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REVIEW / DERLEME

A Review on the Flavonoids – A Dye Source

Doğal Boya Kaynağı – Flavonoidler Üzerine Derleme

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Abstract

In this study, the short information was given about flavonoids giving yellow colour to plants present in nature. In addition to these, flavones, flavonols, flavanones and isoflavonoids as subgroups were also reviewed. Among these subgroups, flavones and flavonols are one of the most important classes of phenolic compounds. The information about the most important dye plants including flavonoids was also given in this study. The investigated plants are weld (*Reseda luteola* L.), onion (*Allium cepa* L.), young fustic (*Cotinus coggygria* SCOP), Anatolian buckthorn (*Rhamnus petiolaris* Boiss), dyer's greenwood (*Genista tinctoria* L.) and Spanish broom (*Spartium junceum* L.). The most important yellow dyestuff and the oldest European dye among these dye sources is known as the luteolin dye. The dye plants were used for yellow color dyeing in ancient and historical textile. Nowadays, flavonoids are reused for sustainable, non-toxic, green textile and environment friendly textile dyeing. In the same time, flavonoids have been used for natural lake organic pigment, cosmetic, pharmaceuitical industries. In recent years, it has been suggested to use flavones in textile dyeing, cosmetic, pharmaceutical, *etc*. industries by the World Health Organization (WHO). Therefore, we have aimed to contribute to similar studies theoretical and experimental in natural dyeing studies.

Keywords: Flavonoid, natural dye, dye plant.

Öz

Bu çalışmada, doğadaki mevcut bitkilere sarı renk veren flavonoidler hakkında kısa bilgi verilmiş olup, ek olarak da, bu bileşiklerin alt grupları olan flavonlar, flavonollar, flavanonlar ve isoflavonoidler hakkında genel bilgiler sunulmuştur. Bu alt gruplar arasında flavonlar ve flavonollar fenolik bileşiklerin en önemli sınıflarından birisidirler. Flavonoidleri içeren en önemli boya bitkileri hakkında bilgiler de bu çalışmada verilmiştir. İncelenmiş bitkiler muhabbet çiçeği (*Reseda luteola* L.), soğan (*Allium cepa* L.), boyacı sumağı (*Cotinus coggygria* SCOP), cehri (*Rhamnus petiolaris* Boiss), boyacı katırtırnağı (*Genista tinctoria* L.) ve katırtırnağı (*Spartium junceum* L.)'dır. Bu boya kaynakları arasında en önemli sarı boyarmaddesi luteolin'dir. Anadolu ve Avrupa'ya özgü boyarmaddenin en önemlilerinden birisi olarak bilinir. Bir çok boya bitkisi antik ve tarihi tekstillerde sarı renk boyamacılığı için kullanılmıştır. Günümüzde, flavonoidler sürdürülebilir, toksik olmayan, eko tekstil ve çevre dostu tekstil boyamacılığı için yeniden kullanılmaya başlanmıştır. Aynı zamanda, flavonoidlerin doğal lak organik pigment, kozmetik ve ilaç endüstrisi için kullanımı yeniden artmıştır. Son yıllarda, Dünya Sağlık Örgütü (WHO) tarafından tekstil boyamacılığında, kozmetik ve ilaç endüstrileri ve benzeri alanlarda flavonların kullanımı önerilmiştir. Bu nedenle, bu çalışmada doğal boyarmaddelerin teorik ve deneysel benzer çalışmalara katkı sağlaması amaçlanmıştır.

Anahtar Kelimeler: Flavonoid, doğal boya, boya bitkisi.

I. INTRODUCTION

Flavonoids have found in nature for over one billion years [1,2]. These compounds were discovered by the Hungarian Nobel laureate Albert Szent-Györgyi in 1936 [3]. "Flava" means yellow in Greek [4]. The components of dyes using in textile

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dyeing are soluble and coloured organic compounds. They are mostly applied to fibres from a solution in water [5]. Flavonoids are usually applied as mordant dyes. As a result of this, the colours from yellow to greenish yellow and brown are obtained [6]. Natural dyes were typically used for the coloring of the food substrate, leather and the natural protein fibres such as wool, silk, and cotton as well as fur since the past [7-9]. At the same time, they were also used to color cosmetic products and to manufacture inks, watercolors and artist's paints [8]. Besides, they were also used for food, buildings and in painting restoration [10]. To give an example, there are about 450 dye plants including dye in India [11]. The use of natural dyes was rapidly reduced after the discovery of synthetic dyes in 1856 [12,13]. Natural dyes in comparison with synthetic dyes are generally environment friendly, anti-allergenic, biodegradable and less toxic [14, 15]. Flavonoids first appeared in green algae 500 million years ago [16]. Flavonoid dyes giving yellow colour to the flowers are important sources of dyes and pigments [17-19]. There are more than 4000 known flavonoids in nature [20]. Flavonoids are abundant in Polygonaceae, Rutaceae, Leguminosae, Umbelliferae and Compositae [21]. Flavonoid compounds consist of a C_6-C_3-C_6 carbon skeleton [22-27]. In Figure 1, the basic chemical structure of flavonoids is given.

