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# Quality attributes of black olives as affected by different darkening methods

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Olives can be darkened by different methods, some of which utilize chemicals and even dyes in some locations. The present study was carried out to evaluate the different darkening methods in terms of acceptance and safety of blackened olives. Olives were blackened naturally (on the tree) as well as artificially. For the latter, air oxidation was conducted on both mature and green olives using different alkalis. Moreover, blackening with nigrosine and hematin dyes was applied, since consumers prefer the appearance of such olives as well as their low price. The artificially blackened olives were compared to their naturally blackened counterparts regarding colour (subjectively and objectively), penetration reading, shrinkage percent and heavy metals content (iron, cadmium and lead). Data showed comparable colour intensity for olives blackened with 4% $Na_2CO_3$ followed by air oxidation for 120 h to those blackened with nigrosine and hematin. Notwithstanding, treatment with $Na_2CO_3$ resulted in the lowest shrinkage percent and heavy metal contents of olives, compared to those treated with other alkalis or dyes. Olives treated with $Na_2CO_3$ most closely resembled those which had been naturally blackened. Immersing $Na_2CO_3$-treated olives in sunflower oil for 1 s prior to air-oxidation significantly lowered the shrinkage percent of olives. © 1997 Elsevier Science Ltd

## INTRODUCTION

Olives (*Olea europaea L.*) are marketed as green, black or discoloured olives, packed with or without brine as whole or chopped, plain or pickled forms. Table olives are consumed on an extremely wide scale all over the world (Sanchez *et al.*, 1991; Vlahov, 1992; Montano *et al.*, 1993).

Among the main quality attributes of black olives, colour is the most organoleptically important. A less mature green olive can be blackened either naturally (developed by maturity), or artificially (developed by oxidation). The natural blackening of olives is mainly attributed to formation and accumulation during maturation of flavonols, flavones and anthocyanins (Marsilio *et al.*, 1990; Vlahov, 1990, 1992).

In Egypt, farmers usually gather their olives all at once regardless of the degree of maturity. Small processors as well as retail merchants generally divide the green fruits into two grades (i.e. very light green and dark green). The price of the first grade and its black product is markedly higher than the other grade. The artificial blackening of olives, however, can be achieved by alkali treatment.

During the alkali treatment of olive, the pH of the fruit's flesh increases and thus the verbascoside (the compound responsible for the bitter taste of olive) decomposes giving caffeic acid. Of the many phenolic compounds of olives, only o-diphenol compounds such as hydroxytyrosol transform following alkali treatment and during the darkening process. Concentrations are directly related to surface colour or surface colour development. Thus, the aforementioned compounds are considered as promoters of the dark colour obtained during the traditional blackening of olive (Marsilio *et al.*, 1990; Brenes-Balbuena *et al.*, 1992).

In Egypt, some small processors of olive darkening, in an attempt to minimize the cost of processing, tend to use a cheap commercial grade of alkali ($Ca(OH)_2$, KOH and NaOH) that is widely used for industrial purposes. Although utilization of such impure chemicals in food processing is forbidden, some small processors use them because of their low prices. Meanwhile, other processors use artificial dyes (i.e. nigrosine or hematin) to blacken olives. However, the different black olives that are sold in low-income public markets are widely different in

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terms of their black colour, texture and degree of surface shrinkage due to the type of alkali, its concentration and treatment time.

The present study was carried out to evaluate the quality of black olives sold in Egyptian public markets. Moreover, some simple and safe methods of blackening olives were applied and evaluated. It is well known that some merchants, especially in public markets, adulterate black olives by adding artificial dyes. Consequently, a simple method of detection of such dyes is required by normal quality control labs.

## MATERIALS AND METHODS

### Materials

For pilot plant experiments, olives (*Olea europaea L.*) were obtained from a farm in Siwa (one of the famous regions for olive production in Egypt). Most of the representative sample was taken immediately after green maturation of fruits. Meanwhile, some fruits were left on the same tree to blacken and ripen naturally (control). Fruits were divided into two grades, namely mature, very light green (Grade A) and green fruits (Grade B).

A sample of dark black olives was collected from the Alexandria public markets. It is known that such olives are preferred by the majority of low-income families due to their low price and attractive black colour. Such samples were analysed qualitatively to detect the presence of artificial dyes and the positive samples were evaluated in the present study.

### Methods

Technological experiments:

The following treatments were applied in order to blacken the less mature green olives:

Experiment no. 1:

1. Commercial KOH (2%).
2. Commercial KOH (2%) + Chemically pure $Na_2CO_3$ (2%).
3. Chemically pure KOH (2%).
4. Chemically pure KOH (2%) + Chemically pure $Na_2CO_3$ (2%)
5. Chemically pure NaOH (2%)
6. Chemically pure NaOH (2%) + Chemically pure $Na_2CO_3$ (2%)
7. Commercial Ca $(OH)_2$ (2%)
8. Commercial Ca $(OH)_2$ (2%) + Chemically pure $Na_2CO_3$ (2%)
9. Chemically pure $Na_2CO_3$ (4%)
10. Chemically pure $NaHCO_3$ (4%).
11. Blackening with technical grade nigrosine dye (0.1%) for 30 min (twice successively in a boiled dye solution).
12. Blackening with technical grade hematin dye (0.1%) as for nigrosine dye.

