Chapter 10

Polyphenols and Herbal-Based Extracts at the Basis of New Antioxidant, Material Protecting Products

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Additional information is available at the end of the chapter

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1. Introduction

Considering that many of the classical corrosion and scale inhibitors are toxic compounds that accumulate in the water and soil, finding natural, eco-friendly inhibitors has represented a constant preoccupation in recent years.

Table 1 shows several examples of vegetal compounds and extracts that have been revealed with anti-corrosive properties.

Given this, it is obvious that the utilization of herbal based extracts as new, ecological, material protecting products is a viable approach mainly because vegetal compounds are able not only to remove oxygen and reactive oxygen species in a biological environment (for example polyphenols, known for their capacity to rapidly oxidize thus being very effective scavenger species), but also to counteract scale formation (for example saponins known for their tensioactive properties) and to inhibit microbial corrosion (the typical example being organosulfur compounds from spices, but also polyphenols). Thus, polyphenols class, especially flavonoids and phenyl-carboxylic acids derivates, likely represent the most feasible alternative of new, natural corrosion inhibitors on basis of their capacity to act as very effective reactive oxygen scavengers, some of them also being antimicrobial species (for example gallic acid, epi(gallo)catechin gallates and tannins). In support, gallic acid has been proved as a double corrosion inhibitor acting as an anodic protector (through capturing oxygen) [36] and also as a microbial development inhibitor by *irreversible changes in membrane properties through hydrophobicity changes, decrease of negative surface charge, and occurrence of local rupture or pore formation in the cell membranes with consequent leakage of essential intracellular constituents* [37].

Moreover, polyphenols compounds have added qualities such as a good thermal stability, high solubility and dispersion into a wide range of solvents, as well as an increasing antioxidant

Investigated sample	**Bibliography**
Acacia and *Pinus tannins*	1, 2, 3
Quercus (oak) and *Castanea* (chestnut) tannins	4, 5
Mimosa tannins	6
Tamarix articulata tannins	7
Thonningia sanguinea ellagitannins	8
Rizophora (mangrove) tannins and catechins	9, 10, 11
Strychnos nux-vomica alkaloidic fraction	12
Cannabis indica alkaloidic fraction	13
Calotropis procera and *Calotropis gigantea* alkaloidic fraction	14
Solenostemma arghel, Chamommile, Halfabar, Black curmin, Kidney bean, *Lupine* and *Damssisa* extracts	15, 16, 17, 18
Opuntia elatior, Acanthocereus pentagonus, Mimosa tenuiflora, Caesalpinia coriaria, Bumbacopsis quinata and *Acacia mangium* extracts	19
Euphorbia falcata, Rosmarinus officinalis, Zenthoxylum alatum, Hibiscus sabdariffa, Aningeria robusta, Euphorbia hirta and *Dialum guineense* extracts	20, 21, 22, 23, 24, 25, 26
Psidium guajava ***seed extract***	27
Spondias mombin ***fruit extract***	28
Phyllanthus amarus leaves extract	29
Cichorium intybus, Arctium lappa, Centaurea cyanus, Pinus caribea, Eucalyptus citriodora, Piper auritum and *Piper guineense* extracts	30, 31
Cuminum Cyminum/cummin, *Ferula assafoetida*/asea, *Capsicum*/chilli, *Allium sativum*/garlic, *Ocimum basilicum*/basil extracts	32, 33, 34, 35

Table 1. Examples of previous work in the field of herbal-based anti-corrosion products

activity into acid medium (explained through the fact that the resulted, partly hydrolyzed, compounds are often more active scavengers' species than the origin homologues).

Summing, polyphenols class seems to convene most of the demands of a composite anti-corrosion/anti-biodeterioration product, also having the advantage of being less toxic than other natural compounds (for example alkaloids).

As for their role, polyphenols are secondary metabolites of the plants involved in defense against ultraviolet radiation and pathogens aggressions. The richest sources of polyphenols are onion, apple, tea, grapes, red wine and grape juice as well as strawberries, raspberries, blueberries and cranberries fruits. They are usually classified into four different groups by their number of phenol rings and by their different structural elements that bind these rings to one another. The four classes are phenolic acids, flavonoids, stilbenes and lignans, also classified as non-flavonoids and flavonoids. In the following are presented general chemical structures of the most commonly vegetal polyphenols, respectively flavonoids (flavonols, flavones, flavanones, flavononols, flavanols, anthocyanidin, isoflavones and chalcones derivates) and phenyl-carboxylic acid (protocatechuic and cinnamic acids derivates) (sub)classes.