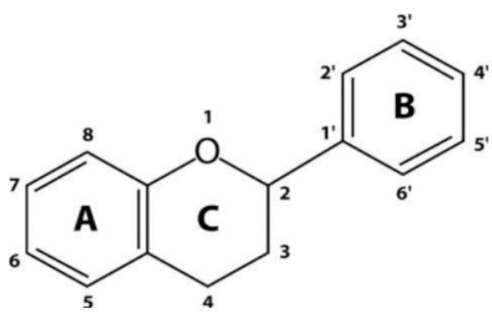


Figure 1. Basic chemical structure of flavonoids

A few nonplant sources also include flavonoids. For example, these compounds are present in the wings and bodies of butterflies in the Satyridae, Lycaenidae, and Papilionidae families. Besides, the only reported mammalian flavonoid source is also obtained from the scent of glands of the Canadian beaver. This flavonoid compound is 4'-methoxyflavan. Besides, flavonoids cannot be synthesized by humans [28].

Most of flavonoids are present in plants as glycoside compounds. Mostly these flavonoid compounds split into to an aglycon and sugar during natural dyeing. The basic structure of the flavonoids is the colourless flavone [29].

Flavones and flavonols (3-hydroxyflavones) are the main chromophores in flavonoids giving yellow colour [30].

Flavonoids occur as aglycones, glycosides and methylated derivatives [31,32]. Flavonoids are often hydroxylated in positions 3, 5, 7, 3', 4' and / or 5' [12,33]. 90 % of all yellow dyes approximately form flavonoids [34]. The hydroxy and methoxy derivatives of flavones and isoflavones include most of naturally occuring yellow colours [35]. The colour index disclosed that nearly 50 % of all natural dyes used in the colouring of textiles are flavonoids [36]. Flavonoids can solubilize commonly in water [10,37].

The possible sugar groups present in the flavonoid molecules increase the water solubility of the hydrophobic flavonoid molecules [18]. However, flavonoids obtain lipophilic feature with metyl groups and isopentyl units [38]. Flavonoids may also help plants living on soils that are rich in metals such as aluminium [39]. Flavonoid derivatives were used in paintings as lake pigments and in historical textiles as mordant dyes until the late nineteenth century [40-42]. According to ancient recipes, the most commonly used mordant material in the natural dyeing giving colour the historical textiles was an aluminium salt in a form of $KAl(SO_4)_2$, also called potash alum [43]. Flavonoids give colour flowers and also protect the plants from microbes and insects [38]. While the less polar solvents are especially important for the extraction of flavonoid aglycones, the more polar solvents are used for flavonoid glycosides or anthocyanins. The less polar aglycones such as isoflavones, flavanones, and dihydroflavonols, or flavones and flavonols which are largely methylated, are usually extracted with solvents such as benzene, chloroform, ether or ethyl acetate [44]. Acylation of flavonoids can effect the solubility of the flavonoids and this situation cause a shift in their absorption spectra [45].

II. SOME SELECTED FLAVONOID CLASSES

2.1. Flavones

The name "flavone" was first suggested by von Kostanecki and Tambor [46]. Flavones have not a 3-hydroxyl group at the C ring, but flavonols have this group [20]. Naturally forming flavones show the most distribution in the plants. Nearly, the flavones are spreaded in the region to be until the bract from the root of a plant [47].

The flavone – based dyes are known to generate stable complexes with metal cations such as aluminium (III), iron(II), and tin (II) [48]. Flavones are colourless organic compounds [49]. These compounds are common in angiosperms [50]. Flavone compound is insoluble in water and it melts at 100°C. At the same time, this compound fluoresces violet in concentrated sulfuric acid. At the resulting of treatment with alcoholic alkali, flavanone is obtained from flavone. Flavones are responsible for ivory and yellow colours in plants and flowers [51].

Nowadays, more than 300 flavone aglycones have been isolated from the plants [52]. The most important flavone – luteolin, is mainly present in vegetables such as artichoke, basil, celery and parsley [53].

