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Editorial

From San Luis, A Few Words of Gratitude†

ABSTRACT

The Photochemical Research Group from San Luis (Argentina) highlights the contributions of Dr. Norman Andino García to the development of the group as a way to show him our gratitude for all his support.

INTRODUCTION

We are very grateful for the opportunity granted by the *Photochemistry and Photobiology* journal to contribute to the Symposium in honor of Dr. Norman Andino García on the occasion of his retirement from the National University of Río Cuarto in Argentina.

In the name of the members of the Photochemical Research Group from San Luis, we will present our experience working together with Dr. Norman García or "Andi," as all of us call him. This is a way of thanking him for all the support, work, guidance and encouragement provided to our research group since the beginning.

ACADEMIC CONTRIBUTIONS TO SAN LUIS NATIONAL UNIVERSITY

Andi has participated, and continues doing so, in various academic activities at the Faculty of Chemistry, Biochemistry and Pharmacy of San Luis National University, including examining doctoral theses or participating in the evaluating committee of candidates for new teaching positions. On every occasion, Andi has shown his usual commitment.

On this occasion, however, we wish to highlight Andi's superlative contribution to the training of researchers in the field of photochemistry at San Luis National University. This was a vacancy research area in our University, and it was Andi's enthusiastic support, his knowledge and his generosity that enabled us to grow as a research group. This is the story we want to share with you.

THE BEGINNINGS IN SAN LUIS

The IX Argentine Congress of Physical Chemistry was held in San Luis in 1994. On this occasion, professors Debattista and Pappano presented a poster on the antimicrobial action of flavonoids obtained from honey of San Luis (1). This work gave rise to the first contact with Andi through Dr. Vicente Ávila, also a professor at the Río Cuarto National University. The structure of the polyphenolic substances suggested that they could interact with reactive oxygen species. But it was necessary to carry out further experiments and research. The purified natural flavonoids and some other synthetic ones were taken to the laboratories of the Department of Chemistry at Río Cuarto National University where experimental measurements were carried out. The results of the study of the capacity of some simple flavonoids as generators and inhibitors of singlet molecular oxygen were reported in the X Argentine Congress of Physical Chemistry held in Tucuman in 1997 (2).

During that year, Paulina Montaña, who was still a Chemistry undergraduate student, started doing research in the Physical Chemistry Area of the Chemistry, Biochemistry and Pharmacy Faculty at San Luis National University. At that time, only a few professors worked in that Area, all of them were over 40 years old and most of them were mainly involved in teaching and research activity was very scarce. This situation had led to an asymmetry in this Area compared to other groups in the faculty: While the professors from other Areas could develop a research career and had the chance to train novel researchers, the Physical Chemistry Area was in disadvantage. This situation constituted an important challenge: If we wanted to grow up and gain research expertise, it was necessary to study, learn, pursue our doctoral projects and open up new research lines; in sum, we had to work and strive.

In this context, Andi was asked to collaborate in the training of young researchers and he accepted without hesitation. Hence, Paulina, the youngest researcher in the area, traveled to Río Cuarto to meet Andi on 1 October 1999. In spite of the torrential rain, Andi went to meet Paulina at the bus station when she arrived in Río Cuarto. He took her to the Río Cuarto National University campus to visit the laboratories and enthusiastically explained his research work to her. It was on this occasion that Paulina heard for the first time terms such as quenching, sensitizer and singlet oxygen. All of this was new to her, as she had never had contact with these concepts during the course of her undergraduate studies. Despite this weakness, or even more, being aware of this, Andi encouraged her to improve her knowledge and taught her to perform experiments of photolysis, oxygen uptake, time-resolved singlet oxygen phosphorescence detection and laser flash photolysis, among others. He not only played an important role in teaching her the phenomena involving excited states but also encouraged her to participate in the discussion of the results.

Regarding the results, there is a particular point we want to highlight: Because of our inexperience, or perhaps because of our aspiration for substrates to be quenchers of reactive oxygen species of riboflavin in the singlet or triplet state, we expected certain experimental values. But, as we know, what you get is not always what you expect. And it was then that Andi used to say: "results are neither good nor bad, they are only results," which impelled us to do the effort to explain the obtained results (Fig. 1).

