Received: 13 June 2014 Accepted article published: 24 June 2014 Published online in Wiley Online Library: 18 July 2014

(wileyonlinelibrary.com) DOI 10.1002/jsfa.6796

Flavonoids protecting food and beverages against light

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Abstract

Flavonoids, which are ubiquitously present in the plant kingdom, preserve food and beverages at the parts per million level with minor perturbation of sensory impressions. Additionally, they are safe and possibly contribute positive health effects. Flavonoids should be further exploited for the protection of food and beverages against light-induced quality deterioration through: (1) direct absorption of photons as inner filters protecting sensitive food components; (2) deactivation of (triplet-)excited states of sensitisers like chlorophyll and riboflavin; (3) quenching of singlet oxygen from type II photosensitisation; and (iv) scavenging of radicals formed as reaction intermediates in type I photosensitisation. For absorption of light, combinations of flavonoids, as found in natural co-pigmentation, facilitate dissipation of photon energy to heat thus averting photodegradation. For protection against singlet oxygen and triplet sensitisers, chemical quenching gradually decreases efficiency hence the pathway to physical quenching should be optimised through product formulation. The feasibility of these protection strategies is further supported by kinetic data that are becoming available, allowing for calculation of threshold levels of flavonoids to prevent beer and dairy products from going off. On the other hand, increasing understanding of the interplay between light and matrix physicochemistry, for example the effect of aprotic microenvironments on phototautomerisation of compounds like quercetin, opens up for engineering better light-to-heat converting channels in processed food to eventually prevent quality loss.

Keywords: food and beverages; polyphenols; flavonoids; food quality; off-flavour; photodegradation; photooxidation

INTRODUCTION: FOOD AND LIGHT

It is well known that light exposure of foods and beverages triggers photoreactions that adversely affect quality, a phenomenon generally referred to as the lightstruck problem. Beer, wine, and dairy products are typically insulted by light as illustrated by their sensitivity for off-flavour formations (perceivable at sub-ppm levels),[1–6] but also meat, fish, vegetable oils, fruit juices and soft drinks suffer from light-induced quality changes.[7–9] A few hours of irradiation, as in display cases or in illuminated cold cabinets, are sufficient for flavours to go off. Beside these changes, also discolouration, loss of nutrients, and perhaps even toxic product formation result from light exposure, each of which can lead to rejection by consumers.[10,11] Despite awareness about the problem, use of transparent packaging is increasing as it is the more attractive material from a marketing point of view. Indeed the package must sell what it protects; however, it remains highly questionable if it still protects what it sells.[12,13] Attempts to change transmission properties without affecting transparency have only been moderately successful and particularly economical viability was questioned due to higher cost, recycling issues, and often lack of local supply of such advanced material.[14] Alternatively, retail conditions may be adapted by selecting appropriate illumination or by simply storing in the dark, although such routine is less practical and difficult to standardise. Therefore, it is worth considering a third (and perhaps most effective) approach to control lightstruck problems. As a result of detailed mechanistic investigations, insights have been produced in the underlying chemistry of light-induced quality changes.[8] In many cases, the generation of strongly oxidising intermediates was identified as crucial step in the development of off-flavours and other defects. Based on this knowledge, it was suggested that the presence of antioxidants, as a built-in protection, possibly mitigates adverse effects associated with light exposure without compromising on the packaging or retail level. For use in foods and beverages only antioxidants of natural origin should be considered as consumers are increasingly reluctant toward synthetic additives.[15] Flavonoids, as found in most fruits and vegetables,[16] are thus particularly suitable compounds as their beneficial effects on food preservation (including prevention of fat oxidation, protection of vitamins and enzymes, and inhibition of microbial growth) have been demonstrated before. Aiming at addition of small amounts in order not to perturb taste or mouthfeel (few hundreds of ppm), their use is generally safe and possibly triggers positive health effects.[17–23]

Briefly, the aim of this review is to evaluate the feasibility of flavonoids protecting foods and beverages against harmful photochemistry. Flavonoids are herein understood as the polyphenolic species having a common diphenylpropane carbon skeleton (C_6—C_3—C_6),[24] with the C_3-link being part of an oxygen-membered 6-ring (hence derivatives of 2-phenylbenzo-γ-pyran) (Fig. 1). Their role as quencher of

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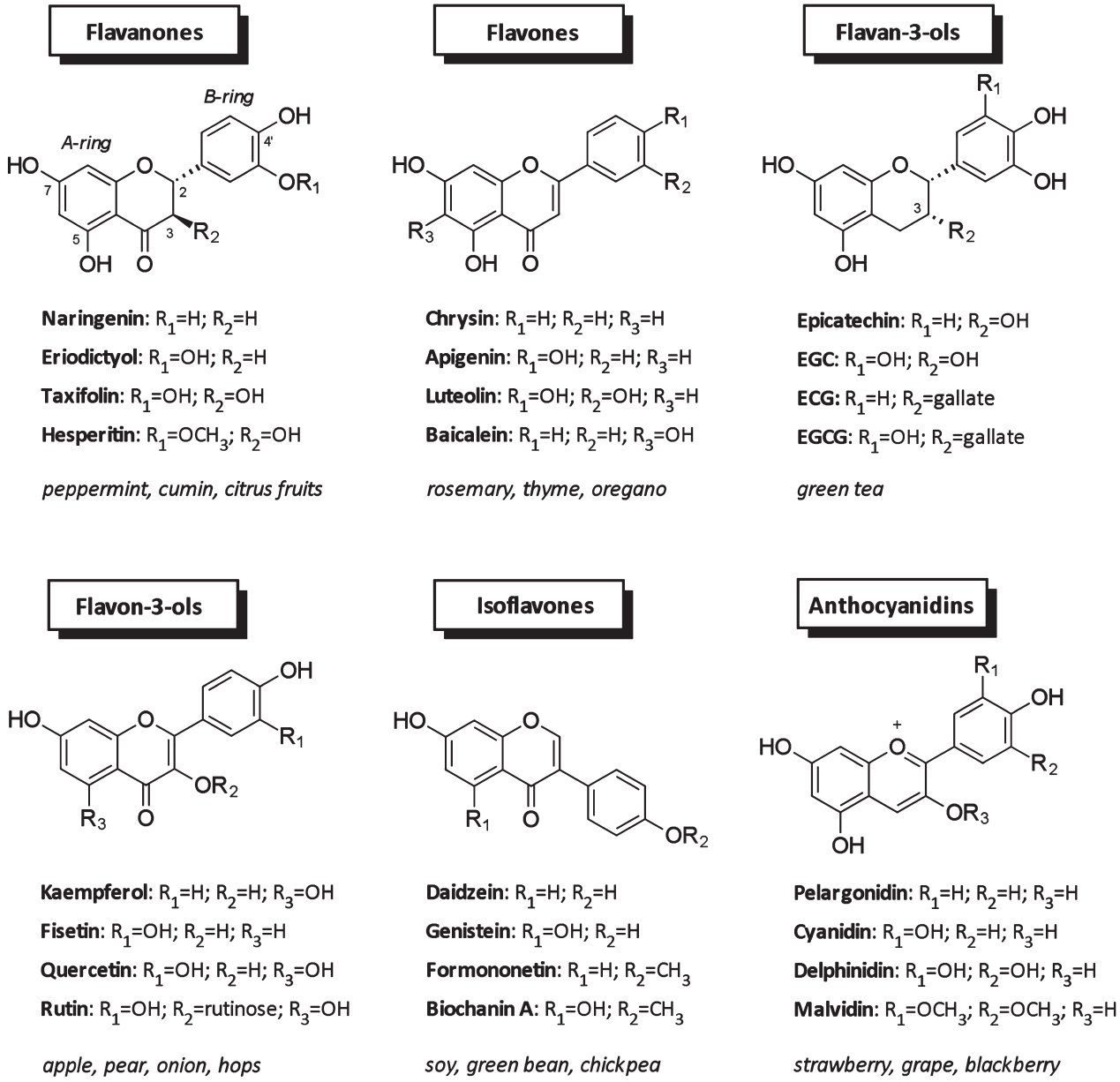


