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6. Solar Chemicals from and for Tropical Australia

Follow-up article to Regional Focus–Australia & New Zealand

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Introduction

At its beginning in the 19th century, synthetic organic photochemistry was a purely solar research area and photochemical reactions were performed 'outdoors' on the roofs of chemical institutes.[i] Despite the often simplified protocols and setups, the potential of solar photochemistry was recognized over 100 years ago by Giacomo Ciamician, the father of modern photochemistry. In his visionary lecture entitled *"The Photochemistry of the Future"* he envisaged the replacement of harmful, at that time coal-based, chemical processes with clean, solar-driven alternatives.[ii] A century has passed and his vision remains largely unfulfilled. Recently, solar photochemistry has seen a remarkable revival within the area of Green Chemistry.[iii] Modern solar reactors furthermore allow a concentration of sunlight, which in return yields to faster reaction rates and subsequently higher space-time-yields.[iv] Cost estimation studies for selected photochemical processes have furthermore shown that solar operations can compete economically with lamp-driven processes.[v] Compared to these traditional 'indoor' processes, solar illuminations often proceed more cleanly with fewer side products, thus reducing the need for exhaustive purification and separation steps.

Figure 1: Solar reactors at James Cook University. The red color of the photosensitizer rose Bengal can be clearly seen.

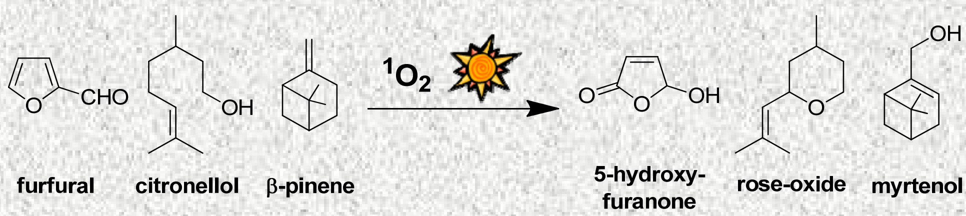
At James Cook University (JCU) in Townsville, Australia, the *Applied and Green Photochemistry Group* utilizes both of tropical North Queensland's abundant natural resources: sunlight and biomass.[vi] Townsville receives over 300 days of direct sunshine per year, which makes it an optimal location for solar research. Likewise, the local sugar and essential oil industry offers a broad portfolio of renewable materials. The *Solar Chemicals from and for the Tropics* activities of the group subsequently focus on the production of commercially important commodity chemicals from these materials.

Solar Reactors

The research group at JCU is equipped with a number of non-concentrating solar reactors (**Figure 1**). Their differing capacities allow for a rapid transfer from demonstration to pilot-scales. The traditional 'flask in the sun' approach of Ciamician is still followed for solar exposures on laboratory-scales. Scale-up is realized in custom-made 1 m^2 flatbed reactors (<8 L scale) or in a commercially available 2 m^2 Compound Parabolic Collector (CPC; <50 L scale). Both reactor models operate in circulation mode and can harvest direct as well as diffuse sunlight. Using these advanced solar reactors, the *Applied and Green Photochemistry Group* has already conducted several kilogram-scale syntheses of valuable commodity chemicals within 1-3 days of illumination. Located in costal North Queensland, the group is furthermore investigating applications of 'solar floats'.[vii] Developed by Prof. Liu at the University of Hawaii, these devices use natural water-reservoirs as heat-sinks, which make them interesting for environmental applications.

Solar Reactions

Photooxygenations are especially suitable model reactions for solar photochemistry. These industrially relevant transformations utilize catalytic amounts of an organic dye, commonly rose bengal, and air for the construction of oxygenated products.[viii] The targeted commodity chemicals examined within the *Solar Chemicals from and for the Tropics* initiative are of particular interest for the Australian economy and allow for value-adding to existing processes and products (**Scheme 1**).



Scheme 1: Solar photooxygenations investigated.

The local sugar industry, for example, offers an easy access to bioethanol and furfural, a sugarcane bagasse-derived compound.[ix] The solar photooxygenation of furfural into the important C5-building block hydroxyfuranone has been realized successfully at JCU on kg-scales.[x] At elevated temperatures, this compound is readily converted *in situ* into its corresponding alkoxy-derivatives, which are useful fragrances. The introduction of solar thermal conditions into the solar photochemical key-process thus opens innovative new markets on demand. Similarly, the Australian essential oils industry is interested in value adding and diversification of its product portfolio. The solar conversion of essential oils into valuable fragrances thus offers a range of new and 'green' products. Two representative processes are currently examined. The conversion of citronellol into the important fragrance rose oxide is performed industrially (<100 t/a) using artificial light.[xi] At JCU, the three-step procedure incorporating a solar-driven photooxygenation step was realized successfully on large-scale. The transformation of β-pinene to the low volume (<10 t/a) fragrance myrtenol is likewise examined but requires prolonged exposure times.[xii]

Conclusion

Tropical North Queensland offers favourable climatic conditions and versatile biomass resources for solar photochemical studies. Dye-sensitized photooxygenations in particular use renewable materials from the local agriculture and forestry industry and convert these sustainable starting materials into high-value chemicals of economic importance to the region. Solar photochemistry can thus contribute substantially to a *Green Chemical Industry*.

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