A low public awareness of illegals red colorants usage: A case study in ketchup and crackers at traditional market of Sukolilo Surabaya

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Abstract. The low public awareness to unhealthy food products causes many unhealthy and unsafe food products still found and distributed, especially in the traditional market. Food additives, synthetic colorants and sweetener, are widely applied in food due to its stability, attractive in colours, and cheaper. Therefore, a survey and determination of illegal reds colorants, Rhodamine B, conducted particularly in ketchups and crackers in Sukolilo Area of Surabaya, East Java, Indonesia as well as three others legal reds colorants red allure, erythrosine, and ponceau 4R. Seven traditional markets at Sukolilo district: Keputih, Gebang Putih, Menur Pumpungan, Nginden Jangkungan, Semolowaru, Klampis Ngasem, and Medokan Semampir, were sampled. Instead of ketchup and crackers, beverages, and traditional cakes are also classified containing reds colorant. They are 38 samples were collected from six traditional markets at Sukolilo district: ketchup 31.58%, crakers 5.26%, beverages 23.68%, traditional cakes 28.95% while the rest is classified as other, i.e. seasonings and sausages. None of those are found at Medokan Semampir traditional Market. None of the collected ketchups contain Rhodamine B. Ponceau 4R and Erythrosine are the common red colorants detected in the ketchups. All the crackers and some samples of traditional cakes that mostly homemade do contain Rhodamine B.

1. Introduction
An effective either information and communication between consumer (read citizen) and government through both Ministry of Health and The National Agency of Drug and Food Control of Republic Indonesia (Badan Pemeriksaan Obat dan Makanan, BPOM) identified as one of an important factor that influencing consumer about healthy food. However, this not yet fully implements. Though, The Minister of Health already issued Permenkes No.1168/MenKes/PER/X/1999 about illegal food additives; Permenkes RI No. 239/MenKes/Per/V/1985 about red illegal colorants; still an illegal food
additives found to be applied at some area in Indonesia. Therefore, an active contribution from either public or government itself for continuous monitoring and controlling is highly needed.

Rhodamine B, methanyl yellow, dulsin (synthetic sweater), and potassium bromate (hardener) are the illegal food additives restricted added to food. While Rhodamine B (CI No. 45170 Food Red 15), Ponceau 3R (Acid Red, CI No. 16155), Ponceau SX (CI. 14700 Food Red 1), and Ponceau 6R (CI No. 16290 Food Red 8) are the illegal red colorants. Those also regulated in BPOM Regulation No.1168/2013 and Permenkes RI No. 37/2013 as well as their maximum allowable concentrations.

Synthetic colorants have more advantages over natural colorants such high stability of color due to food processing, heat exposure such drying process and etc., homogenous results of colors, attractive colors appearance, even cheaper than the natural ones [1]. These advantages of synthetic colorants are the disadvantages of natural colorants. Therefore, many food industries take benefit from it. Hence, public awareness to the importance of unhealthy foods should be developed.

Seven traditional markets at Sukolilo, a high density of population district at East Surabaya area ca. 4227 person/km² (total area 23.69 km²), with various products offered at the traditional market. Rhodamine B, a red illegal colorant, still identified in some snacks at the traditional market area of Genteng, Soponyono, Wonokriti at South Surabaya area [2]. Common illegal preservatives, i.e. formalin and borax, were also identified in seaweed, dried anchovies, dried squid, and wader fish in different traditional market at Surabaya area [3]. Rhodamine B and methanyl yellow, a red and yellow illegal colorant, were also identified in sausages and milk candy [3]. Therefore, there is an obligation for the community to improve awareness to assess unhealthy and unsafe food products by caring their snacks and daily food consumption, finally maintaining their health.

Survey was conducted four times especially to food and beverages that might be contains red colorants at seven traditional market of Sukolilo district. They are at traditional markets of Keputih, Gebang Putih, Menur Pumpungan, Nginden Jangkungan, Semolowaru, Klampis Ngasem, and Medokan Semampir areas. Two times was before Ramadhan festival at 2019 (May 2019) and the rest was afterward. This survey can be act as irregular monitoring and controlling of utilization of legal and safe food additives, indirectly educating community how to identify and know food with legal food additives addition.