**Table 1. C.I.E. units of primary colours for olive fruits as affected by different blackened alkali treatments**

| Treatment | C.I.E. Units | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | X | | | | | Y | | | | | Z | | | | |
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| **Grade (A)** | | | | | | | | | | | | | | | |
| Com. KOH | 0.354 | 0.315 | 0.269 | 0.243 | 0.233 | 0.276 | 0.255 | 0.213 | 0.189 | 0.182 | 0.370 | 0.430 | 0.518 | 0.568 | 0.581 |
| ≫ + $Na_2CO_3$ | 0.338 | 0.304 | 0.265 | 0.236 | 0.230 | 0.262 | 0.224 | 0.215 | 0.183 | 0.182 | 0.400 | 0.472 | 0.520 | 0.581 | 0.588 |
| Pure KOH | 0.350 | 0.288 | 0.266 | 0.235 | 0.230 | 0.265 | 0.232 | 0.214 | 0.183 | 0.181 | 0.385 | 0.480 | 0.520 | 0.582 | 0.589 |
| ≫ + $Na_2CO_3$ | 0.345 | 0.292 | 0.267 | 0.235 | 0.232 | 0.255 | 0.228 | 0.215 | 0.185 | 0.183 | 0.400 | 0.480 | 0.518 | 0.580 | 0.585 |
| Pure NaOH | 0.352 | 0.290 | 0.265 | 0.228 | 0.224 | 0.273 | 0.233 | 0.225 | 0.180 | 0.178 | 0.375 | 0.477 | 0.510 | 0.592 | 0.598 |
| ≫ + $Na_2CO_3$ | 0.345 | 0.290 | 0.255 | 0.225 | 0.223 | 0.255 | 0.233 | 0.210 | 0.175 | 0.175 | 0.400 | 0.477 | 0.535 | 0.600 | 0.602 |
| Com.Ca$(OH)_2$** | 0.314 | 0.305 | 0.286 | 0.245 | 0.245 | 0.296 | 0.290 | 0.275 | 0.220 | 0.220 | 0.390 | 0.405 | 0.440 | 0.535 | 0.535 |
| ≫ + $Na_2CO_3$** | 0.328 | 0.305 | 0.284 | 0.258 | 0.248 | 0.285 | 0.268 | 0.239 | 0.203 | 0.200 | 0.387 | 0.427 | 0.477 | 0.539 | 0.552 |
| $Na_2CO_3$ (4%)** | 0.316 | 0.262 | 0.238 | 0.218 | 0.192 | 0.294 | 0.243 | 0.194 | 0.168 | 0.136 | 0.390 | 0.495 | 0.568 | 0.614 | 0.672 |
| $NaHCO_3$(4%)** | 0.315 | 0.262 | 0.240 | 0.220 | 0.192 | 0.294 | 0.240 | 0.198 | 0.170 | 0.136 | 0.391 | 0.498 | 0.562 | 0.610 | 0.672 |
| **Grade (B)** | | | | | | | | | | | | | | | |
| Com. KOH | 0.318 | 0.274 | 0.254 | 0.236 | 0.226 | 0.273 | 0.239 | 0.196 | 0.196 | 0.188 | 0.409 | 0.487 | 0.530 | 0.568 | 0.586 |
| ≫ + $Na_2CO_3$ | 0.308 | 0.268 | 0.252 | 0.230 | 0.222 | 0.285 | 0.232 | 0.217 | 0.188 | 0.180 | 0.407 | 0.500 | 0.531 | 0.582 | 0.598 |
| Pure KOH | 0.322 | 0.258 | 0.252 | 0.234 | 0.224 | 0.273 | 0.234 | 0.221 | 0.200 | 0.184 | 0.405 | 0.508 | 0.527 | 0.566 | 0.592 |
| ≫ + $Na_2CO_3$ | 0.304 | 0.257 | 0.248 | 0.228 | 0.220 | 0.283 | 0.223 | 0.218 | 0.192 | 0.180 | 0.413 | 0.520 | 0.534 | 0.580 | 0.600 |
| Pure NaOH | 0.315 | 0.260 | 0.255 | 0.228 | 0.221 | 0.280 | 0.220 | 0.216 | 0.190 | 0.179 | 0.405 | 0.520 | 0.525 | 0.582 | 0.600 |
| ≫ + $Na_2CO_3$ | 0.315 | 0.259 | 0.245 | 0.224 | 0.217 | 0.275 | 0.232 | 0.207 | 0.184 | 0.173 | 0.410 | 0.509 | 0.548 | 0.592 | 0.610 |
| Com. Ca$(OH)_2$ | 0.316 | 0.290 | 0.271 | 0.239 | 0.232 | 0.304 | 0.260 | 0.247 | 0.207 | 0.200 | 0.380 | 0.450 | 0.482 | 0.554 | 0.568 |
| ≫ + $Na_2CO_3$ | 0.318 | 0.275 | 0.245 | 0.238 | 0.229 | 0.282 | 0.243 | 0.217 | 0.202 | 0.193 | 0.400 | 0.482 | 0.538 | 0.560 | 0.578 |
| $Na_2CO_3$ (4%) | 0.315 | 0.250 | 0.222 | 0.210 | 0.194 | 0.280 | 0.200 | 0.168 | 0.168 | 0.131 | 0.405 | 0.550 | 0.610 | 0.622 | 0.675 |
| $NaHCO_3$ (4%) | 0.312 | 0.292 | 0.233 | 0.220 | 0.207 | 0.278 | 0.241 | 0.183 | 0.168 | 0.151 | 0.410 | 0.467 | 0.584 | 0.611 | 0.642 |

*1: After 12 h alkali treat.; 2, 3, 4 and 5: After air oxidation for 24, 48, 72 and 96 h, respectively.

