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Pine oil increases spray retention by oats

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Abstract – The effects of the pine-oil-based monoterpene alcohols (Pine-oil), a nonylphenol surfactant and emulsified methylated rapeseed oil (Em-MRO) were evaluated on the dynamic surface tension of water, retention of sprays by oats, contact angle of water drops, and foliar uptake of [¹⁴C]2,4-D-dimethylamine into oats. Pine-oil and emulsified pine oil (Em-pine-oil) produced the quickest drop in dynamic surface tension and the highest levels of retention. Pine-oil and Em-pine-oil had a limited effect on the contact angle, whereas the surfactant greatly reduced the contact angle. Thus, the mode of action of monoterpene alcohols on retention proceeded in a different way than the surfactant. Em-MRO did not increase retention but did stimulate foliar uptake. Em-pine-oil at 0.5% (v/v) had little effect on foliar uptake. An emulsified mixture of the Pine-oil and methylated rapeseed oil (Em-pine-oil-MRO) increased both retention and uptake. In the field, the presence of Em-pine-oil in large droplet sprays should reduce atmospheric pollution and the drift of sprays applied under windy conditions.

herbicide / adjuvant / pine oil / retention / oats

Résumé – L'huile de pin augmente la rétention des bouillies de traitement par l'avoine. Les effets de l'huile de pin à base d'alcools monoterpéniques (Pine-oil), d'un tensioactif nonylphénol, et d'huile de colza méthylée (Em-MRO) sur la tension de surface dynamique de l'eau, la rétention de pulvérisations par l'avoine, l'angle de contact de gouttelettes d'eau, et la pénétration foliaire du [¹⁴C]2,4-D-diméthylamine dans l'avoine ont été évalués. Pine-oil et l'huile de pin émulsifiée (Em-pine-oil) produisent les chutes de tension de surface dynamique les plus rapides et les niveaux de rétention les plus élevés. Pine-oil et Em-pine-oil montrent un effet limité sur l'angle de contact alors que le surfactant l'augmentait grandement. En conséquence le mode d'action des alcools monoterpéniques sur la rétention est différent de celui du tensioactif. Em-MRO n'augmente pas la rétention mais stimule la pénétration foliaire. L'huile de pin apporté à 0,5 % (v/v) a peu d'effet sur la pénétration foliaire. Un mélange émulsifié d'huile de pin et d'huile de colza méthylée (Em-pine-oil-MRO) augmente la rétention et la pénétration foliaire. Au champ, la présence de Pine-oil dans des pulvérisations grossières devrait réduire la pollution atmosphérique et la dérive des pulvérisations appliquées en présence de vent.

herbicide / adjuvant / huile de pin / rétention / avoine

1. INTRODUCTION

Active pesticide ingredients applied with adjuvants are needed to protect crops from diseases, pests and weeds. Effective use requires knowledge of their modes of action and behaviours in the environment. This objective is still a priority since the mode of action of certain adjuvants is still unknown.

Adjuvants may be present in commercial formulations of pesticides. They can also be added just prior to treatment. Since they often improve the performances of active ingredients, adjuvants contribute to decreasing the rates of pesticides used in the environment. This general rule concerning adjuvants is of importance to mineral and vegetable oils, because

they increase the efficacy of numerous herbicides, especially specific graminicides [5, 7]. But the reduction in herbicide rates permitted by addition of oils without reducing control of weeds rarely goes beyond two or three times.

When emulsified pine oil (Em-pine-oil), based on monoterpenes from the tree *Pinus pinaster* Ait., was added in tank-mix to the graminicide clodinafop-propargyl and applied to *Alopecurus myosuroides* Huds., it increased the efficacy of clodinafop-propargyl by four to six times [2]. Moreover, emulsified mixtures of pine oil and methylated rapeseed oil (Em-pine-oil-MRO) increased the efficacy of clodinafop-propargyl by the same magnitude. It was difficult to explain and to improve these results because the mode of action of monoterpenes is not

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known. The aim of this study was to determine the specific effects of Pine-oil on the phases of herbicidal treatment, and to compare it with a surfactant and methylated rapeseed oil.

