Sugar tanning

Karl Flowers, Consultant Technical Editor at ILM with **Andy Schweizer**, R&D Chemist, **Wolfgang Armbruster**, Application Lab Manager and **Dr Daniel Gruseck**, R&D Lab Manager, Schill+Seilacher.

The leather industry is constantly moving into new areas of chemistry and technology. The development of chromium-free leathers is an area of active research with great commercial incentives for tanneries to have a range of tannage types in their portfolio.

The chemical industry is keen to help tanners, including embracing green chemistry principles Kreuder et al. (2017). At the heart of these principles are the adoption of environmentally friendly practices and the use of chemicals that have low environmental and human impact. Low-risk profiles are a major driver for new tanning chemistry.

In terms of low environmental and social impacts, the tannage step is a key driver in determining the fundamental sustainability of a final leather article. A modern tanning chemical must ideally be manufactured of renewable resources that should be of biogenic origin. If a waste biogenic chemical can be sourced, converted into a chemical ideal for tannage and then used with easy application, on multiple leather article types, then it will be of great interest to the international tanning community.

Further, leather manufacturing processes generate trimming and other processing by-products that must be sustainably and profitably managed. If the final leather, the by-products, (and the leather articles) can be part of a circular bioeconomy, then the fundamental chemical building blocks can be recycled back into natural elemental cycles.

This paper will outline a triose chemistry that will introduce new tannage capabilities that will allow even further green chemistry into the global leather industry.

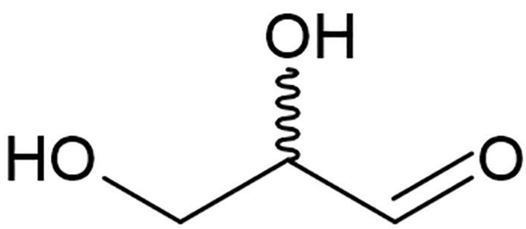

Figure 1. Chemical structure of triose.

Which sugars?

Sugars occur as monomers, dimers or as larger polymers. A curious feature of sugars is that they can occur in a system as a ringed structure or as a simple chain. The sugar structure often flips between the forms or can preferentially form one type depending on the surrounding conditions.

The monomers of sugars range from simple three-carbon structures up to six-carbon structures and are commonly found in food. Three-carbon sugars are found in natural systems and are called trioses, see Figure 1. Bacteria and fungi have evolved to eat all sugars and will actively seek them as a food source. The human body is also very capable of using sugars of all types – especially in a balanced diet.

Chemical reaction

Sugars react with proteins in a process called glycation. The amino group on proteins are nucleophiles and they easily react with sugars at one of their carbonyl groups, see Figure 2. The amino group interaction is of interest to the tanner, as the tanner can exploit the reaction to cause changes to the leather collagen.

The chemical reaction between the amino group and the carbonyl can depend on the conditions and the type of sugar. The size of the sugar also plays a role in the penetration and reactivity of the tanning agent with the pelt. Previous tannages that have attempted to use reactive starches, or modified cellulose have had limited success as the size of the molecules have meant they have not penetrated well into the hide and have left untanned layers (Ozkan and Ozgunay, 2016).

Other researchers examined starch, graft polymers of polysaccharides, and modified carbohydrates to tan collagen. Starch-polyacrylamides and other vinyl derivatives were examined by Liu et al. (2009) and Lu et al. (2005) showing that highly biodegradable polymers can result. Xiaosheng et al. (2012), Zhen and Ma (2000) extended these applications into leathermaking, opening the way for the mindset for the advanced use of polysaccharides in leather. This article introduces a chemical opportunity to use smaller compounds for effective wet-white tanning.

In the use of a small molecule like the triose, the mildness of reaction and the ability to penetrate the pelt ensures that the collagen is modified slowly and evenly.

The chemical reactions between the triose and proteins are identical to the reactions seen in food – as trioses are commonly one of the sugars

