

- J. The State of Nanoparticle-Based Nanoscience and Biotechnology: Progress, Promises, and Challenges. *ACS Nano*. **2012**, *6* (10), 8468-8483.
2. Lundqvist, M.; Stigler, J.; Elia, G.; Lynch, I.; Cedervall, T.; Dawson, K. A. Nanoparticle Size and Surface Properties Determine the Protein Corona with Possible Implications for Biological Impacts. *Proc. Natl. Acad. Sci. USA* **2008**, *105* (38), 14265-14270.
 3. Endo, T.; Kerman, K.; Nagatani, N.; Hiepa, H. M.; Kim, D.-K.; Yonezawa, Y.; Nakano, K.; Tamiya, E. Multiple Label-Free Detection of Antigen–Antibody Reaction Using Localized Surface Plasmon Resonance-Based Core–Shell Structured Nanoparticle Layer *Nanochip. Anal. Chem.* **2006**, *78* (18), 6465-6475.
 4. Röcker, C.; Pözl, M.; Zhang, F.; Parak, W. J.; Nienhaus, G. U. A Quantitative Fluorescence Study of Protein Monolayer Formation on Colloidal Nanoparticles. *Nat. Nanotech.* **2009**, *4*, 577.
 5. Laera, S.; Ceccone, G.; Rossi, F.; Gilliland, D.; Hussain, R.; Siligardi, G.; Calzolari, L. Measuring Protein Structure and Stability of Protein–Nanoparticle Systems with Synchrotron Radiation Circular Dichroism. *Nano Lett.* **2011**, *11* (10), 4480-4484.
 6. Gessner, A.; Lieske, A.; Paulke, B. R.; Müller, R. H. Influence of Surface Charge Density on Protein Adsorption on Polymeric Nanoparticles: Analysis by Two-Dimensional Electrophoresis. *Eur. J. Pharm. Biopharm.* **2002**, *54* (2), 165-170.
 7. Baier, G.; Costa, C.; Zeller, A.; Baumann, D.; Sayer, C.; Araujo, P. H. H.; Mailänder, V.; Musyanovych, A.; Landfester, K. BSA Adsorption on Differently Charged Polystyrene Nanoparticles Using Isothermal Titration Calorimetry and the Influence on Cellular Uptake. *Macromol. Biosci.* **2011**, *11* (5), 628-638.
 8. Lundqvist, M.; Sethson, I.; Jonsson, B.-H. Protein Adsorption onto Silica Nanoparticles: Conformational Changes Depend on the Particles' Curvature and the Protein Stability. *Langmuir* **2004**, *20* (24), 10639-10647.
 9. Jiang, X.; Jiang, J.; Jin, Y.; Wang, E.; Dong, S. Effect of Colloidal Gold Size on the Conformational Changes of Adsorbed Cytochrome C: Probing by Circular Dichroism, UV–Visible, and Infrared Spectroscopy. *Biomacromolecules* **2005**, *6* (1), 46-53.
 10. Raymond-Laruinaz, S.; Saviot, L.; Potin, V.; Marco de Lucas, M. d. C. Protein–Nanoparticle Interaction in Bioconjugated Silver Nanoparticles: A Transmission Electron Microscopy and Surface Enhanced Raman Spectroscopy Study. *Appl. Surf. Sci.* **2016**, *389*, 17-24.

Role of Synthetic Organic Chemistry in Sustainable Agriculture

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Introduction

Undernourishment and malnutrition are major human health concerns in the developing world and these issues are becoming major threats with the increasing population.¹ According to the FOA, in 2050 the world's population is expected to be increased by 2 billion. Providing nutritious foods in adequate amount for the increasing world population is a challenging task.² Sustainable development in agriculture is critically

important to improve the global food security and food nutrition. To achieve this goal world's agriculture has to increase the quantity and diversity of foods.

Synthetic organic chemistry has playing a major role in crop protection and food protection. The control of pathogens, insect pests and weeds has been the major contributor to the agricultural yield. New agrochemicals has got escalating demand. Safe and efficient new organic molecules with new mode of actions will

claim a place in agriculture for many years to come. On this note, synthetic organic chemistry so far has made a huge impact on discovering and manufacturing of new organic molecules for crop protection as well as other critical issues in agriculture. The major aspects we cover from this article are the approaches of synthetic organic chemistry on some of the major concerns in sustainable agriculture such as climate change, minimizing post-harvest losses, reduction of fertilizer consumption and crop protection.