2.2. Flavonols

Flavonols contain widely quercetin, kaempferol, rhamnetin, morin, myricetin and fisetin etc. flavonoids which are known having antioxidant features [54]. Quercetin dye relating to flavonol class was firstly isolated from oak tree (*Quercus rubra*). Interestingly, it can be said that the yellow dye present in the wings of *Melanargea gelatea* butterfly belongs to flavonol class [55]. Kaempferol (3,5,7,4'-tetrahydroxyflavone) shows wide distribution both in free form and in it's glycoside form. Quercetin is a compound which have the most widely distribution among all phenolics present in the nature. It has 135 different glycosides identified. The quercetin-3-rutinosid known as rutin from these compounds is the most common [56]. The most studied flavonols are kaempferol, quercetin, myricetin and fisetin [57].

It can be said that first flavonol dye was obtained from a species of tamarisk (Tamarix sp.). The second flavonol dye was determined in both yellow and green yarns. This plant source is not identified until now [58]. The chemical structures of flavone and flavonol are presented in Figure 2.

Flavone structure **Flavonol structure**

Figure 2. Chemical structures of flavone and flavonol

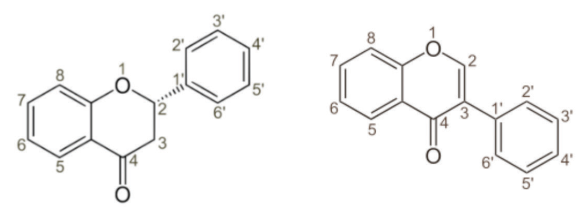
2.3. Flavanones

Flavanones have not the double bond between the positions 2 and 3 and have a chiral center at the position 2 [59]. Linden tea and lemon contain hesperidin and eriocitrin compounds with respect flavanone [60]. Flavanones are extremely reagent compounds and easily to expose hydroxylation, glycosylation and methylation reactions. They are especially found in the crust of the citrus at high concentrations [61]. These compounds are rare and normally present in the form of their glycosides [37].

2.4. Isoflavonoids

Isoflavonoids differ with binding to carbon atom at position 3 of the B – ring from other flavonoid classes as the main structure feature [59]. Isoflavonoids have potentially antibacterial activity [62]. Some isoflavonoids have also been reported to be present in microbes [57]. More than 300 kinds of plants contain isoflavones especially localized in roots and seeds [63]. Isoflavone compounds are only synthesized in legumes such as soy [64].

Dyer's greenweed (*Genista tinctoria* L.) contains genistein (4',5,7-trihydroxyisoflavone) dye which a main isoflavone [65]. Isoflavonoids are isomeric with flavones. These compounds are more limited compared to flavones and flavonols [66]. In Figure 3, the chemical structures of flavanone and isoflavonoid are given.



Flavanone structure **Isoflavonoid structure**

Figure 3. Chemical structures of flavanone and isoflavonoid

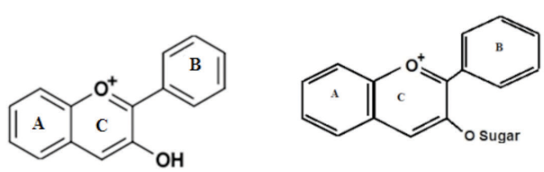
2.5. Anthocyanidins

In Greek, "antho" means flower and "kyanos" also means blue [67]. Anthocyanins are responsible for most red, purple and blue colours. They were introduced as a term by Marquart in 1835. However, the fundamental chemistry of these compounds and flavones were studied about in the nineteenth century by von Kostanecki and Willsätter [68].

Anthocyanidins are basic structures of anthocyanins. These compounds (or aglycones) consist of an aromatic ring (A) connected to one heterocyclic ring (C) including oxygen bonded via C-C bond to an aromatic (B) ring. They are known as anthocyanins if they are found in glycoside forms (bonded to a sugar piece) [69]. Besides, anthocyanins can make complex with metal cations, but it is not clear that wheather or not the chelation can effect the the color of fruit [70]. Teas, honey, fruits, vegetables, nuts, olive oil, cocoa and cereals contain anthocyanidins. Above 500 different anthocyanidins have been known and identified in literature

[71]. The dry weight (up to 30 %) of some flowers includes anthocyanins [37].