2. MATERIALS AND METHODS

2.1. Chemicals

Adjuvants, provided by the French company Action Pin, consisted of partly water-soluble monoterpene alcohols, water-insoluble monoterpene hydrocarbons, and water-insoluble methylated rapeseed oil. Monoterpenes were obtained by industrial distillation so each chemical studied was the major product of a mixture.

Firstly, monoterpene alcohols were dissolved to saturation in water. They included (1) pine oil (Pine-oil), a mixture of terpineol isomers (79.9%), other monoterpene alcohols (9.6%), monoterpene hydrocarbons (7.1%) and other (3.4%), and (2) Terpineol, a mixture of terpineol isomers (97.4%).

Secondly, monoterpene alcohols and water-insoluble chemicals were studied as emulsifiable concentrates coded with the prefix Em. Each concentrate contained the same emulsifier of undisclosed composition (Action Pin). Emulsifier and monoterpenes, or emulsifier and methylated rapeseed oil were mixed in the ratio 3–1 (w/w). Emulsifiable concentrates included (1) Em-pine-oil, (2) Em-terpineol, (3) Em- α -terpineol, a mixture of monoterpene alcohols enriched with α -terpineol (85.1%), (4) Em-*p*-mentane-ol, a mixture of *p*-menthane-ol isomers (99.1%), (5) Em-terpinolene, a mixture of monoterpene hydrocarbons enriched with terpinolene (96.3%), (6) Em-*p*-menthane, a mixture of monoterpene hydrocarbons enriched with *p*-menthane (93.8%), (7) Em-methylated rapeseed oil (Em-MRO) containing 55% oleic acids, and (8) Em-pine-oil-MRO, a mixture of pine oil and methylated rapeseed oil present in the ratio 60–40% (w/w), respectively.

For comparison, Agral 90[®] (Syngenta Agro), a nonyphenol 10 EO surfactant, was used as the additive standard reference. Each adjuvant was added at its recommended rate, namely 0.5% (v/v) for the emulsifiable concentrates, and 0.1% (v/v) for the surfactant.

Two commercial herbicide formulations were used in the retention experiments. They were chosen based on their different effects on retention, namely Roundup[®] (Monsanto), containing glyphosate (360 g L⁻¹), and Célio[®] (Syngenta Agro), which is clodinafop-propargyl plus cloquintocet-mexyl (100 + 25 g L⁻¹). The foliar penetration experiments were conducted with a model-product, U46D[®] (BASF Agro SAS) based on 2,4-D-dimethylamine (480 g L⁻¹) enriched with [¹⁴C]2,4-D-dimethylamine from CEA-France.

2.2. Plant

Germinated seeds of spring oats (*Avena sativa* L. cv. Sirene) were sown in plastic pots on vermiculite irrigated with a complete nutrient solution. They were grown at 11–18 °C (dark-light periods, 16 h photoperiod, 220 μ moles photon m⁻² s⁻¹ PAR). A few days before spraying, the plants were thinned to one per pot. The measurements of retention, droplet surface area, and foliar uptake were initiated at the two-leaf stage (12–13 days after sowing).

2.3. Dynamic surface tension

Data were recorded with a tensiometer Krüss BP 2, using the method of maximum drop pressure. The dynamic surface tension was determined as a function of the age of the newly-created liquid-air interface. This method was applied to the emulsions of chemicals and aqueous solutions containing monoterpene alcohols dissolved to saturation. The time-course of surface tension was established at room temperature.

2.4. Retention

The plants were sprayed using an indoor track-sprayer whose spraying parameters mimicked those used in the field. Unless otherwise indicated, spraying conditions involved flat-fan nozzles, Albus API 110°, VMD from 200 to 250 μ m (VMD = droplet diameter at the volume median, a parameter which characterises the spray droplet population), 200 kPa and 200 L ha⁻¹.

When the study was conducted at a constant volume of 150 L ha⁻¹ with the flat-fan nozzles TeeJet XR 80 03 (blue colour), the VMD was changed by adjusting the pressure to 300, 250, 200, 150 and 100 kPa which gave VMD values of 287, 300, 318, 345 and 391 μ m, respectively. Retention was evaluated by incorporating (0.01% w/v) Na-fluorescein in the spray. Following evaporation of the water retained by the plants, shoots were washed in 5 mM NaOH and the solution filtered. Filtrates were evaluated by spectrofluorimetry at 510 nm. The results were calculated from four plants per sample and three replicates, and expressed in μ L g⁻¹ DW (DW = dry weight).

