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Review Paper

A review on cochineal (*Dactylopius Coccus* Costa) dye

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Abstract

Cochineal (Dactylopius coccus Costa) insect is an important and valuable dye source. Insect red dyes are historically very important. Especially, in the parts of the red or purple coloured of the historical textiles, they were used in the past. It contains 94-98% insect dye which is a carminic acid. A dired type of female of cochineal gives dyes. This insect dye source is an anthraquinone source. It has mostly been used in dyeing of silk, wool, cotton as well as in food colouring, cosmetic sector, pharmaceutical colourants and plastic applications. Natural pigments (lakes) were also obtained from cochineal insect extract in the literature. These lakes were used for paintings, frescoes, restoration and miniature etc. in the past. At the same time, because of its intense hues, colourfastness, and not toxic or carcinogenic, this dye source gained popularity in time. Cochineal produces different colours such as red hues, purple etc. to dye textiles using different mordants. This dye was a symbolizing element of power and prestige in the past.

Keywords: *Dactylopius coccus* Costa, carminic acid, natural dyeing, anthraquinone..

Introduction

Cochineal insects homeland is Central America and it lives on a cactus known as *Nopalea cochenilli*. The brownish-red colour of insect on cactus turns dark red colour later. Only female types of insect contain dyes. The female cochineal insect has not wings and thus it cannot fly. Although it has feet, it cannot act. The male cochineal insect has wings and there is its feet. Therefore, the male insects have ability to fly. Over the cactus, there is a living area relating to the female cochineal insect. The female insects are fertilized by the male insects. In a short time, the female insects lay. After the maturity time of the eggs, these eggs are collected and dried. A few product can be erntened per annum[1].

Literature Review

Cochineal insect as a dye source: The red color source - cochineal (*Dactylopius coccus* Costa) was revealed with attempt of Mexican dyers in very old times[2]. Since the 16th century, this dye insect was one of the most important principal dyes in terms of industry[3]. However, it was mainly used to obtain red dish colorants[4,5]. Ancient North African dyers used animal-based colorants extracted from cochineal (*Dactylopius coccus* Costa) as a source of dye and lake pigment[6]. This dye insect has been used in the objects belonging to the cultural heritage such as textiles and paintings since ancient times[7]. Carmine is a chelate of carminic acid that is a stable red colorant. They are used in world for the colouring of nutrients, beverages, beauty shops and drugs[8]. Carmine contains carminic acid.

The ratio is normally at least 50%[9]. Cochineal containing red coloured bio-colorants was gradually used by Vincent Van Gogh in the second half of his career (1885-1891)[10].

Karadag and Dolen determined carminic acid dye in the red coloured part of the historical textile (Inventory number: 13/1449) by TLC and derivative spectrophotometry. This historical textile piece reaches to the second half of 16th century and afterwards[11]. Cochineal insect contains mostly carminic acid dye. The flavokermesic acid is also found in the acid hydrolysed cochineal extract. Deveoglu et al.[12] produced the natural (lake) pigments - the aluminium-cochineal-walloon oak precipitate, Fe-cochineal-walloon oak precipitateand Sn – cochineal-walloon oak precipitate. Here, production of the pigments was provided with the mixture of the cochineal insect extract and the walloon oak plant extract using the solutions of the aluminium, iron and tin salts. For example, in the iron-cochineal-walloon oak lake pigment, the carminic acid and ellagic acid compounds were only determined. In the tin-cochineal-walloon oak lake pigment, gallic acid and carminic acid were identified. Karadag et al.[13] analysed some historical textiles. Cochineal was used for the red coloured parts.

The inventory numbers are as follows: 13/1515 (silk brocade, red and 16th c.), 13/1449 (silk velvet, red and 17th c.), 13/1960 (silk brocade, red and 16th c.), 13/1507 (silk brocade, red and 16th c.), 13/1671 (silk brocade, red and 17th c.), 13/1918 (silk velvet, red and 16th c.), 13/1673 (silk brocade, red and 16th c.), 13/1900 (silk velvet, red and 16th c.) and 13/1909 (silk caftan, red and first half of 17th c.).