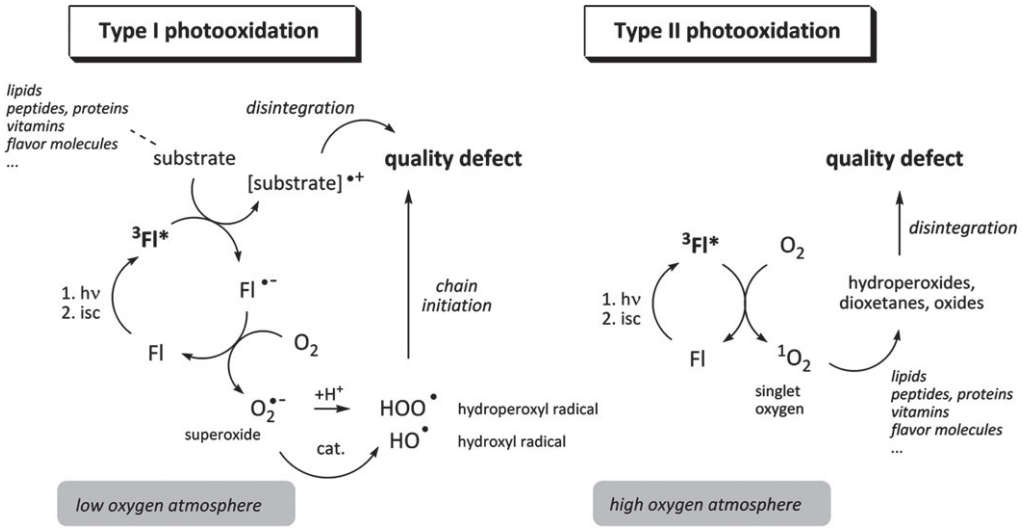
Figure 1. Overview of major flavonoids, as divided into their respective sub-classes. Examples of important sources of the different species are only indicative, as for reasons of conciseness only aglycon structures (except for rutin) are presented.

excited species, as scavengers of photo-induced radicals or as inner optical filters is considered, with particular attention for molecular explanations that support their protective activity. The usefulness of the strategy is further substantiated by a series of examples demonstrating the relevance for real food samples.

PROTECTION MECHANISMS

Under sensitised conditions

Foods and beverages in transparent packaging are inevitably exposed to light during shipping, retailing, and storing. Depending on the transmission properties of the packaging material, the active wavelength range covers most of the visible part, together with UV-A (380–320 nm) and UV-B (320–280 nm) light. Proteins and peptides, carbohydrates, and lipids are usually transparent under these conditions, but colouring agents and natural pigments, including organometal complexes such as chlorophylls, bear strongly absorbing chromophores that harvest light energy with subsequent initiation and acceleration of degradation reactions.[25,26] These so-called sensitised photoreactions are typical for foods and essentially involve two pathways (Scheme 1). Direct interaction of the excited sensitiser (i.e. the light-absorbing species) with food compounds initiates radical processes through electron transfer or hydrogen abstraction and is known as a type I photooxidation. This mechanism is favoured under low oxygen pressure and is for example responsible for lightstruck flavour formation in beer.[27] Under aerobic conditions, excitation energy is preferably transferred to oxygen to generate singlet oxygen, the pivotal intermediate in a type II photooxidation. This reaction is responsible for oxygenation of unsaturated fatty acids in vegetal oils causing high peroxide values and eventually rancidity, while attack of amino acid residues in dairy proteins may give rise to



Scheme 1. Chemistry of type I vs. type II photooxidation mediated by a flavin compound (Fl) as sensitiser. The triplet excited state ($^3Fl^*$), resulting from irradiation followed by intersystem crossing (isc), is the common species in both pathways and is responsible for formation of radicals, reactive oxygen species, and derived oxygenated compounds.

sulfury and potato-like off-flavours.[25] Both photooxidation pathways thus go through a common reactive triplet-excited sensitiser that triggers premature ageing or spoiling of foods and beverages.

Food-related sensitisers

Photosensitivity of foods or beverages is often determined by sensitisers that are naturally present. Riboflavin, also referred to as vitamin B_2, is a vital co-factor in the respiratory chain of living organisms and mostly occurs under the form of flavin adenine dinucleotide (FAD) or the water-soluble flavin mononucleotide (FMN).[28–30] Abundance is high in energy drinks (~12 ppm), meat (particularly liver, ~30 ppm), milk (~1.5 ppm), cheese (~5 ppm), white wine (~0.3 ppm) and beer (~0.2 ppm),[31] products in which their presence was found critical for photodegradation of proteins, unsaturated lipids, flavour molecules, vitamins and other nutrients.[32] Sensitising activity of flavins is due to the isoalloxazine moiety, a strongly conjugated chromophore that accounts for absorption in the blue part of the visible spectrum (hence the pronounced yellow colour).[33] High molar absorptivity ($>10^4$ M^{-1} cm^{-1}) accounts for a $\pi\pi^*$ transition which initially yields the short-lived (~5 ns in water) singlet-excited state ($^1Fl^*$).[34] Efficient intersystem crossing (quantum yield, $\varphi \sim 0.67$) gives a triplet-excited state ($^3Fl^*$) that is significantly longer-lived (~15 ms in water) and thus more damaging for the food matrix. The species allows singlet oxygen formation (type II mechanism) at diffusion-controlled rates ($k \sim 10^9$ to 10^{10} L mol^{-1} s^{-1}),[35,36] while its strong, one-electron oxidising power ($E \sim +1.7$ V)[37] causes degradation of food substrates via radical formation (type I mechanism).[34,38]

Both types of photooxidations have been reported to occur in foods containing flavins,[39–48] while porphyrin derivatives such as chlorophylls are preferentially involved in type II reactions.[30,49] Their presence in dairy products, as influenced by cow feeding patterns, expands the range of harmful wavelengths to the red region[50–52] and accordingly make the efforts to reduce light sensitivity more complex. Sensory analyses of light-exposed milk for example showed that wavelengths longer than 575 nm induced significantly more off-flavours than those shorter than 500 nm, indicating chlorophylls, rather than flavins, are essential mediators of photoactivity.[53]

Beside these typical sensitisers, visible and UV-A light is also absorbed by other sensitising compounds for which photoreactions have not been investigated in detail. Examples include melanoidins, curcumin and curcumoid compounds, carotenes, carmines and carminates, and other natural colourants which may all be involved in food-related photochemistry.[54–59]

Quenching of excited sensitisers by flavonoids

Chemical quenching of excited flavins: the type I mechanism

Sensitisers such as riboflavin and flavin mononucleotide are strongly oxidising species once promoted to their triplet state and ensuing radical formation can initiate a degradation cascade throughout the food matrix. To prevent this chain of reactions occurring, flavonoids are sacrificed to deactivate these electronically excited intermediates before damage to sensitive food compounds has occurred. This quenching process is a typical, and well studied, example of a type I photooxidation involving electron or hydrogen transfer to the excited state. The thermodynamical driving force is the strong overpotential of the triplet flavin ($E \sim 1.7$ V), which is over 1 V higher than the reduction potential at physiological pH ($E_{7.4} \sim 0.3–0.4$ V) reported for quercetin, a flavon-3-ol with strong reducing power.[60,61] Quenching rates are almost diffusion-controlled with rate constants in the order of 10^9 L mol^{-1} s^{-1} (Table 1). In particular, the presence of a catechol-like B-ring was found decisive and much more important than the presence of a C_2—C_3 unsaturation, a C_3-hydroxy substituent, or a C_4-carbonyl moiety.[62,63] Stabilisation of the incipient *ortho*-hydroxy phenoxyl radical, presumably by ensuing formation of a stable radical anion,[64,65] is the driver behind the reducing capacity. In the absence of catechol moieties, quenching from A- or B-ring phenols occurs with formation of the thermodynamically most-favoured radical (mostly on the B-ring).[64,66] This mechanism is still open for debate,[67] as well as is the exact mechanistic interpretation of the quenching reaction. Excitation energy transfer is excluded,[68] but hydrogen atom abstraction (HAT) from a phenolic function next to electron transfer (ET) followed by proton migration have both been claimed feasible. The net result of both mechanisms is identical, but reaction pathways are determined by different thermodynamical and kinetic properties. One-step hydrogen

Table 1. Bimolecular rate constants k_q (in L mol^{-1} s^{-1}), activation enthalpy $\Delta H^{\#}$ at pH 7 (in kJ mol^{-1}), and activation entropy $\Delta S^{\#}$ at pH 7 (in J K^{-1} mol^{-1}) for the chemical quenching of triplet-excited flavin mononucleotide and triplet-excited riboflavin* by flavonoids

Flavonoid[a]	pH 4	pH 7	$\Delta H^{\#}$	$\Delta S^{\#}$
Naringenin	1.2×10^9	1.0×10^9	10.5 ± 3.3	-35 ± 11
Taxifolin	9.3×10^8	1.1×10^9	–	–
Chrysin	9.8×10^8	8.2×10^8	12.3 ± 2.0	-31 ± 7
Apigenin	1.1×10^9	1.1×10^9	–	–
Luteolin	2.0×10^9	2.0×10^9	–	–
Catechin	1.8×10^9	1.6×10^9	11.6 ± 3.6	-29 ± 12
	–	1.4×10^{9} *	–	–
EGCG[b]	–	1.7×10^{9} *	–	–
Kaempferol	1.5×10^9	1.3×10^9	–	–
Quercetin	1.9×10^9	1.9×10^9	13.8 ± 3.3	-20 ± 11
Rutin	1.4×10^9	1.2×10^9	–	–
	–	9.7×10^{8} *	–	–

