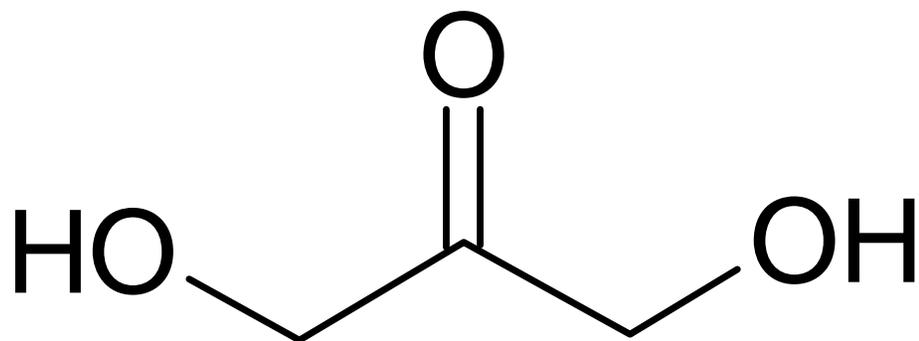


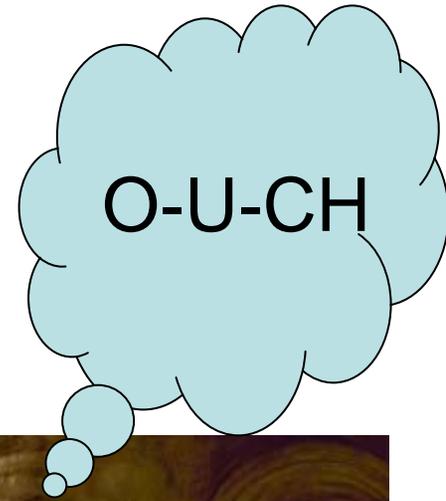
# Self-Tanners



Dihydroxyacetone

# Background

- *The tanned look*: The prevailing cultural esthetic among fair-skinned people in many countries is to have tanned skin
  - Darkening of preformed melanin, accelerated formation of new melanin, and retention of melanin in the epidermis as a result of retardation of keratinization
- Exposure to sunlight carries risks

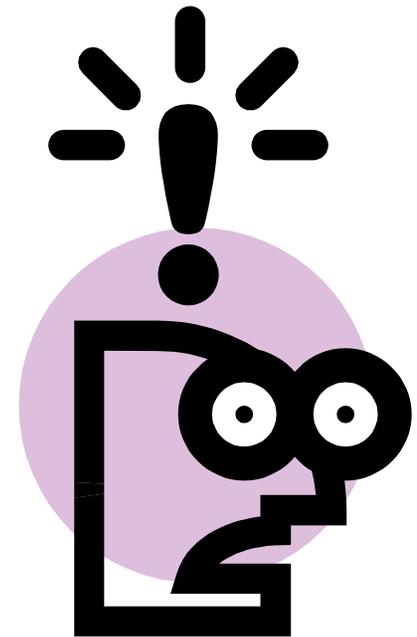


# Discovery of DHA's Browning Effect

- Serendipitous discovery in mid-1950s
- Children's Hospital at the University of Cincinnati
- Dr. Eva Wittgenstein – studying the effect of large oral doses of DHA in children with glycogen storage disease
- Brown spots on their skin after vomiting the sweet concentrated material

# In the beginning...

- Wittgenstien, curious, prepared aqueous solutions of varying concentrations of DHA and was able to reproduce the pigmentation on her own skin
- Kurz, 1994 Review



# Acceptability of DHA's Cosmetic Effect

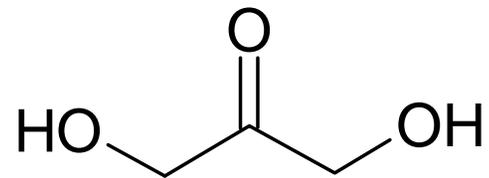
- More natural-appearing brown or golden hues are produced as opposed to more off-color oranges observed with older formulations
- Purer supplies of DHA, refining of DHA-containing vehicles to allow better penetration, recognition of the need for a lower pH, and more rapid color change with a lower concentration of DHA