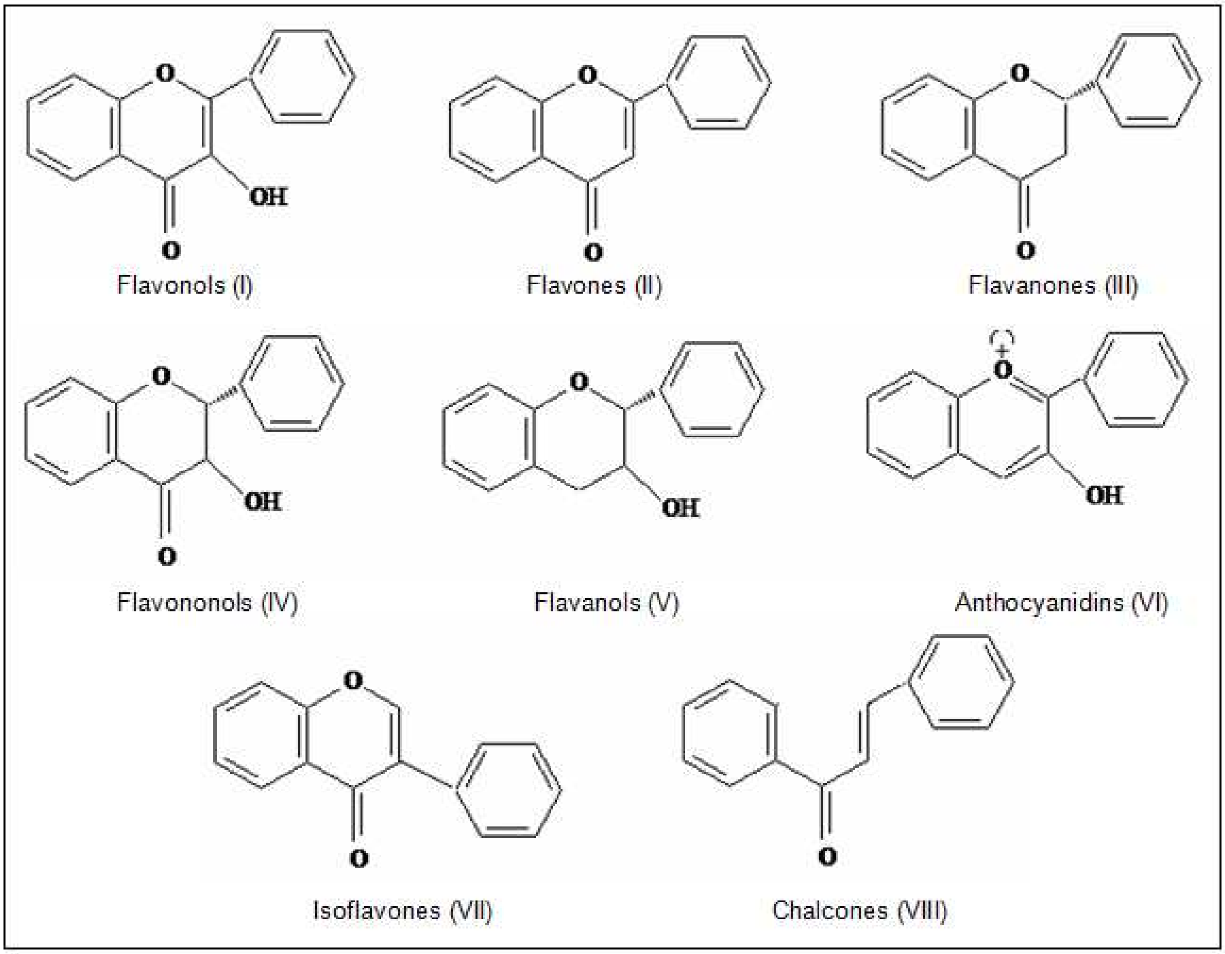

Figure 1. Flavonoids subclasses

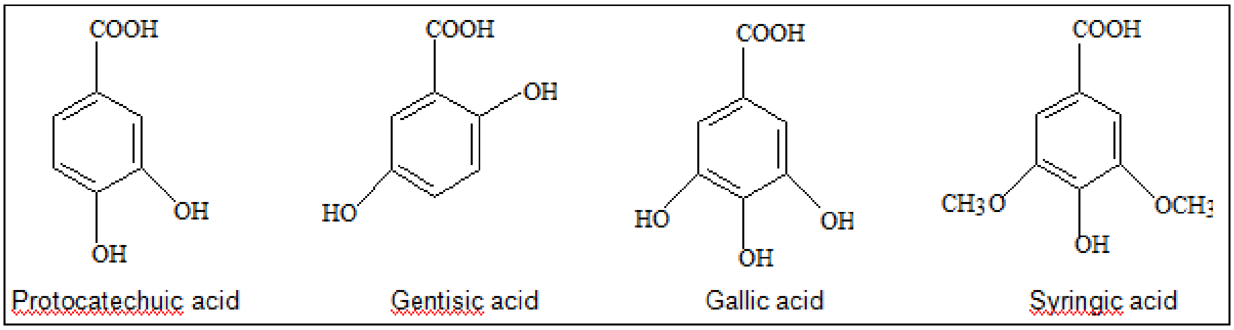

Figure 2. Protocatechuic (phenyl-carboxylic) acid derivates

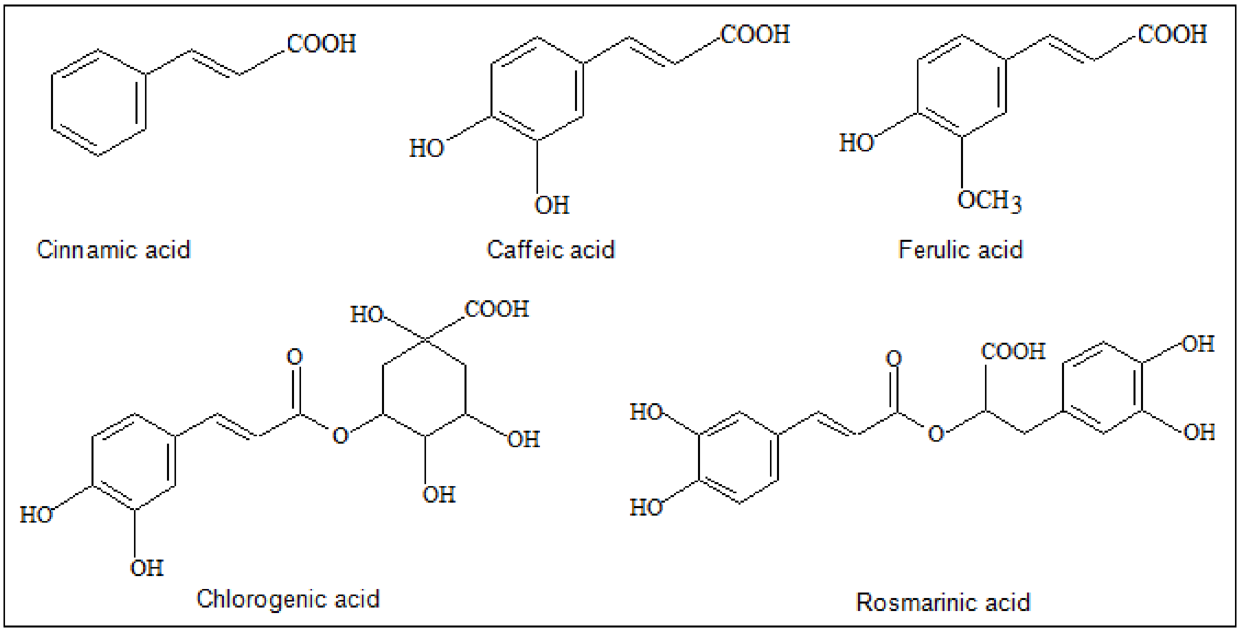

Figure 3. Cinnamic (phenyl-carboxylic) acid derivates

2. Problem statement and application area

Given the complexity of this domain, in fact an inter-, multi- and even trans-disciplinary approach, there is some short-comings need be solved, respectively it should be done much more analytical and microbiological characterization assessments on vegetal extracts tested as new eco-friendly material protecting products for both purposes, practical and scientific, respectively to achieve the quality control of the vegetal extracts and the effectiveness of certain phytocompounds in the ultimate goal of the obtaining of characterized and effective anti-corrosion products.

Data referring to the antioxidant activity of the polyphenols compounds may also be very useful.

For example, some studies [38] carried out on eighteen commonly vegetal polyphenols indicated that the antioxidant activity (AA%) of the flavonoids and phenyl-carboxylic acid compounds depends on both, the number and the position of free hydroxyl (-OH) groups; it should be noticed that studies were made by using chemiluminescence method, luminol/ H_2O_2 system, *p*H=8.6 [39]. Precisely, studies (see Figure 1) has revealed that if (-)-epicatechin, (+)-catechin (belonging to flavan-3-ol subclass), quercetin and kaempferol (belonging to the flavonols subclass) are the most effective antioxidant species (AA% between 90 and 97%), naringin and naringenin (belonging to the flavanones subclass) are the less active (AA% between 32 and 9%). Gallic acid, chlorogenic acid and rosmarinic acid, belonging to the phenyl-carboxylic acid class, are also good scavenger species their antioxidant activities (AA%) varying between 85 and 89% [39].