The carminic acid (trace) was identified in the 13/1561 inventory number silk brocade (green colour) dating back to the first quarter of the 16th century of the Ottoman period obtained from the Topkapi Palace Museum[14]. Deveoglu et al. obtained the lake pigments (aluminium-cochineal lake pigment and iron-cochineal lake pigment) prepared with adding the solutions of the aluminium and iron salts to the cochineal extracts[15]. Arca et al. performed one project that in the dye analyses of caftans belonging to the Ottoman Sultan Bayezid II (1481-1512) and Ottoman Sultan Mustafa II (1695-1703) in the Topkapi Palace Museum collections, it was arised that the cochineal was used in the third quarter of the 16th century[16]. Karadag et al. determined the animal-based and the plant-based red dyes in the historical textiles (the Ottoman Silk Brocades). In the red sample of the inventory number (17624-D.261), only cochineal was identified. Whereas, in the red sample of the inventory number (13/46), both madder and cochineal were identified[17]. Yildiz and Karadag determined carminic acid in the red coloured sample of the historical art object (Inventory number 13/738) - the caftan was dated the second half of 16th century. These parts were dyed with either cochineal (*Dactylopius coccus* Costa) or Ararat kermes (*Porphyrophora hameli* Brand)[18].

Karadag et al. characterized dyes from selected 16–17th century Ottoman Silk Brocades by RP-HPLC-DAD in 2015. The samples related to the inventory numbers of 13/1525 (ground purple), 13/1527 (ground red), 13/1528 (ground red), 13/1539 (ground red) and 13/1550 (ground red) were dyed with either cochineal (*Dactylopius coccus* Costa) or Ararat kermes (*Porphyrophora hameli* Brand)[19]. Karadag and Torgan analysed the selected historical textiles in the Topkapi Palace Museum. The red coloured parts of the samples belonging to 13/156, 13/1005 and 13/1455 inventory numbers were dyed with cochineal (*Dactylopius coccus* Costa)[20]. Nateri et al. investigated the effects of mordanting methods on the absorption behaviour of cochineal red colorant source on polyamide fibers[21]. Cochineal (*Dactylopius coccus* Costa) insect produces carminic acid which constitutes approximately 94-98% weight of the total body mass. Minor compounds of cochineal dye (i.e., the remaining 2-6 %) contain kermesic and flavokermesic acid, dcII, dcIV, and dcVII[22]. In the 16th century, this insect was exported to Europe. Thus, it was began to replace the domestic kermes insect (*Kermes vermilio*)[23]. According to one study performed in 2017, cochineal was found in the red coloured wool piece (Inventory Number: 85) belonging to the Sivas Atatürk Congress and Ethnography Museum[24]. An anthraquinone – carminic acid has a good light stability. According to one work in 2018, alum was used to mordant silk samples. In the work, two dye sources (cochineal and gall oak) were practised to get optimum dyeing parameters. These parameters were obtained with using the different concentrations of these dye sources[25].It is believed that about 4000 years ago, the Chinese dyed silks and leathers with cochineal[26]. This dye source insect is also used nowadays as a valuable red dye source for paintings, lake pigments, dyes, the colouring of food, cosmetic and pharmaceuticals[27,28].

The cochineal insect is peculiar to Peru, Mexico, Bolivia, Chile and Spain (Canary Islands). The color giving cochineal is among orange and red. This situation depends on pH[29]. Carminic acid is soluble in water, alcohol, acid and alkaline solutions[30]. But it is insoluble in petroleum ether, benzene and chloroform solutions[29]. The chemical structure of the carminic acid dye was given in Figure-1.

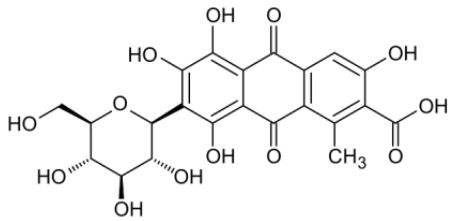

Figure-1: The chemical structure of the carminic acid dye.

Carminic acid obtaining from cochineal insect is a naturally – produced hydrophilic dye compound. This dye is used in the areas of food and cosmetic due to this property. At the same time, the dye can be used in the natural colouring of rubber materials as it is converted to hydrophobic character by means of acetylation or pivaloylation[31]. Because of its hydrophilic nature, the carminic acid–being a dye present in this dye source shows the stability to heat and light[32]. We can say that cochineal can be accepted by the European Union and the United States being a safe substance of consumption in terms of people[26,33]. Cochineal provides the brightness color among all the naturally-producedred dyes[34]. The carminic acids natural color changes depending on pH (namely, if the pH is 8, the color is yellowish; if the pH is above 6.2, the color is bluish-red)[35].