# Structure and Chemistry

- Simple three-carbon “sugar”
- Nontoxic
- An intermediate in carbohydrate metabolism in higher plants and animals
- More rapidly metabolized than glucose in the body
- Prepared by fermentation of glycerol using *Gluconobacter oxydans* (see handout)

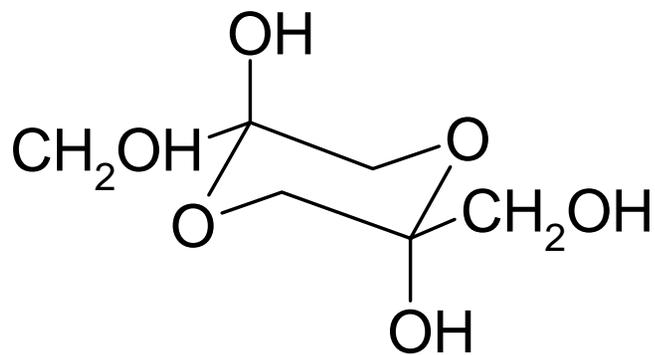
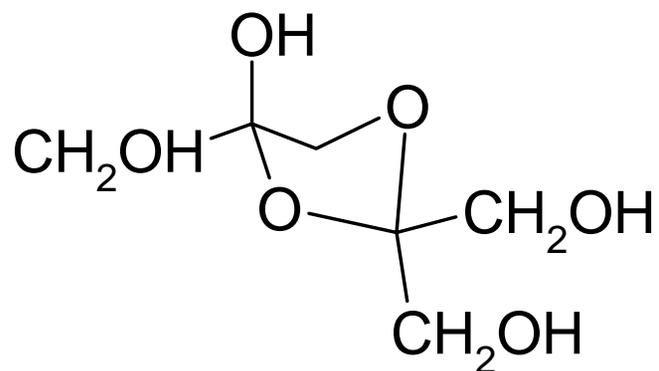
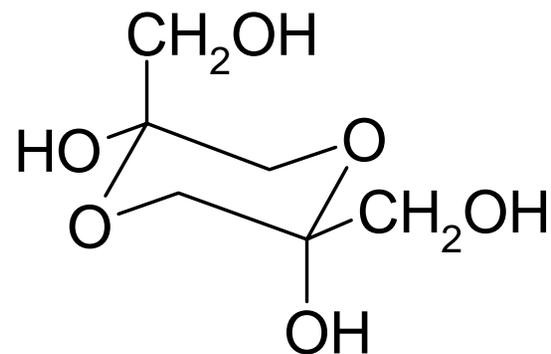
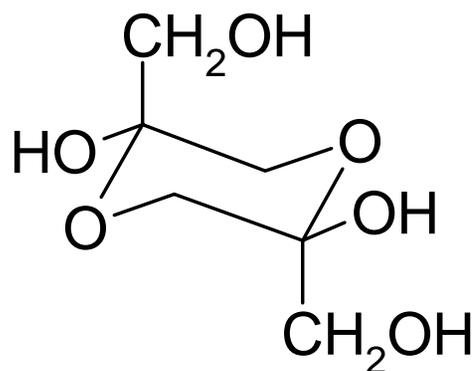
# DHA Chemistry

- Slightly hygroscopic material
- Crystalline form, DHA is a mixture of one monomer and four dimers
- → Intermolecular hemiketal formation
- Dimeric DHA in the form of a cyclic ketal and trimeric DHA in the form of a bicyclic ketal have also been reported



Dihydroxyacetone

monomer



# DHA Chemistry

- Dissolving or heating the dimeric form produces the monomeric form of DHA
- In aqueous solution, DHA occurs as a monomer that can gradually tautomerize into glyceraldehyde
- The equilibrium shifts to DHA at acidic pH or to glyceraldehyde at alkaline pH