Values were taken from Huvaere *et al.*[65] (except for *, which were taken from Becker *et al.*[187]).
[a]For structures, see Fig. 1.
[b]EGCG: Epigallocatechin gallate

atom abstraction depends on the bond dissociation energy (BDE) while electron transfer is determined by the substrate's ionisation potential (IP). According to free energy changes for electron transfer and hydrogen atom transfer, ΔG_{ET} and ΔG_{HAT}, rutin and catechin quench flavin intermediates via HAT[68] while others claim an ET mechanism using similar data.[69] Based on interpretation of activation enthalpies ($\Delta H^{\#}$; relatively low and in agreement with electron transfer) and activation entropies ($\Delta S^{\#}$; negative hence in favour of solvent-assisted electron transfer) (Table 1),[65] an ET mechanism seems to fit best with experimental data.[70]

Chemical quenching of singlet-excited flavin is less relevant due to the short lifetime (~5 ns) and highly efficient intersystem crossing to the longer-lived triplet state.[71] Typically quencher concentrations in the order of 0.25 M would be required to prevent intersystem crossing,[69,72] which is unacceptably high when aiming at real food applications. Moreover, the quenching of excited porphyrins and derivatives via type I mechanism is inefficient, as for example zinc protoporphyrin IX (ZnPP; the red pigment in some dry-cured hams) in its triplet-excited state, ^{3}ZnPP* ($E_0 = 0.44-0.48$ V vs. NHE),[73] was not quenched by flavonoids like quercetin and catechin.[74] Most likely the low over-potential for oxidation kinetically inhibits electron transfer. For sensitisers located inside a protein coat, the spatial proximity of amino acid residues may overrule kinetic inhibition and favour reaction. Quenching of these reactions is unlikely as the pocket is generally not accessible for flavonoids.[75]

Photoprotection mechanism

To understand how flavonoids can efficiently deactivate excited flavin species and how much is needed to save food substrates from degradation, it is vital to understand kinetics of the photooxidation process. Considering the rate of quenching, r_q, by a selected flavonoid [Eqn (1)], then effective protection is obtained only if r_q is faster than r_I, which is the rate of the direct substrate photooxidation:

$$r_q = k_q \left[^3\text{Fl}*\right] [\text{Flav}] \quad (1)$$

$$r_I = k_I \left[^3\text{Fl}*\right] [\text{Sub}] \quad (2)$$

$$r_{II} = k_{II} \left[^3\text{Fl}*\right] [\text{O}_2] \quad (3)$$

As discussed above, the rate constant k_q for the bimolecular interaction of flavonoids with triplet-excited flavins is high (Table 1) which allows fast and efficient quenching at low concentrations. Unfortunately, the same is true for type I oxidation of sensitive substrates [Eqn (2)] as k_I amounts to 10^9 L mol^{-1} s^{-1} for particular amino acids and peptides, 5×10^8 L mol^{-1} s^{-1} for photooxidation of vitamin E, and comparably high values for other nutrients and flavour molecules.[76,77] As a consequence, competitive quenching by flavonoids can only occur at sufficiently high concentrations, i.e. with [Flav] >> [Sub]. The high whey protein presence in milk for example ([Sub] ~ 5–6 g L^{-1}) disfavours such approach, as the amount of flavonoids required would affect flavour quality (astringency), colloidal behaviour, and oxidative stability (prooxidant effects). Lipids, on the other hand, are more readily protected as k_I of polyunsaturated fatty acid chains is significantly lower (~10^5–10^6 L mol^{-1} s^{-1}, depending on the number of unsaturations).[78,79]

At higher oxygen concentrations, the flavin-mediated photooxidation mechanism shifts to a type II pathway with singlet oxygen formation outcompeting the quenching of excited sensitiser by flavonoids (*vide infra*). Indeed the rate constant for quenching of triplet-excited riboflavin by oxygen, k_{II}, is very high (~10^9–10^{10} L mol^{-1} s^{-1})[35,36] which, in combination with the high solubility of oxygen in oils or fatty matrices (~10 mM), makes conditions ideal for a type II process [Eqn (3)]. In aqueous solutions oxygen is less soluble (approximately 10-fold lower), but deactivation by flavonoids (at 1 mM concentration, corresponding to approximately 250 ppm) is still not sufficient to completely inhibit singlet oxygen formation.

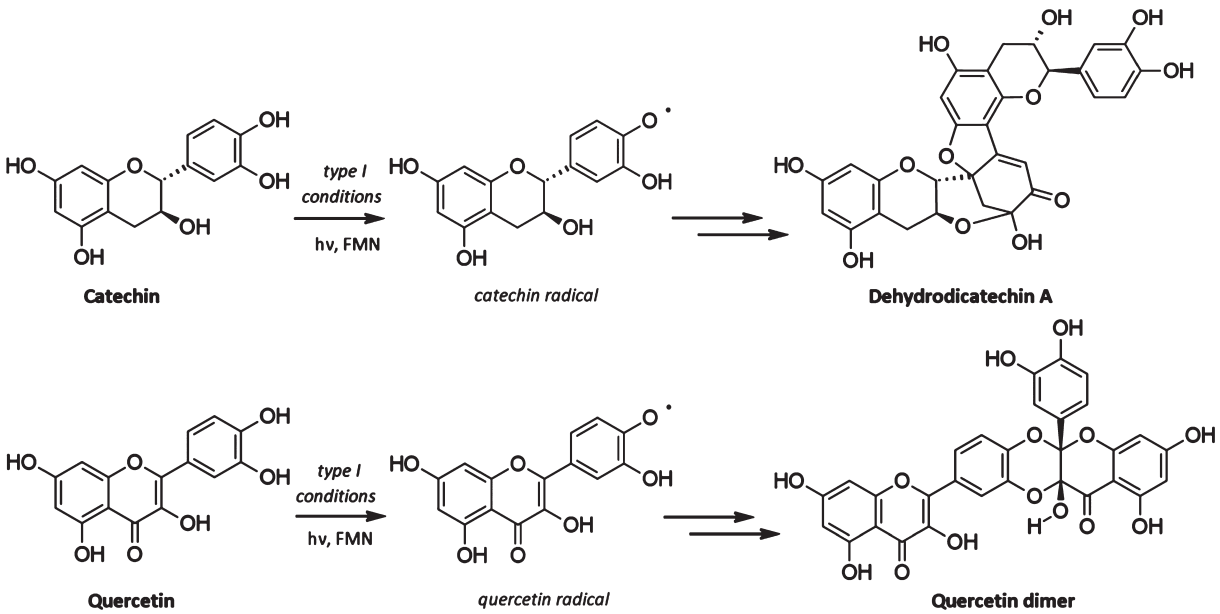
Spent product

A major disadvantage of the deactivation process is that flavonoids, as sacrificial compounds, are consumed with generation of dimeric compounds and other oxidised species (Scheme 2).[80,81] If formed in foods exposed to light, these may alter colloidal stability and affect colour, astringency, and antioxidative capacity. The case was studied in detail for soy isoflavones daidzein and genistein, which were shown particularly vulnerable during exposure of model systems[82] or soymilk.[83] No reaction was observed with typical type II sensitisers such as chlorophyll b,[82] while obvious dimerisation was observed for type I oxidation under the influence of flavins.[84,85] It can thus be concluded that the type I deactivation process gradually decreases quencher concentration, which eventually leaves the matrix unprotected after longer exposure time.

Quenching of reactive oxygen species

The type II mechanism: singlet oxygen

The type II photoreaction differs from type I as it essentially involves oxygen, which is excited to the singlet state by energy transfer from the triplet-excited photosensitiser. Typical examples of species catalyzing this reaction in foods are riboflavin[86] and chlorophylls and related (metallo)porphyrins,[52,87,88] next to other sensitising compounds for which mechanisms have not been elucidated yet. Once excited, the interaction between triplet sensitiser and oxygen is spin-allowed and very effective as revealed by



Scheme 2. Examples of spent product from catechin and quercetin formed after chemical quenching of triplet-excited flavin sensitiser (type I photooxidation).

the high quantum yields ($\varphi = 0.51$ for riboflavin[89] and $\varphi = 0.91$ for zinc protoporphyrin IX[90]). The lowest-lying excited state, $^1O_2$ ($^1\Delta_g$), which is ~ 94 kJ mol^{-1} above ground state energy, is the main oxidant in type II processes. As a highly reactive species with a lifetime of few microseconds in aqueous matrices[91] and 700 μs in apolar media[92] to 86 ms in dry air,[93] $^1O_2$ is capable of oxidising unsaturated lipids, peptides and proteins, and other electron-rich food compounds.

