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Photochemistry Down Under – Solar Chemicals from and for the Tropics

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Introduction – Organic photochemistry started 'outdoors' on the roofs of chemical institutes as a solar discipline in the 19th century.[1] The potential of solar photochemistry was described over 100 years ago by a pioneer in organic photochemistry, Giacomo Ciamician.[2] In his visionary lecture *"The Photochemistry of the Future"* he imagined the replacement of hazardous, at that time coal-based, processes with clean, solar-driven alternatives.[3] A century has passed and his vision remains largely unfulfilled. Recently, the call for sustainable and climate-smart technologies has led to a revival of the sun as an energy and light source.[4] Modern solar concentrators were furthermore developed to accelerate reactions and increase space-time-yields.[5] Likewise, cost estimation studies have demonstrated that solar production can indeed operate economically.[6]

The *Applied and Green Photochemistry Group* at James Cook University (JCU) in Townsville, Australia, has been at the forefront of solar photochemical research and has realized solar transformations from laboratory through to production scales.[7] Located in tropical North Queensland, Townsville experiences over 300 days of sunshine per year, which makes it a favorable location for solar research. The current *Solar Chemicals from and for the Tropics* initiative of the group builds on both of tropical Australia's abundant natural resources, sunlight and biomass, and utilizes these for the bulk production of commercially and tropically relevant chemicals. Since sunlight excludes most of the highly energetic UV light, solarchemical transformations often proceed more cleanly and produce less side products. Compared to lamp-driven processes, this commonly reduces purification steps and results in better product qualities.

Solar reactors – The group at JCU operates a number of solar reactors for small to pilot-scale synthesis in sunlight (**Figure 1**). Small-scale illuminations are still commonly performed following the traditional 'flask in the sun' approach. Larger reactions are conducted in custom-made 1 m^2 flatbed reactors (<8 L capacity) and a 2 m^2 Compound Parabolic Collector (CPC; <50 L capacity). Both reactor types use direct and diffuse light and are operated in circulation mode. The unique "round-W" mirror shape of the CPC reactor additionally allows optimal capture of sunlight.

As part of a recent commercialization grant, the *Applied and Green Photochemistry Group* has synthesized pilot kilogram-batches of valuable commodity chemicals, within 1-3 days of solar exposure using flatbed or compound parabolic concentrator (CPC) reactors. The advantage of operating several different size solar reactors, as seen below, is that it allows for rapid feedback in process development, modifications and refinements. Because of this our preliminary results have received significant attention from local media and industry.

Based in costal North Queensland, the group at JCU is also investigating applications of 'solar floats' (developed by Prof. Liu at the University of Hawaii, USA).[8] These devices use natural water-reservoirs as heat-sinks and thus avoid the high cooling water demand of conventional lamp-driven processes or heat exchangers attached to solar reactors.

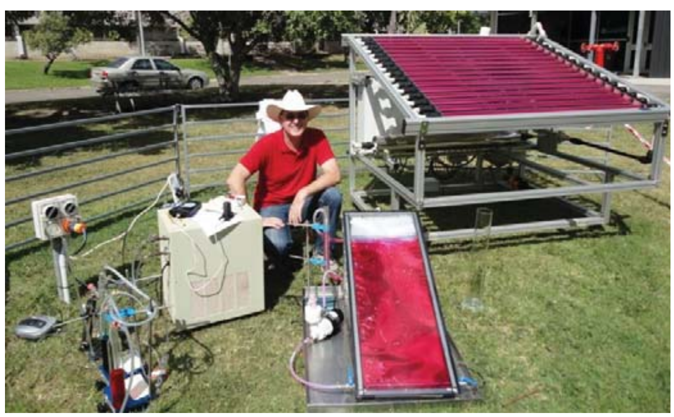
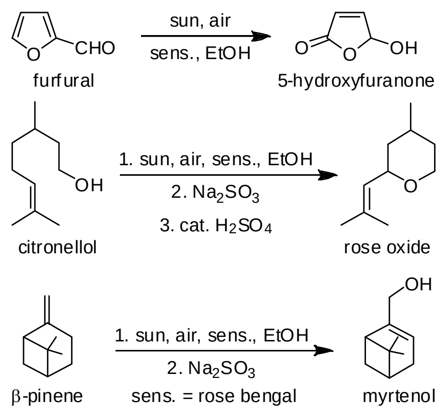


Figure 1. Matthew Bolte in between the solar reactors at James Cook University in Townsville, Australia.

Solar photoreactions – At JCU, the solar research activities are focused on photooxygenations of renewable materials (**Scheme 1**).[9] Air is commonly used as a safe and inexpensive oxygen source. Likewise ethanol, a renewable resource from the sugar industry, is employed as a non-hazardous solvent. The targeted commodity chemicals are of particular economic value for tropical North Queensland.



Scheme 1. Selected photooxygenations investigated.