2.5. Contact angle and drop area

The contact angle of droplets was determined according to a vertical view. Droplets (2 μ L) were set on paraffin and PTFE (teflon), two smooth hydrophobic surfaces, and were observed with a binocular magnifying glass equipped with camera and video-screen. The contact angle was calculated using the equation of Foy and Smith [4].

The initial (a few seconds after deposit) and final (after drying) drop areas were obtained with the same equipment, but using an aerial view. Drops (0.4 μ L) were set on the rough adaxial cuticle of the first leaf of the oats.

2.6. Foliar uptake

A foliar treatment involved the deposit of five droplets of 0.4 μ L on the adaxial outer one-third of the first leaf of the oats. The 0.4 μ L volume resulted from the addition of two droplets of 0.2 μ L: the first one contained 54.3 mM (acid equivalent) formulated 2,4-D-dimethylamine registered as U46D[®] (BASF Agro SAS), applied either alone in a mixture of acetone-water (1–1 v/v), or in water plus adjuvant. The second one contained [¹⁴C]2,4-D-dimethylamine (283 Bq on average).

Foliar uptake took place for 48 h at 11–18°. Then, the treated leaves were washed three times with 0.5 ml acetone-water (1–1 v/v). The radioactivity recovered by washing was quantified by liquid scintillation (Wallac 1409). Shoots and roots that contained the penetrated radioactivity were combusted (Oxidizer OX500, Zinsser Analytic). The resulting ¹⁴CO₂ was determined by liquid scintillation. Each treatment had three replications and the experiments were repeated in time.

Table I. Effects of monoterpenes, methylated rapeseed oil and their mixture on the dynamic surface tension of water. Results expressed as a function of the age of newly created liquid-air interface.

Adjuvant	Dynamic surface tension* (mN m ⁻¹)		
	10 ms*	100 ms	400 ms
Emulsifier (0.125% v/v)	70.0	63.7	58.1
Em-terpinolene (0.5% v/v)	68.0	60.9	56.3
Em- <i>p</i> -menthane (0.5% v/v)	70.2	63.9	57.4
Pine-oil*	43.3	41.0	40.3
Em-pine-oil (0.25% v/v)	46.4	44.9	43.5
Em-pine-oil (0.5% v/v)	43.4	41.0	39.8
Terpineol**	40.7	38.6	37.9
Em-terpineol (0.5% v/v)	41.1	39.0	38.1
Em- α -terpineol (0.5% v/v)	41.9	39.6	38.7
Em- <i>p</i> -menthane-ol (0.5% v/v)	40.5	37.8	36.9
Em-MRO (0.5% v/v)	69.7	60.3	55.6
Em-pine-oil-MRO (0.5% v/v)	47.0	44.2	42.3
Surfactant (0.1% v/v)	66.0	53.3	41.5
Ethanol-water (20–80 v/v)	42.1	41.1	41.0
Octanol*	44.3	38.9	35.0

* ms = millisecond. ** Dissolved to saturation in water. The surface tension of water is 72.8 mN m⁻¹.

3. RESULTS

3.1. Dynamic surface tension

The dynamic surface tension of the newly-created liquid-air interface was recorded from 10 to 400 ms, a period of time that included the fall time of most spray droplets in the field.

Emulsifier, added at 0.125% (v/v) which was the concentration in the 0.5% emulsifiable concentrates, produced about the same drop in dynamic surface tension as the monoterpene hydrocarbons Em-terpinolene and Em-*p*-menthane (Tab. I). By contrast, all the monoterpene alcohols (Pine-oil, Em-pine-oil, Terpeneol, Em-terpineol, Em- α -terpineol and Em-*p*-menthane-ol) gave dynamic surface tension drops about nine-fold higher than monoterpene hydrocarbons at 10 ms. There was not a clear difference between Pine-oil dissolved to saturation in water and Em-pine-oil (0.5% v/v), although the mass of monoterpene alcohols was about two-fold higher in Em-pine-oil than in Pine-oil. A similar observation applied to Terpeneol and Em-terpineol. The drop in dynamic surface tension between 10 and 400 ms in the presence of monoterpene alcohols was less than 5 mN m⁻¹. Hence, the reduction in surface tension by the alcohols mainly occurred within the first 10 ms.

