

Chapter 2

Food

2.1 Test Your Cranberry Pie: Vitamin C and Benzoates

Food dyes, flavor enhancers and preservatives receive the brunt of criticism in the family of food additives. Preservatives do not really deserve this bad reputation as they replaced older, traditional techniques (smoking, curing) that are actually not without dangers.

Benzoic acid and its salts are well known preservatives (E210-E213), their action depending on the inhibition of an enzyme in the citric acid cycle of microorganisms. These preservatives only work well under highly acidic conditions. They are effective against yeasts, mold, and microorganisms producing aflatoxins, but only partially against bacteria. Benzoic acid is often used in combination with potassium sorbate as this mixture is more effective than their individual constituents. Benzoic acid is not effective against oxidation or enzymatic rotting so it is combined with sulfur dioxide in treating fruits. Some people are allergic to benzoic acid; about 4 % of people suffering from asthma develop shortness of breath because of it. Many fruits (blueberries, dry plums, apples) contain benzoic acid in concentrations that exceed the limits set by authorities (Fig. 2.1). These fruits contain vitamin C as well. There is no known human risk of consuming less than 500 mg of benzoic acid daily because it does not accumulate in the body, and it is excreted quite rapidly with urination. Preserved food usually contains 0.05–0.1 % benzoic acid. It is one of the preservatives with the longest known histories, often used in canned fruit, pickle and soft drinks.

Vitamin C (L-ascorbic acid) is probably the best known vitamin, and the daily amount necessary for humans is between 50 and 100 mg depending on age (150 mg for breastfeeding mothers). It is present in many natural sources and is also a common synthetic product.

Suspicion about a possible health risk from the simultaneous consumption of benzoic and ascorbic acid arose in the 1990's in connection with soft drinks. The British daily *The Independent* picked up the line again in 2007 when it claimed that benzoic and sorbic acids may harm mitochondria, the energy producing center of cells. These claims were based on yeast cell experiments carried out by biochemist

Fig. 2.1 Different species of cranberry, especially *Vaccinium macrocarpon* (aka large cranberry, American cranberry, bearberry, shown) is rich in both benzoic and ascorbic acids. (Copyright-free Wikipedia picture)



Peter W. Piper (the name is real!) in the 1990s. There is no unambiguous connection between yeast cells and human cells. For human cells, there is no evidence of any harm done to mitochondria.

Benzoic acid and ascorbic acid are of about the same acid strength. Benzoic acid can be formed in equilibrium between ascorbic acid and benzoic acid salts. Benzoic acid can decompose to give carcinogenic benzene and carbon dioxide under *certain conditions* (Fig. 2.2). How much benzene could be formed in this reaction? There is typically 150 mg of benzoic acid in a liter of soft drink, whereas there are no legal limits for ascorbic acid. The German Federal Institute for Risk Assessment (BfR, *Bundesinstitut für Risikobewertung*) published a recommendation in 2005, which stated that this reaction depends on many external conditions, such as the concentration of the substances involved, the presence of some metal ions (copper and iron), temperature, time, and level of ultraviolet radiation. More importantly, the simultaneous presence of ascorbic acid and benzoates was not obviously connected to the formation of benzene. The amount of benzene formed increased at first when ascorbic acid was added in model experiments, but increasing the amount of vitamin C further actually slowed the reaction down. This is similar to the effect of other antioxidants (e.g. mannitol used as a sweetener or uric acid in urine). The amounts, however, were very low: the concentration remained in the **ppb** or **ppt** range. In the experiments under extreme conditions (45 °C, 20 h of ultraviolet irradiation), the concentration of benzene reached 300 ppb, but this value was much lower under physiological conditions (37 °C, pH 7.4, no ultraviolet irradiation). When experiments were done with food containing both benzoic and ascorbic acids, benzene was formed in concentrations between 0.01 and 38 ppb, but typically below 1 ppb. Just to put this into context: the World Health Organization (WHO) recommends and upper limit of 10 ppb for benzene in drinking water.