The high rates for $^1O_2$ formation complicate deactivation of sensitiser at relevant flavonoid concentrations (*vide supra*), while dedicated type II sensitisers such as porphyrins are not deactivated at all in the presence of flavonoids.[74] Thus, under type II conditions, the prime target for deactivation is $^1O_2$ rather than the excited sensitiser. Fortunately, flavonoids strongly interact with $^1O_2$ in both physical and chemical processes. The rate constants for the observed total deactivation, k_T, is composed of a physical and a chemical component ($k_Q + k_r$) (Table 2). Generally the reaction is dominated by the physical pathway, particularly when the number of phenolic functions increases.[94] The presence of a catechol or pyrogallol rings makes physical quenching a 10- to 100-fold more efficient. For example, epigallocatechin gallate (EGCG), an important green tea flavonoid, is a very efficient $^1O_2$ quencher ($k_T = k_Q \sim 1.5 \times 10^8$ M^{-1} s^{-1}) that is comparable to strong deactivators like α-tocopherol ($k_T \sim 2.1 \times 10^8$ M^{-1} s^{-1}) and γ-tocopherol ($k_T \sim 1.4 \times 10^8$ M^{-1} s^{-1}) but still is significantly slower than β-carotene ($k_T \sim 1.6 \times 10^{10}$ M^{-1} s^{-1}).[95] The EGCG quenching is purely physical,[96] favouring a high turnover number before the quencher is lost. If a 2,3-double bond is present, such as in flavones or flavon-3-ols, chemical deactivation of $^1O_2$ is also feasible. The difference in quenching between apigenin ($k_T \sim 2.8 \times 10^7$ M^{-1} s^{-1}) and naringenin ($k_T \sim 3.7 \times 10^6$ M^{-1} s^{-1}) or the more efficient quenching by quercetin ($k_T \sim 4.6 \times 10^8$ M^{-1} s^{-1}) and rutin $k_T \sim 1.2 \times 10^8$ M^{-1} s^{-1}) as compared to taxifolin $k_T \sim 9.4 \times 10^6$ M^{-1} s^{-1}) may be ascribed to a chemical interaction.[97] For quercetin the 3-hydroxy group stimulates addition of the electrophilic $^1O_2$ by increasing electron density in the double bond, favouring unstable hydroperoxide or 1,2-dioxetane formation with subsequent decomposition (Scheme 3).[96] In the absence of C_3—OH, the electron withdrawing effect of the carbonyl group is more important, which inhibits chemical oxidation and prevents fast depletion of quencher compound.

Photochemical generation of $^1O_2$ in foods is a major cause of formation of hydroperoxides, which are pivotal intermediates in the pathway to oxygenated compounds with unwanted flavour and possibly toxic effects.[11,86] Protein-rich foods are particularly sensitive toward $^1O_2$ as electron-rich amino acid residues from tryptophan, tyrosine, histidine, methionine and cysteine react at significant rates (in the order of 10^7 L mol^{-1} s^{-1}, with cysteine being the most reactive at 5.0×10^7 L mol^{-1} s^{-1}).[86] Similar rate constants are observed for vitamins (vitamin $B_2 \sim 6.0 \times 10^7$ L mol^{-1} s^{-1}, vitamin C $\sim 1.1 \times 10^7$ L mol^{-1} s^{-1}, vitamin D $\sim 2.2 \times 10^7$ L mol^{-1} s^{-1}, and vitamin E $\sim 1.3 \times 10^8$ L mol^{-1} s^{-1}), but their low concentration in foods allows prevention of photooxidation at subtle quencher amounts. Unsaturated lipids interact slower (bimolecular rate constants in L mol^{-1} s^{-1} of $\sim 1.7 \times 10^4$ for oleic acid, $\sim 4.2 \times 10^4$ for linoleic acid, $\sim 6.0 \times 10^4$ for egg yolk phosphatidylcholine, and $\sim 0.9 \times 10^4$ for stearic acid, the latter referring to a pure physical quenching process)[98,99] but their concentrations in food are significantly higher than for vitamins. Moreover, higher oxygen solubility and longer lifetime of $^1O_2$ in lipophilic environments should be accounted for. Still, the effective quenching by flavonoids, with larger k_Q values of up to four orders of magnitude, may prevent lipid peroxidation as pivotal precursor in stale and rancid off-flavour formation. Cholesterol, prevailing along with lipids in meat, dairy products, and fish, is much more sensitive to oxidation (6.9×10^7 L mol^{-1} s^{-1})[78] with formation of possibly toxic oxidation products.[100,101] This rate constant is only slightly below that of rutin, quercetin, and EGCG (1.2×10^8 L mol^{-1} s^{-1}, 4.6×10^8 L mol^{-1} s^{-1}, and 1.5×10^8 L mol^{-1} s^{-1}),[95,97] and quenching will thus be effective only if flavonoid concentration exceeds that of cholesterol. For such highly lipophilic substrates, carotenes, such as lycopene and β-carotene are possibly better alternatives for $^1O_2$ deactivation ($k \sim 1.6 \times 10^{10}$ L mol^{-1} s^{-1}).[97]

Table 2. Rate constants k_T (in L mol^{-1} s^{-1}) for total singlet oxygen quenching by flavonoids; k_T consists of a chemical quenching (k_r) and a physical quenching (k_Q) component

Flavonoid[a]	k_T	k_r[b]	k_Q	Reference
Naringenin	5.0×10^4	No reaction	5.0×10^4	96
	3.7×10^6	No reaction	3.7×10^6*	97
Eriodictyol	1.4×10^6	No reaction	1.4×10^6	96
Taxifolin	1.1×10^6	No reaction	1.1×10^6	96
	9.4×10^6	No reaction	9.4×10^6*	97
Chrysin	2.4×10^6	0.6×10^4 [2.3×10^{-6}]	2.3×10^6	96
	2.0×10^7	NR[c]	NR	97
Apigenin	2.8×10^7	NR	NR	97
Luteolin	1.3×10^6	1.8×10^4 [7.5×10^{-6}]	1.3×10^6	96
Catechin	5.8×10^6	No reaction	5.8×10^6	96
	1.1×10^7	No reaction	1.1×10^7	95
	5.1×10^7	No reaction	5.1×10^7*	94
Epicatechin	1.3×10^7	No reaction	1.3×10^7	95
	5.5×10^7	No reaction	5.5×10^7*	94
EGC[d]	1.7×10^7	No reaction	1.7×10^7	95
ECG[e]	7.8×10^7	No reaction	7.8×10^7	95
EGCG[f]	1.5×10^8	No reaction	1.5×10^8	95
Galangin[g]	1.2×10^6	7.4×10^5 [1.1×10^{-2}]	4.6×10^5	96
Kaempferol	7.1×10^5	4.8×10^5 [9.3×10^{-3}]	2.3×10^5	96
	NR	2.8×10^5	NR	94
Fisetin	3.1×10^6	1.1×10^6 [1.0×10^{-2}]	2.0×10^6	96
Morin[h]	3.9×10^7	3.0×10^7	0.9×10^7*	69
	1.3×10^8	6.6×10^6	1.3×10^8	94
Quercetin	3.1×10^6	1.1×10^6	2.0×10^6*	69
	2.4×10^6	8.9×10^5 [9.7×10^{-3}]	1.5×10^6	96
	4.6×10^8	NR	NR	97
	5.7×10^7	5.7×10^5	NR	94
Rutin	1.6×10^6	0.1×10^6	1.5×10^6*	69
	–	1.1×10^5 [4.6×10^{-5}]	1.5×10^6	96
	2.4×10^7	0.6×10^5	2.4×10^7*	94
	1.2×10^8	NR	NR	97
Myricetin[i]	5.1×10^8	NR	NR	97
	NR	7.3×10^5	NR	94
Biochanin A	1.9×10^8	NR	NR	152
Genistein	5.9×10^7	NR	NR	152

Values of k_Q marked with
*were not reported as such but were obtained from $k_Q = k_T - k_r$.
[a]For structures, see Fig. 1.
[b]Quantum yields are reported between brackets.
[c]NR: not reported.
[d]EGC: Epigallocatechin.
[e]ECG: Epicatechin gallate.
[f]EGCG: Epigallocatechin gallate.
[g]Galangin: similar structure to that of kaempferol, but lacking the C_4'—OH (i.e. unsubstituted B-ring).
[h]Morin: quercetin isomer, but with C_2'—OH instead of C_3'—OH (i.e. resorcinol B-ring).
[i]Myricetin: similar structure to that of quercetin, but with additional C_2'—OH (i.e. pyrogallol B-ring).