†This article is part of a special issue dedicated to Dr. Norman "Andi" García.

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CONTRIBUTIONS TO TRAINING OF HUMAN RESOURCES

Between 1999 and 2003, Andi collaborated in the doctoral training of Paulina Montaña, which consisted of a research on the chemical properties and biological activities of flavonoids. The visible-light irradiation of methanolic solutions containing riboflavin and different flavonoids, under aerobic conditions, produces a complex picture of competitive interactions, which includes mainly the quenching of ^{1}Rf* and ^{3}Rf* excited states, the generation of superoxide radical anion and singlet molecular oxygen, among other reactive oxygen species. The mechanisms that operate are not the same in all cases, but for the most part, flavonoids behave as sacrificial scavengers of reactive oxygen species (3–5).

Andi was also Paulina's advisor in her postdoctoral research work between 2005 and 2007 and in the beginning of her research career (2008–2012) at the National Council of Scientific and Technical Investigations (CONICET). Several investigations were performed in this period, including the generation and quenching of reactive oxygen species by substrates of high biological interest.

The photostability of the neurotransmitter serotonin in the presence of riboflavin upon visible-light irradiation in aqueous medium was investigated to know whether this compound or structurally related ones may act as generators or deactivators of reactive oxygen species. The obtained results showed that the energy transfer from triplet excited state of riboflavin to dissolved oxygen generates singlet molecular oxygen, degrading serotonin via the mentioned species and other nonoxygenated radical-mediated processes (6).

Studies were also carried out of aqueous solutions of the purine bases uric acid, xanthine and hypoxanthine upon visible light in the presence of riboflavin. The observed photodegradation was determined to be caused by singlet molecular oxygen and superoxide radical anion. This species is generated by electron transfer from each purine base to triplet excited riboflavin to produce the radical anion of riboflavin that, after another electron transfer step to ground state oxygen, yields superoxide radical anion and riboflavin. Results indicated that uric acid is the most efficient antioxidant, showing the highest overall rate constant for the singlet molecular oxygen quenching with a very low reactive contribution for the overall process (7).

In view of the possible precursory photoreactions in the generation of humic substances, *Pajares* and coworkers investigated the visible light promoted interaction between riboflavin and gallic acid, a polyphenol naturally formed after lignin degradation. The studies confirmed that singlet molecular oxygen, superoxide radical anion and hydrogen peroxide cause the relatively fast photodegradation of gallic acid in pH 7 aqueous-aerobic medium. These species could contribute to the initiation of polymerization reactions on the polyphenol promoting the generation of humic products in natural waters (8).

More recently, Andi took up the supervision of Gabriela Ferrari′s doctoral work (2007–2012), which focused on the photostability of flavonoid metal complexes and the scavenging ability of free and complexed flavonoids. Flavonoids exhibit biological properties which can be enhanced when complexation occurs. Both the stoichiometry and stability constant of the complexes formed in methanolic solution were determined (9,10). The photophysical properties of complexes and free flavonoids were investigated. The ligands photogenerate singlet molecular oxygen by energy transfer from its excited triplet state to dissolved ground state oxygen. The excited triplet state of the flavonoid is quenched by the metallic ion with a rate constant close to the diffusion-controlled value. The results showed that metallic ion chelation greatly enhances the ability of the flavonoid as an overall singlet molecular oxygen quencher (10).

Andi also trained Gabriela Ferrari during her postdoctoral scholarship (2012–2014), until she became a junior researcher (2015–2018) at CONICET. New investigations were carried out in those years, mainly focused on the scavenging ability of nonsteroidal anti-inflammatory drugs. In this period, two research lines were pursued. Three drugs of the oxicams family were studied in the frame of two specific conditions: (1) their reactive oxygen species scavenging ability, and (2) their

Figure 1. Front of San Luis National University building.

photodegradability under environmental conditions, because oxicams are nowadays considered emerging pollutants. Singlet molecular oxygen and superoxide radical anion were photogenerated through riboflavin photosensitization in aqueous and aqueous-methanolic solutions in the presence of oxicams concentrations in the range 50–500 μM. Under these conditions, the studied substrates quench singlet molecular oxygen showing a significant photodegradation efficiency given by a dominant reactive fashion for deactivation of the oxidative species. However, this is not a desirable property in the context of photoprotection upon prolonged photoirradiation, maybe a way of degradation of nonsteroidal anti-inflammatory drugs in wastewaters (11).