**Alkali treat. for 24 h.

Experiment no. 2:

13. Chemically pure $Na_2CO_3$ (1%)
14. Chemically pure $Na_2CO_3$ (2%)
15. Chemically pure $Na_2CO_3$ (3%)
16. Chemically pure $Na_2CO_3$ (4%)
17. Chemically pure $Na_2CO_3$ (5%)

Immersion in sunflower oil for 1 s prior to darkening by air oxidation to increase intensity of the resultant dark black colour of the olives.

In the light of our preliminary experiments, it was obvious that monovalent cation alkalis penetrate more rapidly (12 h) up to 2/3 of olive flesh than divalent cation alkali (24 h). Accordingly, alkali treatments 1 to 6 were carried out for 12 h, while treatments 7-10 and 13-17 were applied for 24 h. Treated fruits were rinsed with water prior to exposuring to air oxidation (or immersed in oil, exp. 13-17) which was conducted for different periods, (i.e. 12, 24, 48, 72 and 96 h).

**Analytical methods**

Many experimental trials were conducted on blackened olives to extract and detect the dyes using different solvent systems. The ethanol:water mixture was chosen as a safe and simple method which could readily be transferred to a quality control laboratory. Dyes were extracted from black olives using ethanol: $H_2O$ (1:1, v/v). The resultant extract (25 ml) was left to concentrate (~24 h) by natural evaporation under open air. Detection of dyes was carried out using the horizontal paper chromatography technique on filter paper Whatman No. 1 (Cat. No. 1001-110). A good separation was obtained when a mixture of ethanol: $H_2O$ (35:15, v/v)

**Table 2. Brightness, saturation and $\Delta E$ for olive fruits as affected by different blackened alkali treatments**

| Treatment | Brightness (%) | | | | | Saturation (%) | | | | | $\Delta E$ (cm). | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| **Grade (A)** | | | | | | | | | | | | | | | |
| Com. KOH | 29.5 | 28.7 | 28.1 | 22.9 | 21.6 | 18.0 | 18.0 | 21.7 | 27.5 | 33.3 | 6.4 | 5.5 | 3.8 | 2.7 | 2.4 |
| ≫ + $Na_2CO_3$ | 42.6 | 36.3 | 28.1 | 20.8 | 20.4 | 18.9 | 19.0 | 21.4 | 29.9 | 32.8 | 6.2 | 5.1 | 3.8 | 2.5 | 2.3 |
| Pure KOH | 45.7 | 25.7 | 24.2 | 21.8 | 20.8 | 18.5 | 20.0 | 21.5 | 31.3 | 32.8 | 6.3 | 4.6 | 3.7 | 2.4 | 2.3 |
| ≫ + $Na_2CO_3$ | 42.6 | 26.3 | 24.2 | 20.8 | 20.8 | 18.8 | 20.1 | 21.1 | 32.2 | 34.7 | 6.1 | 4.6 | 3.7 | 2.3 | 2.2 |
| Pure NaOH | 46.7 | 32.3 | 30.2 | 21.8 | 20.8 | 18.5 | 19.9 | 20.2 | 34.3 | 34.9 | 6.2 | 4.6 | 3.8 | 2.2 | 2.1 |
| ≫ + $Na_2CO_3$ | 42.6 | 33.1 | 28.1 | 19.0 | 18.6 | 19.2 | 20.1 | 21.7 | 37.3 | 37.5 | 6.0 | 4.6 | 3.4 | 1.9 | 1.8 |
| Com. $Ca(OH)_2$** | 79.4 | 72.4 | 57.5 | 37.1 | 37.1 | 5.5 | 6.5 | 9.3 | 27.8 | 27.8 | 6.0 | 5.7 | 4.8 | 3.4 | 3.4 |
| ≫ + $Na_2CO_3$** | 60.2 | 48.9 | 38.0 | 25.7 | 25.1 | 11.7 | 13.3 | 17.4 | 28.7 | 30.4 | 6.0 | 5.4 | 4.5 | 3.0 | 2.9 |
| $Na_2CO_3$ (4%)** | 74.1 | 44.6 | 23.9 | 18.2 | 12.5 | 9.9 | 20.0 | 29.7 | 41.1 | 60.9 | 5.8 | 4.1 | 2.8 | 1.7 | 0.5 |
| $NaHCO_3$ (4%)** | 74.1 | 42.6 | 26.3 | 18.2 | 12.5 | 10.0 | 20.0 | 32.0 | 41.1 | 60.9 | 5.7 | 4.0 | 2.8 | 1.7 | 0.6 |
| **Grade (B)** | | | | | | | | | | | | | | | |
| Com. KOH | 57.5 | 39.8 | 31.6 | 26.9 | 23.4 | 11.5 | 15.8 | 21.9 | 32.5 | 39.8 | 5.6 | 4.3 | 3.5 | 2.7 | 2.0 |
| ≫ + $Na_2CO_3$ | 66.0 | 36.3 | 32.3 | 23.9 | 22.3 | 9.9 | 16.4 | 24.9 | 34.0 | 40.1 | 5.5 | 4.0 | 3.3 | 2.3 | 2.0 |
| Pure KOH | 52.4 | 34.6 | 33.1 | 26.3 | 23.4 | 16.6 | 21.5 | 28.1 | 35.8 | 40.2 | 5.6 | 3.6 | 3.2 | 2.8 | 2.0 |
| ≫ + $Na_2CO_3$ | 66.0 | 33.8 | 31.6 | 24.5 | 21.8 | 11.6 | 20.1 | 26.4 | 35.7 | 40.0 | 5.5 | 3.5 | 3.2 | 2.4 | 2.0 |
| Pure NaOH | 58.8 | 32.3 | 31.6 | 25.1 | 21.3 | 13.8 | 21.3 | 24.0 | 36.1 | 40.8 | 5.5 | 3.7 | 3.3 | 2.4 | 2.0 |
| ≫ + $Na_2CO_3$ | 58.8 | 34.6 | 30.2 | 23.4 | 21.3 | 11.9 | 19.3 | 27.6 | 36.8 | 43.9 | 5.6 | 3.7 | 3.0 | 2.2 | 1.7 |
| Com. $Ca(OH)_2$ | 79.4 | 52.4 | 44.6 | 31.6 | 28.1 | 7.1 | 12.6 | 16.9 | 30.0 | 33.8 | 6.0 | 4.9 | 4.1 | 3.0 | 2.7 |
| ≫ + $Na_2CO_3$ | 60.2 | 41.6 | 37.1 | 28.8 | 25.1 | 12.5 | 16.7 | 26.9 | 32.6 | 35.4 | 5.7 | 4.3 | 3.3 | 2.7 | 2.4 |
| $Na_2CO_3$ (4%) | 60.2 | 37.1 | 19.0 | 17.7 | 12.5 | 10.9 | 18.3 | 37.8 | 42.6 | 56.5 | 5.6 | 4.5 | 2.0 | 1.5 | 0.4 |
| $NaHCO_3$ (4%) | 58.8 | 38.0 | 21.3 | 19.0 | 15.8 | 11.4 | 19.9 | 23.8 | 39.7 | 48.9 | 5.5 | 4.7 | 3.2 | 1.7 | 0.8 |

