

Biobased Organic Chemistry Laboratories as Sustainable Experiment Alternatives

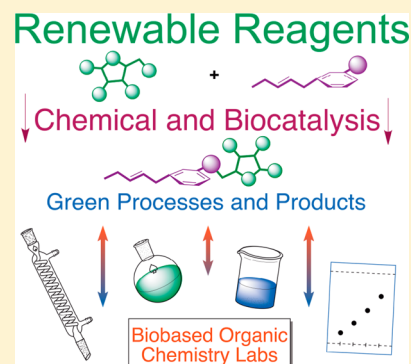
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ABSTRACT: As nonrenewable resources deplete and educators seek relevant interdisciplinary content for organic chemistry instruction, biobased laboratory experiments present themselves as potential alternatives to petroleum-based transformations, which offer themselves as sustainable variations on important themes. Following the principles of green chemistry and the powerful biorefinery model it is possible to create pedagogically sound and modern laboratory experiments employing readily available renewable reactants and reagents to convey important organic chemistry principles. In a reverse approach compared to total synthesis, these experiments should serve to not only make the undergraduate organic chemistry laboratory more green and sustainable but also educate the next generation with both historically important developments and cutting-edge research.

KEYWORDS: Second-Year Undergraduate, Organic Chemistry, Green Chemistry, Natural Products, Biotechnology



Implementing Biobased Protocols in the Laboratory. Since the inception of green chemistry, there has been a concerted effort to develop green educational materials that has resulted in a variety of green chemistry experiments.^{1–4} Notably, many of these have been developed for the organic chemistry curriculum.^{5–8} Despite efforts to achieve truly sustainable experiments, most of the admirable improvements to time honored syntheses focus on the development of greener processes and neglect to afford greener products or vice versa.^{5,7} It should be noted that this is not at the fault of the principles of green chemistry nor the experiment developers but should serve to highlight the difficulty it takes to develop multifaceted sustainable experiments simultaneously following numerous green principles. In an effort to further advance organic chemistry experiments into pedagogy that is both educational and sustainable, it should serve that the next generation of sustainable experiments focuses on the dual development of green processes and products. To aid this development there comes to the forefront a second green chemical ideology to augment the principles of green chemistry: the biorefinery model.⁹

The biorefinery model exists in parallel to the petroleum refinery and represents the industrial handling of biobased materials with biotechnological and chemical processes to afford chemicals, fuels, and materials.^{10,11} Two main advantages to the biorefinery model stem from its use of renewable biomaterials over crude oil distillates as feedstocks and biocatalysis to modify these chemicals, thus taking into consideration both product and process. In viewing the biorefinery model it becomes evident that unlike facile green chemistry efforts the model is wholly sustainable as it incorporates multiple principles of green chemistry into one

paradigm, including renewable feedstocks, design for degradation, safer biocompatible solvents, and potentially others. This combination of green principles should serve to inspire the next generation of sustainable organic chemistry research and pedagogical experiments.

There have been sustainable experiments published in this journal, which serve to promote the use of biobased materials in educational practices (Figure 1).^{12–14} They have well demonstrated the incorporation of either biobased reactants¹⁵ or reagents,¹⁶ and some serve to demonstrate the total synthesis of one natural product into another.¹⁷ Common are laboratories that detail the isolation and identification of biological molecules that may serve the introductory organic chemistry class,^{18–20} but a rare few detail transformations of these molecules^{21,22} truly following the biorefinery model by identifying cheap and readily available starting materials for use. Beyond these, there exists a set of laboratories, polymerizations,²³ and interdisciplinary experiments²⁴ that detail the development of materials from biomass. These are more advanced experiments that serve to connect the organic lab to applied study inviting a wider context into the undergraduate organic laboratory. Lastly, there are a variety of experiments that demonstrate the conversion of oils and fats to biodiesel,^{25–31} a popular experiment that might well be the epitome of the biorefinery model, especially when biotransformations are used.³²

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Biobased Organic Chemistry Experiments		
Experiment	Reaction Scheme	Techniques
Transformations with Castor Oil ¹²	<p>Hydrogenation Transesterification Saponification</p>	Melting Point IR and ¹ H-NMR Spectroscopy
Eugenol Cross Metathesis ¹³	<p>Grubbs' cat.</p>	TLC Chromatography NMR Spectroscopy
Reduction with Carrot Bits ¹⁶	<p>carrot bits water</p>	Column Chromatography
Polymerization of Aspartic Acid ²¹	<p>$\alpha:\beta = 30:70$</p>	Titration
Sorbitol Gelator Synthesis ²²	<p>Novozyme 435</p>	Column and TLC Chromatography IR or NMR Spectroscopy

Figure 1. Biobased organic chemistry laboratories representing a range of topics and techniques.

It must be noted that using complex natural mixtures, and leveraging tools that verge on biochemistry, augments the complexity of these experiments. One common practical observation of those who run these experiments is the extra time some of these transformations take or that workup may entail. Though these may be challenges in the laboratory, each instructor must weigh the advantages of working with biobased materials. Some may come to find these experiments impractical but may be interested in lecturing about them as alternatives, whereas other may find the added time an appropriate introduction for students to real world considerations of organic chemistry transformations.

One of the significant differences between these experiments and traditional total synthesis experiments is the pathway of the biomaterial. While total synthesis experiments utilize petroleum-derived reagents to synthesize a biologically available molecule, these experiments serve to use readily available biomaterials to synthesize products of similar complexity and utility. Thus, by incorporating biobased experiments into a curriculum it should not serve to diminish the impact or relevance of a laboratory, but rather serve to provide a worthwhile learning experience without sacrificing the environmental or economic sustainability of the course.

The arguments for incorporating green chemistry into the curriculum also serve to promote the development and incorporation of biobased reagents and reactants into experiments (following the seventh principle of green chemistry) and thus the promotion of the biorefinery model as a guide for both teaching and research.^{3,33,34} As chemists and educators alike strive to develop sustainable experiments that exist as economically feasible, educational, and environmentally benign experiments, the biorefinery model may serve as a guide alongside the principles of green chemistry. In an effort to effectuate this model, the first step is to push the seventh principle and replace the petroleum-derived materials from at least some of our laboratories and with biobased alternatives. This will serve not only to help to bridge the gap between green

experiments and sustainable experiments but also to inspire the next generation of sustainable scientists when students realize they can use their chemistry to synthesize starting from the biosphere around them. Beyond the inclusion of these experiments and biobased reactants and reagents there needs to be a paradigm shift toward linking applied research and the organic chemistry laboratory. This can be done by taking the sustainable research developments in laboratories and continually and iteratively incorporating elements into the coursework, until the laboratories reflect the topics and work being done by researchers at or near the student's institution, along with the chemistry of natural products specific to their environment. A final step is the permeation of foundational materials into lecture courses such as general chemistry or organic chemistry. Although many green pedagogical developments may begin in the laboratory, more efforts are needed to teach topics including biotransformations, waste recycling, and the production and processing of safe chemicals in lecture so students can connect theory to their experimentation. When the lecture and laboratory can reflect the same principles and ideas, this cohesion should prove to influence and inspire students of all interests. Many inventive and elegant experiments have been created to demonstrate the powerful principles of the using naturally renewable resources; the next step is combining them into a curriculum, which evokes the power of the biorefinery model.