Anthocyanins are water soluble plant compounds. The common anthocyanidin aglycones are cyanidin, delphinidin, petunidin, peonidin, pelargonidin and malvidin. These anthocyanidins differ with the 3' and 5'-positions [72]. Anthocyanins are partially polar molecules. The polar solvents such as water, methanol, ethanol or acetone are used for extraction to a degree [73]. The structure of this compound is derived from flavonol [74]. Generally, anthocyanins have colour diversity because of pH or metal chelation changes [75]. These compounds are also used as natural food colourants [76]. So far, more than 630 anthocyanins have been identified in nature [77]. Anthocyanin molecule contains an ionic site at the charged oxygen. This site increases the polar character of the molecule and supports their water-solubility [78]. As glycosylation increases water solubility, acylation decreases water solubility [79]. Anthocyanin compounds are more stable under acidic conditions [80]. Most of red, purple, and blue-coloured flowers contain anthocyanins [74]. The chemical structures of anthocyanidin and anthocyanin are presented in Figure 4.



Anthocyanidin structure **Anthocyanin structure**

Figure 4. Chemical structures of anthocyanidin and anthocyanin

2.6. Flavanols

Grape and wine contain abundantly flavanols. Flavanols present in grape are found both in the core and the skin [81]. Flavanols are the centre of attraction that due to the important as the units formed proanthocyanins of late years [82]. As examined structurally, flavanols are the most complex flavonoids [61]. In Figure 5, the chemical structure of flavanol is shown.

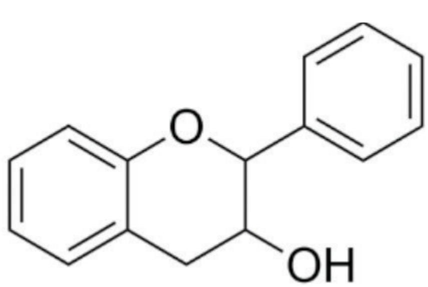


Figure 5. Chemical structure of flavanol

III. DYE PLANTS INCLUDING SOME FLAVONOIDS

3.1. Weld (Reseda luteola L.)

Weld (*Reseda luteola* L.) is called as "Muhabbet cicegi" in Turkey [83]. It is also called "dyer's-weed" [84].

The plant is an annual plant belonging *Resedaceae* family [85]. The seeds of the plant were found in dye waste in places such as York and Scotland (in twelfth century) [86]. Weld (containing luteolin and apigenin) plant was likely the oldest flavonoid dye source which exhibits the most common distribution in the vegetable kingdom and this plant was known by the African tribes in the Neolithic period. In the coptic textiles, this plant was also used by Egyptians [17]. The dyes (mainly luteolin) present in the plant are at the highest level in the blooming season [87]. The seeds related to this plant were found in a lake excavation concerning the Neolithic period in Switzerland. In dye and mordant analyses of the Nubia textiles in the 6th century BC, weld, aluminium (Al) and iron (Fe) salts were determined the used. According to the dye analysis results of the coptic textiles relating the third century and the tenth century, the weld plant was widely used in the Egypt. In the carpet group known as Lotto carpets of XVI. century Usak carpets – one of the periods of the most brigtness of the Turkish carpet art, weld was determined in the yellow coloured parts. The weld plant which is the dye plant quite popular in the Ottoman Empire was frequently used both in the dyeing of wool and silk. Until to the middle of XX.century, the weld was used in the yellow and green parts in the Morocco carpets [83]. The plant was also used by the Gauls in the time of Julius Caesar [88]. The fastness of a mordant dye depends on both the mordant and the mordanting method [89].

Weld lakes were obtained with the adding of the solutions of metal salts to the weld extract prepared with water. Also, the medium relating to the flavonoid-metal complexes was made the alkaline by a base solution which is a sample – K_2CO_3. The lake pigments precipitated with using this method are insoluble metal-dye complexes. They do not solubilize in water. These pigments were prepared and analyzed with HPLC-DAD by Karadag et al. in 2011 [90].

The flavonoid content of weld dye plant was known to average 2 % by weight (2 g dye / 100 g plant). The plant grows as wild in most places of Europe but was also cultivated [30,91]. The luteolin (3',4',5,7-tetrahydroxyflavone) present in weld plant which is mainly a weld flavone is known as the oldest European dye [92-95].This was mentioned in traditional European recipes [96].This dye compound has antibacterial and anti-inflammatory properties [97]. Luteolin has been commonly known to be used as a natural dyeing agent in colouring of natural fibers since prehistoric times [43,98,99].

Weld plant was also used together with indigo to obtain green colour in North Africa. In addition to the luteolin and apigenin present in weld plant, there are also luteolin-7-glucoside and 3,7-glucoside in the plant [100].

The aluminium-luteolin complex stoichiometry was determined as 1:2. For the extraction from the above ground parts of weld plant, the most suitable solvent was methanol. The optimal methanol luteolin extraction was determined to be 8.6 g / kg plant material [101].