*,** as in Table 1.

**Table 3. C.I.E. values of primary colours for artificially darkened olives in comparison with naturally blackened olives**

| Treatment | C.I.E. Units X | C.I.E. Units Y | C.I.E. Units Z | Brightness (%) | Saturation (%) | $\Delta E$ |
|---|---|---|---|---|---|---|
| Naturally Blackened | 0.196 | 0.126 | 0.678 | 11.2 | 48.3 | 0.0 |
| **Grade (A)** | | | | | | |
| Fresh sample | 0.324 | 0.301 | 0.375 | 79.4 | 5.3 | 6.6 |
| Nigrosine (0.1%)* | 0.192 | 0.132 | 0.676 | 12.5 | 58.9 | 0.3 |
| Hematin (0.1%)* | 0.194 | 0.130 | 0.676 | 12.3 | 59.3 | 0.2 |
| **Grade (B)** | | | | | | |
| Fresh sample | 0.302 | 0.288 | 0.410 | 69.1 | 7.3 | 5.8 |
| Nigrosine (0.1%) | 0.194 | 0.131 | 0.675 | 12.5 | 57.1 | 0.3 |
| Hematin (0.1%) | 0.198 | 0.132 | 0.670 | 12.0 | 57.3 | 0.2 |

*Treatment for 30 min×2 times in boiled dye.

was used as a developer. $R_f$ values were found to be 0.40, 0.48 and 0.89 for nigrosine, hematin dyes and natural pigments, respectively.

Moisture determination and ashing process were carried out according to AOAC (1980). Heavy metals were determined by atomic absorption spectrophotometry (Pye Unicam SP 1900).

**Physical properties**

The colour of the olives was assessed by the Lovibond-Schofield Tintometer (The Tintometer Ltd., Salisbury, England) using illuminant C. Lovibond readings were further converted into C.I.E. values as outlined in the manual book supplied with the apparatus. The olives were also presented simultaneously to 10 panellists who were asked to rank the samples on a hedonic scale of 1 (very poor), 2–4 (poor), 5–6 (fair), 7–8 (good) and 9–10 (excellent) to evaluate the colour of black olives as compared to the naturally darkened sample. The volume of olives was measured using the absolute displacement of water for 25 fruits while the shrinkage (%) was calculated as follows:

$$\text{Shrinkage} = (\%)$$

$$= \frac{\text{Volume of fresh fruits} - \text{Volume of treated fruits}}{\text{Volume of fresh fruits}} \times 100$$

Shrinkage is considered as a defect which alters the consumption of olives. Such a defect is attributed mainly to uncontrolled alkali treatment.

The texture of olives was assessed by the Penetrometer (Cat. No. 73510, Precision Scientific Co., Chicago, USA) using the needle (Cat. No. 73520). The weight used on the pan was 50 g.

**Statistical analysis**

All determinations were carried out in triplicate. The data were subjected to analysis of variance and Duncan's Multiple Range test to separate the treatment means as outlined by Steel and Torrie (1980).