Secondary species: superoxide

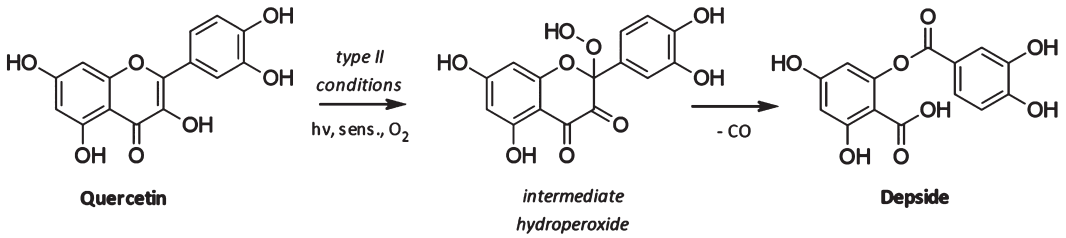
Superoxide ($O_2^{\bullet-}$) is a low reactive, negatively charged radical species that is formed as a side product in type I oxidation (Scheme 1). The electron or hydrogen transfer eventually produces a reduced sensitiser species ($Fl^{\bullet-}$) that readily interacts with residual oxygen ($k_{O2} \sim 1.4\times10^8$ L mol^{-1} s^{-1}) with regeneration of the sensitiser.[35,71,102] Concomitant formation of $O_2^{\bullet-}$ is relatively harmless as such,[103] but as precursor for the more reactive hydroperoxyl radical at low pH (<5; pK_a of $HOO^{\bullet} \sim 4.6$) it causes oxidation of unsaturated lipids or depletion of endogenous antioxidants including cysteine residues and tocopherols.[104,105] Beside this, superoxide yields deleterious hydroxyl radicals through dismutation or by participating in the ferric ion catalysed Haber–Weiss cycle. With generation of these highly reactive species, the impact of type I photoreactions spans well beyond a pure sensitiser–substrate interaction and quenching of the supposedly harmless $O_2^{\bullet-}$ may significantly increase photostability.

Interaction of flavonoids with $O_2^{\bullet-}$ is slow when compared to other radical species: $k \sim 10^2 - 10^7$ M^{-1} s^{-1} vs. $k \sim 10^9$ M^{-1} s^{-1} for the scavenging of $O_2^{\bullet-}$ and $R^{\bullet}$, respectively. Fortunately, $O_2^{\bullet-}$ attacks food substrates even slower ($k \sim$ s^{-1}), therefore few flavonoids are required (~10^{-6} M) for protection ($k = 10^{-6}$ M $\times 10^7$ M^{-1} s^{-1} = 10 s^{-1}).[106] Among the most effective compounds are myricetin, delphinidin, epicatechin gallate, and proanthocyanidins, suggesting a more efficient quenching in the presence of a catechol or pyrogallol group (Table 3).[107,108] In the absence of hydroxyl substituents (e.g. flavone and flavanone) no scavenging activity is observed.[109] The interaction is pH-dependent[108] and most likely involves electron transfer with concerted proton transfer as deduced from the negative activation entropy ($\Delta S^{\#}$).[64] Alternative mechanisms include initial proton transfer[110] or direct hydrogen abstraction by the superoxide anion radical.[111] Flavon-3-ols such as quercetin and kaempferol may interact through a different mechanism with atypical depside formation.[69,80]

The most efficient rate constants (~10^7 L mol^{-1} s^{-1} for gallocatechins and proanthocyanidins) are still far below those for metalloprotein superoxide dismutases (SOD; 1.4×10^9 L mol^{-1} s^{-1}).[112] In this respect, a remarkable increase in quenching efficiency was observed after complex formation between flavonoids and transition metal ions. For example ferrous and ferric complexes of rutin, taxifolin, luteolin, and epicatechin were up to 6× more effective superoxide quenchers, while copper complexes were even more performant.[113–115]

Direct excitation

Next to the occurrence of sensitised reactions, several food molecules interact directly with light without intervention of a sensitiser. Known examples include the degradation of isohumulones in beer,[116,117] the rearrangement of carvone affecting aquavit flavour,[118] the isomerisation of *trans*-anethole in anise-flavoured drinks,[119,120] or the UV-induced lipid and protein degradation in soft cheese.[121,122] The chemistry is considerably different from sensitised conditions as excitation and ensuing events occur intramolecularly. As a consequence, reactions are too fast to be interfered by bimolecular quenching. Preventing excitation is the only option to protect against damage, for example by optically filtering hazardous wavelengths that enter the food matrix. The remarkable properties of flavonoids make them suited for this role too, particularly since they were discovered as an essential part of nature's defence against excessive UV exposure of the photosynthetic apparatus in plants.[123] Their strong



Scheme 3. C_2—C_3 unsaturated flavonoids such as quercetin are chemically consumed during quenching of singlet oxygen in a type II photooxidation.

Table 3. Rate constants k (in L mol^{-1} s^{-1}) for quenching of superoxide by flavonoids as determined at pH 7 and at pH 10.

Flavonoid[a]	pH 7 [b]	pH 10 [c]
Naringenin	–	3.0×10^2
Hesperetin	–	5.9×10^3
Hesperidin	–	2.8×10^4
Catechin	6.4×10^4 *	1.8×10^4
	7.1×10^5	–
Epicatechin	6.8×10^4 *	–
	6.6×10^5	–
EGC[d]	4.1×10^5 *	–
ECG[e]	4.3×10^5 *	–
	1.1×10^7	–
EGCG[f]	7.3×10^5 *	–
Proanthocyanidin oligomer	2.9×10^7	–
Galangin[g]	–	8.8×10^2
Kaempferol	2.0×10^4	2.4×10^3
Fisetin	7.8×10^5	1.3×10^4
Morin[h]	2.9×10^3	1.6×10^3
Quercetin	1.0×10^6	4.7×10^4
Rutin	1.5×10^6	5.1×10^4
Isorhamnetin[i]	7.4×10^4	–
Myricetin[j]	9.0×10^6	–
Delphinidin	8.1×10^6	–
Malvidin	6.0×10^5	–

[a] For structures, see Fig. 1.
[b] Values taken from Taubert *et al.*[112] (except for *, which were taken from Jovanovic and Simic[106]).
[c] Values taken from Jovanovic *et al.*[64]
[d] EGC: Epigallocatechin.
[e] ECG: Epicatechin gallate.
[f] EGCG: Epigallocatechin gallate.
[g] Galangin: similar structure to that of kaempferol, but lacking the C_4'—OH (i.e. unsubstituted B-ring).
[h] Morin: quercetin isomer, but with C_2'—OH instead of C_3'—OH (i.e. resorcinol B-ring).
[i] Isorhamnetin: similar structure to that of quercetin, but with methylated C_3'—OH (i.e. guaiacol B-ring).
[j] Myricetin: similar structure to that of quercetin, but with additional C_2'—OH (i.e. pyrogallol B-ring).

absorption in the UV-B and UV-A region is essential for optical filtering, but it is mainly the ability to convert absorbed photon energy into harmless heat – rather than triggering photochemical transformation – that makes flavonoids efficient photoprotectors.

