CHAPTER I

INTRODUCTION

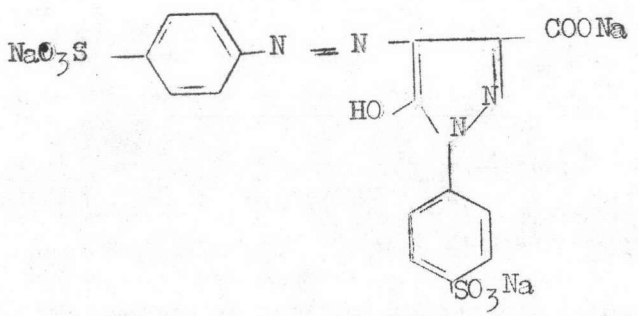
The value of a visual impression of human being is enhanced by the capacity to perceive not only light but also colors. Colors are high in human's favor, for examples, colors on utilized materials, colors on food, colors on cosmetic and even colors on drugs.

Substances used for food coloring can be grouped into natural (vegetable or animal) colors and synthetic dyestuffs. The naturally occurring colors which include substances such as caramel, cochineal, turmeric, chlorophyll and carmine have been employed since originality. Especially, caramel is used in the beverage industry. The synthetic dyes, with the advantages of possessing variety of shades, cheapness and ease of handling, are now extensively used. The compounds are colored depending on the chromophore functional groups, such as azo, azoxy, nitroso, nitrothio, carboxyl and ethylene groups. These dyes cannot be used indiscriminately for coloring food since many dyes are toxic, and food dyes have to be manufactured in a high state of purity and free from harmful constituents. All food dyes, the maximum limits for arsenic as As_2O_3 is 0.00014 % , for lead is 0.001 % ; only a trace of of other heavy metals, precipitable as sulfides, is permitted; and no barium lakes are permitted (1).

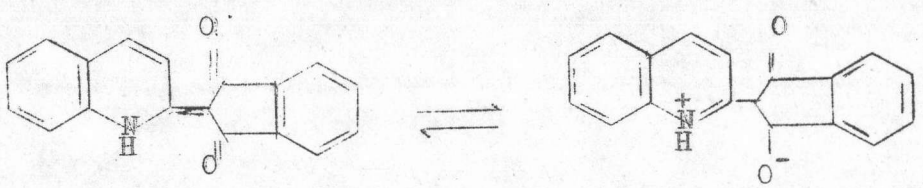
The permitted dyes, Tartrazine, Brilliant Blue FCF and nonpermitted Quinoline Yellow (2) were selected for this study since these dyes have been used for foodstuffs in everyday life. The combination of Tartrazine and Brilliant Blue FCF giving green shade was also studied. Tartrazine and Quinoline Yellow provide yellow colors as well as Brilliant Blue FCF gives blue color.

1.1 Structural formula of the dyes

Tartrazine (Color Index Number (CI. No.) 19140, Food Drug and Cosmetic Number (FD&C No.) 5, Molecular weight (M.W.) 534.37) is a pyrazolone dye. It is trisodium salt of 3-carboxy-5-hydroxy-1-p-sulfophenyl-4-p-sulfophenyl azo pyrazole. The structure is shown below.

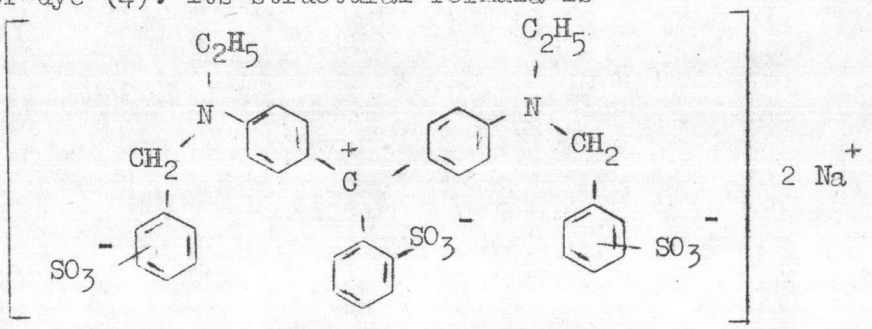


Quinoline Yellow (CI. No. 47005, FD&C No. 10, M.W. 477.38) is a quinophthalone dye. It is sodium salt of a mixture of the mono and disulfonic acids (mainly the latter) of quinophthalene (4). Wizinger (5) proposed the structure of quinophthalene in two resonance forms.



