Sugar to glucaric acid: a sweet path to renewable chemicals

Tyler N. Smith

During the last two years US consumers have seen the introduction of numerous new automatic dishwashing detergents. Almost everyone—from upstarts such as Method Home to majors like Procter & Gamble—has introduced new phosphate-free formulations. With some notable exceptions, these introductions have left consumers with spotting, filming, and frustration. In the same period, a European commission determined that cleaner dishes required the continued allowance of phosphates and declined to ban their use, as several US states have. In both Europe and North America, detergent brands are innovating to recover and gain market share, yet the market is still wide open, as no dominant phosphate replacement has emerged. Finding a suitable phosphate replacement is a complex problem in which formulators must try to balance ingredient cost, performance, and a demand for green chemicals.

One such solution is glucaric acid, a sugar acid identified in a 2004 US Department of Energy report entitled *Top Value Added Chemicals from Biomass* (available from http://www1.eere.energy.gov/biomass/pdfs/35523.pdf) as one of the 12 key "building block" renewable chemicals with great promise in terms of cost, versatility, and sustainability. Glucaric acid is produced from renewable sources, has a favorable environmental profile, and has the potential for widespread applications across many markets. Historically, however, low reaction yields coupled with large waste streams have kept the cost of glucaric acid production prohibitively high, denying formulators the opportunity to incorporate this versatile chemical into their product lines.

Missoula, Montana (USA)-based Rivertop Renewables has developed a breakthrough technology to produce renewable chemicals such as glucaric acid. Based on more than 10 years of research in the labs of Donald E. Kiely, a professor emeritus of carbohydrate chemistry from the University of Montana, Rivertop's proprietary oxidation technology can produce salts of glucaric acid and other building block chemicals at an economical price and at commercial scale.

Rivertop has refined its oxidation technology into a catalytic process that reduces the amount of chemical inputs and consumption, minimizes the production of waste, and increases the yield of valuable end-use products. The oxidation platform is adaptable to feedstocks beyond glucose such as xylose, arabinose, and galactose, as well as other mono- and polysaccharides. As the cost of these feedstocks comes down or as specialty applications drive demand, Rivertop will explore the commercialization of other sugar acids, such as xylaric, arabinaric, and galactaric acids.

A high-performance ingredient in detergents

Using its proprietary oxidation technology, Rivertop has begun to produce glucarate-based products designed as detergent builders. Initially the company aims to replace the legacy ingredient, tripolyphosphate, as well as newer alternatives that are either too costly or that underperform. While phosphates have historically been used due to their effectiveness and low cost, their negative impacts on water supplies have forced governments around the world to ban their use.

Other alternatives to phosphates, such as citrate, can serve as detergent builders in both automatic dishwashing and laundry detergents, but their inability to sequester typical levels of calcium in the wash water has frustrated customers and forced the industry to look

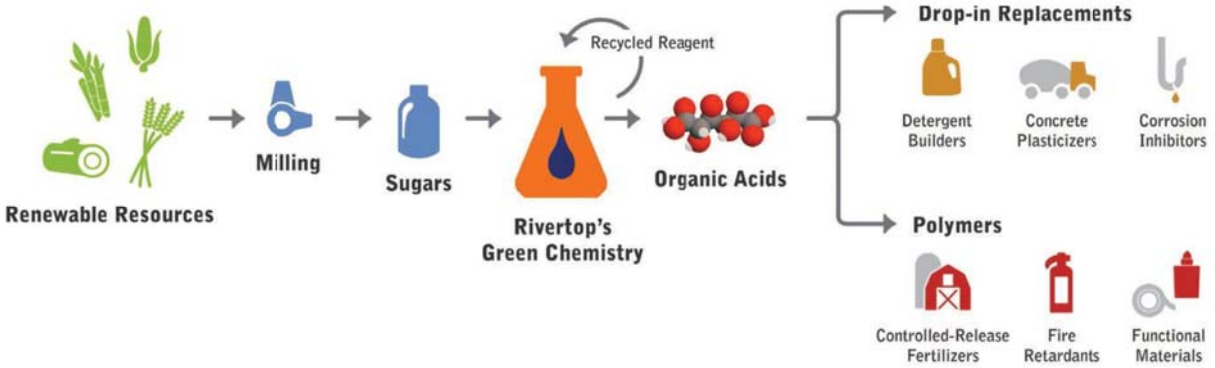

FIG. 1. *The proprietary oxidation technology used to convert sugar into organic acids and products is represented in this flow chart.*