2. Materials and Methodology

2.1. Materials
Some samples were bought and collected from seven traditional markets at Sukolilo district area: Keputih, Gebang Putih, Menur Pumpungan, Nginden Jangkungan, Semolowaru, Klampis Ngasem, and Medokan Semampir. The collected samples might contain red colorant which identified by its appearances. Standard compounds of Rhodamine B, Amaranth, and Red Allure are commercially purchased from Sigma-Aldrich (India) in pro analyst grade whereas both Erythrosine and Ponceau 4R in pharmaceutical grade from Morton Chemical (Netherlands). Silica gel 60 F 254 20×20 cm in size (Merck, Darmstadt, Germany) used for qualitative analysis of dyes. In case of solvents such ethanol (EtOH), ammonia (25%, v/v), and isopropanol (iPrOH) are purchased from Merck (Darmstadt, Germany) in pro analyst grade. A spectrophotometer T60 (PG Instrument, Leicestershire, United Kingdom) were used to quantify the red dyes.

2.2. Method of sampling
Samples that collected at traditional markets may contain red colorant which identified by its appearances. They classified into four groups: beverages, ketchups, crackers and traditional cakes. Two periods of sampling was conducted: before Ramadhan festival at 2019 (May 2019) and afterward. Each period was done in two times. Same samples were bought and collected each time.

2.3. Extraction of red colorants from the sample matrix
Three grams (3 g) of each sample crushed, homogenized with 5 mL 70% EtOH (v/v) swirling in 10 minutes until all the red color came out. Furthermore, centrifugation (3000 rpm, 10 minutes) and the clear solution obtained then separated by filtration [4]. The red colorants then qualitative identified by applying the filtrate to thin layer chromatography (TLC) (subsection 2.4) and further quantified by a spectrophotometer (subsection 2.5).

2.4. Qualitative analysis of red colorants by thin layer chromatography
Thin Layer Chromatography (TLC) conducted red colorants separation and identification. TLC plates (10 cm ×10 cm), Silica gel 60 F 254, prepared, marked 1.5 cm and 0.5 cm, respectively, from the base of plate and top of the plate. A hundred microliter (100 μL) extract of each sample solution (subsection 2.3) applied to the TLC plate in duplicates as well as the standards solution. Mixture of isopropanol: Ammonia (4:1, v/v) was applied as mobile phase.

2.5. Quantitative analysis of red colorants by spectrophotometer UV-Vis
A calibration curve previously conducted for quantifying the red colorant. Calibration curves made by serial dilution of a standard stock solution of red dye. Standard stock solutions made with an accurate weight of 3 g and diluted to 5 mL EtOH 70% (v/v). Calibration carried out using 11 concentrations (7.0, 6.0, 5.0, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, and 0.50 ppm) at maximum wavelength of each red colorants. The quantification of red colorants conducted only to the identified red color by TLC (subsection 2.4).

3. Result and discussion

![Figure 1](image)

**Figure 1.** Red colorants spot from ketchup samples identified with thin layer chromatography (TLC). Spot Rhodamine B (R), Amaranth (A), Ponceau 4R (P), Erythrosine (E), and Red Allure (AR), each spot was 100 ppm. While C spot is mixed standard of all the red colors standard. While samples numbers are different brand of ketchups samples: SS (1); K9 (2); K11 (3); K1-tomato ketchup (4); K1-chili sauce (5); DMT-tomato ketchup (6); ABC (7); INF (8); SS (9); and DMT-chili sauce (10).

Firstly, a survey for identifying types of food and beverages that might contain red colorants was conducted in seven area of traditional market at Sukolilo district: Keputih, Gebang Putih, Menur Pumpungan, Nginden Jangkungan, Semolowaru, Klampis Ngasem, and Medokan Semampir. Subsequently, they were classified into ketchup, crackers, beverages, traditional cakes, etc. (Table 1). However, at Medokan Semampir none of the samples was found. Hence, it was excluded from the Table. They are 38 samples were collected from six traditional markets at Sukolilo district: ketchup (31.58%), crackers (5.26%), beverages (23.68%), traditional cakes (28.95%); while the rest is classified as others sample such instant seasonings and sausages.
**Table 1.** Collected and classified samples from six traditional markets at Sukolilo district.