The plant was the best-known yellow dye source from Roman times up to recent years [102]. The chemical structure of luteolin compound is given in Figure 6.

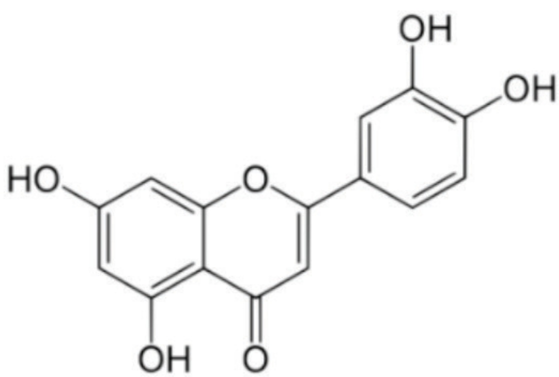


Figure 6. The chemical structure of luteolin compound

Many gut organisms are known to produce extracellular flavonoid compound that can be reduced azo bonds in food colourants [103]. The principal flavonoid component in weld plant is luteolin and apigenin (about 9/1 ratio at 255 nm) [104].

3.2. Onion (Allium cepa L.)

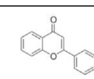
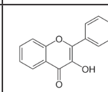
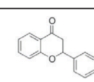
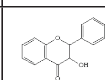
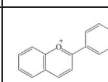
Onion is an edible vegetable apart from its skin [105]. The onion skin contains mainly quercetin (3,3', 4', 5,6-pentahydroxyflavone) which is a flavonol compound. The cultivation of onion (Allium cepa L.) has been performed since about 3000 years. This is a plant which belongs to probably the Central Asia. In the pictures of Egyptian graves, this plant was picturized more of other plants. The onion was also used as a herbal medicine in the past. According to many references, the onion skin was also used in the colouring of eggs in the Eastern ceremony relating to the Christians as a yellow dye source plant [83].

Flavonols (3-hydroxyflavones) can readily undergo photo-oxidation, resulting in fading or discoloration. Unlike it, if the flavonol is substituted, e.g. with a glycosyl group, the present flavonol derivative is comparatively stable [58]. Quercetin compound produces from yellow to brown tones for the natural fibers such as silk and wool [106]. Quercetin is found in abundance in the products such as onions, broccoli, apples and berries [31]. These foods may protect against certain forms of lung cancer [107]. Over 450.000 tonnes of onion wastes are annually produced in the European Union (mainly in UK, Holland and Spain) [108]. Skin of Allium cepa L. which is a kitchen waste material has dyeing potential on different textile materials [109].

In Anatolia, onion skins have been used for the dyeing of wool since past [110].

The cultivated onion, *Allium cepa*, includes about 89 % water, 4 % sugar, 1 % protein and 2% fiber. Besides, it also contains the compounds like vitamin B1, vitamin B2, vitamin B3 and vitamin C. In addition to these, it also contains phenolics, flavonoids, as well as elements (for example; iron, calcium, magnesium, manganese and zinc) [111]. Electronic transitions appear in the spectrum as individual bands, described by three basic parameters (position, intensity and width), which can be used for estimations of the characteristics as well as for qualitative and quantitative analysis. Table 1 shows the UV absorption bands of some flavonoids.

Table 1. UV absorption bands of some flavonoids [55]

Flavonoid	Structure	Band I	Band II
Flavones		240-285	304
Flavonols		240-285	352
Flavanone		270-295	300
Dihydroflavonol		270-295	300-320
Anthocyanidin		270-280	465-550

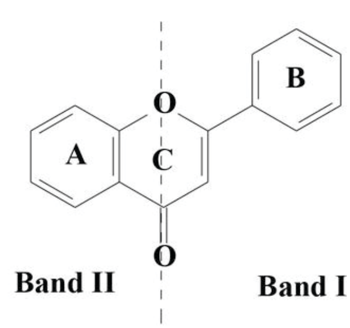


Figure 7. The division of bands I and II related to UV–VIS absorption bands

Flavones and flavonols have generally two primary absorption bands. While band II (250-285 nm) related to the A ring absorption, band I (320-385 nm) represents the B ring absorption. The lack of a 3-hydroxyl group in flavones divorces from flavonols. Functional groups can effect a shift in absorption. For example, this shift suites to 367 nm in kaempferol, 371 nm in quercetin and 374 nm in myricetin. Flavanones show a very strong band II absorption maximum between 270 and 295 nm. The following sample compounds can be given that 288 nm (naringenin), 285 nm (taxifolin) and it has only a shoulder for band I at 326 and 327 nm [112,113]. Flavonoids absorb light in the visible spectrum between 400 and 700 nm [54]. Figure 7 shows the division of bands I and II related to UV–VIS absorption bands.

3.3. Young fustic (Cotinus coggygria SCOP)

Young fustic (Cotinus coggygria SCOP) is also known as "Duman Agaci" and "Peruk calisi". This plant can be mostly seen at maquis areas in the Mediterranean coasts in Turkey. The plant is bise and China origin. Young fustic is a shrub that grows to a height of 2-5 m and is a beardless and defoliates in the winter. It has leaves in a length of 2 and 3 centimetres. The seeded watery fruits are like a awry pear. In form of kidney inside the fruits, there is only a seed. The upper surface of the plant's leaves is beardless. The lower surface of the plant's leaves is also purple green. In its leaves, it is appeared a staining such as dark red close to violet purple in the autumn. In plant of the petalled flowers, the blooming takes a very short time. They are found in the case of fibrous-branched, flossy and clusters. It's fruits are shiny green and blue-green appearance similar to wig. In the fall, the fruits hang off on the feathery stems. We see a view the coloured fledged when we looks it from a distance.

This plant is known as a dye source since the Roman Empire. It was commonly used in Europe at medieval times and has economically an important location. According to Roman Pilinus living between 1923 and 1979 years, the plant was also used for the dyeing of leather at the old times. In Europe, especially for the dyeing of silk, the plant was used to obtain yellow colour at 19th century. The leaves and twigs related to this plant were used to dye the Turkish soldiers's uniforms and tents in World War I. The plant was also used to dye the yellow yarns in the carpets at 19th century. Especially, the yellow colours present in Taspinar carpets were obtained with using this plant [83].

Cotinus coggygria Scop. (young fustic) was a flavonoid source and also an important source of tannin [17]. The plant includes a flavonol compound fisetin and a flavanonol compound fustin yellow flavonoids [114,115]. The dye components present in young fustic dye plant are given in Figure 8. This plant is also known as "smoke tree" in English [116]. The plant was probably an important dye plant in the past. We can see that to be used in the dyeing of ecclesiastical/liturgical garments [117].

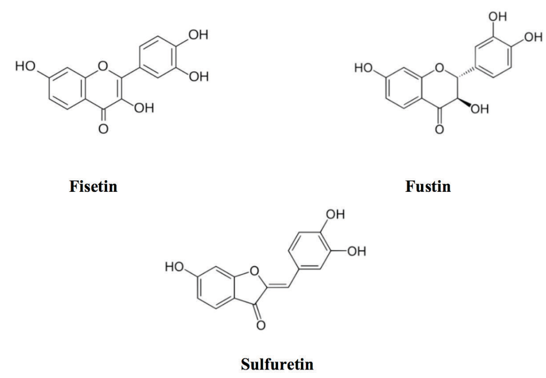


Figure 8. Dye components of young fustic dye plant

The main fisetin colourant present in the plant was isolated by Michel-Eugène Chevreul (the French chemist) at the beginning of the 19th century. During the same time, this compound was called as fustin by his. But this dye was given to a flavanone present in the plant. An orange colorant as a sulfuretin relating to a group of aurones was recently identified in the plant. The wood concerning the plant also contains tannin compounds (3 % on average). Also, the branches and leaves of the plant contain fisetin, myricetin, quercetin, kaempferol, and some flavonol glycosides, anthocyanins and tannins (from an average of 18-20 % up to 35 %) [118].

Fisetin dye is easily soluble in the solutions such as ethyl alcohol, acetone and acetic acid. But it is almost insoluble in water, ethyl ether, benzene and chloroform [119]. The plant's leaves include mainly tannins. They were used to obtain brown, gray and black with using iron mordant salt [85]. The plant grows largely in central and southern Europe and Turkey. Besides, it was also used for tanning of leather [86].

The lightfasness of dyeing with this dye plant is poor [120].

3.4. Anatolian buckthorn (Rhamnus petiolaris Boiss)

Anatolian buckthorn (Rhamnus petiolaris Boiss) is also known as altın agaci, alacehir, boyaci dikeni, and akdiken in Turkey. It is a thorny or bush plant growing up to 3 m in height. The plant grows on mountainy, hilly, rocky, sunny braes and in the sides or under of the rare forest at 1000 and 1300 m in height. There is twenty – two kinds of the plant. Although Rhamnus petiolaris defoliates, some of these kinds does not defoliate. The plant blooms the small yellow-green coloured in the months of May and June. These blooms form the seeds (fruits). After the seeds have been green for a long time, it's fruits convert into brown or black colour. The outer shell of the fruits at 6 and 7 mm in diameter is brown colour and the interior of fruit's is also yellow colour. Rhamnus petiolaris grows as endemic in Central Anatolian. The plant was used to obtain yellow colours of a lot of carpets weaved in the 15th and 17th centuries. Also, until the beginning of 20th century, it was exported from the Anatolian to many countries of the world for the dyeing of silk and wool. The plant was used to obtain the yellow colour in the composition of yellow and green colour in 16th century Ottoman textiles.In the first samples of Hereke carpets, the plant was generally used in the part of yellow [83]. Buckthorn berries are an old Turkish dye source [121]. The obtaining dye from Rhamnus is known since ancient time. This dye was extensively used for dyeing textiles from middle age to 19th century as a lake pigment [122]. The dye components of Anatolian buckthorn dye plant were presented in Figure 9.

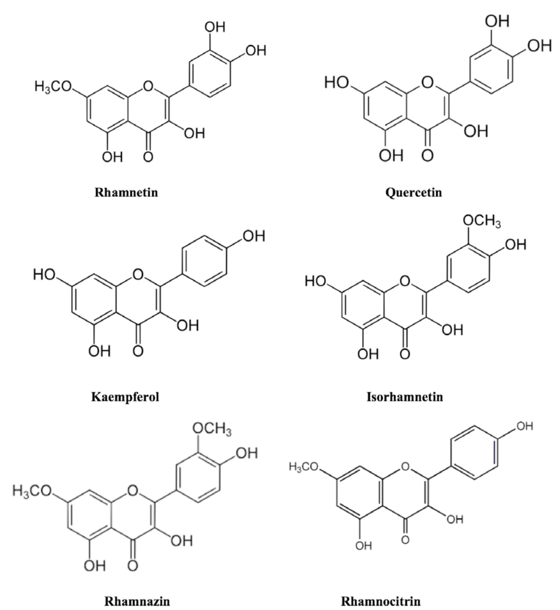


Figure 9. Flavonoid dye components of Anatolian buckthorn dye plant [123]

A flavonol quercetin and rhamnetin were determined in the Anatolian buckthorn aqueous extract and together with rhamnetin and emodin were identified in the natural pigments precipitated by Al(III), only emodin was determined in the natural pigments precipitated by Sn(II) and Fe(II) [121].

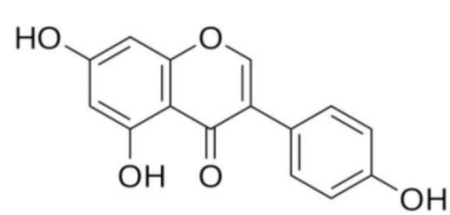
Rhamnetin is slightly soluble in water and soluble in concentrated sulphuric acid. This dye is freely soluble in sodium hydroxide 10 %. In addition to this, it is sparingly soluble in acetic acid and alcohol [119].

According to the work published in 2012, Deveoglu et al. determined quercetin-3-arabinosid and possible quercetin glucosides in the non-hydrolysed *Rhamnus petiolaris* extract. In the acid hydrolysed extract, rhamnetin, isorhamnetin (flavonoids) and emodin (anthraquinone) were identified. In the acid hydrolysed alum-mordanted buckthorn dyed wool fibre, rhamnetin and isorhamnetin were determined [124].

In 2013, the according to the work of the examination on dyeing of silk with buckthorn and walloon oak, Deveoglu et al. identified quercetin, kaempferol or isorhamnetin, rhamnetin, rhamnazin (dimetylquercetin) and emodin in the acid hydrolysed buckhtorn extract [125].

3.5. Dyer's greenwood (Genista tinctoria L.)

Dyer's greenwood (Genista tinctoria L.) is a perennial and bushy plant that has yellow flowers. The plant grows up to 1 and 1.5 m in hight. It is sparse branch and thornless. The young twigs are petite, light green colour and it is longitudinal grooved. The plant blooms in the months of June and August. The flowers were gathered in the peak of the branchs and they are golden blond. It's fruits are in the form of the broad bean and 2 cm in the length. The homeland of this plant is the South and Central Europe, the Caucasus, the Anatolian and the North Iran. The plant is widely seen in the north of the Anatolian in Turkey. Also, it is frequently coincied in the thrace and the black sea region. At the digs making in the city of Bristol relating to the 13th and 14th centuries and in the some archeological digs relating to the 9th and 11th centuries in the city of York in the England, dyer's greenwood seeds, weld and other plant seeds were found together. The plant was used as a dye plant in Europe during the Middle Ages. At the time of Edward III (1312-1377) in England, the plant was used together with woad in the dyeings of green colour. The dyeing was become famous as Kendel green. The one of dye components of dyer's greenweed dye plant was given in Figure 10.