(i) Climate Change

Climatic changes due to fluctuations in temperatures and rainfall patterns are playing an essential role in global agricultural productivity.³ Plants respond to these climatic changes by altering metabolism pathways.⁴ It has been recognized that most of these metabolic pathways mediated by plant based small peptides.⁵ The essential role of these small peptides (<100 amino acids) in plant growth and development can be used to mitigate the plant stress during climatic changes. Naturally these peptides are produced in plant cells. Some of these essential plant peptide sequences have already been recognized and summarized in Table 1.

Table 1

Peptide	Function
CLE 25 ⁶	Resistance to dehydrative stress
Calreticulin ⁷	Drought and high salt tolerance, better root growth
Ph-AMP ⁸	Broad spectrum antifungal activity
BPCH7 ⁹	Effective gene transfer in cells

These peptides can be synthesized using solid phase peptide synthesis (SPPS)¹⁰ and use as plant external stimuli to relieve the plant stress during extreme conditions.

(ii) Water scarcity

Global agriculture accounts for about 70% of global water withdrawals, and also constantly competing with domestic, industrial and environmental uses even with limited availability.¹¹ Scarcity of water for agriculture is one of the future challenges to overcome to increase the crop production for the increasing population. Sustainable use and water management are critically important to conserve water for agriculture and other

uses. Innovations are required to manage sustainable irrigation practices for the crop production.

The three dimensional polymeric network materials which are capable of absorbing large amounts of water are termed as hydrogels.¹² These hydrogels can be able to retain water and nutrients as well as release them accordingly when the root zone of plants start to dry up. Harnessing the high swelling and slow water retention of hydrogels opens the novel avenues in agricultural applications.¹³ Most of the developments in the area of hydrogel are based on natural polymers. However polypeptides,¹⁴ polysaccharides¹⁵ and synthetic polyvinyl and polyester can also be used as alternatives. These polymers can be synthesized and optimized using Synthetic organic techniques.¹⁶

(iii) Minimizing post-harvest losses

One-third of the global food production (worth about US \$1 trillion), is lost during postharvest operations every year.¹⁷ The reduction of postharvest losses can give higher returns compared to increasing crop production to meet escalating global food demand. Novel strategies to reduce postharvest losses can be achieved by using innovative multidisciplinary approaches involving synthetic organic chemistry.

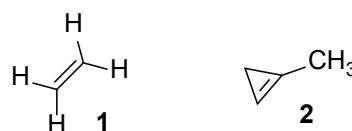
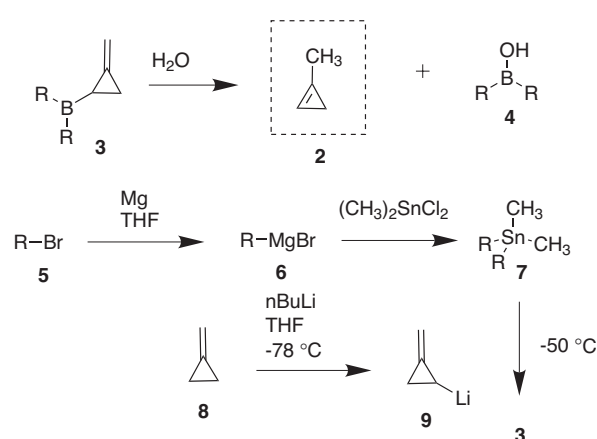


Figure 1: Structure of plant hormone ethylene, 1 and ethylene inhibitor 1-methyl cyclopropene, 2

Plant hormone ethylene can play a significant role in ripening fruits and yellowing leaves.¹⁸ Uncontrolled ethylene exposure can induce significant changes in quality parameters of perishable plant products during the post-harvest storage. 1-methyl cyclopropene (1-MCP) is one of the competitive inhibitors in ethylene receptors of the plant and this compound can prevent ethylene binding even at minimum concentrations.¹⁹

Gaseous nature of 1-MCP at ambient temperature renders its usage in open field applications. Therefore stable complexes which can release 1-MCP gradually at ambient temperature could be much effective. These stable 1-MCP complexes can be synthesized using

synthetic organic techniques. Scheme 1 depicted the synthesis of stable Boronated-1-MCP complex²⁰ which releases the active component upon contact with water.