## RESULTS AND DISCUSSION

**Darkening process**

Data presented in Tables 1 and 2 illustrate the effects of different treatments on the colour of olives as assessed objectively. As can be seen for grade A olives (mature), the effects of 4% $Na_2CO_3$ and 4% $NaHCO_3$ on blackening were superior to treatments with other alkalis that are frequently used on the commercial scale. It was obvious that as the air oxidation period elapsed, the olives being darker as indicated by the highest saturation and the lowest brightness. Moreover, $\Delta E$ (the distance between position of a sample on the chromaticity diagram and corresponding point of the naturally blackened sample) further confirmed this finding. Such an effect was not pronounced for grade B (green) olives. On the other hand, blackening of olives with artificial dyes (0.1% nigrosine and 0.1% hematin), resulted in the darkest olives of all chemical treatments applied in the present study (Table 3). This agrees with Marsilio *et al.*, 1990 who found that oxidation of olives in alkaline medium followed by aeration maintained the dark colour of olives.

**Table 4. C.I.E. units for $Na_2CO_3$-treated olives (2$^{nd}$ exp.)**

| Treatment | $Na_2CO_3$ (1%) CIE units | | | $Na_2CO_3$ (2%) CIE units | | | $Na_2CO_3$ (3%) CIE units | | | $Na_2CO_3$ (4%) CIE units | | | $Na_2CO_3$ (5%) CIE units | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | X | Y | Z | X | Y | Z | X | Y | Z | X | Y | Z | X | Y | Z |
| **Grade (A)** | | | | | | | | | | | | | | | |
| Fresh sample | 0.324 | 0.299 | 0.377 | 0.324 | 0.299 | 0.377 | 0.324 | 0.299 | 0.377 | 0.324 | 0.299 | 0.377 | 0.324 | 0.299 | 0.377 |
| After treat. for 24 h | 0.315 | 0.295 | 0.390 | 0.318 | 0.295 | 0.387 | 0.318 | 0.295 | 0.387 | 0.316 | 0.292 | 0.392 | 0.316 | 0.292 | 0.392 |
| Air oxidation for | | | | | | | | | | | | | | | |
| 24 h | 0.286 | 0.264 | 0.450 | 0.283 | 0.250 | 0.467 | 0.273 | 0.250 | 0.477 | 0.266 | 0.242 | 0.432 | 0.270 | 0.247 | 0.483 |
| 48 h | 0.258 | 0.218 | 0.524 | 0.252 | 0.213 | 0.535 | 0.240 | 0.202 | 0.558 | 0.238 | 0.194 | 0.568 | 0.236 | 0.190 | 0.574 |
| 72 h | 0.241 | 0.183 | 0.576 | 0.236 | 0.180 | 0.584 | 0.222 | 0.163 | 0.615 | 0.217 | 0.165 | 0.618 | 0.216 | 0.164 | 0.620 |
| 96 h | 0.223 | 0.167 | 0.610 | 0.222 | 0.167 | 0.611 | 0.207 | 0.141 | 0.652 | 0.198 | 0.139 | 0.663 | 0.196 | 0.139 | 0.665 |
| 120 h | 0.215 | 0.155 | 0.630 | 0.211 | 0.151 | 0.638 | 0.197 | 0.137 | 0.666 | 0.195 | 0.135 | 0.670 | 0.195 | 0.283 | 0.670 |
| **Grade (B)** | | | | | | | | | | | | | | | |
| Fresh sample | 0.305 | 0.290 | 0.405 | 0.305 | 0.290 | 0.405 | 0.305 | 0.290 | 0.405 | 0.305 | 0.290 | 0.405 | 0.305 | 0.290 | 0.405 |
| After treat. for 24 h | 0.300 | 0.285 | 0.415 | 0.300 | 0.285 | 0.415 | 0.302 | 0.283 | 0.415 | 0.300 | 0.285 | 0.415 | 0.302 | 0.282 | 0.415 |
| Air oxidation for | | | | | | | | | | | | | | | |
| 24 h | 0.277 | 0.253 | 0.470 | 0.268 | 0.247 | 0.485 | 0.265 | 0.235 | 0.500 | 0.266 | 0.239 | 0.495 | 0.263 | 0.233 | 0.504 |
| 48 h | 0.247 | 0.205 | 0.548 | 0.242 | 0.202 | 0.556 | 0.240 | 0.202 | 0.558 | 0.229 | 0.191 | 0.580 | 0.226 | 0.194 | 0.580 |
| 72 h | 0.235 | 0.181 | 0.584 | 0.227 | 0.169 | 0.604 | 0.220 | 0.162 | 0.618 | 0.215 | 0.159 | 0.626 | 0.218 | 0.162 | 0.620 |
| 96 h | 0.219 | 0.155 | 0.626 | 0.208 | 0.144 | 0.648 | 0.202 | 0.139 | 0.659 | 0.198 | 0.136 | 0.666 | 0.199 | 0.138 | 0.663 |
| 120 h | 0.203 | 0.141 | 0.656 | 0.200 | 1.140 | 0.660 | 0.196 | 0.136 | 0.668 | 0.193 | 0.133 | 0.674 | 0.195 | 0.133 | 0.672 |