# FTIR Study

- Interconversion of DHA and glyceraldehyde was studied in different solvents and temperatures by FTIR spectroscopy
- Dissolution in water and increasing temperatures caused the dissociation of the dimeric forms of both compounds into monomers and the subsequent inter-conversion of DHA and glyceraldehyde

# FTIR Study

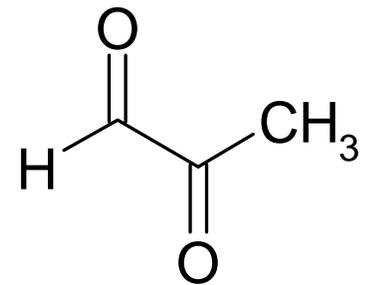
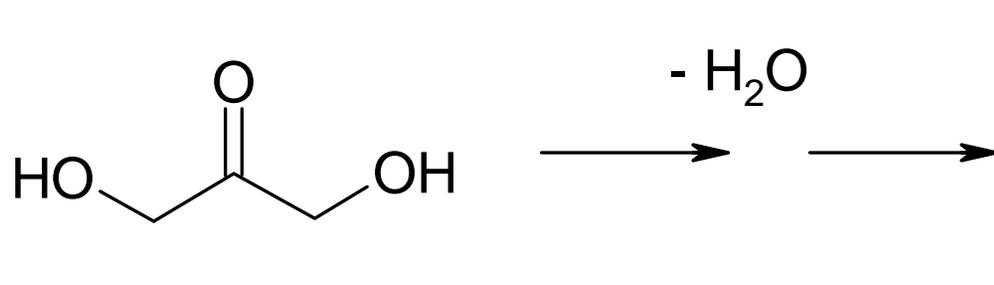
- A five-membered ring form was predominant in aqueous solutions of the dissociated glyceraldehyde dimer, whereas a six-membered ring form was preferred in aqueous solutions of dissociated DHA dimer

# FTIR Study

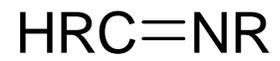
- DHA predominantly converted to the six-membered H-bonded conformation of glyceraldehyde when dissolved in water
- → Attributed to the preferential formation of the trans- or E-enediol as an intermediate
- Temperature-dependent spectra have indicated that increasing the temperature favored the formation of glyceraldehyde in the aqueous equilibrium mixtures of dimeric glyceraldehyde and DHA

# Chemistry

- Stratum Corneum site of action
- Resulting products when applied to skin are cyclic and linear polymers having yellow or brown color
- Only the monomeric form undergoes the Maillard reaction that leads to tanning



Pyruvaldehyde



Imine



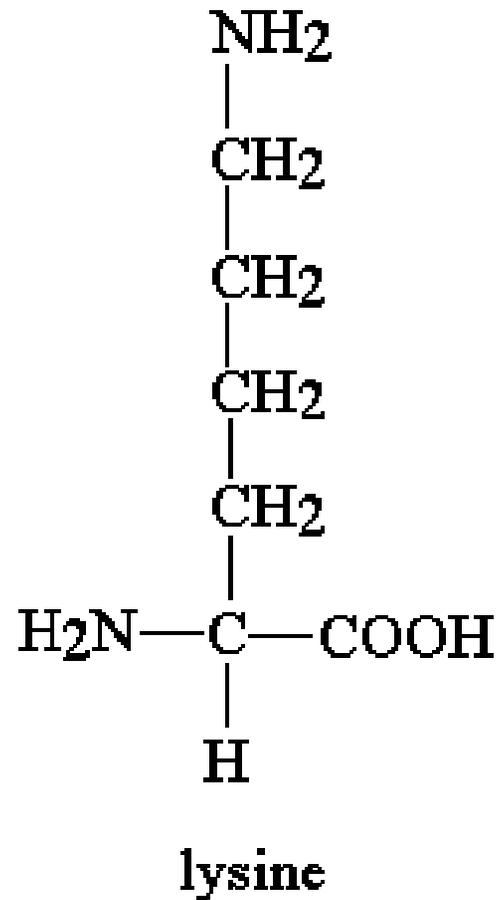
Melanoidins  
Yellow or Brown color

# Louis-Camille Maillard

- 1912
- Amino acids interact with sugars to create brown or golden brown compounds
- Maillard reaction defined currently as the reaction of the amino group of amino acids, peptides, or proteins with the glycosidic hydroxyl group of sugars, forming brown products referred to as melanoidins