Irrational fears might result in irrational precaution. The US Food and Drug Administration published data on benzoic acid and ascorbic acid in 2007. Although no connection was established between the amount of these substances and the concentration of benzene, recommendations for the reduction in benzoate use were made for manufacturers in a few cases, which were duly followed. The British supermarket chain Sainsbury's removed sodium benzoate from 120 products because of consumer concerns.

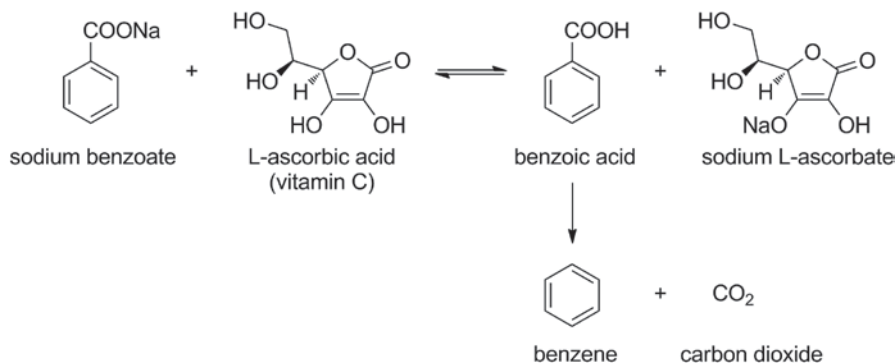


Fig. 2.2 Reaction of sodium benzoate and L-ascorbic acid (vitamin C) in a model experiment. (Authors' own work)

The majority of human exposure to benzene comes not from food but air (smoke and car exhaust). The concentration of benzene inside a car might be as high as 20 ppb, at the gas pump it may even be 1000 ppb. In the US, the average benzene concentration in the air is 2–10 ppb. Typically, 0.01 ppb is detected even in the air above the Pacific Ocean. Smoking a single cigarette produces about 500 μg of benzene, which of course makes its way to exhaled air. The British Food Standards Agency estimated that consuming about 20 l of soft drinks a day poses the same benzene exposure as other environmental sources.

The reader may rightly feel that this story is getting complicated. Or is it? In everyday life, people continuously face risks when choices are made on food, transportation, family care and so on. Society is aware of some potential hazards (e.g. transportation), but is less aware of others (food additives etc.). Naturally, there is more fear about the latter. People choose between trying to understand risks or continuing to live in irrational fear. The reader may certainly make his or her own choice.

2.2 Food Dyes: The Good, the Bad and the Ugly

Food dyes, especially the artificial ones (\rightarrow 1.4), are probably the most controversial group of food additives. The proven risk of allergic human reactions to these substances is seldom larger than for other substances, but their unnecessary use should no doubt be avoided: blue triple sec, green ketchup, or soft drinks containing 8–10% of orange, cherry or other fruit are made more attractive by dyes. However, natural substances may also be problematic, and some of them are banned today.

From a chemical point of view, most synthetic dyes are azo dyes, some of them from the triphenylmethane dye family, whereas there are a few whose structure does not belong to the two large, predominant groups. Why are synthetic dyes advantageous? Primarily, because synthetic dyes are more stable than natural dyes. Most

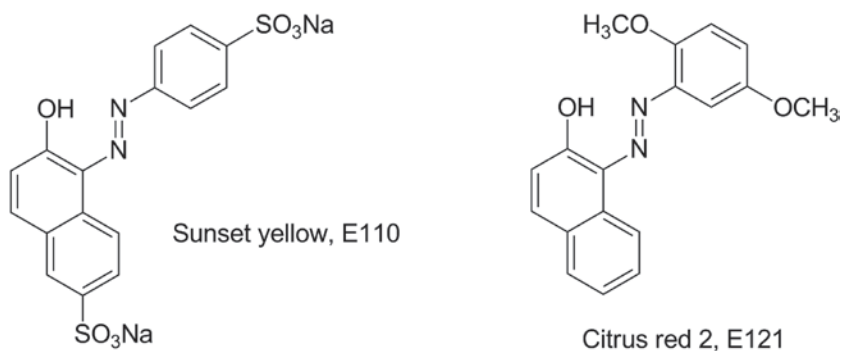


Fig. 2.3 The chemical structures of two azo dyes. (Authors' own work)

natural dyes cannot tolerate heat treatment, the oxygen in air or changes in pH. Nature did not develop them for human kitchen use. The juice of red cabbage turns an ugly grey upon pH change.