Em-MRO containing methylated rapeseed oil reduced the dynamic surface tension in a similar way to the emulsifier (Tab. I). Em-pine-oil-MRO, which included monoterpene alcohols mixed with methylated rapeseed oil, decreased the dynamic surface tension by more than 25 mN m⁻¹ at 10 ms, close to Em-pine-oil (0.25% v/v).

Unlike the monoterpene alcohols, the decrease in dynamic surface tension obtained with surfactant was dependent on time (Tab. I). A mixture of ethanol-water (20–80 v/v) reduced

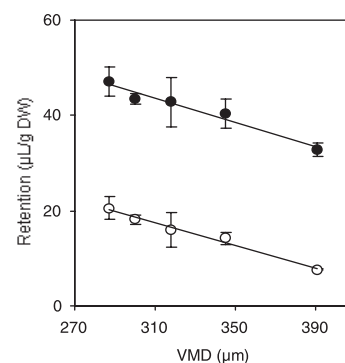


Figure 1. Retention of water enriched with Em-pine-oil (0.5% v/v) and surfactant (0.1% v/v) by oats as a function of VMD of sprays applied at a constant volume of 150 L ha⁻¹. Mean \pm SD (■ Em-pine-oil; ○ Surfactant).

the dynamic surface tension of water as quickly as the monoterpene alcohols. The effect of the monoterpene alcohols on dynamic surface tension could be mimicked with octanol dissolved to saturation in water (540 mg L⁻¹).

3.2. Retention by oats

The experiments were conducted with oats, a difficult-to-wet plant. When water was sprayed alone, retention ranged from 11.8 to 16.1 $\mu\text{L g}^{-1}$ DW (Tab. II). Emulsifier significantly increased retention relative to water alone (experiments C and E). The effects of Em-terpinolene, Em-*p*-menthane and Em-MRO were not different from emulsifier (experiment E). By contrast, all monoterpene alcohols (dissolved or emulsified) increased retention by an average of seven times than without additives. The effect of Em-pine-oil-MRO was significantly different from Em-MRO and intermediate between Em-MRO and Em-pine-oil (experiment B). The surfactant increased the retention compared with water alone and water plus emulsifier, but its effect on retention was always less than Em-pine-oil (experiment C). Other results indicated that the benefit of monoterpene alcohols on retention also occurred using Turbo TeeJet® nozzles, which produced a VMD of 558 μm (not shown).

The effects of Em-pine-oil and surfactant were also compared by applying sprays of different VMDs at a constant volume of 150 L ha⁻¹. When the VMD increased from 287 to 391 μm , retention decreased with both Em-pine-oil and surfactant (Fig. 1). However, the retention ratios (Em-pine-oil/surfactant at identical VMDs) ranged from 2.3 to 4.3 when the VMD increased from 287 to 391 μm . Moreover, the retention ratio (Em-pine-oil at 391 μm /surfactant at 287 μm) was 1.6. Again, similar results were found using Turbo TeeJet® nozzles (not shown).

The effects of monoterpene alcohols (Em-pine-oil and Em-pine-oil-MRO) were assessed with commercial herbicide formulations since the formulations alone increased the levels of retention by oats. Glyphosate and clodinafop-propargyl at two rates were applied alone or with adjuvant (Tab. III). The two formulations were retained differently by the oats, with the greatest retention by the glyphosate formulation. A rate effect

Table II. Effects of monoterpenes, methylated rapeseed oil and their mixture on retention of water by oats. Sprays were applied with flat fan nozzles Albus 110° under 200 kPa and at 200 L ha⁻¹. A, B, C, D and E corresponded to five independent experiments, the number of replications being indicated in brackets. Mean ± SD.

Adjuvant	Retention (μL g ⁻¹ DW)				
	A (6)	B (6)	C (4)	D (6)	E (4)
None	16.1 ± 2.1		13.3 ± 1.5		11.8 ± 3
Emulsifier			27.4 ± 1.3		23.4 ± 4
Em-terpinolene					26.6 ± 8
Em- <i>p</i> -menthane					23.0 ± 4
Pine-oil*				103.4 ± 6	
Em-pine-oil	116.5 ± 8.8	63.5 ± 12	99.2 ± 5.5	109.0 ± 9	97.7 ± 14
Em-terpineol					106.7 ± 21
Em- α -terpineol					100.6 ± 22
Em- <i>p</i> -menthane-ol					98.8 ± 18
Em-MRO	21.7 ± 1.4	14.7 ± 3			18.0 ± 4
Em-pine-oil-MRO		37.1 ± 6			
Surfactant			36.9 ± 1.3		
LSD (<i>P</i> = 0.05)	6.5	9.8	4.6	10	19

* Dissolved to saturation in water. Emulsifier, emulsified concentrates and surfactant applied at 0.125, 0.5 and 0.1% (v/v), respectively.

Table III. Effects of monoterpene alcohols and their mixture with methylated rapeseed oil on retention of glyphosate and clodinafop-propargyl by oats. Mean ± SD.

Adjuvant (0.5% v/v)	Retention (μL g ⁻¹ DW)			
	glyphosate (g a.i. ha ⁻¹)		clodinafop (g a.i. ha ⁻¹)	
	1080	4320	20	60
None	54 ± 2	73 ± 1	24 ± 4	24 ± 1
Em-pine-oil-MRO	107 ± 1	113 ± 8	78 ± 6	85 ± 12
Em-pine-oil	152 ± 9	139 ± 13	131 ± 18	138 ± 16
LSD (<i>P</i> = 0.05)	12.5		19.5	

was recorded with glyphosate applied alone. Nevertheless, the addition of Em-pine-oil and Em-pine-oil-MRO increased the retention with both herbicide formulations.

3.3. Contact angle and drop area

The effects of adjuvants on the contact angle were examined by placing 2 μL-drops of water either alone or plus adjuvant on paraffin and PTFE. The contact angle with pure water was 108 ± 3° on both hydrophobic surfaces (Tab. IV). Emulsifier reduced the contact angle of water to 78–82°. Pine-oil and Terpineol dissolved to saturation in water produced a contact angle ranging from 81 to 84°, as did emulsifier. The mixture ethanol-water (20–80 v/v) gave 87°. For the first time in this research, Em-MRO and Em-pine-oil showed effects of the same magnitude, especially on PTFE. It was clear that the smallest contact angle (36 ± 3°) was associated with the surfactant.

When the hydrophobic surface was the rough adaxial cuticle of oats, the effects of adjuvants were determined by evaluating the initial droplet area (a few seconds after deposit) and the final drop area (after drying) by an aerial view. The adjuvants sorted on the basis of the initial drop area followed the same order as the contact angle, namely: emulsifier < monoterpene alcohols dissolved to saturation < Em-pine-oil and Em-MRO < surfactant (Tab. V). However, the dry drops resulted

Table IV. Effects of monoterpene alcohols and methylated rapeseed oil on the contact angle of a 2 μL drop of water applied alone or in the presence of an adjuvant on two smooth hydrophobic surfaces (paraffin and PTFE). Mean ± SD.

Adjuvant	Contact angle (°)	
	Paraffin	PTFE**
None	108 ± 3	108 ± 2
Emulsifier (0.125% v/v)	78 ± 3	82 ± 2
Pine-oil*	84 ± 13	
Terpineol*		81 ± 3
Em-pine-oil (0.5% v/v)	61 ± 11	60 ± 9
Em-MRO (0.5% v/v)	51 ± 4	64 ± 4
Surfactant (0.1% v/v)	36 ± 3	
Ethanol-water (20–80 v/v)		87 ± 3

* Dissolved to saturation in water. ** PTFE = polytetrafluoroethylene (teflon).

Table V. Effects of monoterpenes, methylated rapeseed oil and their mixture on the initial and final areas of 0.4 μL droplet of water applied alone or with an adjuvant on the rough adaxial cuticle of the first leaf of oats. Mean ± SD.

Adjuvant	Droplet area (mm ²)	
	Initial**	Final**
None	-	-
Emulsifier (0.125% v/v)	0.68 ± 0.01	0.83 ± 0.01
Terpineol*	0.74 ± 0.03	0.84 ± 0.04
Em-pine-oil (0.5% v/v)	0.88 ± 0.05	0.88 ± 0.26
Em-MRO (0.5% v/v)	0.86 ± 0.11	2.26 ± 0.55
Em-pine-oil-MRO (0.5% v/v)	0.77 ± 0.07	3.05 ± 0.62
Surfactant (0.1% v/v)	1.47 ± 0.17	3.63 ± 0.40

* Dissolved to saturation in water. ** Initial area evaluated few seconds after deposit. Final area evaluated after drying.

Table VI. Effects of monoterpenes and methylated rapeseed oil on the uptake of [^{14}C] 2,4-D-dimethylamine to the adaxial surface of the first leaf of oats. Mean \pm SD.

Experiment	Adjuvant	% of applied radioactivity				Uptake**
		Wash	Combustion	Deficit*		
A	Acetone-water (1-1 v/v)	69.8 \pm 2.3	25.9 \pm 2.0	4.3 \pm 0.1	30.2 \pm 1.8 (a)	
	Emulsifier (0.125% v/v)	57.4 \pm 3.3	34.4 \pm 2.4	8.2 \pm 0.5	42.6 \pm 2.7 (b)	
	Em-pine-oil (0.5% v/v)	59 \pm 3.3	37.4 \pm 2.4	3.6 \pm 2.7	41.0 \pm 2.7 (b)	
	Em-MRO (0.5% v/v)	28.6 \pm 2.3	60.1 \pm 7.7	11.3 \pm 11.7	71.4 \pm 1.9 (c)	
	Em-pine-oil-MRO (0.5% v/v)	29.6 \pm 2.5	64.2 \pm 2.1	6.2 \pm 5.0	70.4 \pm 2.0 (c)	
B	Acetone-water (1-1 v/v)	73.9 \pm 0.7	24.5 \pm 0.6	1.6 \pm 0.2	26.1 \pm 0.5 (a)	
	Surfactant (0.1% v/v)	60.9 \pm 2.6	34.7 \pm 3.4	4.4 \pm 1.6	39.1 \pm 2.2 (b)	
	Em-pine-oil (0.5% v/v)	58.7 \pm 2.8	37.9 \pm 0.7	3.3 \pm 3.6	41.2 \pm 2.3 (b c)	
	Em- α -terpineol (0.5% v/v)	56.9 \pm 6.4	36.9 \pm 6.5	6.2 \pm 3.0	43.1 \pm 5.3 (b c)	
	Em-pine-oil-MRO (0.5% v/v)	48.9 \pm 10.6	49.0 \pm 8.9	2.1 \pm 3.8	51.1 \pm 8.7 (c)	

* Deficit = applied ^{14}C - (washed ^{14}C + combusted ^{14}C). ** Uptake % = combustion % + deficit %. Uptake means followed by the same letter did not differ significantly (LSD at $P = 0.05$).

in final drop areas which were different from the initial drop areas according to the adjuvants. Final drop areas with the emulsifier, Terpineol and Em-pine-oil were not very different from initial drop areas, but were increased 2.6 and 4.0 times in the presence of Em-MRO and Em-pine-oil-MRO, respectively. The drop area with the surfactant increased throughout evaporation to 3.6 mm². Hence, the evaporation of water induced an area difference between Em-pine-oil and Em-MRO. Moreover, Em-pine-oil-MRO showed the behaviour of Em-MRO.

3.4. Foliar uptake

When 2,4-D salt was applied to the oats cuticle in acetone-water (1-1 v/v), 26-30% of the active ingredient penetrated the foliar cuticle in 48 h (Tab. VI). The radioactivity detected in the wash and from combustion did not represent all of the administered radioactivity, so a deficit appeared. Foliar uptake was estimated by adding the combusted radioactivity and deficit (see discussion).

The emulsifier and Em-pine-oil significantly increased the foliar uptake of 2,4-D relative to acetone-water, but with no difference between them (Tab. VI, experiment A). Em-MRO and Em-pine-oil-MRO stimulated more than two-fold the uptake of 2,4-D relative to acetone-water. Surfactant (0.1%), Em-pine-oil (0.5%) and Em- α -terpineol (0.5%) exhibited beneficial effects, but with no difference between them (experiment B). By contrast, the effect of Em-pine-oil-MRO was significantly higher than surfactant.