These resonance forms were confirmed lately by Kuhn and Bar (6).

Brilliant Blue FCF (CI.No.42090, FD&C Blue No. 1, M.W. 792.86) is the disodium salt of dibenzyldiethyldiaminotriphenyl carbinol-trisulfonic acid anhydride. It belongs to the triphenyl methane group of dye (4). Its structural formula is



1.2 Preparation of the dyes

Tartrazine is made by treating two moles of phenylhydrazine-p-sulfonic acid with one mole of dioxytartaric acid. Alternatively, it is prepared by coupling the diazotized sulfanilic acid with oxalacetic acid ether, condensing the product with phenylhydrazine-p-sulfonic acid and finally hydrolyzing the ester with sodium hydroxide solution (3).

Quinoline Yellow is prepared by treating two moles of quinoline with one mole of phthalic anhydride at 200°C in the presence of zinc chloride and sulfonating with 24 % of fuming sulfuric acid (3,14).

Brilliant Blue FCF is prepared by condensing one mole of benzaldehyde-o-sulfonic acid with two moles of benzylethylaniline sulfonic acid, following by oxidation and converting into disodium salt (3).

1.3 Properties of the dyes

Tartrazine and Quinoline Yellow are yellow powder and readily soluble in water, giving yellow solutions. Tartrazine is slightly soluble in 95 % alcohol but it is readily soluble in glycerol and glycols (3). It has good resistance to light, acetic acid, hydrochloric acid and 10 % sodium hydroxide solution. However, towards 30 % sodium hydroxide solution its resistance is only fair and it turns redder in hue. Ferrous sulfate tends to make the hue of the dye duller. However, the aqueous solution of Tartrazine is not affected by aluminum.

Brilliant Blue FCF is a bronze-purple powder and readily soluble in water, giving a greenish blue solution. It is moderately soluble in 95 % alcohol, and is soluble in glycerol and glycols (2). It is fairly fast to light and has good resistance to the action of acetic acid giving green color. Its resistance to 10 % hydrochloric acid is moderate, the dye turning green in hue; to 30 % hydrochloric acid is poor, the dye turning yellow-green in hue. Brilliant Blue FCF is moderately resistant to 10 % sodium hydroxide whereas 30 % sodium hydroxide solution causes a change in shade to wine red on standing.

Its resistance to reducing agents is better than that of azo colors. It has little resistance to oxidising agents. Brilliant Blue FCF is unaffected by contact with copper and aluminum in either water or acid solution (3).

1.4 Applications of the dyes

Tartrazine, Quinoline Yellow and Brilliant Blue FCF are used for coloring soaps, casein plastics, leather, and anodized

aluminum ; for the manufacture of light filters in photograph as well as for the manufacture of inks and wood stains. The barium lakes are used for paper coating. Lakes on aluminum hydroxide are used for transparent effects in tin printing.

Pure grades of the dyes are used for coloring cosmetics. Tartrazine and Brilliant Blue FCF are used for coloring food and drugs. Tartrazine is used as a biological stain, as an adsorption elution indicator for chloride estimation in biochemistry (7).

In carbonated beverages; Tartrazine is used alone for lemon shade and it is mixed with Brilliant Blue FCF to produce lime shade.