**Table 5. Brightness, saturation and ΔE for $Na_2CO_3$-treated olives (2nd exp.)**

| Treatment | $Na_2CO_3$ (1%) | | | $Na_2CO_3$ (2%) | | | $Na_2CO_3$ (3%) | | | $Na_2CO_3$ (4%) | | | $Na_2CO_3$ (5%) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Brightness (%) | Saturation (%) | ΔE cm | Brightness (%) | Saturation (%) | ΔE cm | Brightness (%) | Saturation (%) | ΔE cm | Brightness (%) | Saturation (%) | ΔE cm | Brightness (%) | Saturation (%) | ΔE cm |
| **Grade (A)** | | | | | | | | | | | | | | | |
| Fresh sample | 79.4 | 6.5 | 6.0 | 79.4 | 6.5 | 6.0 | 79.4 | 6.5 | 6.0 | 79.4 | 6.5 | 6.0 | 79.4 | 6.5 | 6.0 |
| After treat. for 24 h | 72.4 | 6.9 | 5.8 | 74.1 | 6.9 | 5.3 | 74.1 | 6.9 | 5.8 | 70.8 | 6.9 | 5.8 | 70.8 | 6.9 | 5.8 |
| Air oxidation for | | | | | | | | | | | | | | | |
| 24 h | 54.9 | 10.8 | 5.0 | 51.2 | 10.9 | 4.7 | 47.8 | 15.1 | 4.4 | 44.6 | 16.5 | 4.2 | 42.6 | 17.2 | 4.1 |
| 48 h | 31.6 | 22.3 | 3.6 | 30.2 | 23.6 | 3.3 | 27.5 | 28.0 | 3.0 | 26.3 | 31.5 | 2.7 | 23.4 | 31.8 | 2.6 |
| 72 h | 19.9 | 29.6 | 2.5 | 19.9 | 31.4 | 2.3 | 16.6 | 38.9 | 1.7 | 18.2 | 41.6 | 1.5 | 17.7 | 41.7 | 1.5 |
| 96 h | 16.9 | 36.7 | 1.7 | 17.3 | 39.9 | 1.7 | 14.1 | 49.6 | 0.7 | 17.4 | 52.3 | 0.5 | 13.8 | 53.3 | 0.5 |
| 120 h | 15.4 | 44.7 | 1.2 | 15.1 | 45.9 | 1.2 | 12.5 | 53.4 | 0.5 | 12.8 | 55.3 | 0.4 | 13.1 | 54.8 | 0.4 |
| **Grade (B)** | | | | | | | | | | | | | | | |
| Fresh sample | 70.8 | 7.4 | 5.5 | 70.8 | 7.4 | 5.5 | 70.8 | 7.4 | 5.5 | 70.8 | 7.4 | 5.5 | 70.8 | 7.4 | 5.5 |
| After treat. for 24 h | 69.1 | 7.6 | 5.4 | 69.1 | 7.6 | 5.4 | 67.6 | 7.6 | 5.4 | 67.6 | 7.6 | 5.4 | 67.6 | 7.6 | 5.4 |
| Air oxidation for | | | | | | | | | | | | | | | |
| 24 h | 48.9 | 13.1 | 4.5 | 42.6 | 15.7 | 4.2 | 40.7 | 17.3 | 4.0 | 41.6 | 17.5 | 4.0 | 46.7 | 18.0 | 3.9 |
| 48 h | 29.5 | 24.2 | 3.2 | 26.9 | 29.5 | 2.9 | 28.1 | 29.2 | 2.8 | 25.1 | 33.1 | 2.5 | 36.3 | 33.4 | 2.5 |
| 72 h | 19.9 | 31.0 | 2.3 | 16.9 | 34.8 | 2.0 | 15.8 | 39.1 | 1.6 | 16.9 | 40.6 | 1.5 | 16.9 | 39.6 | 1.5 |
| 96 h | 14.7 | 41.2 | 1.5 | 13.4 | 47.6 | 0.8 | 12.8 | 49.0 | 0.6 | 13.4 | 51.8 | 0.5 | 12.8 | 51.4 | 0.6 |
| 120 h | 12.8 | 45.5 | 1.1 | 13.1 | 52.5 | 0.6 | 12.3 | 53.4 | 0.3 | 12.5 | 54.9 | 0.4 | 12.5 | 53.7 | 0.4 |

**Table 6. C.I.E. values of primary colours for market olives in comparison with Lab. and control samples**

| Type and number of sample | C.I.E. Units X | Y | Z | Brightness (%) | Saturation (%) | ΔE |
|---|---|---|---|---|---|---|
| Market samples | | | | | | |
| 1 | 0.198 | 0.136 | 0.666 | 13.1 | 48.9 | 0.4 |
| 2 | 0.198 | 0.140 | 0.662 | 14.1 | 49.2 | 0.4 |
| 3 | 0.200 | 0.144 | 0.656 | 14.4 | 49.2 | 0.4 |
| 4 | 0.188 | 0.134 | 0.678 | 13.1 | 50.7 | 0.4 |
| 5 | 0.195 | 0.133 | 0.672 | 12.8 | 50.7 | 0.4 |
| 6 | 0.200 | 0.138 | 0.660 | 12.5 | 47.9 | 0.5 |
| 7 | 0.194 | 0.134 | 0.672 | 13.1 | 50.3 | 0.3 |
| Lab. prepared samples | | | | | | |
| $Na_2CO_3$ | | | | | | |
| 3%(A) | 0.198 | 0.136 | 0.666 | 13.1 | 48.9 | 0.4 |
| 3%(B) | 0.196 | 0.136 | 0.668 | 13.4 | 49.3 | 0.3 |
| Naturally blackened sample | 0.196 | 0.126 | 0.678 | 11.2 | 48.3 | 0.0 |

In the light of the effective role explored in the present study regarding $Na_2CO_3$, different concentrations were investigated. Tables 4 and 5 show colour values of olives as measured by the Lovibond Tintometer. It was obvious that for both grade A and B olives, the Z value and saturation (%) increased while X value, brightness and ΔE decreased as concentration of $Na_2CO_3$ was increased. In particular, the air oxidation process is considered a key element in achieving blackening of olives and as air oxidation proceeds, the olives become darker. The point of interest is that when olives were treated with 3% $Na_2CO_3$ followed by air oxidation for 120 h, the ΔE value amounted to 0.4 and 0.3 for grades A and B, respectively, which are very close to the counterparts (0.3 and 0.2) for nigrosine and hematin treatments. Moreover, raising the concentration of $Na_2CO_3$ to 5% led to comparable Z values, equal to those obtained by adding nigrosine and hematin dyes. Such a finding confirms the possibility of using a mild and safe alkaline solution instead of artificial dyes to darken olives, and therefore preventing the health hazards of such dyes.