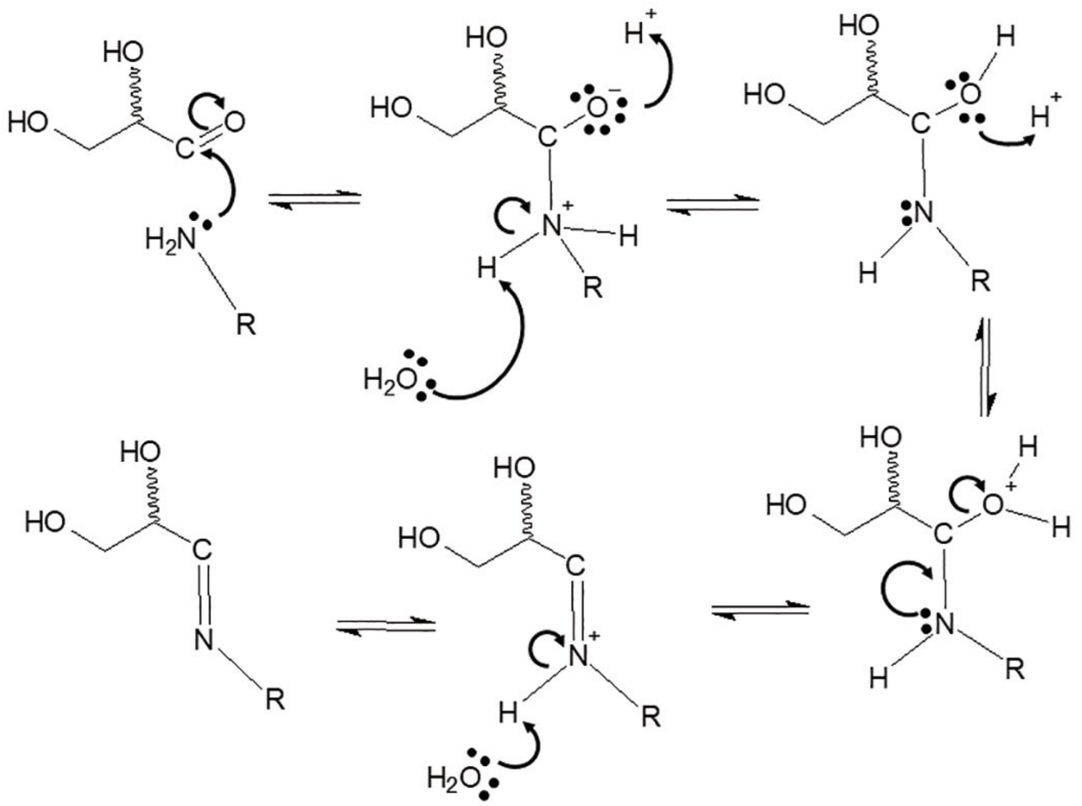

Figure 2. Nucleophilic attack on the tanning agent (ε-amino group targeting triose carbonyl).

that react with proteins during cooking. The umami taste in food is also associated with chemicals that have resulted from a sugar/protein reaction. Covington (2011) postulated that bog-body type reactions would be exploitable by tanners and, 11 years later, these natural reactions are now being introduced into leathermaking.

Manufacture science

Trioses occur naturally and are synthesized as part of the glycolysis cycle. While the main glucose reactions are taking place, the body is also using enzymes to catalyse the conversion of glycerol (a by-product of fat metabolism) into triose sugars, see Figure 3. Triose-3-phosphate and dihydroxyacetone phosphate are also parts of the glycolysis reactions.

Manufacturers of a triose take biogenic glycerol, a major waste output of vegetable oil industry, and convert it into a renewable and scalable ingredient for tanning. A high biogenic: fossil carbon content is highly desired by brands, product manufacturers and tanners, who opt for 100% biogenic chemicals. The triose from a waste vegetable oil source will pass through ASTM D-6866 (ISO 16620-2) with a fully biogenic nature – which is very useful to the tannage end-of-life credentials (ASTM, 2022; ISO, 2019).

The conversion of vegetable oils in processing plants around the world, yields large sources of waste glycerol, allowing the manufacture of triose close to all tanneries – significantly reducing carbon miles to the tannery.

The process, as can be seen in Figure 3, is very simple and requires little energy (the process generates its own heat) - resulting in what preliminary results show to be a small carbon footprint (low energy, low carbon miles), and being a waste, means they get zero allocation from upstream process impacts. The short process conversion of glycerol to triose means the outputs of the reaction are few, with the oxidation of a hydroxyl group into a carbonyl, leaving virtually no residue.

Process science

Processing developments were examined in the research and development laboratory and at full tannery scale. Triose does not appear on any current manufacturing restricted substance lists and is not flagged for action in any global rolling action plans (chemicals for scrutiny). The tanning agent reacts with the leather substrate and produces a tanning float with little active substance as a residue. The residues that

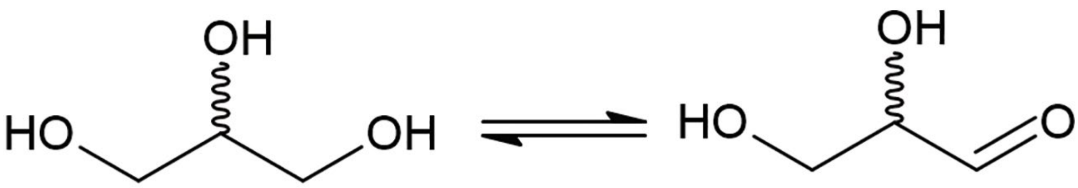

Figure 3. Chemical manufacture of triose.