Scheme 1: Synthesis of 1-MCP boron complexes

(iv) Reduction of fertilizer consumption

Synthetic inorganic fertilizers are playing a key role in enhancing crop production.²¹ However, overuse of these inorganic fertilizers in many parts of the world has contributed to soil, water and air pollution. The demand for inorganic fertilizers in the future is predicted to be increased further with the world's population growth. New technologies employing to increase nutrient use efficiency (NUE)²² and thereby reduction of fertilizer usage can be used as effective mitigation alternatives to control the environmental impacts of the inorganic fertilizers.

Chemically decomposing organic compounds such as isobutyridene-diurea (10)²³ and crotonylidene-diurea (11)²⁴ can be used as controlled release N-fertilizers. These compounds can be prepared by using excess urea aldehyde condensation reaction.

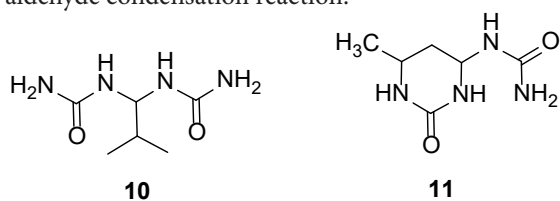


Figure 2: Chemically decomposing urea compounds

Inhibition of the conversion of ammonium-N to nitrate-N by soil bacteria can be a useful process to prevent leaching and denitrification.²⁵ Several small organic molecules can be used in this regard as

inhibitors as shown in figure 3. Substituted schiff base type compounds have also been synthesized as potential inhibitors.²⁶

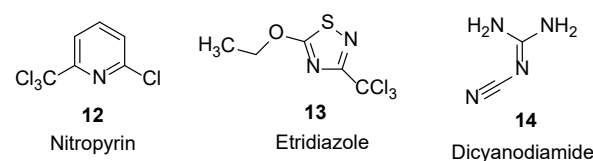


Figure 3: Key Inhibitors of nitrification reaction

(v) Modern Crop protection chemicals

Crop protection by using chemical strategies have been in practice for many decades. However the industry is constantly demanding new molecules due to changing the agricultural environment and the crop resistance.²⁷ The three main groups of agrochemicals are herbicides, insecticides and fungicides. Among these, half of the crop protection chemicals are in fact herbicides. However, it has been noted that the resistance is appearing even for the most used herbicide Glyphosate.²⁸

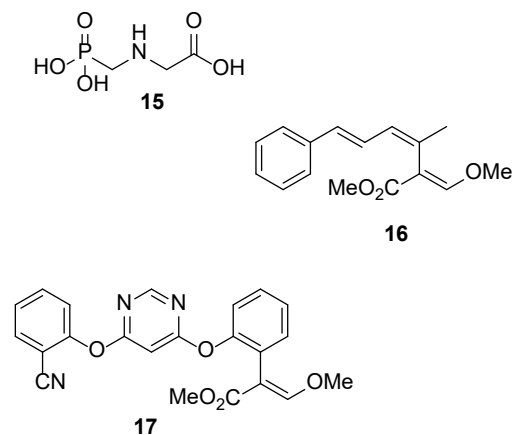


Figure 3: Structure of Glyphosate (15), natural product stobilurinA (16) and Azoxystrobin (17)

The resistance breaking nontoxic molecules with broad weed spectrum activity are constantly in need for the industry. Natural product stobilurin-A derived fungicide, azoxystrobin is a good example of broad spectrum fungicide which is effective against over 400 crop disease systems.²⁹ The invention of new agrochemicals is exclusively relying on biological efficacy. However, there is a well establishing way of developing safe, effective and economical agrochemical leads. This involves screening of the biological target, use of bioactive natural products and their rationally designed analogs and mechanism based design.