The comparative effect of adjuvants, applied at various concentrations, was established on the basis of the uptake ratio

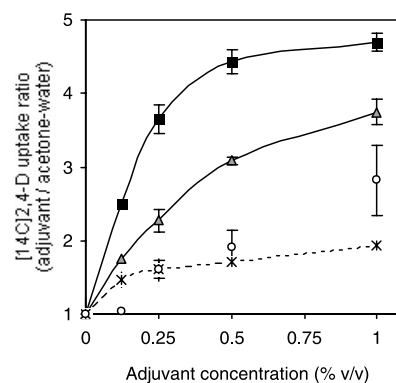


Figure 2. Uptake ratio of [^{14}C] 2,4-D-dimethylamine between water containing an adjuvant and the acetone-water reference. Penetration as a function of adjuvant concentration into the first leaf of oats for 48 h. Results from 4 independent experiments. Mean \pm SD (■ Em-MRO; Δ Em-pine-oil-MRO; \circ Em- α -terpineol; * emulsifier).

between water plus adjuvant and acetone-water, taken as a reference in each experiment (Fig. 2). Emulsifier present at 0.125% gave a 1.5 \pm 0.2 ratio which was significantly different from acetone-water. The ratio became 1.9 at 1%. The effect of Em- α -terpineol was dependent on its concentration, the uptake ratio ranging from 1.9 \pm 0.5 to 2.8 \pm 0.2 at 0.5% and 1%, respectively. The effect of Em-MRO increased with its concentration, more than four times at 0.5% and nearly five times at 1%. The uptake with Em-pine-oil-MRO gave a

response curve which was intermediate between Em-MRO and Em- α -terpineol.

4. DISCUSSION

4.1. Dynamic surface tension

Pine-oil and Em-pine-oil strongly reduced the dynamic surface tension of water in less than 10 ms while Em-terpinolene and Em-*p*-menthane reduced the dynamic surface tension less dramatically and in a similar way to the emulsifier supplied by Action Pin. Pine-oil and Em-pine-oil mainly contained cyclic saturated and unsaturated monoterpene alcohols (terpineol isomers and *p*-menthane-ol). We previously reported that their generally similar effects on surface tension depended very little on the degree of saturation of molecules or their cyclic or alkyl shape, but on the presence of the hydroxyl group [3]. The hydroxyl group is polar. It provides partial solubility in water. For example, the water solubility of α -terpineol ranges from 1360 to 1980 mg L⁻¹ according to the sources of information [8, 10]. Conversely, the monoterpene ring is a hydrophobe, so monoterpene alcohols would not be homogeneously distributed throughout the water phase but would preferably adsorb to the water-air interface. That could explain that (1) monoterpene alcohols exhibit surface activity and (2) ethanol, that is freely soluble in water, should be present in the mixture 20–80 (v/v) at a concentration about 100 times higher than monoterpene alcohols dissolved to saturation in water to reduce the dynamic surface tension of water with the same magnitude. The mimicking effect of octanol (little solubility in water) of monoterpene alcohols agrees with this hypothesis. However, unlike the volatile or toxic alkyl alcohols, such as ethanol and octanol, respectively, the biodegradable monoterpene alcohols have been classified as neither volatile nor toxic [3].

Pine-oil produced the same decrease in dynamic surface tension of water as Em-pine-oil (0.5% v/v), which had a concentration of monoterpene alcohols about two-fold higher (Tab. I). This response revealed that (1) about half of the monoterpene alcohols of Em-pine-oil were located in the micelles of emulsifier, (2) the measurement of surface tension did not relate to this micelled fraction, and (3) the effect of emulsifier was negligible relative to monoterpene alcohols.

The effect of Em-pine-oil-MRO (0.5% v/v) was similar to Em-pine-oil (0.25% v/v) and close to Em-pine-oil (0.5% v/v). It was not surprising since the drop in dynamic surface tension in relation to the concentration followed a logarithmic relationship and that 0.5% was near the horizontal asymptote (data not reported).

4.2. Retention

Oats plants retained very little water applied without adjuvants, being a difficult-to-wet plant (Tab. II). Pine-oil dissolved to saturation and Em-pine-oil (0.5% v/v) gave the highest ratios of retention relative to water (7.2 ± 1.3). Thus the solutions of Pine-oil probably contained enough dissolved monoterpene alcohols to meet the increase in the newly-created interface at spraying and droplet impact.