| TYPE of Sample | Gebang Putih | Klampis Ngasem | Semolowaru | Keputih | Menur Pumpungan | Nginden Jangkungan |
|----------------|--------------|----------------|------------|---------|----------------|------------------|
| K1             | √            |                |            |         |                |                  |
| K2             | √            |                |            |         |                |                  |
| K3             | √            |                |            |         |                |                  |
| K4             |              |                |            | √       |                |                  |
| K5             |              |                | √          |         |                |                  |
| K6             |              |                | √          |         |                |                  |
| K7             |              |                | √          |         |                |                  |
| K8             |              |                | √          |         |                |                  |
| K9             |              |                |            | √       |                |                  |
| K10            |              |                |            |         |                |                  |
| K11            |              |                |            |         |                |                  |
| K12            |              |                |            |         |                |                  |

**KETCHUP**

| C1             |                |                |            |         |                |                  |
| C2             |                |                |            |         |                |                  |

**CRACKER**

| M1             |              |                |            |         |                |                  |
| M2             |              |                |            |         |                |                  |
| AA1            |              |                |            |         |                |                  |
| AA2            |              |                |            |         |                |                  |
| JL             |              |                |            |         |                |                  |
| DWT1           |              |                |            |         |                |                  |
| DWT2           |              |                |            |         |                |                  |
| DWT3           |              |                |            |         |                |                  |
| DWT4           |              |                |            |         |                |                  |

**BEVERAGES**

| BK1            |              |                |            |         |                |                  |
| BK2            |              |                |            |         |                |                  |
| KT1            |              |                |            |         |                |                  |
| KT2            |              |                |            |         |                |                  |
| KT3            |              |                |            |         |                |                  |
| KB1            |              |                |            |         |                |                  |
| KB2            |              |                |            |         |                |                  |
| RK             |              |                |            |         |                |                  |
| KB3            |              |                |            |         |                |                  |
| AS             |              |                |            |         |                |                  |
| RG             |              |                |            |         |                |                  |

**TRADITIONAL CAKES**

| S1             |              |                |            |         |                |                  |
| S2             |              |                |            |         |                |                  |
| SS             |              |                |            |         |                |                  |
| J              |              |                |            |         |                |                  |

*a* Sample without registered brand.

Abbreviation of samples: ketchup/sauce (K), crackers (C), mutiara beverage (M), seaweeds beverage (AA), jelly beverage (JL), dawet = Javanese traditional beverage with santan (DWT), bolu kukus (BK), kue tok (KT), kue-kue basah = traditional cakes (KB), rambutan kelapa = dry shredded coconut meat (RK), astor = cigarette shaped of snack with strawberry flavour (AS), rengginang = traditional snack made from dried glutinous rice (RG), seasoning (S), sausage (SS), and jam (J) while ordered number indicated different sample.

Most of the ketchup samples have either PIRT or MD code but none of the crackers has. All the traditional cakes do not have of either PIRT or MD code; meaning they are homemade. PIRT-code (*Izin Pangan Industri Rumah Tangga*, PIRT) is a certificate for food and beverage of home industry company,
while MD is a legal permission code (from government) for large scale and local industries. Local here is a large-scale industry that produces his or her own products. Gratefully, none of the collected samples of ketchup contains Rhodamine B. Ponceau 4R and Erythrosine are the common red colorants detected in the ketchups samples (Figure 1). While some of them i.e. sample number 6-10, does not use Amaranth, Red Allure, Erythrosine, and Ponceau 4R. Therefore, none of the red colorants are detected; they are favorites and branded ketchup products. All the collected samples were abbreviated for ethical purposes.

Both of crackers (C1 and C1) contain Rhodamine B, some samples of DWT (dawet) and traditional cakes such BK, KB3, AS, RK, RG do contain Rhodamine B (Figure 2). Most of them are homemade industries products. Therefore, monitoring and controlling especially homemade products should receive a great attention. In case of instant seasonings samples, the red colorants were not well separated, due containing some oils.

![Figure 2](image)

Figure 2. Some samples that qualitatively detected of Rhodamine B. Crackers (C1 or C2), DWT, AS, and RG (respectively from left to right).

Rhodamine B particularly can be identified by its bright fluorescence pink color (Figure 2). Increasing public awareness to unhealthy food by educating community, i.e. family based, is the first action can be reached.

4. Conclusion

Public awareness to unhealthy food need to be improved and maintained. Government (BPOM) with the help of community need to regularly monitor and control utilization of legal and safe food additives. Those, indirectly educating community how to identify and know food with legal food additives addition. Improving their awareness to unhealthy food products and finally maintaining their health

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