**Table 7. Sensory evaluation for the colour of blackened olive fruits as affected by different alkali treatments (first exp.)***

| Colouring treatments | | Grade (A) out of 10 | Grade (B) out of 10 |
|---|---|---|---|
| Com. KOH | (2%) | 3.6 ± 0.2 h | 3.8 ± 0.2 fg |
| Com. KOH ± $Na_2CO_3$ | (2%) | 4.3 ± 0.2 gh | 4.2 ± 0.2 fg |
| KOH | (2%) | 4.5 ± 0.2 fg | 4.9 ± 0.2 ef |
| KOH ± $Na_2CO_3$ | (2%) | 4.9 ± 0.2 ef | 5.5 ± 0.3 de |
| NaOH | (2%) | 5.1 ± 0.2 ef | 5.6 ± 0.3 d |
| NaOH ± $Na_2CO_3$ | (2%) | 5.0 ± 0.1 ef | 5.8 ± 0.2 d |
| Com. $Ca(OH)_2$ | (2%) | 5.1 ± 0.2 ef | 5.0 ± 0.3 e |
| Com. $Ca(OH)_2$ ± $Na_2CO_3$ | (2%) | 5.6 ± 0.3 e | 5.1 ± 0.2 e |
| $Na_2CO_3$ | (4%) | 7.6 ± 0.3 cd | 7.4 ± 0.3 c |
| NaH $CO_3$ | (4%) | 7.3 ± 0.3 d | 6.9 ± 0.2 c |
| Nigrosine | (0.1%) | 8.7 ± 0.3 ab | 9.1 ± 0.3 a |
| Hematin | (0.1%) | 8.9 ± 0.2 a | 8.8 ± 0.3 ab |
| Control (naturally blackened) | | 8.1 ± 0.3 bc | 8.5 ± 0.2 b |

*Mean of ten panelists ± standard error.
**Means in a column not sharing the same letter are significantly different at $P < 0.01$.

Seven olive samples obtained from Alexandria public markets had C.I.E. values quite consistent and comparable to naturally blackened olives and those treated with 3% $Na_2CO_3$ for grades A and B (Table 6).

## Subjective evaluation of colour

Table 7 reveals that panellists preferred olives darkened by adding nigrosine and hematin dyes to those which had been blackened by alkali followed by air oxidation. Olives treated with 4% $NaCO_3$ were almost comparable to the control (i.e. naturally blackened olives). However,

**Table 8. Subjective evaluation of colour of blackened olive obtained from Alexandria markets in comparison with control and lab. samples (2nd exp.)**

| Treatment | Colour evaluation (out of 10)* |
|---|---|
| **Market samples**: | |
| 1 | 8.2 ± 0.4 a** |
| 2 | 7.8 ± 0.2 bc |
| 3 | 7.8 ± 0.3 bc |
| 4 | 8.3 ± 0.3 a |
| 5 | 7.9 ± 0.3 ab |
| 6 | 8.1 ± 0.3 a |
| 7 | 7.5 ± 0.2 c |
| **Grade A**: | |
| $Na_2CO_3$ (1%) | 5.7 ± 0.3 f |
| (2%) | 6.4 ± 0.2 e |
| (3%) | 7.3 ± 0.3 cd |
| (4%) | 8.0 ± 0.3 a |
| (5%) | 8.3 ± 0.3 a |
| **Grade B**: | |
| $Na_2CO_3$ (1%) | 6.4 ± 0.2 c |
| (2%) | 6.8 ± 0.3 de |
| (3%) | 8.0 ± 0.3 a |
| (4%) | 8.4 ± 0.4 a |
| (5%) | 8.3 ± 0.2 a |
| Naturally blackened olive | 8.2 ± 0.3 a |

*Mean ± standard error of 10 panellists.
**Means in a column not sharing the same letter are significantly different at $P < 0.01$.

when olives treated with different concentrations of $Na_2CO_3$ (i.e. 1, 2, 3, 4 and 5%) were kept under open air for 120 h and subjected to organoleptic evaluation along with the control, acceptabilities for the colour of 4% and 5% $Na_2CO_3$ treatments and the control were almost comparable. This was true for both grades A and B of olives (Table 7).

Data in Table 8 indicate that the colour of olives which had been naturally blackened and that treated with 3% $Na_2CO_3$ were quite comparable in terms of acceptability by panellists. However, four (out of seven) market samples exhibited the same acceptability as the aforementioned treatments regarding colours.

**Shrinkage and texture of olives**

It was obvious that the volume of the olives declined significantly as a result of the treatments with alkalis followed by air oxidation. The reduction was least, however, for those treated with $Na_2CO_3$ for both grades of olives (A and B) as shown in Table 9.