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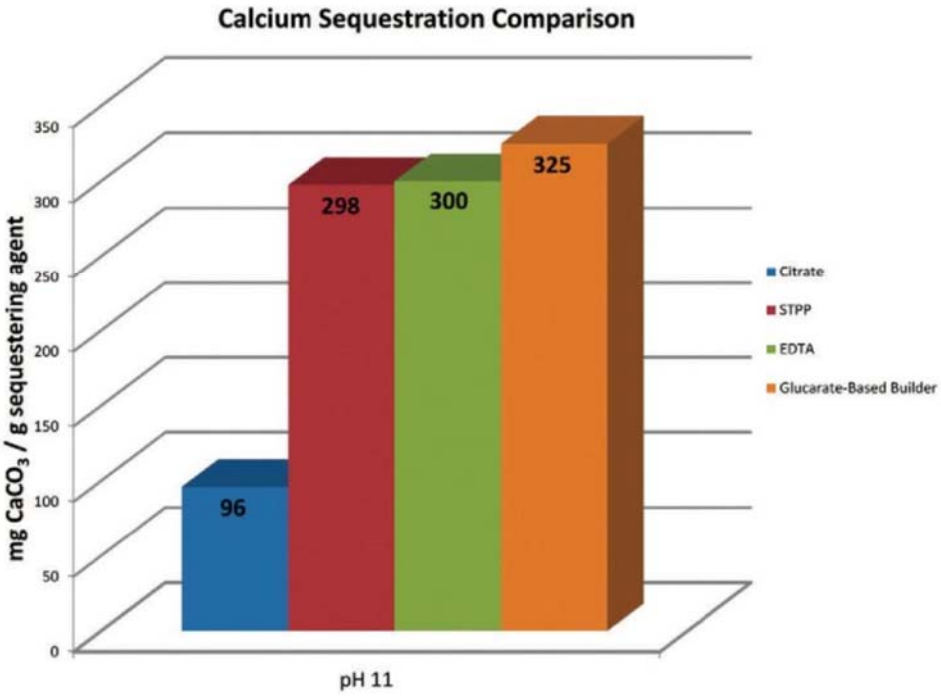

FIG. 2. *This bar graph compares calcium sequestration for citrate, sodium tripolyphosphate (STPP), ethylenediamine tetraacetic acid (EDTA), and glucaric acid. Courtesy of Rivertop Renewables.*

for better solutions. Polymer dispersants offer a partial alternative, but their applications are limited by cost and concentration constraints.

Research has shown that glucarate is a highly effective calcium sequestering agent when formulated with aluminate or borate at pH levels typical to automatic dishwashing detergents. Additionally, glucarate is an effective corrosion inhibitor, an added benefit for the protection of silverware and dishwashers.

Rivertop's chemists began testing their glucarate builders in consumer dishwashers under controlled conditions in the third, quarter of 2011, and they have begun to work with industry partners on advanced formulations to meet specific needs of manufacturers and consumers.

Ultimately Rivertop hopes to provide a suite of cleaning product solutions capable of meeting the growing global demand for phosphate replacement.

Beyond detergents

While detergents will serve as the initial and lead application of Rivertop's glucarate products, the versatility of this green chemical will allow the company to enter additional markets that are in need of cost-competitive chelating agents, corrosion inhibitors, concrete additives, and starting materials for bio-based polymers and chemicals.

Many of the best innovations in industrial water chemistries have come from the detergent industry. Research by Rivertop and others strongly suggests that glucaric acid salts can prevent both scale and corrosion in critical water systems, including manufacturing equipment, bridges, and highways. The company's third-party tests have demonstrated effective corrosion prevention in road de-icers. The biodegradability of Rivertop's glucarates adds value as demands for water conservation increase.

Glucaric acid has also shown broad potential in functional materials such as concrete admixtures and wallboard dispersants. As a concrete admixture, glucaric acid has already met ASTM standard C494 for set retarding and water reduction, adding strength, increasing flowability, and managing set time.

Early research suggests glucaric acid-based polymers are also applicable for adhesives, films, and gels, where they allow for high performance with increased biodegradability.

Feedstocks

Glucose will serve as the initial feedstock for the company's green chemistry technology, but Rivertop's oxidation process offers versatility as a platform process for producing value-added products from a wide variety of

FIG. 3. *Rivertop's product testing automatic dishwasher machines. Photo by Todd Goodrich/ University of Montana.*

renewable, agricultural feedstocks. The process can use a variety of sugar feedstocks, including mono- and polysaccharides, to produce a portfolio of renewable chemicals. Although future chemicals will be alike in basic form, the products from different sugars offer unique properties that will enable the company to fine tune performance in different applications as well as open up entirely new uses.

Currently Rivertop sources its glucose from corn—the cheapest and most abundant source of sugar in the United States. However, the company continues to investigate other potential sources for low-cost sugars such as algae and biomass.

Commercialization plans

Beginning in 2012, Rivertop plans to start production with capacity capable of up to 6–10 million pounds (2.7–4.5 million kg) of product annually through contract manufacturing. To further optimize the cost efficiency of the process and achieve additional cost optimization, Rivertop will build a "semi-works" production facility (the last step in scaling the

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SOY & BREAST CANCER (CONTINUED FROM PAGE 546)

"I believe that early exposure is the key in order to see the protective results in adult life," Hilakivi-Clarke said. "For that reason, we cannot make recommendations based on the Shu data—the exposure of Chinese women to isoflavones is very different."

Would she recommend soy foods to her best friend if the friend had breast cancer?