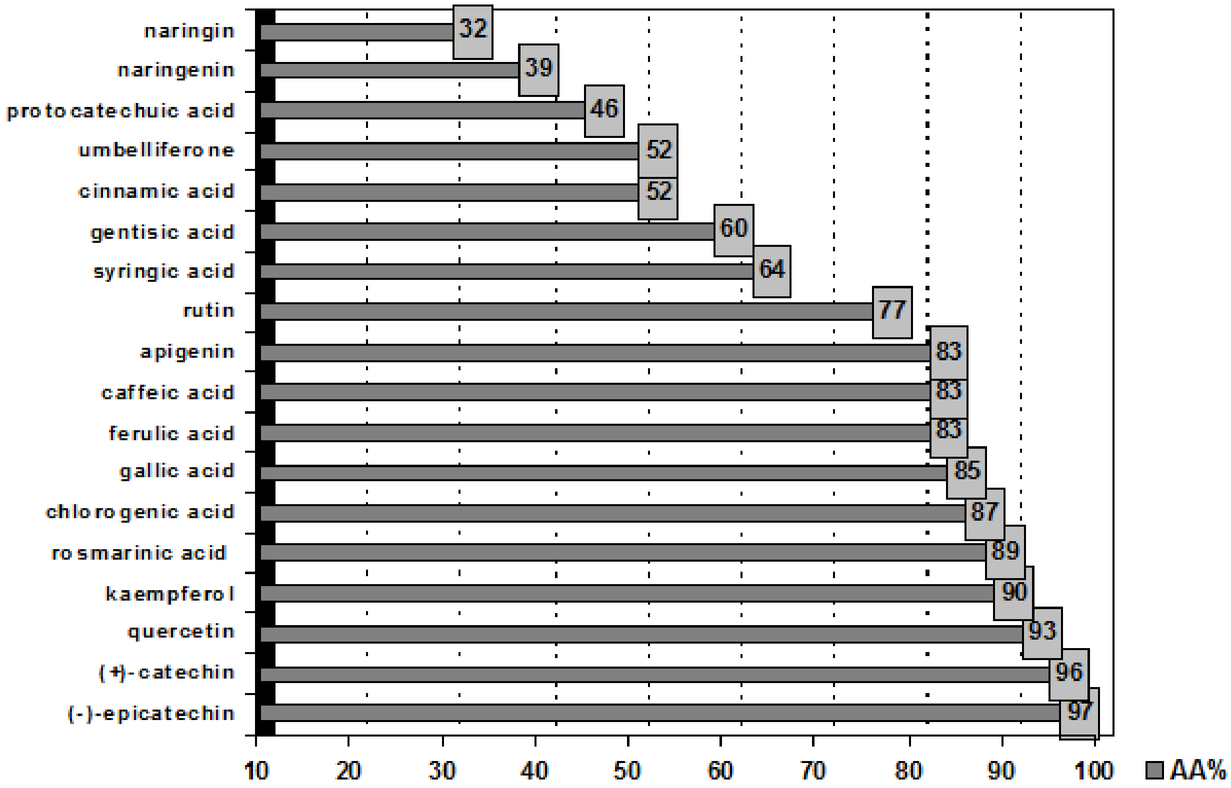

Figure 4. Antioxidant activity (CL method) of eighteen (18) commonly vegetal polyphenols

As for the capacity of the vegetal polyphenols to stop bacterial corrosion, on basis of a comprehensive review [40], structure–activity relationship for antibacterial activity of flavonoids compounds has been summarized as follows:

- 2_,4_- or 2_,6_-dihydroxylation of the B ring and 5,7-dihydroxylation of the A ring in the flavanone structure is important for their antimicrobial/anti-methicillin resistant *Staphylococcus aureus* (MRSA) activity;

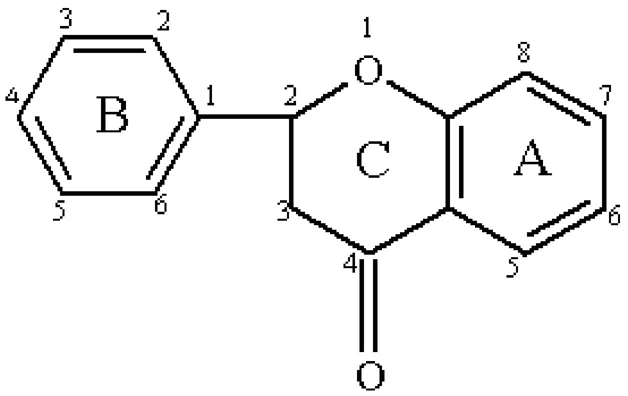

Figure 5. Flavonoid general structure

- substitution at the 6 or 8 position with a long chain aliphatic group such as lavandulyl (5-methyl-2-isopropenyl-hex-4-enyl) or geranyl (trans-3,7-dimethyl-2,6-octadienyl) enhance antimicrobial activity, and substitution with C8 and C10 chains enhanced the activity of flavonoids belonging to the flavan-3-ol class;
- 5-hydroxyflavanones and 5-hydroxyisoflavanones with hydroxyl group at position 2_ are also very active;
- chalcones are more effective against MRSA than flavanones or flavones, hydroxyl groups at the 2_ position being very important for their anti-staphylococcal activity;
- methoxy groups drastically decrease the antibacterial activity of flavonoids.

For example, using *Staphylococcus aureus* to guide the isolation process, some studies [41] on a methanolic extract isolated from dried leaves of *Physena madagascariensis* indicated two monomeric flavanones containing lavandulyl units in the limonene form as being very active against this bacterium. Similarly, studies [42] on some butanol and dichloromethane extracts of root of *Flemingia strobilifera* (a flowering plant in the legume family, *Fabaceae*) indicated flemingiaflavanone (8, 3-diprenyl-5, 7, 4'-trihydroxy flavanone) with significant antimicrobial activity against Gram-positive (*Staphylococcus aureus*, *Staphylococcus epidermidis*, methicillin resistant *Staphylococcus aureus*/MRSA), Gram-negative bacteria (*Pseudomonas aeruginosa*, *Escherichia coli*) and fungi (*Candida albicans*); genistin (5, 4 dihydroxy isoflavone7-O-glucoside) showed moderate activity against Gram-positive, Gram-negative bacteria and fungi.

Other studies [43] on some crude methanolic extracts isolated from *Grewia asiatica*, *Eugenia jambolana* and *Carissa carandas* separated, each one, into four major fractions respectively, 1)phenolic acids, 2)flavanols, 3)flavonols and 4)anthocyanins fractions indicated that, besides being the most active on microbial strains, phenolic acid fractions also inhibited all tested fungal species. Similarly, studies on Tunisian Quince (*Cydonia oblonga* Miller) pulp and peel polyphenolic extracts [44], shown as very reach in caffeoyl derivates demonstrated that chlorogenic acids acts in synergism with other components of the extracts to exhibit their total antimicrobial activities. Other comparative studies [45] on some common phytochemicals respectively, 5 simple phenolics - tyrosol, gallic acid, caffeic acid, ferulic acid, and chlorogenic acid; chalcone - phloridzin; flavan-3-ol - (-)epicatechin; seco-iridoid - oleuropein glucoside; 3 glucosinolate hydrolysis products - allylisothiocyanate, benzylisothiocyanate and 2-phenylethylisothiocyanate, but also on some dual combinations of streptomycin with these phytochemicals against *Escherichia coli*, *Pseudomonas aeruginosa*, *Listeria monocytogenes* and *Staphylococcus aureus* indicated that the isothiocyanates had significant antimicrobial activities, while the phenolics were much less efficient; no antimicrobial activity was observed in the case of phloridzin (chalcone derivate).

Differently, studies [46] reported that the marine paint mixed with 2-methoxy-2',4'-dichloro chalcone considerably reduced the formation of biofilm by *Vibrio natriegens*, a marine bacterium, on polycarbonate (PC), polymethylmethacrylate (PMMA) and glass fiber reinforced plastic (GFRP). Precisely, it has been revealed that the surfaces coated with dichloro chalcone containing marine paint had the lowest number of colony forming units (CFU)(1-5×10(6)), proteins (20-30 μg/cm2) and carbohydrates (5-10 μg/cm2) attached to them after 28 days of exposure to the organism when compared to surfaces coated with $CuSO_4$ mixed paint (20-40×10(6) CFU/ml, proteins of 50-60 µg/cm2 and carbohydrates of 40-50 µg/cm2) or plain marine paint (30-40×10(6) CFU/ml, proteins of 120-150 µg/cm2 and carbohydrates of 40-60 µg/cm2). Also, results indicated that the biofilm on PMMA was 7, 10 and 12 µm thick on chalcone, copper and plain paint coated surfaces, respectively. Furthermore, the first two paints increased the surface roughness but decreased the surface hydrophobicity when compared to the plain paint. The obtained results suggested that the low amount of biofilm formed in the presence of dichlorochalcone can be associated to its antibacterial and slimicidal activity and also its ability to reduce the hydrophobicity of the surface.

As for the solvent effectiveness, some studies [30] on different aqueous, acetonic, and ethanol extracts of *Cichorium intybus* L., *Arctium lappa* L., *Centaurea cyanus* L. (Asteraceae), *Allium sativum* L. (Liliaceae), *Pinus caribea* Mor. (Pinaceae), *Eucalyptus citriodora* Hook. (Mirtaceae) and *Piper auritum* Kunth (Piperaceae) against different microorganisms (*Pseudomonas fluorescens, Bacillus cereus, Bacillus polimixa, Enterobacter agglomerans and Streptomyces* sp.,) associated with biodeterioration indicated that the aqueous extracts did not show any antibacterial activity, the antimicrobial activity from bacteria isolated from biofilms being present only in the ethanol extracts.

Referring to the scale issue, with their well known tensioactive properties, triterpenic (acidic) saponins appears as the most viable approach, the neutral ones, respectively sterolic saponins, being very toxic (see bellow the general chemical structure of sterolic and triterpenic saponins, respectively spirostane and oleanolic acid types).

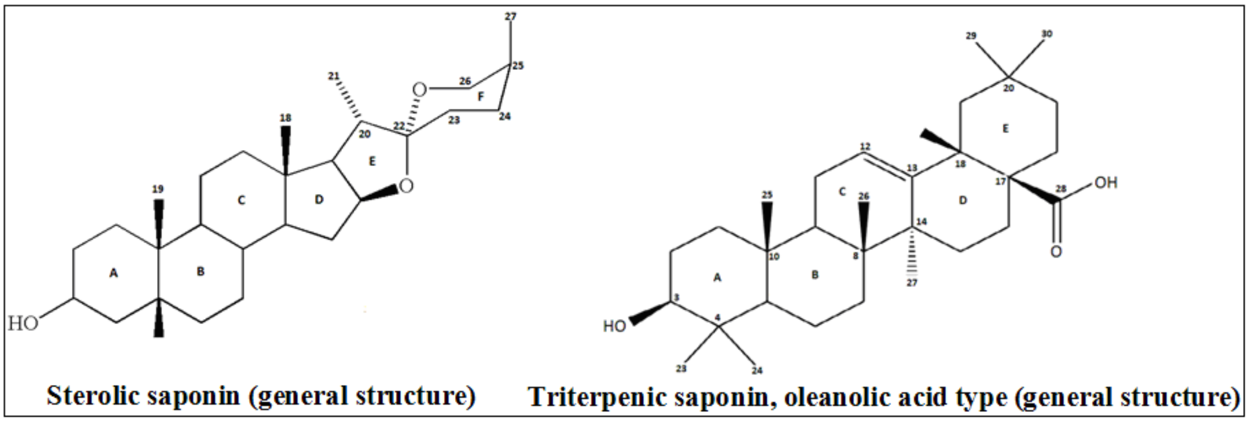

Figure 6.