In the Ottoman manuscripts, cochineal insect was used in the La'li inks. The main component of the La'li ink was *Dactylopius coccus* Costa[36]. Since old times, cochineal is an important valuable dye insect for societies[37]. The anthraquinone compounds can likely help for the resistance of the plant to the fungi in the soil[38]. These compounds are rather important in the point to protect photooxidative fading[39]. It can probably say that approximately 100.000 insects can equal to 1kg of dried cochineal[40,41]. It is known that anthraquinone dyes have a rather good status in terms of light fastness[42]. The paintings on the pyramids of Teotihuacan made in pre-Christian times included cochineal[43]. The British officiers' uniforms which have a scarlet broadcloth were dyed with cochineal till about 1952[44]. Cochineal is more stable in comparison with kermes in terms of a dye source. May be due to this reason, it was used in carpet making and in art works[45]. Cochineal was used as a red dye in the most of British (and Portuguese) postage stamps between XIXth and XXth centuries[46]. Carminic acid is also a more stable dye molecule in comparison with many synthetic food colorants. This dye takes brownish color at 135°C and it decomposes at 205°C. Its whole and complete structural formula was determined by Overeem and van der Kerk in 1964 and confirmed in 1965 by Bhatia and Venkatamaran[47].

The carmine obtaining from cochineal has a good stability and an unaffected position towards oxygen, light, sulphur dioxide, heat and water[48]. The Aztec, Incan and Mayan peoples were utilized from cochineal dye insect as a paint and a natural dye source to provide colorful situation the robes[49,50]. Cochineal was also used by Mexican Indians since slippery time[51].

This dye source is one of the mainly animal - origin sources which give a natural dye[52]. Anthraquinones – a class belonging to carminic acid – are of the oldest dyes which were determined in the wrappings of mummies thousand of years ago[53]. Cochineal insect was important to get natural red dyes for pre-Hispanic Mexico[54]. This dye source is a defenceless insect in terms of climatic factors[55]. The molecular formula of the carminic acid anthraquinone compound is $C_{22}H_{20}O_{13}$ and its molecular weight is 492.28[56-58]. We can say that carminic acid has a precipitation at pH 3, a good stableness at pH 4 and subsequently, a quite stableness at pH 5 to 8[59]. Cochineal insect produces carminic acid molecule to preserve themselves counter to predators[60]. Since the 16th century, this dye source was used as a mercantile factor in the world[61]. Cochineal insects belong to the coccoidea family of the homoptera class. These insects are not bigger than one centimeter diameter[62]. The female of cochineal insect is known as "*coccus*". Carminic acid can be used for the spectrophotometric and the quantitative analysis of too much elements. Especially, this compound is a reagent using for boron[63]. Schweppe and Roosen-Runge informed that cochineal was almost early times used as a natural dye source by Peruvian Paracas culture in 700 BC[64]. Because of the phenolic groups of carminic acid, it is a fairly acidic molecule. We know that its solution color depends on pH[65].

In the past, cochineal was used to dye the cloths wearing in the religious and political ceremonies by the senior executives, especially[66]. The carminic acid which is an anthraquinone was already isolated from cochineal insect by Maier et al.[67]. Cochineal insect is a natural dye source. In many cases, animal-based dyes are superior to vegetable dyes. But vegetable dyes are mostly preferred to dye. This situation can be arised from a clean technology and an environmental policy[68]. The female insects were used as a red dye source in the textile, art and wine industries in the regions of mediterranean, middle east and central asia[69]. After these insects are completed their evolution, they can reach to the big time in terms of the dye[70]. The past of natural dyes dates back to about 4000 years old[71]. In Table-1, some application areas of cochineal insect dye were given.

Conclusion

The dried female insects are natural dye source to obtain red colour. Anthraquinones are main chromophores in the most commonly used red dyes. The dried cochineal insect contains mostly carminic acid dye. Besides, this dye source includes also kermesic acid and flavokermesic acid except carminic acid dye. These are metal chelating agents. The dyeings with this dye insect are realized in the literature.

The natural pigments (lake pigments) with using the solutions of some metal salts (such as aluminium, iron, and tin) with this dye insect extract were obtained. These pigments can especially be used for wall paintings and historical manuscripts. Carminic acid ($C_{22}H_{20}O_{13}$) is one dye derived from biological sources. The dyeing of fabrics was traditionally realized with cochineal. We can say that cochineal was also used for different purposes in daily life.

Table-1: Some application areas of cochineal insect dye.

Application area	References
Historical textiles	13, 14, 18-20, 72-75
Textile dyeing	25, 29, 76-84
Natural lake pigment	12, 15, 85
Food	29, 82, 83, 86-88
Cosmetic	29, 82, 83, 86-89
Plastic	29
Pharmaceutical	29, 89
Icons	90, 91
Paintings	92
Medicine	83, 88
Paint	83
Watercolor	93

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