"If she had never consumed soy before and wants to improve her overall diet by adding it, it would be fine to include at the level of about 1/2 serving per day (or several full servings per week). But I would tell her she absolutely should not take isoflavone supplements."

Shu herself says that questioning the applicability of data in Asian women "is understandable." Thus, she and others pooled data from three US studies with her original data from Chinese women. In all, the team evaluated postdiagnosis soy food intake and breast cancer outcomes of 18,312 women between the ages of 20 and 83 years.

The pooled study was presented at the 102nd Annual Meeting of the American Association for Cancer Research in April 2011 (http://tinyurl.com/AACR-pooled). "We did not see any adverse effect related to eating soy food," Shu said of the study, adding that there was no sign of a risk of recurrence. "There was some suggestion that soy foods may be beneficial."

One of the pooled US cohorts in the research presented at AACR is from a study led by Bette Caan of Kaiser Permanente in Oakland, California, USA. Entitled Women's Healthy Eating and Living (WHEL), the study is a randomized, controlled trial of more than 3,000 early-stage breast cancer survivors, with a median follow-up of 7.3 years from the time of enrollment (*Cancer Epidemiology, Biomarkers & Prevention 20*:854–858, 2011). Results showed that consuming up to 1/2 serving of soy foods per day did not increase breast cancer recurrence among women previously diagnosed with breast cancer, and was associated with lower mortality among such women. (Neither result reached significance.)

"When one considers the limitations of animal research, that the clinical data show isoflavone exposure doesn't adversely affect markers of breast cancer risk, and the epidemiologic data from China and the United States indicating postdiagnosis soy consumption improves the prognosis of women with a history of breast cancer, it is pretty clear that the totality of the evidence has shifted in favor of the safety and potential benefit of soy foods," says Mark Messina.

Moving forward

As is the case with all things scientific, more work is needed. But my months of research and reading have left me feeling perfectly comfortable with continuing to eat a variety of whole soy foods. [A note of caution: Each breast cancer patient needs to do her own review of the research and make her own decision. If it isn't wise to generalize data from Asian women to Western women, it is even less wise to blindly follow the decision of one health and nutrition writer.]

My daily—costly—supplement regimen now includes long-chain omega-3 fatty acids in the form of triglycerides, curcumin with piperine, glucosamine and chondroitin, and 600 International Units of vitamin D3 with co-factors.

Curcumin (a phytochemical in turmeric) has shown promise as an anticancer agent; I added it (with co-factor piperine, which is necessary to increase the bioavailability of curcumin) to my armamentarium. Resveratrol (one of the bioactive phytochemicals in red grapes) has also shown promise, but it is a mixed agonist/antagonist. Until there is more literature to review demonstrating that it doesn't aid cell proliferation, I will not take it in supplement form.

Why the D3? Studies show that women with serum 25-hydroxyvitamin D levels above 40 nanograms/milliliter have less debilitating joint pain and stiffness, a very common side effect of adjuvant therapy with aromatase inhibitors. Why omega-3 fatty acids? Because an observational study focusing on post-initial treatment breast cancer patients monitored over a seven-year period found that women in the highest third of long-chain omega-3 consumption (more than 153 mg/day) were 40% less likely to die from breast cancer compared with women in the lowest third.

Even more important, however, in terms of holding recurrence at bay—or reducing the risk of breast cancer, for that matter—is weight loss and exercise. Adipose tissue manufactures estradiol, the most potent of the body's estrogens, and outcomes of obese breast cancer patients are not as good as slender patients. Then, too, at least 15–20 metabolic equivalents of exercise per week has been associated with a significant reduction in the risk of recurrence of breast cancer. (To learn more about metabolic equivalents, see www.dslrf.org/pdfs/Great_Reads_MarieMurphyBCRisk.pdf.)

And now for the question that remains unanswered: Have I pulled the welcome mat for recurrent cancer or am I just making very expensive urine? Only time will tell.

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company's technology prior to a full commercial facility), co-located with the company's headquarters in Missoula. A larger, global-scale glucaric acid production facility will follow, with an anticipated capacity of 60 million pounds per year. Rivertop's first commercial facility is expected to be built in the Midwestern United States, in proximity to an abundant supply of low-cost, readily available glucose.

Only the beginning

The future of the cleaning products industry is one in which high product performance and competitive pricing will continue to be the benchmark; however, the growing importance to consumers of product sustainability and environmental impact will play a larger role in purchasing decisions. Manufacturers already see this coming and, in turn, are searching for cost-effective, reliable solutions. Of course, consumer preference is not the only power at play in this process, as increasingly stringent governmental regulations will also drive the movement toward sustainable materials.

With low-cost, biodegradable glucaric acid, Rivertop Renewables has found a phosphate replacement for detergents that is effective and cost competitive. It has also identified a product that can move beyond the cleaning industry to serve multiple industries now and in the future. Glucaric acid may just be the start, as Rivertop's oxidation technology can utilize a variety of sugars from numerous renewable, sustainable feedstocks such as cellulosics and algae.

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