Nature has been a frequent resource for many bioactive molecules. Even though most of the natural products are lacking the properties required for successful crop protection, they have provided better leads for crop protection chemicals. The structurally optimized target molecules then can be synthesized using synthetic organic chemistry.³⁰ Synthetic pyrethroid insecticides were perhaps the most enduring example in this regard which were derived from pyrethroids natural products (figure 4).³¹

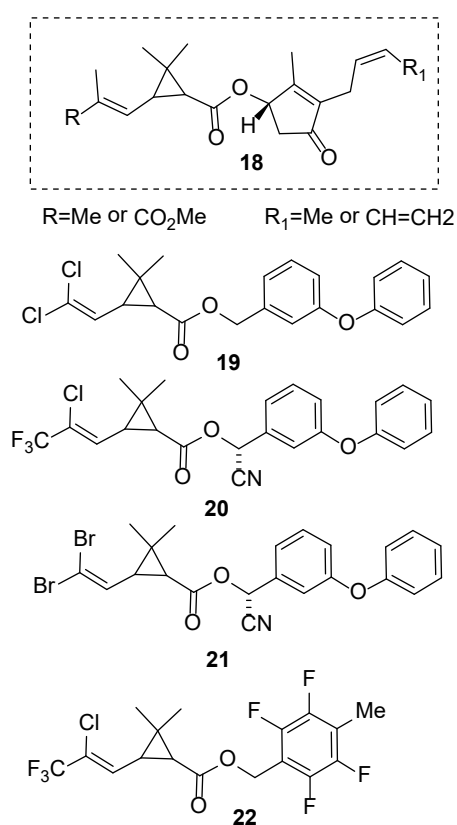


Figure 4: Natural and synthetic Pyrethroids

Summary

Constant supply of food for the growing world is critically important. With its unique ability of bridging the structure and function, organic synthesis became an enabling science for many applied disciplines. In concert with other key science segments, organic synthesis is poised to address the key issues in global agriculture and food safety. Continuous multidisciplinary research on agriculture organic interface will immensely contribute to economic development via producing new compounds for safe, efficient agricultural practices. These new molecular architectures will facilitate the novel approaches to

mitigate some of the key challenges in agriculture in order to increase the crop production especially in an agriculture dependent tropical country like ours.

References

- O. Müller and M. Krawinkel, *CMAJ*, **2005**, *173*, 279-286.
- H. Meyers William and N. Kalaitzandonakes, in *Food Security in an Uncertain World*, Emerald Group Publishing Limited, **2015**, vol. 15, pp. 161-177.
- R. M. Adams, *American Journal of Agricultural Economics*, **1989**, *71*, 1272-1279.
- S. B. Gray and S. M. Brady, *Developmental Biology*, **2016**, *419*, 64-77.
- S. Ali, B. A. Ganai, A. N. Kamili, A. A. Bhat, Z. A. Mir, J. A. Bhat, A. Tyagi, S. T. Islam, M. Mushtaq, P. Yadav, S. Rawat and A. Grover, *Microbiological Research*, **2018**, *212-213*, 29-37.
- T. Araya, M. Miyamoto, J. Wibowo, A. Suzuki, S. Kojima, Y. N. Tsuchiya, S. Sawa, H. Fukuda, N. von Wirén and H. Takahashi, *Proceedings of the National Academy of Sciences*, **2014**, *111*, 2029-2034.
- X.-Y. Jia, L.-H. He, R.-L. Jing and R.-Z. Li, *Physiologia Plantarum*, **2009**, *136*, 127-138.
- H. Mkrtchyan, S. Gibbons, S. Heidelberger, M. Zloh and H. K. Limaki, *International Journal of Antimicrobial Agents*, **2010**, *35*, 255-260.
- J.-A. Chuah and K. Numata, *Biomacromolecules*, **2018**, *19*, 1154-1163.
- M. Amblard, J.-A. Fehrentz, J. Martinez and G. Subra, *Molecular Biotechnology*, **2006**, *33*, 239-254.
- L. R. Brown, *Water Science and Technology*, **2001**, *43*, 17-22.
- A. S. Hoffman, *Advanced Drug Delivery Reviews*, **2012**, *64*, 18-23.
- W. E. Rudzinski, A. M. Dave, U. H. Vaishnav, S. G. Kumbar, A. R. Kulkarni and T. M. Aminabhavi, *Designed Monomers and Polymers*, **2002**, *5*, 39-65.
- E. K. Johnson, D. J. Adams and P. J. Cameron, *Journal of Materials Chemistry*, **2011**, *21*, 2024-2027.
- T. Coviello, P. Matricardi, C. Marianecchi and F. Alhaique, *Journal of Controlled Release*, **2007**, *119*,