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Notes

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REFERENCES

- (1) Doxsee, K. M.; Hutchison, J. E. *Green Organic Chemistry: Strategies, Tools, and Laboratory Experiments*; Brooks/Cole: Pacific Grove, CA, 2004.
- (2) Dicks, A. P. *Green Organic Chemistry in Lecture and Laboratory*; Taylor & Francis: Boca Raton, FL, 2012.
- (3) Levy, I. J.; Haack, J. A.; Hutchison, J. E.; Kirchoff, M. M. Going Green: Lecture Assignments and Lab Experiences for the College Curriculum. *J. Chem. Educ.* **2005**, *82* (7), 974–976.
- (4) Roesky, H. W.; Kennepohl, D. K.; Lehn, J.-M.; Luque, R.; Clark, J. H.; Macquarrie, D. J.; Carril, M.; SanMartin, R.; Dominguez, E.; Gossage, R. A.; et al. *Experiments in Green and Sustainable Chemistry*; Wiley-VCH: Weinheim, Germany, 2009.
- (5) Yadav, U.; Mande, H.; Ghalsasi, P. Nitration of Phenols Using Cu(NO₃)₂: Green Chemistry Laboratory Experiment. *J. Chem. Educ.* **2012**, *89* (2), 268–270.
- (6) Ter Meer Guardia, L.; Belli, A.; Molta, G.; Gordon, P.; Jaworek-Lopes, C. Green Crossed Aldol Condensation Reactions Using Trans-Cinnamaldehyde. *Chem. Educ.* **2011**, *16*, 23–25.
- (7) Birdwhistell, K. R.; Nguyen, A.; Ramos, E. J.; Kobelja, R. Acylation of Ferrocene: A Greener Approach. *J. Chem. Educ.* **2008**, *85* (2), 261–262.
- (8) Dintzner, M. R.; Kinzie, C. R.; Pulkrabek, K.; Arena, A. F. The Cyclohexanol Cycle and Synthesis of Nylon 6,6: Green Chemistry in the Undergraduate Organic Laboratory. *J. Chem. Educ.* **2012**, *89*, 262–264.
- (9) Clark, J. H.; Budarin, V.; Deswarte, F. E. I.; Hardy, J. J. E.; Kerton, F. M.; Hunt, A. J.; Luque, R.; Macquarrie, D. J.; Milkowski, K.; Rodriguez, A.; Samuel, O.; Tavener, S. J.; White, R. J.; Wilson, A. J. Green Chemistry and the Biorefinery: A Partnership for a Sustainable Future. *Green Chem.* **2006**, *8* (10), 853–860.
- (10) Kamm, B.; Kamm, M. Principles of Biorefineries. *Appl. Microbiol. Biotechnol.* **2004**, *64* (2), 137–145.
- (11) Clark, J. H.; Luque, R.; Matharu, A. S. Green Chemistry, Biofuels, and Biorefinery. *Annu. Rev. Chem. Biomol. Eng.* **2012**, *3*, 183–207.
- (12) Alwaseem, H.; Donahue, C. J.; Marincean, S. Catalytic Transfer Hydrogenation of Castor Oil. *J. Chem. Educ.* **2014**, *91* (4), 575–578.
- (13) Taber, D. F.; Frankowski, K. J. Grubbs's Cross Metathesis of Eugenol with Cis-2-Butene-1,4-Diol To Make a Natural Product. An Organometallic Experiment for the Undergraduate Lab. *J. Chem. Educ.* **2006**, *83* (2), 283–284.
- (14) Besse, P.; Bolte, J.; Veschambre, H. Baker's Yeast Reduction of Alpha-Diketones: A Four-Hour Experiment for Undergraduate Students. *J. Chem. Educ.* **1995**, *72* (3), 277–278.
- (15) Miles, W. H.; Connell, K. B. Synthesis of Methyl Diantilis, a Commercially Important Fragrance. *J. Chem. Educ.* **2006**, *83* (2), 285–287.
- (16) Ravia, S.; Gamenara, D.; Schapiro, V.; Bellomo, A.; Adum, J.; Seoane, G.; Gonzalez, D. Enantioselective Reduction by Crude Plant Parts: Reduction of Benzofuran-2-Yl Methyl Ketone with Carrot (*Daucus Carota*) Bits. *J. Chem. Educ.* **2006**, *83* (7), 1049–1052.
- (17) Touaibia, M.; Guay, M. Natural Product Total Synthesis in the Organic Laboratory: Total Synthesis of Caffeic Acid Phenethyl Ester (CAPE), A Potent 5-Lipoxygenase Inhibitor from Honeybee Hives. *J. Chem. Educ.* **2011**, *88* (4), 473–475.