For example, studies on 39 plant materials indicated that the birch bark (containing betulinic acid), plane bark (also containing betulinic acid), olive leaves, olive pomace, mistletoe sprouts and clove flowers (all containing oleanolic acid), apple pomace (containing ursolic acid) and rosemary leaves (containing an equal mixture of these three triterpene acids) are the richest sources of triterpenic saponins [47]. Other vegetal materials demonstrated as being abundant in triterpenic acids are *Satureja parvifolia* and *Eucalyptus* species. Thus, in the first case, studies on methanolic extracts lead to the isolation of eriodictyol, luteolin and ursolic and oleanolic acids [48]. In the second case, studies on the outer bark of *E. globulus*, *E. grandis*, *E. urograndis*, *E. maidenii* and *E. nitens* indicated triterpenic acids contents varying between 4.5 g/kg in E. urograndis and 21.6 g/kg in E. Nitens, but out of these species, temperate and Mediterranean *E. nitens* and *E. globulus* were also revealed as very rich in triterpenic acids; precisely, E. globulus outer bark was found as the richest source of ursane acids, while E. nitens outer bark was revealed as the richest source of oleanane and lupane acids [49].

Summing, olive oil appears as one of the most complete source of corrosion inhibitors on basis of its content in phenolics (4-hydroxybenzoic acid, protocatechuic acid, syringic acid, 4-hydroxy-phenylacetic acid, homovanillic acid, ferulic acid, sinapic acid), flavonoids (apigenin and luteolin derivates), lignanes, isochromans, tyrosol and hydroxytyrosol derivates [50] as well as in triterpenic acid derivates (oleanolic, ursolic and maslinic acids) [51] theoretically able to manage all, oxidative stress, microbial development, and scale formation.

3. A case study

Below it is presented a case study on four vegetal extracts for the purpose of assessing scavenger/antioxidant activity and corrosion inhibition effectiveness of certain flavonoids and phenyl-carboxylic acid derivates combinations.

Thus, there were compared four series of whole and selective ethanolic extracts, respectively:

- extracts containing $^{2)}$chlorogenic acid derivates aside small quantities of kaempferol, apigenin, quercetin and catechin derivates isolated from leaves of *Fagus sylvatica* L. (see Figure 2, T4-T8 tracks, respectively Table 2);
- extracts containing $^{1)}$quercetin and derivates isolated from scales of *Allium cepae bulbus* (see Figure 2, T11-T15 tracks, respectively Table 2);
- extracts containing a mixture of $^{3)}$quercetin and chlorogenic acid derivates isolated from leaves of *Juglans regia* L. (see Figure 3, T4-T9 tracks, respectively Table 3) and
- extracts containing a mixture of $^{4)}$quercetin, luteolin and apigenin derivates aside small quantities of chlorogenic acid isolated from *Agrimonia eupathoria* L.-herba (see Figure 3, T10-T15 tracks, respectively Table 3).

Chemiluminescence studies (luminol/H_2O_2 system, *p*H=8.6) carried out on these four series of whole and selective vegetal extracts isolated from scales of *Allium cepae bulbus*, leaves of *Fagus sylvatica* [52], leaves of *Juglans regia* and the aerial part (*herba*) of the *Agrimonia eupathoria* [53] indicated maximum antioxidant activities (AA%) of 91% to 97% for *total phenols content* ranging between 3 and 57mg *per* 100mL ethanolic extract (see Table 4).

Subsequently comparative studies [55] on carbon steel corrosion in acidic (0.5M H_2SO_4) solution model indicated that all studied extracts presented anti-corrosion properties, *Fagus sylvatica* L. leaves whole ethanol extract being the most potent anti-corrosion product, also presenting anti-scale properties. Results were patented [56].

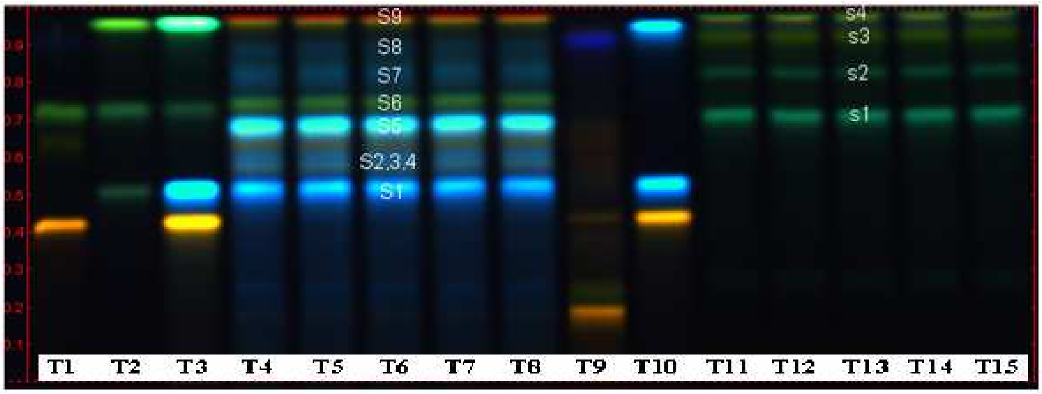

Figure 7. (HP)TLC aspects of *Fagus sylvatica* L. leaves (T4-T8 tracks) and *Alii cepae bulbus* L. scales (T11-T15 tracks) whole ethanol extracts [52]