2.2.1 Azo Dyes

The largest group of synthetic dyes is called azo dyes. The name refers to the azo group, which is two nitrogen atoms connected by a double bond: $R-N=N-R'$. R and R' stand for various aromatic ring structures, which influence the acidity, alkalinity, and color, among others. The azo group maintains a continuous conjugation between the π electron systems of the aromatic rings, and this causes the vivid color of these compounds. Two examples are shown in Fig. 2.3. Sunset yellow (E110) is still in use, whereas Citrus red 2 (E121) has already been phased out.

An older name of this group is aniline dyes, which refers to the compound aniline, the simplest aromatic amine. Aniline is substance that has had a very high, but largely unrecognized impact on modern society. The names of two huge multinational chemical companies founded in Germany in the 1860s, BASF (Badische Anilin- und Soda-Fabrik) and AGFA (Aktiengesellschaft für Anilinfabrikation) are a testament to the true importance of this unsung chemical hero. Azo dyes were discovered in the middle of the nineteenth century and generated a major development in the organic chemical industry. Tens of thousands of different dyes were prepared mostly to color textile, leather or fur, but inks, paper and wall paints also benefitted greatly. One of the first commercial products introduced in the 1870s was chrysoidine, used for making yellow wool or silk. The nineteenth century dye industry was also the cradle of the later developing pharmaceutical industry. One of the first true antibacterial drugs, sulfonamide *Prontosil rubrum* (Domagk, 1935) was in fact an azo dye. Strict health and environmental criteria has only left 12–13 azo dyes for use in the modern age as food additives.

Azo dyes today are considered harmless at the concentration level of their typical Usage. Although azo dyes do not occur in nature, human metabolism can cope with

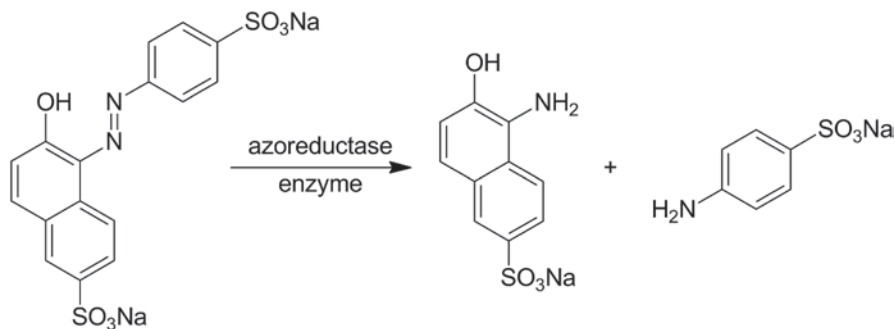


Fig. 2.4 The primary reductive transformation of an azo dye into the two constituent amines. (Authors' own work)

them easily. There are azoreductase enzymes in the body that reduces the azo group to produce two compounds with amino groups (Fig. 2.4).

The toxicity or the proven carcinogenic nature of some azo dyes is primarily caused by these amines or their further decomposition products. These dyes (e.g. Butter yellow or Citrus red) have been phased out. There are heated debates about the possible allergies caused by these compounds. All substances (medicines, cosmetics, even staple food included) may have this effect, typically at concentration levels of 100 or 10 **ppm**. The use of the azo dye tartrazine, which is thought to be more problematic because of allergies, is not recommended in infant formula. A 2007 report from Southampton University has received a great deal of publicity as it questioned the safety of azo food dyes in 3–9 year old children on the grounds that they cause hyperactivity. However, several scientific experts voiced serious concerns about the methodology of this study. The first counterpoint was that the reasons for selecting the dyes and their particular mixtures were unclear. In addition, measuring hyperactivity in children is by no means exact, and the statistical evaluation of the results was not rigorous.

