Characterization data and kinetic studies of novel lipophilic analogues from 2,4-dichlorophenoxyacetic acid and Propanil herbicides

Larissa M. Porciuncula, Alex R. Teixeira, Maria F.C. Santos, Marcelo G.M. D'Oca, Elisa S. Orth, Caroline R.M. D'Oca

Laboratório Kolbe de Síntese Orgânica, Escola de Química e Alimentos, Universidade Federal do Rio Grande, Av. Itália, Km 08, s/n, Rio Grande, RS, Brazil
Grupo de Catálise e Cinética, Universidade Federal do Paraná, Curitiba, PR, Brazil
Laboratório de Ressonância Magnética Nuclear, Departamento de Química, Universidade Federal do Paraná, Curitiba, PR, Brazil

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This work describes the data collection of new lipophilic esters and amides herbicides, analogues to 2,4-dichlorophenoxyacetic acid (2,4-D) and Propanil. The data include $^1$H and $^{13}$C NMR spectra and UV–VIS spectroscopic experiments, from the work “Novel lipophilic analogues from 2,4-D and Propanil herbicides: Biological activity and kinetic studies”. The UV–VIS and $^1$H NMR spectra were employed to kinetic degradation design, and could be used to access new herbicides derivatives with better environmental properties.

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Specifications Table

| Subject          | Organic chemistry |
|------------------|-------------------|
| Specific subject area | Organic synthesis; Physico-Chemistry. |
| Type of data     | NMR experiments were performed on a Bruker AVANCE 400 NMR spectrometer operating at 9.4T, observing $^1$H and $^{13}$C at 400.13 MHz and 100.50 MHz, respectively, equipped with a 5 mm direct detection probe (BOO) with gradient along the z-axis in CDCl$_3$ or DMSO-d$_6$ solution with TMS as the internal standard. For qNMR $^1$H experiments, pulse was calculated by pulsecal. The relaxation delay for use in the acquisition of the quantitative $^1$H NMR spectra was determined by T1 measurements with the aid of the pulse sequence inversion recovery, with same parameters as for $^1$H spectra changing the $\tau$ values from 0.01 to 15 s. $^1$H spectra were acquired by using a 30° pulse sequence (zg) with the following parameters: 30 s of relaxation delay (D1), 16 transients, a spectral width (SW) of 4789.27 Hz ($\sim$ 12.0 ppm), 64 K numbers of data (TD), and 6.84 s of acquisition time (AQ). The experiments were performed at 298 K. FIDs were Fourier transformed with line broadening (LB) = 0.3 Hz. The resulting spectra were manually phased and baseline corrected, and referenced to the TMS at δ 0.0 ppm. The kinetic studies were carried by UV–Vis spectroscopy (Agilent Cary). Infrared (IR) spectra were acquired on a Schimadzu IR PRESTIGE-21. |
| Data format      | Raw and analyzed data |
| Parameters for data collection | The kinetic UV–Vis spectroscopy (Agilent Cary) monitored the region of 190–800 nm under pseudo-first order conditions. An aliquot of 20 μL stock MeCN solution (0.01 mol.L$^{-1}$) was added to a quartz cuvette (10 mm optical path) containing 3 mL of the reaction medium: acid solution (HCl 0.1 mol.L$^{-1}$) or alkaline solution (NaOH 0.1 mol.L$^{-1}$). The reactions were monitored for at least five half-life times, by following the reactant consumption and product formation. The kinetic profiles were fitted with equations, using iterative least-squares software. |
| Description of data collection | The NMR spectroscopic data were collected from isolated product, from chromatographic column. Kinetic data (UV–VIS and $^1$H NMR) were collected from aliquots directly retired from reaction, under alkaline or acid conditions. |
| Data source location | Universidade Federal do Pará, Centro Politécnico, Curitiba, Paraná, Brazil. |
| Data accessibility | With the article |
| Related research article | L. M. Porciuncula, A. R. Teixeira, M. F. C Santos, M. G. M. D’Oca, L. S. Santos, F. Nachtgall, E. S. Orth, C. R. M. D’Oca, Novel lipophilic analogues from 2,4-D and Propanil herbicides: Biological activity and kinetic studies, Chem. Phys. Lipids. DOI: 10.1016/j.chemphyslip.2020.104947 |

Value of the Data

• These data are useful or important because describe the spectroscopic data of the lipophilic amides and esters analogs from classical organochlorides herbicides. In addition, the data showed the kinetic parameters obtained in acid and alkaline hydrolysis after the incorporation of fatty long-chains in herbicides.

• This dataset could be useful for other research groups interesting in the characterization of new derivatives of organochlorides herbicides and can benefit kinetic parameter studies relational to organochlorides herbicides degradation in the environmental.