1.5 Toxication of the dyes

Regulations promulgated under the U.S: Federal Food, Drug and Cosmetic (FD&C) Act of 1938 affected to elimination of undesirable contamination from dyes used in food and these dyes must contain no harmful impurities (8). Safety data based on animal tests were supplied to support the continued listing of specified colors under the new act regulations for permitting to use as FD&C colors under Section 406 (b). Food and Drug Administration (FDA) defined "harmless" to mean a substance incapable of producing "harm" in test animals in any quantity or under any conditions (8).

FDA issued regulations permitting the permanent listing of FD&C Blue No. 1 (Brilliant Blue FCF) and FD&C Yellow No. 5 (Tartrazine) for use in food (2) and nonpermitting Quinoline Yellow as food color (9). The toxicological data of permitted food colors

were studied and the acceptable daily intakes for these colors have been established by the Joint FAO/WHO Expert Committee on Food Additives as listed in Table 1.

In Thailand, the Ministry of Industry issued an announcement in September 1976 suggesting the use of Tartrazine instead of Quinoline Yellow (10).

Biological aspects of Tartrazine reported by FAO/WHO (11); Tartrazine was given to rats, rabbits and man, showed that Tartrazine can be reduced in vivo when it is given orally but it cannot be reduced when it is given intraperitoneally. The reduction is then carried out by the gastro-intestinal flora. No mutagenic effect was found when this color was tested in cultures of Escherichi coli (11). No tumor was observed in rats and dogs for long term studies at the level 1.5 % in the rat diet, and 2 % in the dog diet (11).

For Quinoline Yellow, the available data are not fully adequate for evaluation but a substantial amount of detailed information is available concerning results of long-term tests (11). Further work required metabolic studies in animals and man.

For Brilliant Blue FCF, no evidence of carcinogenic action was found in mouse (12) and rats (13).

1.6 Literature survey of the dyes

The polarographic behaviors of some azo food dyes such as Tartrazine, Sunset Yellow FCF and Orange RN were suggested to be a two-electron transferred reduction process (15,16). The interaction of azo dyes with proteins was studied by Forbes (17). It was reported

Table 1 The acceptable daily intakes for FD&C Blue No 1 and FD&C Yellow No 5 (8)

Color	No-adverse Effect Dietary Levels Animal Study	Safe Level for man mg / day	Estimated Max. Ingestion mg/day/capital	Acceptable Daily Intake mg/Kg FAO/WHO
FD&C Blue No 1	5.0 % Rats 2.0 % Dogs	363	1.23	0-12.5
FD&C Yellow No 5	2.0 % Rats 2.0 % Dogs	363	16.3	0-7.5

that the para hydroxyazobenzene was bound by bovine serum albumin with the intermolecular hydrogen bonding as well as the sulfonate group of azo dyes were bound by electrostatic forces.

The polarographic reduction of the single carbon-nitrogen bond was studied by Zuman and Horák (18). It was reported that the reduction of triethylamino acrolein $OHC-CH=CH-\overset{+}{N}-(C_2H_5)_3$ involved two two-electron steps. The reduction of the $C-\overset{+}{N}$ bond was the first wave and the more negative wave at higher pH value was identical with acrolein. In addition, substances bearing the $\overset{+}{N}HR_3$ group were more easily reducible than those with $\overset{+}{N}HR_2$ and these even more than NR_2.

The polarographic reduction of ketones was explained by a free radical mechanism (19).

The polarographic reduction of 1,3-indandione was complicated, such as 2-phenyl-1,3-indandione which resulted in four waves and the occurance of each reduction wave was affected by pH of the solution (20).

From the above toxicological data, the announcement of the Ministry of Industry of Thailand (10), and the biological aspects of the reduction of food colors in vivo; the reduction mechanism of Tartrazine, Quinoline Yellow, Brilliant Blue FCF and the combination of Tartrazine and Brilliant Blue FCF to produce green shade are of interest. Therefore, the polarographic reduction behaviors of these dyes are studied in this present work.