the surface. The remainder was obtainable by rupturing the trapped cells in the interior of the starch matrix through trituration with hexane with a mortar and pestle. Trifluralin adsorbed onto SX of similar mesh contained 12.3% a.i., and all of this was desorbed by hexane.

Adsorption of Trifluralin onto Encapsulated Trifluralin. Encapsulated trifluralin was mixed with an acetone solution of trifluralin, followed by evaporation of acetone. Exactly 1.0000 g of encapsulated trifluralin was mixed with a solution of 0.0423 g of trifluralin in 2 mL of acetone and evaporated on a dish 1 h prior to analysis. The product was calculated to contain 15.7% trifluralin.

Encapsulation of Trifluralin Adsorbed onto Starch Xanthide. A mixture of 5.0 g of SX containing 12.3% adsorbed trifluralin and 5.0 g of starch xanthate was treated with 5.0 mL of an aqueous solution containing 0.075 mL of 30% hydrogen peroxide and 0.093 g of sulfuric acid and stirred to complete solidification. The product, after air-drying, contained 11.5% trifluralin.

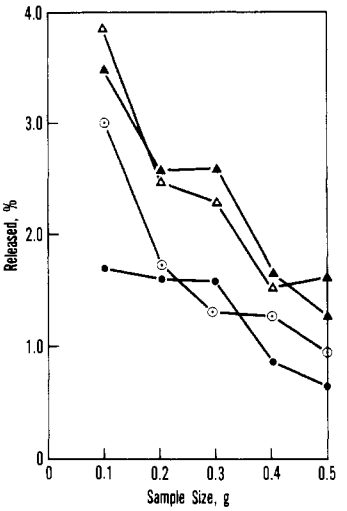

Figure 1. Volatilization of trifluralin into Whatman No. 2 filter paper. (⊙) 12.1% a.i. encapsulated in starch xanthide to pass 12 mesh and (●) with an equal amount of water; (△) 12.3% a.i. adsorbed onto starch xanthide to pass 12 mesh and (▲) with an equal amount of water.

Encapsulation of Trifluralin Adsorbed onto Pearl Starch. A mixture of 2.0 g of trifluralin adsorbed onto pearl starch (14.5% a.i.) and 6.0 g of starch xanthate was treated with 3.0 mL of the hydrogen peroxide–sulfuric acid solution (as above) and mixed until solidification was complete. After water was expressed, the product was air-dried overnight at room temperature. Total trifluralin was 10.1% by trituration with methanol and 10.9% by trituration with hexane.

RESULTS AND DISCUSSION

The amounts of trifluralin volatilized into filter paper over 24 h are expressed as percent of total trifluralin (Figure 1). It is seen that the amounts released relative to the total present increase with decreasing sample weight. This observation indicates that volatilization takes place not only into the filter paper but also onto neighboring particles of the sample. In smaller samples there are fewer neighboring particles and hence greater relative volatilization into the filter paper.

Samples containing trifluralin adsorbed mostly on the surface volatilize more than samples containing trifluralin encapsulated within the particles. When water is added to these samples, the volatility of trifluralin is altered. The success of these experiments is limited by difficulties in controlling the path through which the trifluralin is volatilized.

The results of desorption into hexane appear to be less dependent upon sample size, and both desorption and release are measured more accurately. Desorption into hexane is suitable for measuring the influence of water adhering to the formulation, since water is not soluble in hexane. Water causes an initial decrease of desorption into hexane through a barrier effect. Subsequently there is diffusion of the trifluralin through the barrier into hexane.

Trifluralin release from the various formulations into hexane, both with and without water, is summarized in Table I. The amount released into hexane without added water (0:1) represents trifluralin adsorbed at or near the surface of the particles. Additional trifluralin present was not desorbed but only released by crushing or triturating the formulation in the presence of an organic solvent. The most efficient encapsulation is achieved when melted trifluralin is used (formulations 10 and 11). For these two products, about 90% of the trifluralin was encapsulated

Table I. Effect of Water upon the Release of Trifluralin from Encapsulated and Adsorbed Formulations Suspended in Hexane

formulation[a] containing trifluralin	time, days	% release for water:formulation 0:1	1:1	2:1	3:1
1, physical mixture of SX encapsulated[b] and SX adsorbed	0	40	32	32	20
	7	43	55	73	48
2, SX encapsulated[b] containing adsorbed	0	42	30	23	14
	7	42	50	57	39
3, SX adsorbed encapsulated with SX	0	81	40	29	13
	7	100	100	93	36
4, pearl starch adsorbed encapsulated with SX	0	47	9	2	2
	7	53	53	7	7
5, SX adsorbed	0	94	99	72	42
	7	93	99	100	76
6, SX encapsulated,[c] 20-30 mesh	0	32	18	6	3
	7	33	44	39	24
7, SX encapsulated,[c] 30-40 mesh	0	33	17	6	3
	7	36	47	41	19
8, SX encapsulated,[c] 40-60 mesh	0	34	17	5	2
	7	39	51	45	24
9, SX encapsulated,[c] 60-120 mesh	0	48	17	4	4
	7	51	66	45	21
10, SX encapsulated,[b] 60-120 mesh	0	8	3	2	1
	7	8	70	41	18
11, SX encapsulated,[b] passing 120 mesh	0	9	4	2	1
	7	10	88	50	19

[a] SX is starch xanthide. [b] Melted trifluralin was used for encapsulation; ~90% encapsulated. [c] Trifluralin in acetone solution was used for encapsulation; ~50-70% encapsulated.

and 10% was adsorbed. When an acetone solution of trifluralin was used, as in formulations 6–9, about 50–70% was encapsulated and 30–50% was adsorbed. There are only slight changes in release for most of the dry samples over extended periods but very marked changes when water is first added. The addition of water causes an initial decrease in desorption, followed by a continuous rise, to where the release from the dry formulation may be exceeded. This observation may account for reports of poor initial control with trifluralin–starch xanthide formulations but good control after several weeks (Foley and Wax, 1978; Coffman and Gentner, 1978, 1979, 1980). It would also be expected that the release of trifluralin from formulations containing encapsulated trifluralin would not be immediately responsive to soil moisture as would purely adsorptive formulations or trifluralin adsorbed onto the soil (Harper et al., 1976; Hollingsworth, 1980). Maximum release is attained at 1:1 and 2:1 water:formulation ratios. Ratios of water:formulation greater than these cause decreases in the release, possibly due to saturation of the capsules and formation of a surface barrier of adsorbed water.

Figure 2 shows the effect of water on a product (formulation 9 of Table I) of 60–120 mesh containing ~50% adsorbed trifluralin prepared by encapsulation from acetone solution. Such a product might be fine enough for spray applications and have a potential for good release characteristics. Where the 1:1 water:formulation ratio is used, the initial lag in release is overcome in 2 days with a sustained release thereafter.

Figure 3 compares rates of release in 1:1 water:formulation ratio with different particle sizes. It may be seen that after the initial release suppression, there is a rapid rise over 1–3 days, followed by a steady, slower rise. The overall release increases with decreasing particle size, and it is greatest for the finest particles over 120 mesh. The influence of the amount initially adsorbed in the dry

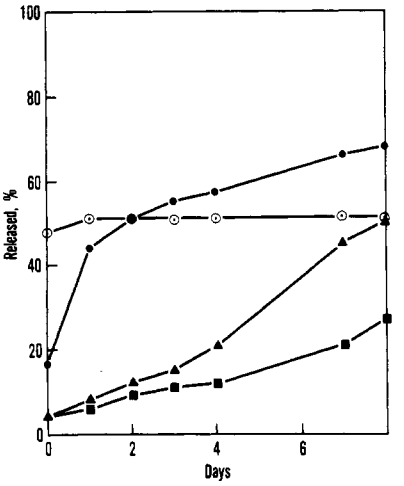

Figure 2. Effect of water:formulation ratio upon the release of trifluralin from SX, 15.4% a.i., 60–120 mesh; (⊙) 0:1, (●) 1:1, (▲) 2:1, and (■) 3:1 water:formulation (acetone solution of trifluralin used for encapsulation).

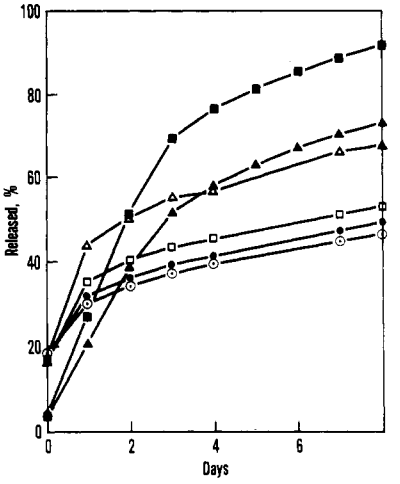

Figure 3. Effect of particle size and content of adsorbed trifluralin upon the release of trifluralin from SX-encapsulated formulations containing equal amounts of water. (⊙) 20–30, (●) 30–40, (□) 40–60, and (△) 60–120 mesh (acetone solution of trifluralin used for encapsulation); (▲) 60–120 and (■) passing 120 mesh (melted trifluralin used for encapsulation).

formulation can be seen by comparing the 60–120-mesh products encapsulated from acetone solution (△) and from melted trifluralin (▲). The benefit of adsorbed trifluralin is seen in the first 3 days and indicates the advantage that might derive from formulations that contain both adsorbed and encapsulated trifluralin. There would be satisfactory release of active agents initially, followed by a continuous prolonged release.