Within the pollution-related research line, a study of a removable chitosan-derivatized polymeric sensitizer was carried out. The sensitizer system, soluble in the aqueous acidic medium, was employed in the singlet oxygen-mediated photodegradation of hydroxybenzenes, model molecules of water contaminants. The polymer quenches the oxidative species, the process being mostly attributable to a physical interaction and promotes the photoprotection of the same sensitizer. The polymeric sensitizer, totally insoluble in neutral medium, can be removed from the solution after the photodegradative cycle by precipitation through a simple pH change (12).

Andi has also worked in the doctoral training of Vanesa Muñoz since 2012, studying, both experimentally and theoretically, the stability of flavonoid metal complexes, and the scavenging ability toward photogenerated reactive oxygen species of free and complexed flavonoids. Visible-light irradiation of aqueous-ethanolic solutions of riboflavin in the individual presence of chrysin and its complex with Cu(II) generates singlet molecular oxygen, which interacts with both systems. Metal chelation greatly enhances the scavenging ability of the free ligand toward singlet molecular oxygen through a predominantly physical mechanism. In this way, practically all singlet molecular oxygen is deactivated by the complex without significant loss of the quencher while chrysin quenches singlet molecular oxygen in a prevailing reactive fashion (13).

Last but not least, Andi has been supervising Frida Dimarco's doctoral research since 2015, which focuses on the interaction of essential oils with photogenerated singlet molecular oxygen. Essential oils are a mixture of volatile compounds, products of the secondary metabolism of plants. Once these oils are extracted, they can be degraded losing their organoleptic and therapeutic properties due to various environmental factors. Exposure to light upon aerobic conditions is the main cause of this decomposition. These degradations can be caused by reactive oxygen species photogenerated from endogenous sensitizers. The Rf-sensitized photodegradation of the essential oil of oregano, thymol and carvacrol was studied. The mechanism involves singlet molecular oxygen mainly through a physical process (14).

During this time, and thanks to Andi's support and guidance, we set up a basic photochemical laboratory in the Physical Chemistry Area at National University of San Luis. Andi's