For the second experiment, it was clear that immersing $Na_2CO_3$-treated olives in sunflower oil for 1 s prior to air oxidation significantly lowered the shrinkage percent of olives (Table 9).

Table 10 reveals that no significant differences could be traced regarding the penetrometer readings of grade

**Table 9. Volume and percentage of reduction (shrinkage) of blackened olive fruits as affected by different discoloration treatments.**

| Sample | | Grade A | | Grade B | |
|---|---|---|---|---|---|
| | | Volume of 25 fruits (ml)* | Red. (%) | Volume of 25 fruits (ml)* | Red. (%) |
| Fresh | | 167 ± 3.6 a | — | 161 ± 2.8 a | — |
| 1st exp. | | | | | |
| Com. KOH | (2%) | 110 ± 3.1 g | 34.1 | 105 ± 2.7 h | 34.8 |
| Com. KOH ± $Na_2CO_3$ | (2%) | 118 ± 2.8 f | 29.3 | 116 ± 2.0 fg | 28.0 |
| KOH | (2%) | 118 ± 2.5 f | 29.3 | 120 ± 3.5 ef | 25.5 |
| KOH ± $Na_2CO_3$ | (2%) | 124 ± 3.3 e | 25.7 | 126 ± 2.9 cd | 21.7 |
| NaOH | (2%) | 117 ± 4.8 f | 29.9 | 113 ± 3.3 g | 26.7 |
| NaOH ± $Na_2CO_3$ | | 127 ± 4.7 de | 23.9 | 122 ± 4.0 de | 24.2 |
| Ca $(OH)_2$ | (2%) | 123 ± 5.0 ef | 23.3 | 121 ± 2.3 de | 24.8 |
| Ca $(OH)_2$ ± $Na_2CO_3$ | (2%) | 130 ± 2.8 d | 22.1 | 127 ± 4.2 c | 21.1 |
| $Na_2CO_3$ | (4%) | 137 ± 5.0 c | 18.0 | 131 ± 3.7 c | 18.6 |
| $NaHCO_3$ | (4%) | 135 ± 2.9 cd | 19.1 | 130 ± 4.3 c | 19.3 |
| 2nd exp. | | | | | |
| $Na_2CO_3$ (1%) | | 145 ± 2.8 b | 13.1 | 140 ± 4.1 b | 13.0 |
| (2%) | | 148 ± 3.8 b | 11.4 | 143 ± 2.8 b | 11.2 |
| (3%) | | 143 ± 2.8 b | 14.3 | 141 ± 3.3 b | 12.4 |
| (4%) | | 148 ± 4.2 b | 11.4 | 145 ± 2.8 b | 10.0 |
| (5%) | | 142 ± 3.7 b | 14.9 | 141 ± 3.3 b | 12.4 |

*Mean ± standard error of 10 panellists.
**Means in a column not sharing the same letter are significantly different at $P < 0.01$.

**Table 10. Penetrometer reading for blackened olive fruits as affected by different treatments of discoloration***

| Sample | | Grade A | Grade B |
|---|---|---|---|
| Fresh** | | 60.1 ± 1.1 g | 37.8 ± 1.3 f |
| Com. KOH | (2%) | 101.7 ± 2.1 bcd | 83.6 ± 1.8 a |
| Com. KOH + $Na_2CO_3$ | (2%) | 105.2 ± 1.7 ab | 83.0 ± 1.4 a |
| KOH | (2%) | 103.7 ± 1.7 ab | 80.5 ± 1.2 ab |
| KOH + $Na_2CO_3$ | (2%) | 107.0 ± 1.5 a | 82.8 ± 1.2 a |
| NaOH | (2%) | 100.1 ± 1.7 bcd | 81.4 ± 1.5 a |
| NaOH + $Na_2CO_3$ | (2%) | 102.9 ± 2.0 abc | 80.2 ± 1.2 ab |
| Com. Ca $(OH)_2$ | (2%) | 79.6 ± 1.7 f | 59.8 ± 1.2 e |
| Com. Ca $(OH)_2$ + $Na_2CO_3$ | (2%) | 88.8 ± 1.4 e | 71.7 ± 1.5 d |
| $Na_2CO_3$ | (4%) | 95.1 ± 1.1 d | 78.3 ± 1.7 b |
| $NaHCO_3$ | (4%) | 90.7 ± 2.0 e | 69.9 ± 1.3 d |
| $Na_2CO_3$ | (1%) | 90.8 ± 1.3 c | 72.1 ± 0.9 d |
| $Na_2CO_3$ | (2%) | 98.2 ± 1.7 cd | 67.3 ± 1.6 c |
| $Na_2CO_3$ | (3%) | 96.1 ± 1.1 d | 80.2 ± 1.1 ab |
| $Na_2CO_3$ | (4%) | 95.7 ± 1.5 d | 78.7 ± 1.5 bc |
| $Na_2CO_3$ | (5%) | 99.2 ± 1.9 bc | 80.3 ± 1.1 ab |

*Mean ± standard error of 25 fruits.
**Values for the naturally blackened fruits = 102.4 ± 1.4.
***Values in a column not sharing the same superscript are significantly different at $P < 0.01$.

**Table 11. Detection of artificial dyes, moisture content and some heavy metals of commercially produced and laboratory made blackened olive fruits.**

| Type and no. of sample | Detection of Dye | Moisture content % | Fe* W.W.B** | