The mechanism of organosilicone surfactant-induced uptake of amine and ester formulations of triclopyr.

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Summary
Addition of the organosilicone surfactants DC X25152 or Silwet L77 to triethylamine formulations of triclopyr reduced surface tension to < 25 mN m^{-1} and contact angles with leaf surfaces to < 20°. Rapid stomatal entry and herbicide uptake were determined. The organosilicone DC 57 did not perform similarly. Addition of DC X25152 or Silwet L77 to triclopyr butoxyethyl ester did not reduce surface tension significantly, being maintained at a minimum of 28 mN m^{-1}. No rapid uptake or stomatal entry of triclopyr butoxyethyl ester was determined and herbicide was shown to enter by a trans-cuticular pathway.

Introduction

The development of organosilicone compounds as adjuvants for improving the efficacy of herbicides has been beneficial in improving control of difficult to kill weed species (2). Organosilicone surfactants enhance both the magnitude and rate of herbicide uptake, although they may act antagonistically, (1,2).

Gorse (*Ulex europaeus* L.) has been a major weed target but is not an ideal experimental plant for uptake studies. Field bean (*Vicia faba* L.) has similar stomatal characteristics and has proved to be an excellent model experimental system (1).

This paper demonstrates the importance of solution surface tension, organosilicone chemistry and herbicide formulation in determining the magnitude, rate, and pathway of triclopyr uptake.

Materials and Methods

Plant material and experimental conditions: Plants of field bean and gorse were grown at 20-23 /15°C with a 14 h photoperiod, 70% RH and PPFD of 300 µmoles m^{-2} s^{-1} in a soil-based medium. Field bean was grown from seed and gorse from cuttings. The third leaf of field bean and mature spines of gorse were selected for experimentation. All experiments were fully randomised designs with a minimum of eight replicates.

Herbicide formulations: Triclopyr as the triethylamine salt or butoxyethyl ester was used at 4 kg a.i. ha^{-1} with the addition of ^{14}C triclopyr where necessary (1). The organosilicone surfactants DC 57 and DC X25152 (Dow Corning) and Silwet L77 (Union Carbide) were added on a volume basis.

Experimental methods: Uptake was determined by application of 0.25 µl droplets of an appropriate formulation, removal by washing with 70% aqueous methanol after a predetermined period and quantification of radiolabel by liquid scintillation counting (1). Wax extraction involved removal with chloroform. Uptake was expressed as a percentage of applied radiolabel.

Surface tension was measured by an adapted droplet-volume technique (1) and contact angle calculated using Mack's equation (2). Formulation behaviour on the leaf surface was visualised by adding a fluorescent indicator (Uvitex 2B, at 1 g l^{-1}) and observation by UV microscopy, following deposit removal with 70% aqueous methanol after 60 s or 1 h (1).

Results
Aqueous solutions of DC X25152 and Silwet L77 had surface tension values <25 mN m^{-1}, with an appoximately constant value of 21 mN m^{-1} at concentrations >0.05% (v/v). The critical micelle concentration (cmc) for DC X25152 and Silwet L77 was between 0.05 and 0.1% (v/v). The surfactant DC57 did not behave in the same manner and the low point surface tension values were 40-45 mN m^{-1}, within a concentration range of 0.1-0.5% (v/v). Surface tension values showed reasonable correspondence with contact angles when droplets were applied to the adaxial surface of field bean leaves. At ≥ 0.25% (v/v) Silwet L77 gave instantaneous complete wetting, with a similar result for DC X25152. Addition of triclopyr triethylamine did not vary the surface tension values significantly from those in pure water, while addition of the butoxyethyl ester had a very marked effect. Ester formulations with DC X25152 and Silwet L77 had a low point value of 28 mN m^{-1} at 0.5% (v/v), and were slightly higher at lower surfactant concentrations. No cmc value could be calculated and contact angles were >30°.

The low surface tension values for aqueous and triethylamine solutions permitted rapid stomatal entry, particularly at 0.25-0.5% (v/v). Visualisation of this phenomenon by UV microscopy was confirmed by measurement of herbicide uptake into both the adaxial surface of field bean leaves and gorse spines (Table 1). The rapid uptake during the initial 20 min. was followed by a slower uptake phase by 120 min. There was no evidence of major solution infiltration through stomata with the addition of DC 57 at 0.5% (v/v). With the butoxyethyl ester UV microscopy produced localised fluorescence around stomata but no signs of spreading fluorescence, consistent with solution infiltration into substomatal cavities and intercellular spaces.

There were marked differences in uptake between triclopyr triethlamine and butoxyethyl ester, depending on the presence of surfactant (Table 2). The control treatment of the butoxyethyl ester had the greatest uptake and the addition of Silwet L77 did not enhance uptake. Silwet L77 had a marked effect on enhancing the uptake of the triethylamine salt. A separate analysis revealed 3.3 -3.9% of herbicide was incorporated into epicuticular wax with the butoxyethyl ester, but only 0.4-0.6% with the triethylamine formulation.

Table 1. Percentage uptake of triclopyr triethylamine by field bean and gorse, with and without the addition of Silwet L77.

	Uptake (%)					
	Field Bean			Gorse		
Silwet L77 % (v/v)	20	60	Time 120	(min.) 20	60	120
0	0.9	2.7	8.4	2.0	6.5	10.8
0.25	5.6	10.0	16.8	8.9	12.3	16.6
S.E. mean	1.46			1.65		

Table 2. Percentage uptake of triclopyr triethylamine (A) and triclopyr butoxyethyl ester (E) by field bean and gorse with and without addition of Silwet L77, after 6h.

	Uptake (%)			
Silwet L77 % (v/v)	Field Bean		Gorse	
	A	E	A	E
0	3.1	23.3	1.1	36.8
0.25	19.0	25.8	18.2	39.2
S.E. mean	2.09			

Discussion

The key requirement for enhanced herbicide uptake following addition of organosilicone surfactants was reduced surface tension and the consequential low contact angle of droplets with the target surface. Both DC X25152 and Silwet L77 meet the requirement of surface tension of <25 mN m^{-1} but this was not satisfied by DC 57, with consequentially poor uptake characteristics. The low surface tension required for stomatal entry was achieved by triclopyr triethylamine with rapid initial uptake (Table 1). The result is similar to that for glyphosate isopropylamine (2) but different to that for triclopyr butoxyethyl ester, (Table 2). The latter does not show appropriate reductions in surface tension and the present results indicate that triclopyr in this formulation enters the leaf or spine by a trans-cuticular pathway rather than by infiltration into sub-stomatal cavities.

Acknowledgements

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References

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