- 5-24.
16. M. F. Akhtar, M. Hanif and N. M. Ranjha, *Saudi Pharmaceutical Journal*, **2016**, *24*, 554-559.
 17. R. J. Hodges, J. C. Buzby and B. Bennett, *The Journal of Agricultural Science*, **2010**, *149*, 37-45.
 18. E. C. Sisler and S. F. Yang, *BioScience*, **1984**, *34*, 234-238.
 19. C. B. Watkins, *Biotechnology Advances*, **2006**, *24*, 389-409.
 20. S. Majher, T. Peggy and L. LinShu, *Journal of Plant Studies*, **2016**, *5*, 1-10.
 21. G. Ge, Z. Li, F. Fan, G. Chu, Z. Hou and Y. Liang, *Plant and Soil*, **2009**, 326, 31.
 22. V. C. Baligar, N. K. Fageria and Z. L. He, *Communications in Soil Science and Plant Analysis*, **2001**, *32*, 921-950.
 23. T. D. Hughes, *Agronomy Journal*, **1976**, *68*, 103-106.
 24. M. Yasuhara and T. Inoi, *Journal of the Science of Soil and Manure, Japan*, **1970**, *41*, 83-88.
 25. *in Nitrification Inhibitors—Potentials and Limitations*, DOI: 10.2134/asaspecpub38.c2, pp. 19-32.
 26. N. Aggarwal, R. Kumar, P. Dureja and D. S. Rawat, *Journal of Agricultural and Food Chemistry*, **2009**, *57*, 8520-8525.
 27. K. Smith, D. A. Evans and G. A. El-Hiti, *Philos Trans R Soc Lond B Biol Sci*, **2008**, *363*, 623-637.
 28. S. O. Duke and S. B. Powles, *Pest Management Science*, **2008**, *64*, 319-325.
 29. X. Zhang, Y.-X. Gao, H.-J. Liu, B.-Y. Guo and H.-L. Wang, **2012**, 33.
 30. M. W. Walter, *Natural Product Reports*, **2002**, *19*, 278-291.
 31. F. O. Silvério, E. S. de Alvarenga, S. C. Moreno and M. C. Picanço, *Pest Management Science*, **2009**, *65*, 900-905.

Chemical Nature of Pesticides

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The phrase, “The Granary of the East” was used to describe the success of agriculture-based economy of our ancient nation. After European invasion, we lost our self-sustaining golden era, and gradually we started begging from developed countries and now we depend on their monetary loans and products. Pesticides are one of the major hazardous products, which we import without proper specifications, guidelines and monitoring. Today, it seems that these pesticides are making us sick or killing silently, particularly those who live in cultivating areas of Sri Lanka.

The substances or mixtures that use for controlling, preventing, destroying, repelling or attacking any biological organism are known as “**pesticides**”. First historical evidence of pesticides came from Sumerian civilization, 2000 BCE. According to the archeologists, they have used sulfur to control mites and insects. Presently, about 2 million tons of pesticides are utilized globally, out of which 47.5% are herbicides, 29.5% are

insecticides, 17.5% are fungicides and 5.5% are other pesticides.

Pesticides can be classified into two main groups based on;

- **Targeted use** - e.g. Algaecide (for algae), Acaricide (for mites), Avicide (for birds), Bactericide (for bacteria), Fungicide (for fungi), Herbicide (for weeds), Insecticide (for insects), Biopesticide (derived from natural materials, e.g. baking Soda), etc.
- **Chemical nature** - This article intends to shine some light in this regard.

Pesticides based on chemical nature

Pesticides are classified depending on their chemical compositions, and are broadly classified as either organic or inorganic pesticides.

Inorganic pesticides are simple compounds