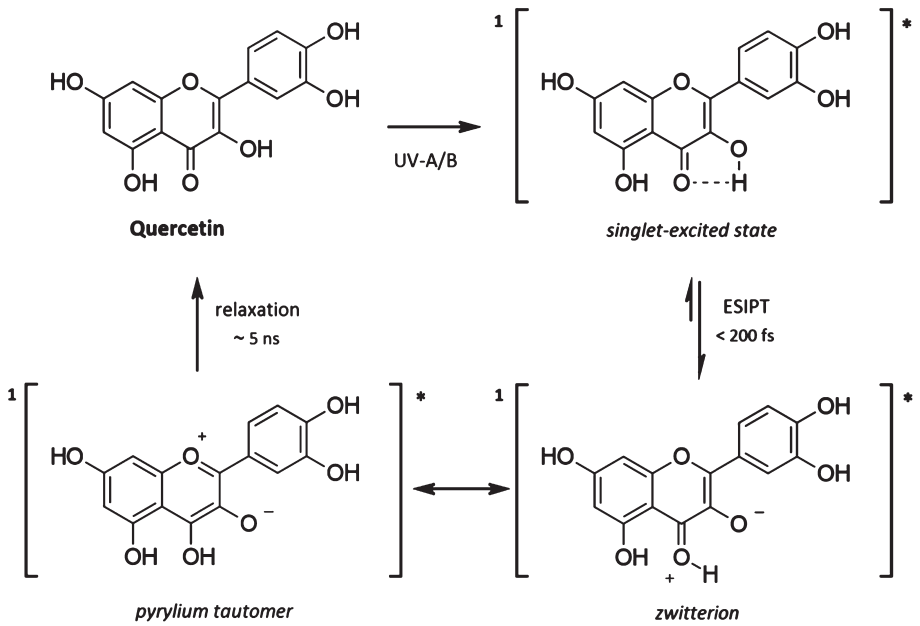
Flavon-3-ols and flavones

Flavon-3-ols such as quercetin and its glycosides are widespread and their photochemical and photophysical properties are probably the best studied of all flavonoid species. Similar to flavones, flavon-3-ols show strong UV absorption due to B–C ring conjugation (between 320 and 385 nm, the so-called band I) and the presence of a hydroxylated A-ring (band II, between 250 and 285 nm).[124] Band I corresponds to a $S_0 \rightarrow S_1$ transition (a $\pi\pi^*$ transition with $n\pi^*$ character; $\epsilon \sim 2.8 \times 10^4$ L mol^{-1} cm^{-1}),[125] which for flavone (no substitutions) is followed by intersystem crossing (isc) to a longer-lived, chemically reactive triplet state ($\varphi_{isc} \sim 0.9$; $k_{isc} \sim 2 \times 10^{10}$ s^{-1}).[126–128] On the contrary, a very low quantum yield for intersystem crossing is observed for flavon-3-ols such as quercetin because the presence of the C_3-hydroxyl causes efficient transient tautomerism from the singlet excited state.[129–131] The mechanism involves ultrafast intramolecular proton transfer from the C_3-hydroxyl to the neighbouring carbonyl,[132] followed by relaxation to the ground state with dissipation of excitation energy into heat (Scheme 4). This so-called excited-state intramolecular proton transfer (ESIPT) is driven by electronic rearrangements in the first singlet excited state, accounting for a pK_a decrease for the C_3—OH by almost 10 units while basicity of the C_4 carbonyl is increased by more than 4 units.[133] The mechanism works for flavones too, as the C_5—OH neighbouring the carbonyl or the more distal C_7—OH group (which is the most acidic as the pK_a decreases from 7.4 in the ground state to −2.2 in the first excited singlet state)[134] take over the role of proton donor.[135] Particularly the C_5—OH favours ESIPT over intersystem crossing (due to a so-called 'proximity effect')[136] although hydrogen bonding with the matrix may compromise effectivity.[137]

The dissipation of photon energy into heat is an appealing strategy to protect against light-induced changes in food systems. The process is very efficient and provides a way to deflect UV light from food molecules without sacrificing the optical filter.[138–140] For example, the low quantum yield of photodegradation of quercetin (approximately 10^{-4})[141] in combination with a high molar absorptivity makes inner filtering effective at low concentrations. Still decomposition sets in after longer exposure time with formation of 2,4,6-trihydroxybenzoic acid and 3,4-dihydroxybenzoic acid,[142,143] but derived glycosides like rutin are generally better resistant to photodegradation.[144,145] It is worth noting, however, that in the presence of metal ions, a condition which is not unlikely in food matrices, a significantly different photoreactivity is observed. Rather than dissipating to heat, photon energy induces ligand (e.g. quercetin or rutin) to metal charge transfer (I to 400–550 nm; $\epsilon \sim 10^3$ L mol^{-1} cm^{-1}) with resulting radicals degrading according to known mechanisms.[146–149]

Isoflavones

Isoflavones, which differ from other flavonoids by the B-ring attachment at the C_3-position, are characterised by three band maxima (for example, at 340 nm, 280 nm and at 260 nm for genistein in ethanol).[150] Similar as for the 5-hydroxyflavones, radiationless transition, via ESIPT, is very efficient and supports a better photostability of genistein and biochanin A when compared



Scheme 4. Ultra-fast excited state intramolecular proton transfer (ESIPT) with subsequent tautomerisation efficiently dissipates excitation energy in flavon-3-ols, as exemplified by UV irradiation of quercetin.

to daidzein and formononetin. [150] The latter two, both lacking a C_5—OH (Fig. 1), undergo radical formation[151] but quantum yields strongly depend on pH.[152,153] The ESIPT mechanism also affects sensitising activity, as the low yield of triplet excited states makes genistein and daidzein unsuitable as singlet oxygen sensitisers.[153]

Flavanones and flavanonols

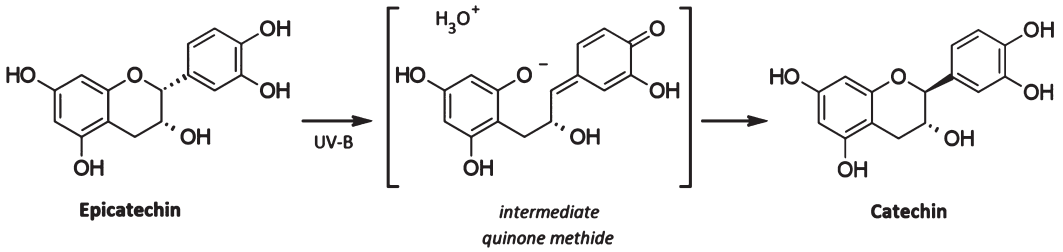
Absorption maxima of flavanones appear at considerably shorter wavelengths than for the corresponding flavones, as shown for example for naringenin and apigenin (288 nm vs. 337 nm). This difference is essentially ascribed to the lack of conjugation between the A and B ring, leaving band II situated between 270 and 295 nm. The absorption range is therefore limited, which makes this flavonoid class less useful as optical filters.

Flavan-3-ols and proanthocyanidins

Flavan-3-ols and derived proanthocyanidins lack a carbonyl moiety which excludes them from the phenone photochemistry as discussed for flavones, flavon-3-ols, and isoflavones. Excitation maxima are at shorter wavelengths (~275 nm for catechin in water, shifting to ~300 nm for corresponding anions) hence they are mainly active in the UV-B range.[67] Photolysis at 300 nm gives epimerisation at C_2, with thermodynamical preference for the more stable *trans*-configuration (Scheme 5).[154] The reaction proceeds via a $\pi\pi^*$ singlet state (1–10 ns lifetime) with considerably higher acidity ($pK_a \sim 4$) than the S_0 state ($pK_a \sim 10$).[155] Deprotonation facilitates cleavage of the benzylic C—O bond to give the intermediate quinone methide,[156] which undergoes recyclisation to finalise the isomerisation process. It is unclear whether green tea catechins such as EGCG undergo similar rearrangements, but the shorter lifetime of the excited state (only few picoseconds) and the low quantum yield for fluorescence perhaps suggest an even faster process.[157] This effective and non-destructive way to sink UV energy makes flavan-3-ols excellent optical filters, but like flavanones their operating range is limited to UV-B light.

Anthocyanins and anthocyanidins

The core structure of anthocyanins consists of a positively charged 7-hydroxy flavilium ion that is typically glycosated at the C_3—OH and C_5—OH positions. Anthocyanidins are the corresponding aglycons which, together with the anthocyanins, account for the bright colours among others in blackberries, strawberries, grapes, blueberries, aubergine and avocado. Ranging from pale yellow over purple–blue to red, colour and light absorption are strongly pH-dependent. One of their suggested biological roles is to protect photosynthetic tissues against excessive light stress by strongly absorbing blue–green and ultra-violet light.[158,159] Moreover, anthocyanins have the capability to deactivate their excited singlet states back to the ground state almost instantly with transformation of light energy into harmless heat. The mechanism is pH dependent as under acidic conditions anthocyanins prevail as red-coloured, protonated species with a pK_a (asigned to C_7—OH) of approximately 4–5.[160] Upon excitation, the excited singlet state behaves as superphotoacid ($pK_a \sim 0$) and transfers a proton to water via sub-nanosecond excited state proton transfer (ESPT, ~ 10–20 ps) (Scheme 6).[161] The corresponding excited base returns to its ground state and reclaims the proton from water, accounting for a total process time of < 200 ps.[162,163] This highly effective deactivation cycle accounts for low quantum yields of degradation, as for example observed for an elderberry extract rich in anthocyanins ($\varphi \sim 0.4 \times 10^{-4}$ mol einstein^{-1}, $\lambda_{exc} = 440$ nm, pH ~ 3–4).[164] The process differs from the intramolecular ESIPT (as described for carbonyl-bearing flavonoids), the latter which may lose efficiency by solvent interaction (*vide supra*). The tolerance of water in the dissipation mechanism makes anthocyanins a preferred candidate for protecting foods and beverage against light-induced degradation. However, the fact that most flavylium cations become unstable at the pH of most food matrices (pH > 3) and add water to form a pale yellow, ineffective hemiacetal is a serious drawback. To be useful, anthocyanins should be accompanied by other phenolic species (such as phenolic acids or other flavonoids) with which they form a stable complex.[165–169] This co-pigmentation, as the phenomenon is referred to, accelerates