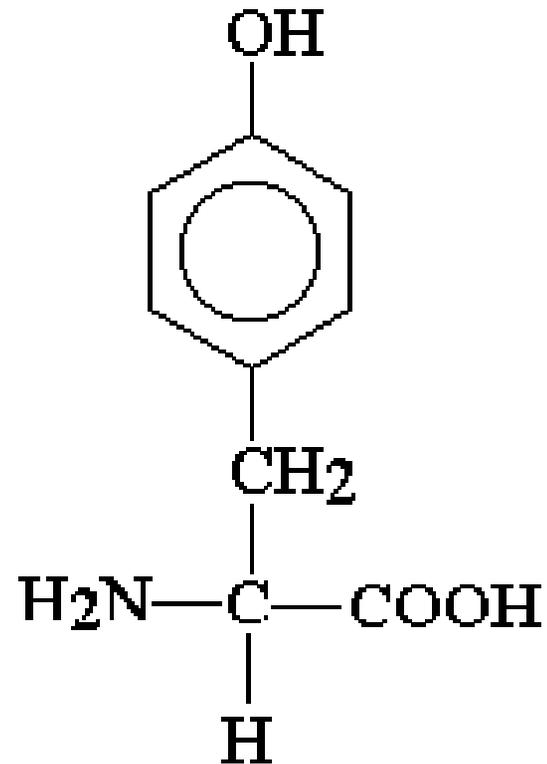
# Melanoidins

- Polymeric
- Linked by lysine side-chains to the proteins of the SC
- Different than formation of melanin, some properties are similar (absorption spectra)



# Melanoidins

- Melanins consist of aromatic amino acids  
→ tyrosine
- Melanoidines, consist mainly of an aliphatic moiety with very few aromatic functions in the side chains



tyrosine

# SPF of DHA



- Treatment with a 3% DHA solution overnight provides SPF of at least 3 in the UVB region
- SPF of 10 in UVA region on skin treated with a 15% solution of DHA

# Formula Types



- Wash-offs and Wear-offs
- Wash-offs are cosmetic tanning products in cream or gel formulas, without DHA, that give the appearance of a tan, but wash-off in the shower at the end of the day

# Formula Types

- Wear-off formulations containing DHA are the true self-tanning products
- Available in creams, lotions, milks, gels, or sprays
- Develop a tan in a matter of hours and wear off in a matter of days
- O/W emulsions

# Formulation Guidelines

- Normally 4-8% (wt/wt)
- Store in a cool temperature to prevent destabilization (DHA not stable above 40 °C)
- Use skins own buffers to achieve optimal pH of 5-6 for Maillard reaction to occur (original formulation pH 3-4)

# Formulation Guidelines

- Selection ingredients
- Emulsifiers – nonionic over ionic to improve stability
- Emollients – all compatible with DHA
- Thickeners – hydroxyethylcellulose, methycellulose, and silica
- Moisturizers – water-free systems not useful (propylene glycol 20% in w/w formulation)

# Formulation Guidelines

- Compounds containing nitrogen – avoid
- Fragrance oils – kept to a minimum (degradation)
- Tinting – combining with other dyes to enhance coloration (avoid iron oxides)

# Conclusion

- DHA used for more than 30 years
- Safe alternative
- Formulate with proper pH and storage conditions
- Provides some photo-protection
- DHA used in the treatment of psoriasis