2.2.2 Triphenylmethane Dyes

Triphenylmethane dyes are characterized by a central carbon atom which is bonded to three aromatic systems, most often phenyl rings (Fig. 2.5). There are additional basic or acidic functional groups on these rings, which change the distribution of conjugated electrons to form quinoidal structures, which in turn results in a color change. A number of these compounds are also used as acid-base indicators in chemical laboratories. The archetype of triphenylmethane dyes, magenta colored fuchsine, was accidentally discovered and purposefully patented by Frenchman François-Emmanuel Verguin in 1859 during experiments aimed at the oxidation of aniline.

It has long been known that triphenylmethane dyes with aromatic rings bearing basic, mostly dialkylamino substituents, have significant antibacterial effects. They

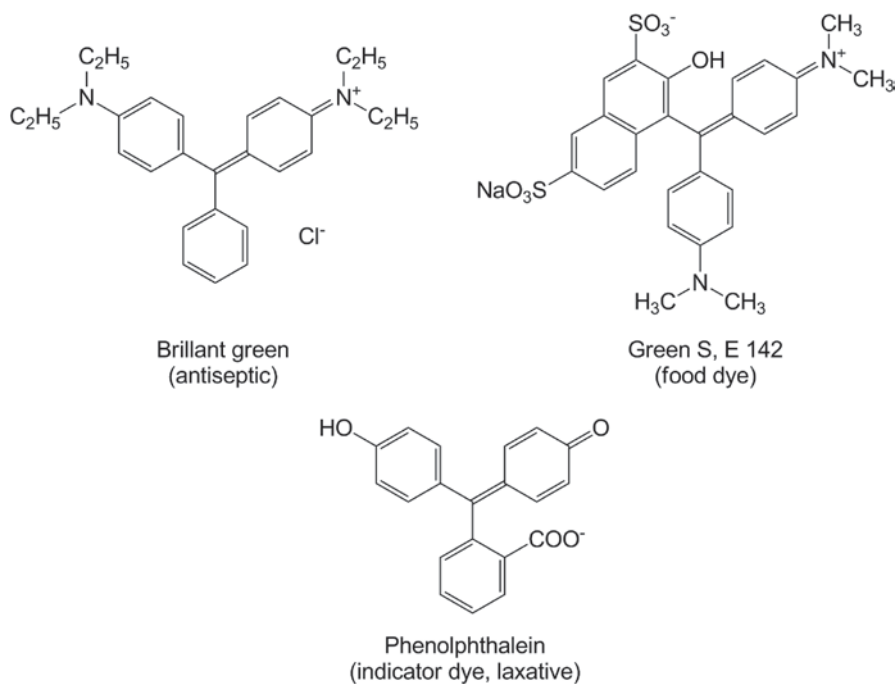


Fig. 2.5 Examples of triphenylmethane dyes. (Authors' own work)

are also effective against fungal skin infections. Castellani's paint, which is a red solution of carbol (phenol) fuchsin, or crystal violet, are still used occasionally, but this practice is presently discouraged in developed countries. There are better and longer-lasting dyes today, such as Green S (Fig. 2.5). Significant harmful effects of triphenylmethane dyes have not been detected thus far. They may cause local tissue death when injected in concentrated solution, but this is not a reasonable health risk. Their non-toxic nature is nicely illustrated by the fact that some members of this group of dyes have been used as a laxative for more than a century. For this purpose, phenolphthalein is still one of the most reliable and safest alternatives.

2.3 The Organic Vegetable Hype

2.3.1 *A Question for Eternity: Natural or Artificial Fertilizers?*

This question is not that difficult to answer: avoiding too much of a good thing is an excellent guideline. Neither plants nor animals enjoy an overabundance of nutrients. Obesity and the resulting health problems (diabetes, cardiovascular diseases,

and joint aches) have received copious media attention lately. Ironically, parents of overweight children are often quite proud of their offspring. Sagging and loose tissues are not only characteristic of obese people, they are found in 'overfed' plants as well. The problem is not the synthetic fertilizer, as it contains the same nutrients as the natural variety. No plant can utilize the organic components of manure directly; they need to wait for soil bacteria to change them into inorganic nitrate, phosphate and other salts. The difference lies in the speed of the chemical and biological reactions. Soil bacteria work slowly, so there is never a surplus of nitrate available and, therefore, plants cannot consume excess nitrates.