Sugarcane bagasse from the local sugar industry, for example, represents an important fuel source and potential renewable feedstock. The transformation of furfural, a bagasse-derived compound, into high value chemicals is thus of strategic importance.[10] The photooxygenation of furfural into the versatile building block hydroxyfuranone proceeds in one step, without the need of further reduction.[11] In contrast, elevated temperatures furnish directly the corresponding alkoxy-derivatives as novel fragrances.[12] Similarly, Australia was a major producer of essential oils, however, increasing pressure from Asia and customer demands have seen a declining share of the world market. This has created a need for value adding and diversification of product portfolios. The conversion of essential oils into high end, natural fragrances thus addresses this need and opens innovative new markets.[13] The transformation of citronellol to the important fragrance rose oxide, for example, follows a simple three-step procedure.[14] The crucial photooxygenation step has been previously realized on large-scale using concentrated sunlight. The conversion of β-pinene to the low volume fragrance myrtenol via a two-step protocol is likewise investigated at JCU.[15]

Conclusion – Tropical Australia offers excellent opportunities for solarchemical research. Solar photooxygenations in particular allow for the easy conversion of renewable materials from the local agriculture and forestry industry into high-value chemicals of industrial importance.

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References.

1. H. D. Roth "The beginnings of organic photochemistry" *Angew. Chem. Int. Ed. Engl.* 1989, 28: 1193-1207.

2. G. Nebbia, G. B. Kauffman "Prophet of solar energy: a retrospective view of Giacomo Luigi Ciamician (1857-1922), the founder of Green Chemistry, on the 150th anniversary of his birth" *Chem. Educator* 2007, 12: 362-369.

3. G. Ciamician "The photochemistry of the future" *Science* 1912, 36: 385-394.

4. P. Esser, B. Pohlmann, H.-D. Scharf "The photochemical synthesis of fine chemicals with sunlight" *Angew. Chem. Int. Ed. Engl.* 1994, 33: 2009-2023.

5. (a) A. Fernandez-Garcia, E. Zarza, L. Valenzuela, M. Perez "Parabolic-trough solar collectors and their applications" *Renew. Sust. Energy Rev.* 2010, 14: 1695-1721; (b) K.-H. Funken, J. Ortner, "Technologies for the solar photochemical and photocatalytic manufacture of specialities and commodities: a review" *Z. Phys. Chem.* 1999, 213: 99-105.

6. (a) N. Monnerie, J. Ortner "Economic evaluation of the industrial photosynthesis of rose oxide via lamp or solar operated photooxidation of citronellol" *J. Sol. Energy Eng.* 2001, 123: 171-174; (b) K.-H. Funken, F.-J. Müller, J. Ortner, K.-J. Riffelmann, C. Sattler "Solar

collectors versus lamps – a comparison of the energy demand of industrial photochemical processes as exemplified by the production of ε-caprolactam" *Energy* 1999, 24: 681-687.
7. (a) M. Oelgemöller, C. Jung, J. Mattay "Green photochemistry: Production of fine chemicals with sunlight" *Pure Appl. Chem.* 2007, 79: 1939–1947; (b) M. Oelgemöller, C. Jung, J. Ortner, J. Mattay, E. Zimmermann "Green Photochemistry: solar photooxygenations with medium concentrated sunlight" *Green Chem.* 2005, 7: 35-38.
8. Y.-P. Zhao, R. O. Campbell, R. S. H. Liu "Solar reactions for preparing hindered 7-cis-isomers of dienes and trienes in the vitamin A series" *Green Chem.* 2008, 10: 1038-1042
9. (a) K. Gollnick "Photooxygenation and its application in chemistry" *Chim. Ind.* 1982, 63: 156-166; (b) W. Rojahn, H.-U. Warnecke "Die photosensibilisierte Sauerstoffübertragung – eine Methode zur Herstellung hochwertiger Riechstoffe" *DRAGOCO-Report* 1980, 27: 159-164; (c) M. Fischer "Industrial applications of photochemical synthesis" *Angew. Chem. Int. Ed. Engl.* 1978, 17: 16-26.
10. A. Mamman, J. Lee, Y. Kim, T. Hwang, N. Park, Y. Hwang, J. Chang, J. Hwang "Furfural: Hemicellulose/xylosederived biochemical" *Biofuels Bioprod. Bioref.* 2008, 2: 438-454.
11. (a) S. Marinković, C. Brulé, N. Hoffmann, E. Prost, J.-M. Nuzillard, V. Bulach "Origin of chiral induction in radical reactions with the diastereoisomers (5R)- and (5S)-5-l-menthyloxyfuran-2[5H]-one" *J. Org. Chem.* 2004, 69: 1646-1651; (b) G. O. Schenck "Über die unsensibilisierte und photosensibilisierte Autoxydation von Furanen" *Liebigs Ann. Chem.* 1953, 584: 156-176.
12. P. Esser, R. Pelzer, F. Völkl "Verwendung substituierter Lactone als Riechstoffe" *EP-0761808A2*, 1996 [*Chem. Abstr.* 1997, 138: 220667].
13. J. L. Bicas, A. P. Dionisio, G. M. Pastore "Bio-oxidation of terpines: an approach for the flavour industry" *Chem. Rev.* 2009, 109: 4518-4531.
14. G. Ohloff, E. Klein, G. O. Schenck "Darstellung von Rosen-oxyden und anderen Hydropyran-Derivaten über Photohydro-peroxyde" *Angew. Chem.* 1961, 73: 578.
15. G. O. Schenck, H. Eggert, W. Denk "Über die Bildung von Hydroperoxyden bei photosensibilisierten Reaktionen von O_2 mit geeigneten Akzeptoren, insbesondere mit α- und β-Pinen" *Liebigs Ann. Chem.* 1953, 584: 177-198.