Tested sample	Spot	*Rf~*	Colour spot	Attributed compound
Fagus sylvatica L. leaves extracts	S1	0.52	Light blue, fluorescent (fl.)	Chlorogenic acid
	S2	0.56	Brown, non-fl.	Catechin derivate
	S3	0.58	Blue, fl.	Neochlorogenic acid
	S4	0.64	Brown, non-fl.	Catechin derivate
	S5	0.69	Blue-green, fl.	Kaempferol derivate (likely Lespedin)
	S6	0.75	Green, fl.	Apigenin derivate (likely Vitexin)
	S7	0.83	Blue, fl.	Isochlorogenic acids (two isomers)
	S8	0.90		
	S9	0.97	Yellow, fl.	Quercetin
Alii cepae bulbus L. scales extracts	s1	0.72	Green-blue, fl.	Quercetin-4'-O-glycosides (also called spiraeosides)
	s2	0.84	Green-blue, fl.	
	s3	0.94	Green and Yellow fl.	Isorhamnetin and Quercetin
	s4	0.98		

Table 2. Chemical qualitative composition of *Fagus sylvatica* leaves and *Alli cepae bulbus* scales extracts [52]

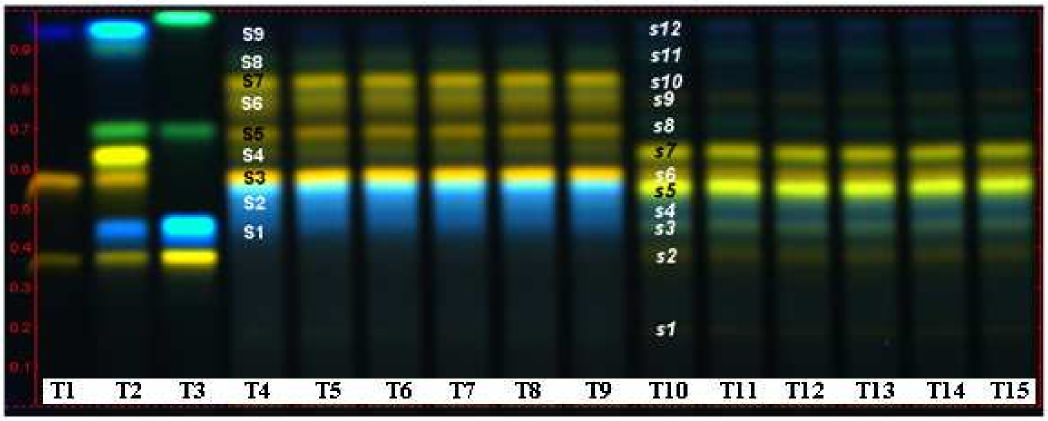

Figure 8. (HP)TLC aspects of *Juglans regia* L. leaves (T4-T9 tracks) and *Agrimonia eupathoria* L. aerial part (T10-T15 tracks) whole ethanol extracts [53]

Tested sample	Spot	*Rf~*	Colour spot	Attributed compound
Juglans regia L. leaves extracts	S1	0.45	Light-blue, fl.	Chlorogenic acid
	S2	0.50	Light-blue, fl.	Neochlorogenic acid
	S3	0.56	Orange, fl.	Quercetin derivate (likely Hyperoside)
	S4	0.63	Green, fl.	Apigenin derivate (likely Isovitexin)
	S5	0.69	Orange, fl.	Quercetin derivate (likely Isoquercitrin)
	S6	0.76	Orange, fl.	Quercetin derivate (likely Avicularin)
	S7	0.81	Orange, fl.	Quercetin derivate (likely Quercitrin)
	S8	0.87	Green-blue, fl.	Quercetin derivate (likely Juglanin)
	S9	0.96	Dark-blue, fl.	Protocatechuic acid
Agrimonia eupathoria L. aerial part extracts	s1	0.20	Orange, fl.	Quercetin derivate
	s2	0.38	Orange, fl.	Quercetin derivate (likely Rutin)
	s3	0.44	Orange, fl.	Quercetin derivate
	s4	0.50	Light-blue, fl.	Neochlorogenic acid
	s5	0.55	Yellow, fl.	Luteolin derivate (likely Isoorientin)
	s6	0.58	Orange, fl.	Quercetin derivate (likely Hyperoside)
	s7	0.63	Yellow, fl.	Luteolin derivate (likely Orientin)
	s8	0.73	Green, fl.	Apigenin derivate (likely Cosmosiin)
	s9	0.78	Orange, fl.	Quercetin derivate
	s10	0.80	Blue, fl.	Isochlorogenic acid isomer
	s11	0.87	Green, fl.	Apigenin derivate
	s12	0.98	Deep-blue, fl.	Rosmarinic acid