The chemical process to make saltpeter is identical to the one used in the Middle Ages: manure was mixed with straw and ash in compost piles and left alone for as long as a year with an occasional sprinkling of urine, which contains nitrogen. Bacteria slowly turned organic nitrogen into nitrate, the salts of which crystallized on the surface of the compost piles very much like soda-salts do in dry flatlands. At the end of the process, the saltpeter was collected and purified.

In the case of artificial fertilizers, there is no such natural speed-limitation; farmers can distribute as much as they wish on their lands. Excess fertilizers can cause overstimulation of growth and while the farmers make a clear profit from the increased crop, quality usually suffers. The results are similar to a person who eats constantly. The wisest course of action is to use fertilizers only to replenish nutrients in soil without creating an overabundance of them.

2.3.2 *Nitrates in Vegetables*

Potassium nitrate (KNO_3 , saltpeter) and sodium nitrate (NaNO_3 , Chilean salt-peter) have been known for a long time, and used in explosives, fertilizers and preservatives. They also have a long history for curing meat products (\rightarrow 2.8). Nitrates themselves are not toxic. However, nitrites, which often form from nitrates, compete in an entirely different league. On average, about 5 % of nitrates are transformed to nitrites in the bowels. Poor quality drinking water may also contain nitrates and this may be especially harmful for infants. It is not particularly beneficial for adults, either. Nitrite reacts with the oxygen-carrying molecule hemoglobin in blood: it oxidizes iron(II) in hemoglobin into iron(III). The resulting compound is called methemoglobin, since it is unable to carry oxygen, the body begins choking. Sometimes this appalling phenomenon is called blue-baby syndrome.

It seems much less publicized that certain vegetables are also significant sources of nitrates in the human diet. Serious research in this field began only a few years ago. Spinach is a prime suspect as its nitrate content may vary widely from 700 to 4000 mg/kg. Is it not ironic that spinach could actually be harmful for children? (\rightarrow 2.11) Whatever Popeye might say, children might have more common sense than their parents do. Table 2.1 present the nitrate contents of a few vegetables.

Table 2.1 Nitrate contents of some vegetables

Nitrate content (mg/kg)	Plant
Very high (>2500)	Beetroot, chard, radish, lettuce, spinach, chervil, celery, cress, salad rocket
High (1000–2500)	Fennel, endive, kohlrabi, Chinese cabbage, parsley, leek, celery root
Average (500–1000)	Dill, cabbage, Savoy cabbage, parsnip
Low (200–500)	Broccoli, chicory, cauliflower, turnip, squash, cucumber
Very low (<200)	Artichoke, bean, pea, potato, sweet potato, garlic, mushroom, watermelon, onion, eggplant, green pepper, tomato, melon, asparagus

The nitrate content of a vegetable depends on the season, and even upon the time of day, the quality of the soil, and the use of fertilizers. Boiling dissolves about 70–75 % of the nitrate content, so it is advisable to discard the water used for boiling after the first 2 min. The highest value (9300 mg/kg) ever found was for salad rocket (rucola). In most European countries, laws have set a highest tolerable limit for the nitrate content of certain vegetables, e.g. they are in the range from 3000 to 4500 mg/kg for beetroot. The European Commission has set a legal limit of 200 mg/kg for the nitrate content of infant formula and food specifically intended for children. The WHO (World Health Organization) recommends an **allowable daily intake** (ADI) of 3.7 mg/kg of body weight/day, which translates into approximately 200 mg of nitrate for an adult. Consuming vegetables could well be a source of larger amounts. Even if this were the case, consuming large amounts of nitrates almost never happens on a regular basis, so it is not a cause for alarm.

To sum up: vegetables are often surprisingly rich in nitrates. If surplus fertilizers are used to increase the amount of nitrogen in soils, this may further exacerbate the problem. The solution is controversial: artificial fertilizers with reduced nitrogen content must be used, and natural fertilizers should also be applied with extra care. Needless to say, these precautions will decrease the yield of the vegetables.