Beyond 300 μm , retention levels decreased in the presence of surfactant and Em-pine-oil (Fig. 1). However, the retention of coarse spray (VMD = 391 μm) in the presence of Em-pine-oil was 1.7 times higher than that of finer spray (VMD = 287 μm) with surfactant. Hence, monoterpene alcohols appeared to increase spray retention by difficult-to-wet plants, even when the VMD was about 400 μm . Concerning retention, the Em-pine-oil-MRO mixture was similar to the Em-pine-oil.

The benefits of monoterpene alcohols on spray retention by oats also occurred when using commercially-formulated active ingredients. The effect was more pronounced with clodinafop-propargyl than glyphosate, i.e. with the formulation that worked with the lowest rate of product per hectare.

4.3. Contact angle

Pine-oil and Terpineol reduced the contact angle of water by 24% on paraffin and 27% on PTFE. The surfactant reduced the contact angle three-fold more than the monoterpene alcohols. Thus the alcohols were more active than the nonylphenol surfactant for reducing the dynamic surface tension of water and retention, but they were less effective on the contact angle. Unlike a wetter that is known to reduce the contact angle by reducing the surface tension of the two interfaces (water-air and water-solid) of the deposited drop, the monoterpene alcohols greatly reduced the surface tension of the water-air interface only. Their enhancement of retention would mainly result from their speed in reducing this surface tension.

The ability of monoterpene alcohols to increase retention would be related to their small molecular weight (about 150) which is lower than Agral 90® (660 on average). Since the rate of diffusion to the droplet surface tends to be inversely related to molecular size [9], the diffusion coefficient of monoterpene alcohols in water is much higher than surfactant. This property allows a reduction in surface tension in 2–3 ms of relatively high VMD droplets that are flattened on impact, and a reduction in their bounce. Monoterpene alcohols would appear to be agents reducing bounce.

The behaviour of droplets containing adjuvants was not the same on smooth and rough surfaces. On a smooth surface (PTFE), the areas of droplets containing adjuvants spread very little or not at all during drying (not shown). By contrast, on a rough surface (cuticle of oats), an increase in spreading occurred following the evaporation of water with Em-MRO, Em-pine-oil-MRO and surfactant (Tab. V). Hence, Em-pine-oil and Em-MRO induced different spreading on oats, and Em-pine-oil-MRO exhibited the behaviour of Em-MRO.

4.4. Foliar uptake

The summation of radioactivity recovered during the experiments of foliar uptake revealed a deficit or ¹⁴C loss (Tab. VI). On the one hand, there was a proportional relationship between the magnitude of the deficit and the combusted radioactivity in seven independent experiments (not shown). On the other hand, numerous researchers have reported leakage of phenoxy herbicides from roots [1, 6]. Thus the deficit found in the experiments was interpreted as the result of a leakage, and

the combusted fraction and deficit were added to estimate uptake. On this basis, the two oils differently increased the foliar uptake of 2,4-D-dimethylamine, the effect of Em-pine-oil (0.5% v/v) being lower than Em-MRO (0.5% v/v). Em-pine-oil-MRO showed an intermediate effect between Em-MRO and Em-pine-oil (Fig. 2).

The word oil present in Pine-oil and rapeseed oil refers to two modes of action. Pine-oil, composed of monoterpene alcohols, increased retention of droplets probably by reducing their bounce, whereas rapeseed oil increased the spreading of drops and foliar uptake of 2,4-D-dimethylamine. A mixture of these two oils combined the two effects. Other results are still missing to explain how the merging of these effects allowed clodinafop-propargyl to always be more effective when mixed with Em-pine-oil-MRO than Em-MRO, and equal to or more effective than Em-pine-oil [2].

4.5. Practical application

Greater understanding of the mode of action of monoterpene alcohols suggests some practical application of the information. By producing a very quick drop in the dynamic surface tension of the air-water interface, the monoterpene alcohols increase retention of sprays by difficult-to-wet plants, even if the spray droplets are relatively large. Since the application of sprays with large droplets leads to fewer fine droplets, the presence of monoterpene alcohols added as tank-mix to sprays with large droplets should reduce (1) the atmospheric pollution and (2) the drift of sprays applied under windy conditions in the field.

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