The advantage that many of the new generation tannages have over older tannages is that they produce a stable half tannage, but the collagen is not too heavily modified, hence making it easy for the bacteria to assimilate it.

remain, are the type of residues that biological effluent treatment plants readily degrade. Straganz et al. (2002) has shown that diketones can be easily degraded by bacteria that use it as a sole carbon source. Likewise, Wang et al. (2011) showed the viability of converting trioses into lactic acid for use in biodegradable plastics. As a monomer or a polymer, triose can easily be used as a carbon source for fermenting bacteria.

Trimmings, shavings and tanned splits are easily disposed of through composting or anaerobic digestion. Depending on the post-tannage chemistry, the same solid waste management versatility is also possible. Sampathkumar (2001) showed that the composting of wastes and sludge is dependent on the carbon to nitrogen ratio of the incoming waste streams. Triose tanned leather has a carbon to nitrogen content that is within the 20:1 to 40:1 range required for effective breakdown. Triose as a biogenic short carbon chain means that the carbon content of protein is not significantly raised.

The chemistry of the triose makes its use quite unique. The chromium-free tannage means that the types of articles using first-generation tanning agents could be limited due to fundamental restrictions associated with the tannage. Dye uptake by the triose is unlike other chromium-free leathers – uptake is high, colour shades (without additional fixatives) are deep, and rubfastness test results are excellent. Bienkiewicz (1983) outlines the dyeing kinetics and draws attention to the dipole-dipole interactions or hydrogen bonding that can occur between the polar, hydroxyl-rich sidechains (that results from the reaction between the triose and the collagen) and many of the leather dyes.

Triose tannage also has multiple entry points, which is good as the versatility of the starting point is important to a factory. Tanners can use material entering a tanning process as: after bating, after pickling or as pickled material shipped to another tannery and the tanning then started there. Starting a process from any three of those positions can be difficult with other tannages due to chemistry limitations – the triose can be started from multiple points because the reactivity of the tanning agent is controlled by its process conditions – the tanning bath is simply adjusted to suit the starting condition.

Figure 4. Photo of disintegration of triose tanned leather on day 11 of the ISO 20200 test.

Biodegradability science

The tannage from a triose tanning agent will raise the collagen shrinkage temperature to over 70°C. It achieves this through the reaction with the amino acid side chains of the collagen, such as modified triazine, dyes and fatliquors. The reaction is very different to chromium which links to the acid side chains, or vegetable tannins which link to the peptide group of collagens. The size and nature of the triose tannage is also very important, it does not polymerise (to any great extent) and therefore does not form bulky structures within the collagen – keeping the options open to make soft, firm, tight-grained and milled grain articles. It also appears to leave many amino groups unreacted to allow dye and fatliquor reactions.

The leather is thus susceptible to peptide bond attack during biodegradation. Collagenase or nonspecific proteases attack the vulnerable peptide bonds. Short dipeptides or amino acids with a glycated side chain are assimilated by the bacteria or fungi with relative ease resulting in a high degree of ultimate biodegradation. Tests on tanned leathers showed a 28-day ISO 20136 biodegradability of 69% and materials had fully disintegrated (in ISO 20200) in under 20 days, see Figure 4 (ISO, 2015; ISO 2020). The advantage that many of the new generation tannages have over older tannages is that they produce a stable half tannage, but the collagen is not too heavily modified, hence making it easy for the bacteria to assimilate it.

Figure 5. Plant ecotoxicity studies of triose showing vibrant top growth.

The triose half tannages produce leather that performs with no problems during its working life (low moisture, low bacterial/fungal load and a pH of 4) where the properties of post tannage and tannage dictate the performance properties. In the leather product's end-of-life, the leather can end up in a composting environment (high moisture, high bacterial/ fungal load and a pH greater than 7). In the end-of-life, the triose-tanned leathers are rapidly broken down by the environment through the action of abiotic and biotic components.