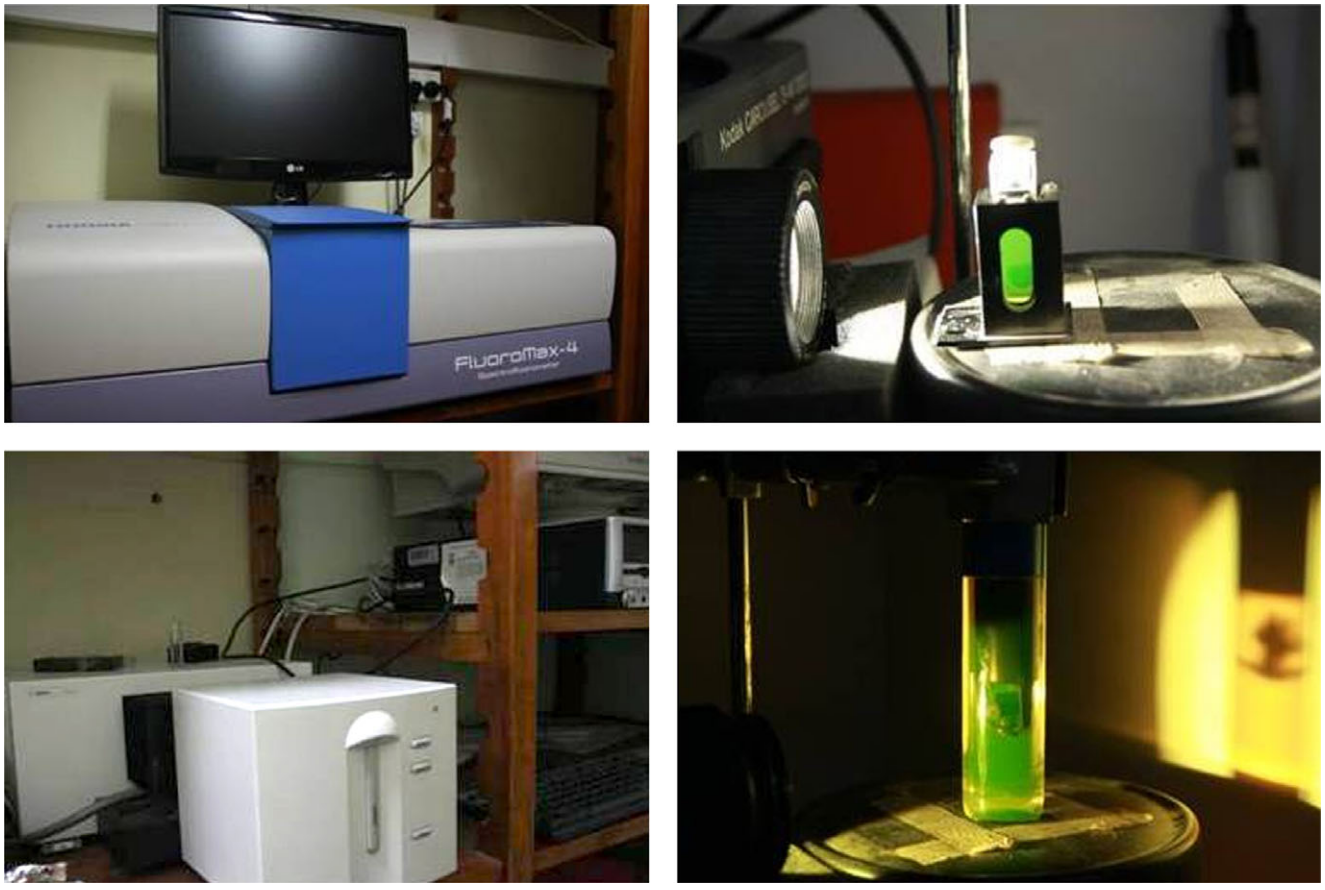

Figure 2. Photochemical Laboratory in Physical Chemistry Area of the Chemistry, Biochemistry and Pharmacy Faculty at San Luis National University.

Figure 3. Photochemical Research Group: from left to right: M. Paulina Montaña; Norman García; Vanesa Muñoz; Frida Dimarco; and Gabriela Ferrari.

dedication and effort are qualities that transcend his life as a researcher. Every time we traveled to Río Cuarto to do experimental measurements, Andi invited us to share dinner with his kind wife Marta. Andi was aware that we had to resign spending time with our family in order to study and grow in the academic field, and these friendly moments were truly helpful.

In all these years of working together, we also experienced Andi's generosity. We always received financial support for conference registration fees and travel expenses for carrying out experimental measurements, for work meetings and for purchasing materials or repair laboratory equipment.

Andi not only gave us his knowledge and financial support, but also shared his family time with us and opened his house, where we met many times to analyze results, or to write applications for scholarships or research funding. This also allowed us, besides the strictly academic discussions, to enjoy Marta's delicious cooking.

Thanks to Andi's generous support and advice as an external collaborator of our research project in San Luis National University, we have also been able to pursue the training of new researchers in our group (Fig. 2).

CONCLUDING REMARKS

In addition to the long list of Andi's academic qualities, we especially want to emphasize some of its many human qualities, those that have strengthened and maintained our bond over time. Andi always showed his commitment, responsibility, ability to work, integrity, cordiality, dedication, honesty and generosity. He stimulated good professional practice through his own example, perhaps without even intending to do so, but as a natural result of his attitude to work.

It is a pleasure and an honor for us to participate in this acknowledgment of Andi's work, by highlighting not only his academic excellence but also his human values, which constitute a way to show the scientific community in general, and young researchers in particular, that both academic and human virtues are worth highlighting and promoting among researchers. People like Andi print their indelible mark on those who meet them. All the members of the Photochemical Research Group from San Luis wholeheartedly appreciate everything Andi has done for us, and we will forever be grateful. We wish Andi all the best for the years to come together with his wife, children and grandchildren (Fig. 3).

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