Scheme 5. Photoisomerisation is the main pathway for dissipation of excitation energy in flavan-3-ols. Recyclisation of the pivotal quinone methide intermediate gives the thermodynamically more stable *trans*-configuration.

internal conversion to the ground state via ESPT and brings lifetime of the excited singlet state to a sub-picosecond level.[170]

PHOTOPROTECTION IN PRACTICE

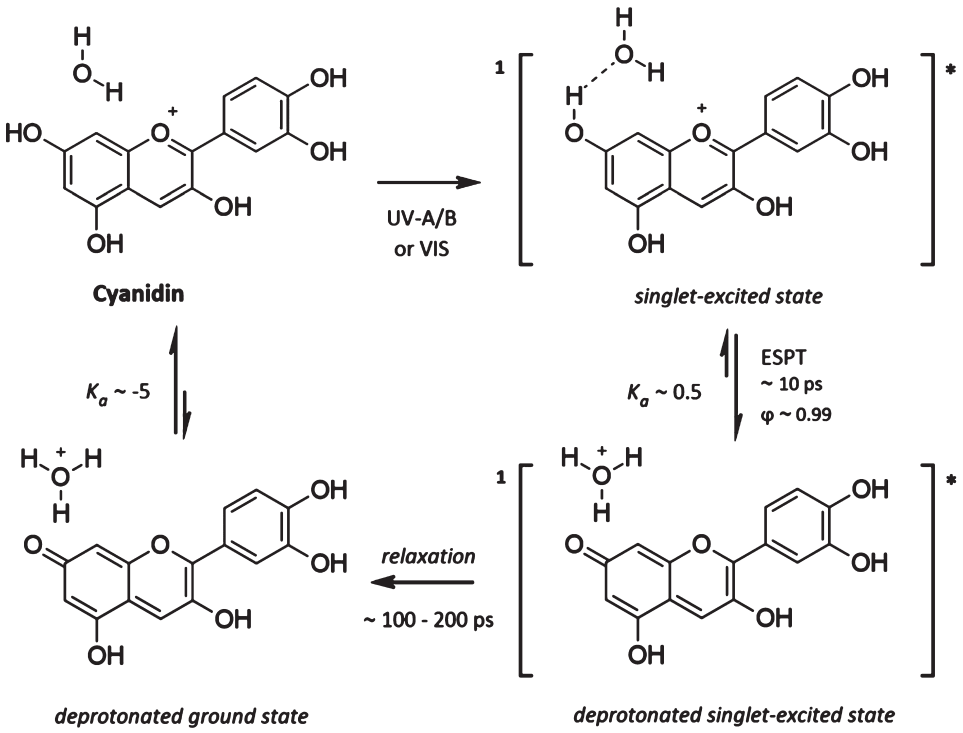
Examples

The rate at which light exposure shortens shelf life depends on several factors including light intensity, the light source, exposure time, the packaging material, and, obviously, the sensitivity of the matrix. Light penetrates deep into beverages and makes them highly photosensitive, probably with beer as the best-known example. Light exposure generates an obnoxious off-flavour after a complex interplay of light, riboflavin (acting as natural sensitiser), isohumulones (the hop-derived bitter agents), and sulfur-containing amino acids, peptides and proteins.[45,47,77,171] The radical degradation path results in 3-methylbut-2-ene-1-thiol (MBT), the benchmark off-flavour that characterises light-exposed beers. It resembles the foxy odour secreted by skunks hence the trivial name skunky thiol, although other sulfury compounds have been identified which contribute to lightstruck perception.[172,173] Beer ingredients malt and hops are natural sources of flavonoids and should therefore offer protection against the reactive riboflavin triplet according to quenching mechanisms as described above. Malt naturally contains proanthocyanidins, dimers and trimers of catechin and gallocatechin, while hops are rich in flavon-3-ols and their glycosides, catechins and proanthocyanidins.[174–177] However, despite their potential to deactivate excited sensitisers and protect against MBT formation, most of the naturally present flavonoids are removed deliberately because of their undesirable tendency to destabilise colloidal properties and promoting haze formation.[178,179] Moreover, astringency, a sensation characterised by dry and puckering mouthfeel, is mainly ascribed to complexation of proanthocyanidins with lubrication proteins in saliva and adversely impacts beer quality.[180–182] Catechin monomers and other flavonoids have less influence on haze formation and can be introduced in a post-filtering step. Sensory analysis indeed confirmed protection against light, but relatively high concentrations possibly affect taste perception.[183] From kinetic analyses of phenolic interactions with triplet-excited flavins, it was shown that ~0.36 mM (approximately 100 ppm) may effectively quench 90% of the reactive intermediates.[72]

Milk is highly photosensitive, with both lipids and proteins being oxidised under sensitised conditions due to natural presence of riboflavin and chlorophylls.[30,52,184] Formation of carbonyl compounds such as pentanal, hexanal, heptanal, 2-nonenal, 2,4-nonadienal and 2,4-decadienal all attributed to lipid photooxidation, deters freshness of milk and imparts green, metallic and fatty off-flavours.[185] On the other hand, light-induced protein and amino acid degradation is likely to produce sulfury off-flavours, including methional, dimethyl disulfide, and dimethyl trisulfide that give rise to the typical cabbage and 'burnt feather' smell. Methionine is a pivotal precursor and disintegrates via a radical mechanism (type I),[45] as well as through interaction with singlet oxygen.[5] In model systems (aqueous solution at pH 3.5 with 500 ppm methionine and 0.5 ppm riboflavin), epigallocatechin (EGC) and EGCG, the principal antioxidants from green tea, were found powerful inhibitors of sulfury volatiles and decreased formation up to 60% with reference to untreated samples.[186] At a concentration of ~50 ppm, they performed significantly better than Trolox (a model representing vitamin E), BHA, a major synthetic food antioxidant, and rutin. The latter is supported by advanced kinetic measurements, showing that EGCG deactivates excited flavins via electron transfer almost twice as fast as rutin ($k \sim 1.7 \times 10^9$ L mol^{-1} s^{-1} vs. 1.0×10^9 L mol^{-1} s^{-1}).[187] Also, lipid photooxidation in milk, which is very significant with $k \sim 8.1 \times 10^5$ L mol^{-1} s^{-1},[188] is potentially inhibited by the presence of flavonoids. Both EGC and EGCG were effective against type II photooxidation of conjugated linoleic acid and performed significantly better than apple polyphenols (consisting mainly of procyanidins and quercetin compounds) in an oil-in-water emulsion model system.[189] Green tea extract (at 150–500 ppm) was better than α-tocopherol in protecting linoleic acid against hydroperoxide and conjugated diene formation in model systems, mainly because the catechins remained stable during longer exposure.[190]

Formulating these catechins in real milk samples (at 100 ppm) corroborated results from model systems and proved epicatechin (together with chlorogenic acid, the major coffee polyphenol) to be a practically quantitative inhibitor of lipid-derived aldehydes such as (*E*,*E*)-2,4-nonadienal, (*E*)-2-nonenal, and (*E*,*E*)-2,4-decadienal.[185] Despite moderate reduction of methional formation, epicatechin ranked best in preventing overall lightstruck character and performed significantly better than endogeneous antioxidants such as α-tocopherol. When administered as a green tea extract, epicatechin, EGC and EGCG reduced formation of hydroperoxides, malondialdehyde, and aldehyde off-flavours and protected nutrients like retinol and tocopherol in light-exposed milk.[191] About 90% reduction of hexanal and heptanal formation and approximately 50% better preservation of retinol and α-tocopherol were obtained with only 25 ppm of extract, which is at least four times more effective than ascorbic acid.