Table 3. Chemical qualitative composition of *Juglans regia* leaves and *Agrimonia eupathoria* aerial part extracts [53]

Parameters	Raw material description							
	Allium cepae bulbus L. scale		*Fagus sylvatica* L. leaves		*Juglans regia* L. leaves		*Agrimonia eupathoria* L. aerial part	
Type of extract: Whole (W) or Selective (S)	W	S	W	S	W	S	W	S
Antioxidant activity: (AA%)	92	95	91	94	95	97	94	97
Total phenols content: mg/100mL (expressed as gallic acid equivalents)	3.1	6.7	20.2	39.2	35.6	64.4	48.4	56.8
Total flavones content: mg/100mL (expressed as quercetin* or rutin equivalents)	2.3*	4.6*	7.2	10	23.2	58.6	21.6	17.6

Note: Analytical measurements were done by using classic methods [54], respectively total phenols content was measured by using *Folin* reagent and the results were expressed as gallic acid equivalents and total flavones content was measured by using $AlCl_3$ in base (sodium acetate) medium and the results were expresses as quercetin*, respectively, rutin equivalents

Table 4. Antioxidant activities of the four series of whole and selective vegetal extracts

4. Results and comments

This case study has revealed the following aspects:

- *whole* vegetal extracts presented similar antioxidant activities (AA%) with selective vegetal extracts but at the lesser amounts of total phenols, thus suggesting the benefit of the vegetal compounds, respectively polysaccharides and proteins, lacking in the selective extracts;

- *Allium* polyphenols (quercetin and derivates) indicated the highest antioxidant effectiveness, meaning that *Allium cepae bulbus* extracts presented the maximum antioxidant activity (respectively, 92%) at the lowest total phenols content (respectively, 3.1 mg/100mL whole ethanol extract).
- *Fagus sylvatica* leaves extracts (containing mainly chlorogenic acid derivates added to only small quantities of flavonoid derivates) also were very effective antioxidant products emphasizing an augmented antioxidant activity (91%) at moderate total phenols content (respectively, 20.2 mg/100mL whole ethanol extract);
- *Juglandis* leaves extracts (containing dominantly quercetin derivates aside moderate levels of chlorogenic acid derivates), similar to *Agrimony herba* extracts (containing a mixture of quercetin, luteolin and apigenin flavonoids aside small quantities of chlorogenic acid derivates) both required high total phenols contents (35.6 mg/100mL and, respectively, 48.4 mg/100mL extract) in order to present the same magnitude of the antioxidant activity (95% and, respectively, 94%);
- *Fagus sylvatica* leaves whole ethanol extract was the most potent anti-corrosion product presenting anti-scale properties, as well.

5. Conclusion

Literature data driven indicated that phytocompounds and herbal-based extracts are of increasing interest in this field of new, eco-friendly material protecting products. Accordingly, it has been revealed that on basis of their capacity to consume oxygen and reactive oxygen species added to the capacity to inhibit microbial development, polyphenols based extracts seems to convene most of the demands of a composite anti-corrosion/anti-biodeterioration product, also having the advantage of being less toxic than other vegetal extracts (for example alkaloids extracts). With effective tensioactive properties, triterpenic saponins also appear as very useful anti-corrosion ingredients by decreasing scale formation and increasing phytocompounds solubility.

In support, a case study aiming the comparison of the antioxidant activity and corrosion inhibition effectiveness of four whole and, respectively, selective vegetal extracts isolated from four vegetal species selected in a manner to contain different combinations of flavonoids and phenyl-carboxylic acid derivates revealed that quercetin compounds had the highest antioxidant/scavenger activity at the lowest concentration in respective environment, thus suggesting high anti-corrosion potential of quercetin based extracts. Subsequently, comparative anti-scale/anti-corrosion studies indicated that, besides containing polyphenols species with high antioxidant/scavenger activity, the co-presence of other protecting, synergetic or boosting compounds seems to be more important for the final anti-corrosion effect. As proof, *Fagus sylvatica* leaves whole ethanol extract abundant in chlorogenic acid derivates aside only small quantities of flavonoid (quercetin, apigenin, kaempferol and catechin) derivates, but containing some saponins derivates [57] offered the most proper protecting conditions on carbon steel corrosion in acidic (H_2SO_4) solution model.

Given these, it has been concluded that it should be done much more analytical and microbiological characterization assessments on vegetal extracts tested as new eco-friendly material protecting products for both purposes, practical and scientific, respectively to achieve the quality control of the vegetal extracts and the effectiveness of certain phytocompounds in the ultimate goal of the obtaining of characterized and effective anti-scale/anti-corrosion products.

Therefore, further studies in this area may be done on those vegetal extracts or combinations of vegetal extracts offering the whole range of material protecting compounds, respectively polyphenols with augmented antioxidant activity and/or polyphenols with strong antimicrobial activity, saponins with tensioactive properties and other vegetal macromolecules, such as polysaccharides and proteins, with protective, synergistic or boosting effects all contributing to the achieving of a highly effective corrosion, biodeterioration and scale inhibitor product.

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