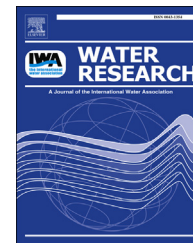


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# Photolysis of natural $\beta$ -triketonic herbicides in water

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## ABSTRACT

The fate of four natural  $\beta$ -triketones (leptospermone, isoleptospermone, grandiflorone and flavesone,  $pK_a = 4.0$ – $4.5$ ) in aqueous solution, in the dark and upon simulated solar light irradiation was investigated. In anionic form,  $\beta$ -triketones undergo slow dark oxidation and photolysis with polychromatic quantum yields varying from  $1.2 \times 10^{-4}$  to  $3.7 \times 10^{-4}$ . Leptospermone and grandiflorone are the most photolabile compounds. In molecular form,  $\beta$ -triketones are rather volatile. Polychromatic quantum yields between  $1.2 \times 10^{-3}$  and  $1.8 \times 10^{-3}$  could be measured for leptospermone and grandiflorone. They are 3–5 times higher than for the anionic forms. Photooxidation on the carbon atom bearing the acidic hydrogen atom is the main oxidation reaction, common to all the  $\beta$ -triketones whatever their ionization state. However, leptospermone shows a special photoreactivity. In molecular form, it mainly undergoes photoisomerization. Based on this work, the half-lives of  $\beta$ -triketones in surface waters should be comprised between 7 and 23 days.

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## 1. Introduction

One of the major challenges facing agriculture is to increase food production to feed the continually expanding world population while decreasing the environmental impact associated with pesticide crop treatments. Biopesticides are attractive alternative pest management tools because they often present lower toxicity and faster environmental degradation than their synthetic counterparts. Research in the field

of biocontrol has consequently intensified. An interesting case is the one of  $\beta$ -triketones herbicides. Commercial synthetic  $\beta$ -triketones derivatives, sulcotrione, mesotrione and tembotrione, were designed after the discovery of the herbicidal properties of leptospermone, the primary component of Manuka essential oils (see Table 1) (Dayan et al., 2011; Douglas et al., 2004; Hellyer, 1968; van Klink et al., 1999; Beaudegnies et al., 2009; Bick et al., 1965). All these compounds have  $\beta$ -triketones backbones that inhibit the *p*-hydroxyphenylpyruvate

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**Table 1 – Chemical structure of natural  $\beta$ -triketones (leptospermone, grandiflorone, isoleptospermone and flavesone) and commercial synthetic  $\beta$ -triketones<sup>a</sup> (sulcotrione, mesotrione and tembotrione). Asterisks denote the position of the acidic functionality.**

Structure	Name	Abbreviation	R <sub>1</sub>
	Leptospermone	L	
	Grandiflorone	G	
	Isoleptospermone	I	
	Flavesone	F	
	Sulcotrione	S	R <sub>2</sub> Cl
	Mesotrione	M	NO <sub>2</sub>
	Tembotrione	T	NO <sub>2</sub>
			R <sub>3</sub> H
			CH <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>

<sup>a</sup> The term “natural  $\beta$ -triketone” describing the compounds tested in this study (leptospermone, grandiflorone and flavesone) was first introduced to acknowledge that their biosynthesis followed a phloracetophenone-type cyclization to form a triketide phloroglucinol-like ring (Hellyer, 1968). But this is a misnomer because these natural products actually possess four keto groups. Later on, leptospermone served as a template from which the triketone herbicides (i.e., sulcotrione and mesotrione) were developed as inhibitors of *p*-hydroxyphenylpyruvate dioxygenase (Lee et al., 1997). We later demonstrated that leptospermone also inhibited the same enzyme and referred to it as a natural triketone herbicide in reference to the original literature from Hellyer and to the synthetic triketone herbicide class that was derived from it (Dayan et al., 2007).

dioxygenase (HPPD) enzyme by complexing with Fe<sup>2+</sup> within the catalytic domain (Dayan et al., 2007).

An important issue concerning pesticides regardless of their synthetic or natural origin, is their environmental fate. Phototransformation is a potential degradation pathway for compounds that absorb solar radiations, in particular its ultraviolet component. The photolysis of sulcotrione and mesotrione has already been studied in simulated solar light. In neutral water these reactions are very slow. Registration reports give half-lives of 100 d for sulcotrione (EPA, 2002) and 86–96 d for mesotrione (Onisko, 1988).

In the case of mesotrione, the main photoproducts is MNBA (4-(methylsulfonyl)-2-nitrobenzoic acid) produced by photohydrolysis, i.e. addition of OH on the CO in the  $\alpha$  position to the carbon atom bearing the acidic hydrogen and denoted by an asterisk in Table 1. Minor photoproducts also result from photohydrolysis and opening of the cyclohexanedione ring (Ter Halle and Richard, 2006). A number of unidentified oxidation photoproducts have also been observed in these studies. Interestingly, data shows that the triplet excited state of mesotrione is involved in the reaction. First, the rate of mesotrione photolysis is 3-fold faster in deoxygenated solution than in air-saturated medium. Second, mesotrione sensitizes the photooxidation of phenols (e.g., phenol, 2,4,6-trimethylphenol or coniferyl alcohol) while phenols inhibit the photolysis of mesotrione. These reactions are explained by an initial H-atom transfer from phenols to triplet mesotrione to yield radicals and then H-atom transfer from the reduced radical arising from mesotrione to oxygen

regenerating mesotrione. Third, irradiation of mesotrione generates singlet oxygen (Ter Halle and Richard, 2006).

The photolysis of sulcotrione in simulated solar light is pH-dependent and the rate increases upon medium acidification. In neutral medium, the main photoproduct is CMBA (2-chloro-4-(methylsulfonyl)-benzoic acid) produced by photohydrolysis. This reaction is similar to that yielding MNBA in the case of mesotrione. A chromone derivative is also detected. This compound that is formed subsequently to HCl elimination and cyclisation becomes the major photoproducts in very acidic medium (pH < 3) (Ter Halle et al., 2006). Photocyclisation was also observed in the case of tembotrione upon irradiation at 254 nm (Calvayrac et al., 2013).

In this study, we evaluated the photodegradation of natural  $\beta$ -triketones in water and identified the main photoproducts. As with their synthetic counterparts, natural  $\beta$ -triketones bear an acidic hydrogen and can exist in molecular or anionic forms depending on the pH. However, their photoreactivity may be different because the natural products studied do not contain an aromatic ring directly linked to the carbonyl and electron-withdrawing atom or groups (-NO<sub>2</sub>, -SO<sub>2</sub>Me, -Cl).

## 2. Experimental section

### 2.1. Chemicals

All chemicals were used as received. Methanol was purchased from Aldrich (Chromasolv, 99.9%) and acetonitrile from VWR

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