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Synthesis and Plant Growth Regulatory Properties of Substituted 2-(2,2,2-Trichloroethylideneamino)phenols, 2-(Trichloromethyl)benzoxazoles, and Benzothiazoles

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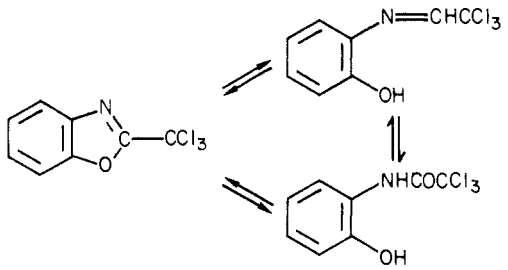
2-(2,2,2-Trichloroethylideneamino)phenols and 2-(trichloromethyl)benzoxazoles and benzothiazoles were synthesized. Their effects were compared on the growth of a number of broad-leaved weeds. Several compounds were shown to be good plant growth retardants. The unsubstituted phenol and benzoxazole showed particularly good plant growth retardant properties and substitutions in the benzene nucleus resulted in loss of activity or an increase in phytotoxicity.

2-(Trichloromethyl)benzoxazole, acquired as an inter-



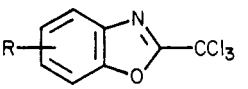
mediate during a synthesis program, showed plant growth retardant properties when passed through a general herbicide screen. The extent of plant miniaturization accompanied by minimal phytotoxicity prompted a more extensive study of this compound. A literature survey revealed that the parent compound and some derivatives had been shown to possess herbicidal properties (Holan, 1967; Holan and Samuel, 1970). The potential products of reduction and hydrolysis, and therefore possible metabolites, 2-(2,2,2-trichloroethylideneamino)phenol and α,α,α-trichloro-2-hydroxyacetanilide, respectively, were also synthesized and screened as potential plant growth retardants.

2-(2,2,2-Trichloroethylideneamino)phenol was found to possess excellent plant growth retardant properties but α,α,α-trichloro-2-hydroxyacetanilide was essentially inactive. Accordingly, a series of ring-substituted derivatives, 2-(trichloromethyl)benzoxazoles and 2-(2,2,2-trichloroethylideneamino)phenols were synthesized and their effects on plant growth observed.

CHEMICAL METHODS

Analyses were performed by Strauss, Oxford. Infrared spectral data were recorded as nujol mulls on a Perkin-Elmer 157 recording spectrophotometer. Where analyses are indicated by symbols of the elements, analytical results obtained for those elements are within 0.4% of the theoretical values.

Table I. Physical Properties of 2-(Trichloromethyl)benzoxazoles



R	formula	mp, °C	% yield	analyses
4-CH_3	$C_9H_6Cl_3NO$	68	13	C, H, N
6-CH_3	$C_9H_6Cl_3NO$	69	30	C, H, N
7-CH_3	$C_9H_6Cl_3NO$	56	47	C, H, N
4,6-$(CH_3)_2$	$C_{10}H_8Cl_3NO$	103.5	28	C, H, N
5,7-$(CH_3)_2$	$C_{10}H_8Cl_3NO$	65	64	C, H, N
4,5,6-$(CH_3)_3$	$C_{11}H_{10}Cl_3NO$	117	26	C, H, N
4-Cl	$C_8H_3Cl_4NO$	100	18	C, H, N

2-Aminophenols were prepared by the reduction of the appropriate 2-nitro- or 2-phenylazophenols with alkaline dithionite. The method was new for the reduction of the following 2-nitrophenols to known amines (percentage yields in parentheses), 6-methyl (42), 3,5-dimethyl (67), 3,6-dimethyl (49), and 3-chloro (60), and also for 3,4,5-trimethyl-2-phenylazophenol to 2-amino-3,4,5-trimethylphenol (85).

The 2-(trichloromethyl)benzoxazoles were prepared by procedures based upon published methods (Stephens and Bower, 1950); Holan et al., 1967). Equimolar amounts of the appropriate 2-aminophenol and methyl trichloroacetimidate were heated under gentle reflux for 1–4 h in a 10% solution with ethanol. Removal of the solvent followed by repeated crystallizations of the residue gave analytically pure samples.

The 2-(2,2,2-trichloroethylideneamino)phenols were prepared from 2-aminophenols by reaction with anhydrous chloral in acetic acid for 15 min at 60 °C according to the method previously described (Stephens and Bower, 1950). The physical properties and deviations from the standard

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