Genistein

Figure 10. One of dye components of dyer's greenwood dye plant

Effective dyes including the plant are the flavone luteolin (0.3 % by weight of plant material) and the isoflavone genistein dyes [30,83]. The branches of the plant contain luteolin dye. Genistein is soluble in water, alcohol and ether [119]. Apart from luteolin and genistein dyes, the flavone apigenin and the glycosides of these flavonoid compounds are known as dye components present in Genista species [126]. Genistein (4',5,7-trihydroxyisoflavone) is a polyphenolic isoflavone and was mainly obtained from Genista tinctoria L. in 1899 [127]. Genistein is also present in the form of the glucoside genistin [119]. The glycoside (7-D-glucoside) is called as genistin [115] (Figure 11).

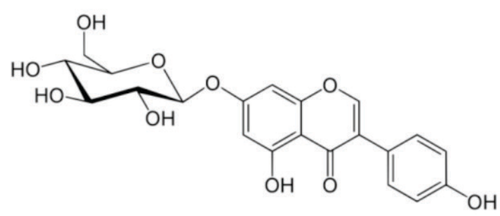


Figure 11. One of dye components of dyer's greenwood dye plant

3.6. Spanish Broom (Spartium junceum L.)

Spanish Broom (Spartium junceum L.) is known as "Katirtirnagi" in Turkey. It is a without thorns perennial and sylindirical shrub and 1 and 3 m in height. It's leaves are simple. It's flowers exist together 5 and 20 pieces. They have a gold colour. This plant is spread over a wide area in the Black Sea, the Aegean, the Mediterranean regions. Especially, it shows a wide distribution in the shrubberries close to the sea. This plant is known as a good dye plant due to the hight fastnesses of the dyes present it. It was also used for the wool dyeing in the past. The plant's dried flowers contain luteolin and quercetin dyes [83]. Spanish broom (*Spartium junceum* L.) is a plant relating to a member of Leguminosae family [128]. The plant has been known in the all of Mediterranean since the ancient times. The Greeks, Romans and Carthagians have been used the plant for manufacturing ropes, nets, bags, sails, clothing and for covering roofs [129].

The flavonoids were used for many application areas (textile dyeing, food, painting, leather dyeing, cosmetic *etc.*) In Table 2, some application areas of flavonoids are summarized.

Table 2. Some application areas of flavonoids as a dye source

Application area	Reference
Historical textiles	[17], [30], [94], [130-137]
Textile dyeing	[5], [7-9], [14], [26], [42], [87], [89], [106], [111], [124], [125], [138-141]
Natural lake pigment	[41], [90], [95], [97], [121], [142-145]
Medieval manuscript, easel painting	[18], [146]
Mural painting, icons	[83]
Cosmetic	[8], [57]
Food	[10], [31]
Leather	[7-9]
Ink, watercolors, artist's paints	[8], [147]
Medicine	[57]
Solar cell	[148]

Conclusion

Generally, flavonoids are yellow coloring compounds and their application fields are quite common. In other words, flavonoids have been used as coloring agent for food, textile, painting, leather, cosmetic, etc. Many flavonoids are known as antioxidant substances and many vegetables and fruits contain flavonoid or flavonoids. Approximately 90 % of the yellow natural dyes contains flavonoid molecules. The flavonoids have been also used for textile dyeing of art objects (carpet, kilim, fabrics, etc.) since ancient times. In this sence, we can say that the most used natural dye compounds are probably flavonoids in the natural dyeing. The another chemical properties of flavonoids are the metal chelating of metal ions. With greatest probability, the dyes containing flavonoids are commonly used for the dyeing of mordanted silk and wool, etc. after pre-operation of dyeing procedure on textile materials. The flavonoids are one of the most common dye family of polyphenolic compounds produced in nature. The dyeing spectrum of flavonoids on textile can be in the range from yellow to brown.

Nowadays, flavonoids are used for sustainable and environment friendly textile dyeing. Besides, they are also being used in pharmaceutical and cosmetic industries. In addition, many flavonoids have been utilized for solar cells in recent years. The yellow colors of the textile in art works in all museums are based on the flavones. Flavonoids were used for coloring of painting, mural painting, icon, etc. in the ancient times.

As a result, we can come across flavonoid molecules and flavonoid-based dyes in everywhere at all times from the ancient times to now.

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