Due to the presence of similar constituents as found in milk, photooxidation is likely to affect cheese and butter flavours. Light penetration is less effective for these solid and semi-solid matrices and light-induced changes are merely a surface phenomenon.[121] Both riboflavin and chlorophylls are involved as sensitisers, but also protoporphyrin and hematoporphyrin have been identified as



Scheme 6. Fast excited state proton transfer (ESPT) to water with subsequent tautomerisation efficiently dissipates excitation energy in anthocyanidins such as cyanidin (or in corresponding anthocyanins). The mechanism works under UV as well as visible light irradiation.

photoactive compounds in dairy products.[30,52,184] The presence of these sensitisers makes cheese and butter particularly vulnerable to visible light-induced changes through both type I and type II oxidation mechanisms. Typical off-flavours include stale aldehydes and volatile disulfides,[1,2,192] but addition of green tea extract (750 ppm) effectively reduced formation of lipid-derived aldehydes in soft cheese with possibly improved flavour stability as result.[193]

Edible oils are ideal environments for type II photooxidation. Their lipophilic nature allows high concentrations of oxygen, while natural sensitisers such as chlorophylls are well soluble and easily extracted in the matrix during production. Naturally occurring flavonoids like fisetin and baicalein (present at ppm levels) efficiently inhibit linoleic acid peroxidation by quenching $^1O_2$ without being consumed.[194,195] It may be argued that the natural presence of carotenes, which are excellent $^1O_2$ quenchers, offers good protection against photooxidation and possibly makes addition of flavonoids superfluous. However, flavonoids are more versatile and quercetin and rutin for example were found to protect flax seed oil against UV-induced oxidation due to strong inner-filtering ($\epsilon \sim 1.1 \times 10^4$ L mol^{-1} cm^{-1} and $\epsilon \sim 1.2 \times 10^4$ L mol^{-1} cm^{-1} for quercetin and rutin).[196] Catechin, with $\epsilon \sim 110$ L mol^{-1} cm^{-1} at 300 nm excitation, was ineffective in this case.

Light exposure not only affects flavour; discolouration or colour fading is also a quality defect attributed to photooxidation. As a natural colour of many juices and other fruit and vegetable products like tomato paste for pizza and carrot paste for infant nutrition, carotenoids are typically affected by light and by concurrent oxidation of lipids and proteins. Paprika oleoresin, a common colouring agent for meat products, cheese, and sauces is an example of a carotenoid-based colouring agent that is affected by light exposure.[197] Upon evaluation of naturally occurring flavonoids, EGCG and quercetin were found to protect with efficacies of ~ 50% and ~35% compared to α-tocopherol and ~ 40% and ~27% compared to BHT. Green tea extracts offered protection too, but catechin was inefficient.[198] In this respect, it was recently investigated how plant phenols including quercetin and rutin regenerate carotenoids from their first oxidation product, the radical cation. Remarkably, plant phenols with average reducing power, rather than the strong reducing ones, were demonstrated to provide the most efficient regeneration of carotenoids (Fig. 2), an observation that was rationalised in agreement with the Marcus theory for electron transfer.[199]

Practical application

The examples as described have demonstrated that introduction of flavonoids is an effective strategy to inhibit light-induced quality changes. Still, implementation of the technology is delicate as physical and organoleptical features may change due to bitter taste and astringency[200,201] and due to the tendency to perturb colloidal stability.[202] Applying a vegetal extract, composed of different flavonoids, probably performs better than spiking a single flavonoid compound when considering changes in taste and mouthfeel. Food grade extracts from blueberries, dark chocolate, grape skin, green tea, clover, and many more are commercially available today. Tea extracts are rich in flavonols (EGC and EGCG make up ~35% of the dry matter in green tea),[203] as are extracts from dark chocolate (610 mg kg^{-1} catechins in black chocolate).[204] Apples and pears are also a good source of catechins and have been shown to provide protection against singlet oxygen-induced protein oxidation.[205] Grape skin and hop extracts contain more proanthocyanidins (i.e. polymerised flavanols) which are less useful due to the astringent sensations and colloidal instability they provoke.[178,179] Flavon-3-ols and their glycosides, such as quercetin and rutin, are excellent photoprotectors, but their prevalence in fruits or vegetables is much lower compared to flavanols (concentrations below 10 mg kg^{-1}) and

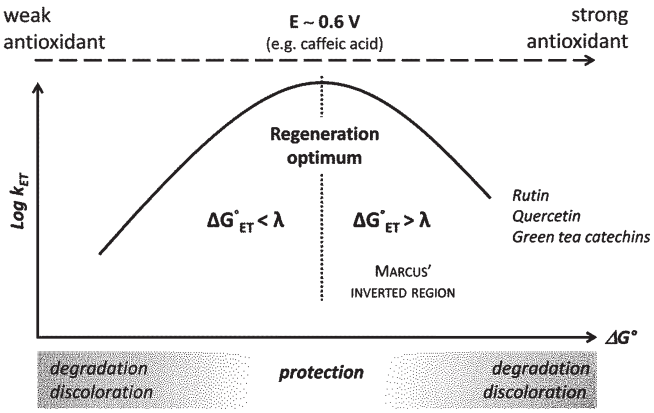


Figure 2. Marcus plot for electron transfer from plant phenols to carotenoid radical cations shows that flavonoids with strong antioxidative power were less efficient for regeneration of carotenoids than moderate antioxidants. For quercetin, rutin, and green tea catechins the standard free energy change for electron transfer (ΔG^0) exceeds the reorganisation energy (λ) for charge distribution in the donor–acceptor transition state and results in increased activation energy as compared to less exergonic reactions (e.g. with caffeic acid). As a consequence, slower electron transfer (Marcus' inverted region) is observed with carotenoid radical cation degradation as preferred pathway over regeneration.

possibly limits utilisation.[206] Flavones like luteolin are found in herbs, including thyme, green pepper, and oregano, and may be used for more specific applications in foods. Flavanones are typical of citrus fruits, with naringenin, hesperetin, and eriodictyol occurring in grapefruit, in oranges, and in lemons, respectively. They prevail mostly as glycosides (at the C_7 position) and taste bitter (such as naringin from grapefruit). Isoflavones mainly occur in soy (and derivatives) and prevail as glycosides of genistein, daidzein, and glycitein.[207] Their unpleasant bitter and astringent taste practically refutes their use as extracts, although hydrolysis to the corresponding aglycones may soften organoleptic perception. Anthocyanins and anthocyanidins are common to many fruits and are particularly important for the colour in berries and grapes.[208] In strawberries, for example, cyanidin-3-glucoside and pelargonidin-3-glucoside prevail, while in grapes mainly cyanidin-, pelargonidin-, delphinidin- and malvidin glucosides and diglucosides are found.[209,210] These compounds are excellent inhibitors of photoreactions, but it is worth considering addition of a co-flavonoid to stabilise anthocyanidins and anthocyanins against hydrolysis.

To determine which extract is most suitable for a specific application, much will depend on economy, effectivity to inhibit the consequence of light exposure, and the physical compatibility of the extract with the matrix. For example, colour stability may be affected by the flavonoid itself (e.g. with anthocyanins) or by (photo)oxidised flavonoids, the latter giving rise to yellowish di- and oligomers.[211] This was demonstrated by colour changes in white wines, which gradually darken upon ultraviolet and visible light exposure due to interactions between riboflavin and flavan-3-ols.[212] Also availability of the flavonoid in the matrix is key to effectively protect against light-induced changes. As for beverages, water solubility is essential and favours the use of glycosides, such as rutin, or flavon-3-ols like catechin and derivatives. Extracts rich in quercetin and kaempferol, both effective photoprotectors, are poorly soluble in aqueous systems and are used preferably in more hydrophobic environments.[113] They are excellent inhibitors of lipid peroxidation (soy bean lecithin) under continuous UV irradiation, with consumption of the antioxidant, however.[213,214] Protection is even more effective in liposomes (e.g. from egg yolk) as the aprotic microenvironment of the bilayer appears to stabilise the ESIPT tautomer,[215] which results in a very effective light-to-heat conversion.[216] The former illustrates the importance of understanding both the physical interaction of flavonoids with food components as well as the photochemistry affecting the matrix to determine which flavonoid is most effective to protect against light-induced changes.

CONCLUSIONS

An estimated 90 million tons of food is wasted annually in Europe alone, with almost half of it being discarded at retail and consumer level.[217] Among major causes of rejection are aesthetic issues (e.g. discolouration) and premature spoiling due to inadequate storage or packaging. Next to the economic impact of food wasting by households, retailers and processors, the issue is core to a larger ethical debate on resource management. In order to reduce food waste, it is essential to identify all possible culprits affecting quality and to mitigate their effects. Arguably a major factor affecting food quality, light exposure is perhaps equally influential as temperature. Despite this pivotal role, remarkably little effort was put in increasing photostability of foods or beverages. In this review it has been demonstrated that flavonoids are versatile compounds with peculiar (photo)chemical properties that may be effective against harmful light-induced changes. As quenchers of excited sensitisers in bimolecular reactions they prevent typical type I and type II oxidations, while efficient conversion of photon energy into harmless heat protects against direct damage by UV or visible light. Taking into consideration that flavonoids are safe, cheap (often extractable from food processing waste streams), abundant, and, as natural compounds, exempt from food additives certification,[218] most likely they are competitive with synthetic preservatives and eventually contribute to the sustainability of food industry. In combination with a thorough insight in photochemistry of light-induced changes to select the most effective quenching route, without doubt these compounds are capable of protecting food and beverages against undesired effects of light exposure to prevent premature quality loss.

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