As aerobic composting and biodegradation convert carbon-based materials into CO_2, water, and biomass, there is some concern over what form of carbon is released as a gas. A fossil carbon-based plastic if it can decompose, will produce fossil carbon, as a gas. Triose tannage produces 100% biogenic CO_2 allowing a perfect cycling of natural carbon. A tanner that then carefully chooses biogenic post tanning and finishing chemistry will guarantee the circular bioeconomic properties of these leathers.

The high biodegradability of the material means that carbon in the leather is largely bio-assimilated and respired, shown by the high absolute and relative biodegradability (69% absolute and 77% relative biodegradability). The speed and extent of disintegration, coupled with a high biodegradability, is boosted by the fact that the leather compost poses no soil toxicity issues. Figure 5 shows the plant response of the triose tannage. The plants are within 12% of the control plants suggesting that the plants showed little concern for soils that contained the triose leather composts. A tannery or product manufacturer could easily compost their cutting floor and leather scraps to produce a compost that is completely soil friendly.

Conclusions

Tanning trials using a triose as the main tanning agent have been performed on multiple scales in multiple geographic locations with great success. This scientific paper has highlighted the chemistry and science associated with a second-generation chromium-free tanning agent. The sustainability of the triose can be summarised as follows:

- Renewable ingredient from non-food waste stream that has a significantly low environmental chemical production footprint. The production does not use intermediates, solvents, and low energy.
- The triose chemistry is 100% biogenic carbon.
- The leathers produced have versatile starting and exit points and have performance capabilities that will meet most specifications.
- The biodegradability and compost disintegration capabilities produce leather composts that have no ecotoxicity issues and rapid breakdown times. The off gasses from disintegration of the tannage will be 100% biogenic due to the nature of the collagen and the tanning agent.

References

Bienkiewicz, K. (1983) Physical chemistry of leather making. Robert E. Krieger Publishing Company, Florida, USA. p. 454-455.

Covington, A. (2011) Tanning chemistry – the science of leather. RSC Publishing, Cambridge, UK. p. 455-456.

Straganz, G. D., Brecker, L., Weber, H. J., Steiner, W., Ribbons, D.W. (2002) A novel β-diketone-cleaving enzyme from Acinetobacter johnsonii: acetylacetone 2,3-oxygenase. Biochem. Biophys. Res. Commun. 297:232–6.

Ozkan, C. K. and Ozgunay, H. (2016) Usage of starch in leather making. Proceedings of the 6th International Conference on Advanced materials and Systems (ICAMS). (DOI:10.24264/icams-2016.IV.10)

Sampathkumar, S. (2001) Composting of tannery sludge. A United Nations Industrial Development Organisation (UNIDO) Regional Programme for pollution control in the South-East Asia. US/RAS/92/120. UNIDO, Vienna, Austria. p. 1-57.

Kreuder, A. D., House-Knight, T., Whitford, J., Ponnusamy, E., Miller, P., Jesse, N., Rodenborn, Sayag, S., Gebel, M., Aped, I., Sharfstein, I., Manaster, E., Ergaz, I., Harris, A., and Grice, L. N. (2017) A method for assessing greener alternatives between chemical products following the 12 principles of green chemistry. ACS Sustainable Chem. Eng. 5: 2927-2935.

ISO (2019) Plastics – biobased content – Part 2: determination of biobased carbon content (ISO 16620-2: 2019). International Standards Organisation, Geneva, Switzerland.

ISO (2020) Leather – determination of degradability by micro-organisms (ISO 20136: 2020). International Standards Organisation, Geneva, Switzerland.

ISO (2015) Plastics – determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test (ISO 20200: 2015). International Standards Organisation, Geneva, Switzerland.

ASTM (2022) Standard test methods for determining the biobased content of solid, liquid, and gaseous samples using radiocarbon analysis (ASTM D-6866-22), ASTM International, West Conshohocken, PA, US.

Liu, G, Lv, S., and Ma, Y. (2009) Synthesis and leather-tanning properties of a starch-polyacrylamide graft copolymer by means of HRP, (available online: http://www.aaqtic.org.ar/congresos/china2009/ download/2-4/2-122.pdf (accessed 7 September 2022)

Lu, S., Liang, G., Ren, H., Wang, J., and Yang, Q. (2005) Synthesis and application of graft copolymer retannage of degraded starch and vinyl monomers. J. Soc. Leath. Tech.Ch. 89: 63-66.

Xiaosheng, D., Hui, C., Rui, D. and Zhihua, S. (2012) Preparation and application of denatured starches. J. Soc. Leath. Tech. Ch. 96: 189-194.

Zhen, J. and Ma, J. (2000) Modification of starch and its application in leather making. J. Soc. Leath. Tech.Ch. 86: 93-95.