• This dataset can be used for application and in the development of experiments in agricultural practices with environmental-friendly agrochemicals. Annually, around 2.5 million tons of agrochemicals are used worldwide and this causes an impact on the environment such as water suppliers and soil.

1. Data Description

The dataset referring to lipophilic analogues from herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and Propanil that were obtained from fatty common alkyl chains. The synthesis of new lipophilic esters 6a-c was realized from esterification reaction of herbicide 2,4-D with palmitic (C16:0), stearic (C18:0) and oleic (C18:1) fatty alcohols. The experiments were performed according to previous work using sulfamic acid ($H_2NSO_3H$) catalyst [1]. After synthesis of the fatty esters
esters, the synthesis of lipophilic amides 8a-c from 2,4-D was investigated from different methodologies. The synthesis of new fatty amines 11a-c was derived from 3,4-dichloroaniline, common core present in Propanil, Linuron and Diuron agrochemicals. The lipophilic esters and amides synthesized from 2,4-D and 3,4-dichloroaniline were characterized by $^1$H and $^{13}$C NMR, infrared spectroscopy. Afterwards, the lipophilic herbicides 6a-c, 8a-c and 11a-c were submitted to studies of kinetic behavior in aqueous medium, under basic and acid conditions. The degradation’s profile was studied by kinetic UV–vis and $^1$H NMR experiments.

1.1. Characterization data by NMR experiments

The characterization dates of lipophilic herbicides 6a-c, 8a-c and 11a-c are showed in the Figs. 1–20, Figs. 21–30.

1.2. Kinetic studies by $^1$H NMR and UV–vis

The lipophilic herbicides and 2,4-D were submitted to studies of kinetic behavior to determine the degradation’s profile in aqueous medium, under basic and acid conditions. The degradation’s profile studied by kinetic $^1$H NMR and UV–vis are showed in Figs. 31–38.

2. Experimental design, materials and methods

2.1. NMR characterization experiments

The NMR characterization experiments of lipophilic herbicides 6a-c, 8a-c and 11a-c were performed in NMR 5 mm tube on a Bruker AVANCE 400 NMR spectrometer operating at 9.4T,
Fig. 2. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 6a.

Fig. 3. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound 6b.
Fig. 4. $\text{^{13}C NMR (CDCl}_3$, 100 MHz) spectrum of compound 6b.

Fig. 5. $\text{^1H NMR (CDCl}_3$, 400 MHz) spectrum of compound 6c.
Fig. 6. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 6c.

Fig. 7. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound 6d.
Fig. 8. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 6d.

Fig. 9. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound 8a.
Fig. 10. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 8a.

Fig. 11. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound 8b.
Fig. 12. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 8b.

Fig. 13. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound 8c.
Fig. 14. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 8c.

Fig. 15. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound 11a.
Fig. 16. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 11a.

Fig. 17. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound 11b.
Fig. 18. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 11b.

Fig. 19. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound 11c.
Fig. 20. $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of compound 11c.

Fig. 21. IR (cm$^{-1}$, KBr) spectrum of compound 6a.
Fig. 22. IR (cm$^{-1}$, KBr) spectrum of compound 6b.

Fig. 23. IR (cm$^{-1}$, KBr) spectrum of compound 6c.
Fig. 24. IR (cm$^{-1}$, KBr) spectrum of compound 6d

Fig. 25. IR (cm$^{-1}$, KBr) spectrum of compound 8a.
Fig. 26. IR (cm$^{-1}$, KBr) spectrum of compound 8b.

Fig. 27. IR (cm$^{-1}$, KBr) spectrum of compound 8c.
Fig. 28. IR (cm$^{-1}$, KBr) spectrum of compound 11a.

Fig. 29. IR (cm$^{-1}$, KBr) spectrum of compound 11b.
Fig. 30. IR (cm\(^{-1}\), KBr) spectrum of compound 11c.

Fig. 31. Comparison between NMR \(^1\)H (400 MHz, D\(_2\)O) spectra from acid hydrolysis of fatty derivatives ester 6c (right) and amide 8c (left); Conditions: [6c] = 6.67 × 10\(^{-5}\) mol L\(^{-1}\); [8c] = 6.67 × 10\(^{-5}\) mol L\(^{-1}\); [HCl]=0.1 mol L\(^{-1}\); 60 °C.
Fig. 32. Spectra 2,4-D in neutral, acid and basic medium, showing the characteristic band of 2,4-D between 280 and 300 nm.