2.3.3 *Are Organic Vegetables More Nutritious than Others?*

This question was carefully studied using **meta-analysis**, in which relevant experimental reports were re-evaluated using identical and very strict criteria. All scientific articles were excluded which did not describe reproducibility, analytical techniques or statistical methods in enough detail, or presented other reasons to doubt the reliability of the conclusions. Out of 318 studies reviewed, only 55 were deemed reliable. In these well-crafted studies, nitrogen, phosphorus, vitamin C, magnesium, calcium, potassium, zinc, copper and oil contents were compared during the analysis, and the bottom line was unambiguous: organically grown products were not significantly different in any way from non-organically grown. The nitrogen and phosphorus contents of organic vegetables were a few percent higher on average, but the scattering of measured data was much larger than this difference.

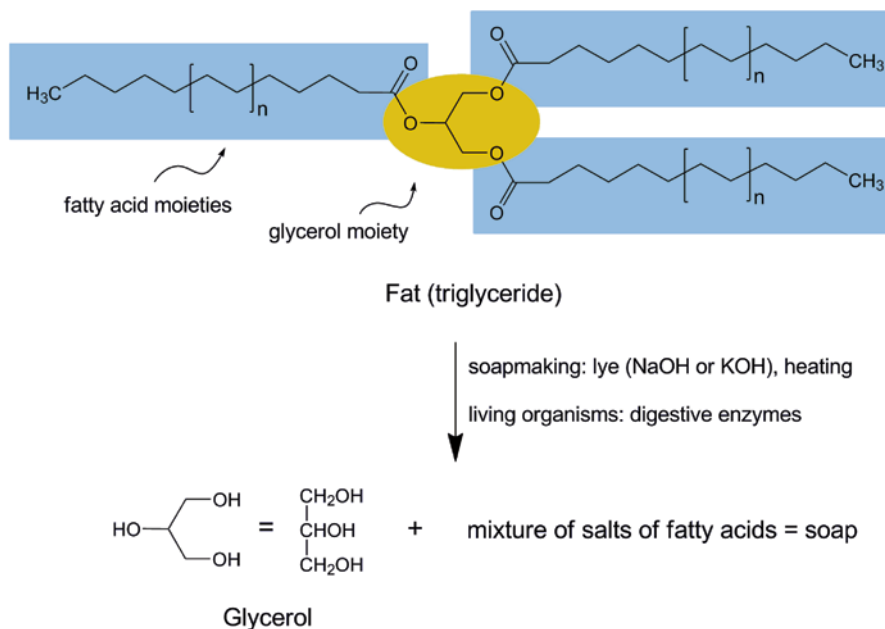


Fig. 2.6 Saponification of fats. (Authors' own work)

2.4 “You’re the One for Me, Fatty”: Concocted Fats

If we wish to start the story where it began, we should travel back in time to an Ancient Age when soap-making was first discovered. What is soap? If fats are boiled together with some aqueous alkali for a lengthy time, they will decompose. Chemically, they undergo alkaline hydrolysis (Fig. 2.6). Glycerol and soap are formed in this process: soap is a mixture of the sodium (or potassium) salt of different fatty acids. In an ever-popular novel, *The Mysterious Island* (*L'Île mystérieuse*), French science-fiction writer Jules Verne very nicely described that soap could be made even on a deserted island (the movies supposedly based on this novel seldom make a point of this part).

In a chemical sense, fats are triglycerides. This word may sound familiar to many as it is often used in the mass media. In blood tests, the level of triglycerides is often measured in addition to cholesterol. Triglycerides are compounds formed from glycerol (an alcohol with three hydroxyl groups) and fatty acids known as *esters*. They are fundamental substances in all living organisms, bacteria and humans alike.

This decomposition process is called saponification. It can be halted at intermediate stages to produce mono- and di-glycerides. These are compounds in which only one or two of the hydroxyl groups of glycerol form ester bonds (Fig. 2.7). In layman's terms: some of the fatty acids from the fat have been removed. In the human body, these intermediate compounds are formed when fats are broken down, and they are also formed when fat-containing ingredients are boiled for a long time

100 Chemical Myths

Misconceptions, Misunderstandings, Explanations

Kovács, L.; Csupor, D.; Lente, G.; Gunda, T.

2014, XXII, 396 p. 175 illus., 75 illus. in color., Hardcover

ISBN: 978-3-319-08418-3