- (18) Wagner, C. E.; Cahill, T. M.; Marshall, P. A. Extraction, Purification, and Spectroscopic Characterization of a Mixture of Capsaicinoids. *J. Chem. Educ.* **2011**, *88* (11), 1574–1579.
- (19) Walsh, E. L.; Ashe, S.; Walsh, J. J. Nature's Migraine Treatment: Isolation and Structure Elucidation of Parthenolide from *Tanacetum Parthenium*. *J. Chem. Educ.* **2012**, *89* (1), 134–137.
- (20) Chrea, B.; O'Connell, J. A.; Silkstone-Carter, O.; O'Brien, J.; Walsh, J. J. Nature's Antidepressant for Mild to Moderate Depression: Isolation and Spectral Characterization of Hyperforin from a Standardized Extract of St. John's Wort (*Hypericum Perforatum*). *J. Chem. Educ.* **2014**, *91* (3), 440–442.
- (21) Green, B.; Bentley, M. D.; Chung, B. Y.; Lynch, N. G.; Jensen, B. L. Isolation of Betulin and Rearrangement to Allobetulin. A Biomimetic Natural Product Synthesis. *J. Chem. Educ.* **2007**, *84* (12), 1985–1987.
- (22) LeFevre, J. W.; McNeill, K. I.; Moore, J. L. Isolating Friedelin from Cork and Reducing It to Friedelinol and Epifriedelinol. A Project Involving NMR Spectrometry and Molecular Modeling. *J. Chem. Educ.* **2001**, *78* (4), 535–537.
- (23) Bennett, G. D. A Green Polymerization of Aspartic Acid for the Undergraduate Organic Laboratory. *J. Chem. Educ.* **2005**, *82* (9), 1380–1381.
- (24) Hwang, H. L.; Jadhav, S. R.; Silverman, J. R.; John, G. Sweet and Sustainable: Teaching the Biorefinery Concept through Biobased Gelator Synthesis. *J. Chem. Educ.* **2014**, *91*, 1563–1568.
- (25) Goldstein, S. W. Biodiesel from Seeds: An Experiment for Organic Chemistry. *J. Chem. Educ.* **2014**, *91* (10), 1693–1696.
- (26) Pohl, N. L. B.; Streff, J. M.; Brokman, S. Evaluating Sustainability: Soap versus Biodiesel Production from Plant Oils. *J. Chem. Educ.* **2012**, *89* (8), 1053–1056.
- (27) Stout, R. Biodiesel from Used Oil. *J. Chem. Educ.* **2007**, *84* (11), 1765–1771.
- (28) Behnia, M. S.; Emerson, D. W.; Steinberg, S. M.; Alwis, R. M.; Dueñas, J. A.; Serafino, J. O. A Simple, Safe Method for Preparation of Biodiesel. *J. Chem. Educ.* **2011**, *88* (9), 1290–1292.
- (29) Bucholtz, E. C. Biodiesel Synthesis and Evaluation: An Organic Chemistry Experiment. *J. Chem. Educ.* **2007**, *84* (2), 296–298.
- (30) Daconta, L. V.; Minger, T.; Nedelkova, V.; Zikopoulos, J. N. Organic Chemistry and the Native Plants of the Sonoran Desert: Conversion of Jojoba Oil to Biodiesel. *J. Chem. Educ.* **2015**, *92* (10), 1741–1744.
- (31) Bendinskas, K.; Weber, B.; Nsouli, T.; Nguyen, H. V.; Joyce, C.; Niri, V.; Jaskolla, T. W. A Teaching Laboratory for Comprehensive Lipid Characterization from Food Samples. *J. Chem. Educ.* **2014**, *91* (10), 1697–1701.
- (32) Fjerbaek, L.; Christensen, K. V.; Norddahl, B. A Review of the Current State of Biodiesel Production Using Enzymatic Trans-esterification. *Biotechnol. Bioeng.* **2009**, *102* (5), 1298–1315.
- (33) Kitchens, C.; Charney, R.; Naistat, D.; Farrugia, J.; Clarens, A.; O'Neil, A.; Lisowski, C.; Braun, B. Completing Our Education. Green Chemistry in the Curriculum. *J. Chem. Educ.* **2006**, *83* (8), 1126–1129.
- (34) Cann, M. C.; Dickneider, T. A. Infusing the Chemistry Curriculum with Green Chemistry Using Real-World Examples, Web Modules, and Atom Economy in Organic Chemistry Courses. *J. Chem. Educ.* **2004**, *81* (7), 977–980.