Fig. 33. Typical consecutive spectra for the acid (A) and basic hydrolysis (C) of 2,4-D, and corresponding kinetic profile at 300 nm for the acid hydrolysis (B); The basic hydrolysis was too slow to be followed. Solid line corresponds to the fits according to a pseudo-first order equation.\(^3\) Conditions: [2,4-D]= 6.67 x 10\(^{-5}\) mol L\(^{-1}\); [HCl]=0.1 mol L\(^{-1}\); 60°C.

observing \(^1\)H and \(^{13}\)C at 400.13 MHz and 100.50 MHz, respectively, equipped with a 5 mm direct detection probe (BBO) with gradient along the z-axis in CDCl\(_3\) or DMSO-d6 solution with TMS as the internal standard. Figs. 21–30.
Fig. 34. Typical consecutive spectra for the basic hydrolysis of 6c (A); Kinetic profile at 230 nm for the basic hydrolysis of 6c (B); Solid line corresponds to the fits according to a pseudo-first order equation; Condition: 60 °C, [6c] = 6.67 × 10^{-5} mol L^{-1}; [NaOH] = 0.1 mol L^{-1}.

Fig. 35. Typical consecutive spectra for the acid hydrolysis of 6c (A); Kinetic profile at 230 nm for the acid hydrolysis of 6c (B); Solid line corresponds to the fits according to Eq. (1); Condition: 60 °C, [6c] = 6.67 × 10^{-5} mol L^{-1}; [HCl] = 0.1 mol L^{-1}.

Fig. 36. Typical consecutive spectra for the basic hydrolysis of 8c (A); Kinetic profile at 230 nm for the basic hydrolysis of 8c (B); Solid line corresponds to the fits according to a pseudo-first order equation; Condition: 60 °C, [8c] = 6.67 × 10^{-5} mol L^{-1}; [NaOH] = 0.1 mol L^{-1}.

2.2. Kinetic studies by UV–Vis

The kinetic studies were carried by UV–Vis spectroscopy (Agilent Cary) monitoring in the region of 190–800 nm under pseudo-first order conditions [2]. An aliquot of 20 mL stock solution of the target compounds (6c, 8c and 11c; 0.01 mol.L^{-1} in acetonitrile) was added to a quartz cuvette (10 mm optical path) containing 3 mL of the reaction medium: acid solution (HCl 0.1 mol.L^{-1} – acid hydrolysis) or basic solution (NaOH 0.1 mol.L^{-1} – alkaline hydrolysis). The
Fig. 37. Typical consecutive spectra for the acid hydrolysis of 8c (A); Kinetic profile at 230 nm for the acid hydrolysis of 8c (B); Solid line corresponds to the fits according to Eq. (1). Condition: 60 °C, [8c] = 6.67 × 10⁻⁵ mol L⁻¹; [HCl] = 0.1 mol L⁻¹.

Fig. 38. Typical consecutive spectra for the acid (A) and basic hydrolysis (C) of 11c, and corresponding kinetic profile at 300 nm for the acid hydrolysis (B) and at 230 nm for the basic hydrolysis (D); Solid line corresponds to the fits according to a pseudo-first order equation. Conditions: [11c] = 6.67 × 10⁻⁵ mol L⁻¹; [HCl] = 0.1 mol L⁻¹; 60 °C.

reactions were monitored for at least five half-life times, by following the reactant consumption and product formation. The kinetic profiles (absorbance vs time) were fitted with equations, using iterative least-squares software.

2.3. Kinetic studies by RMN

The experiments were performed in NMR 5 mm tube using aliquot of 20 mL stock solution of the target compounds (6c, 8c and 11c; 0.01 mol L⁻¹ in acetonitrile) containing 3 mL of
the reaction medium: acid solution (HCl 0.1 mol.L\(^{-1}\) – acid hydrolysis) or basic solution (NaOH 0.1 mol.L\(^{-1}\) – alkaline hydrolysis).

For qNMR \(^1\)H experiments, pulse was calculated by pulsecal. The relaxation delay for use in the acquisition of the quantitative \(^1\)H NMR spectra was determined by T1 measurements with the aid of the pulse sequence inversion recovery, with same parameters as for \(^1\)H spectra changing the \(\tau\) values from 0.01 to 15 s. \(^1\)H spectra were acquired by using a 30\(^\circ\) pulse sequence (\(zg\)) with the following parameters: 30 s of relaxation delay (D1), 16 transients, a spectral width (SW) of 4789.27 Hz (\(\sim 12.0\) ppm), 64K numbers of data (TD), and 6.84 s of acquisition time (AQ). The experiments were performed at 298 K. FIDs were Fourier transformed with line broadening (LB) = 0.3 Hz. The resulting spectra were manually phased and baseline corrected, and referenced to the TMS at \(\delta\) 0.0 ppm.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.dib.2020.106202.

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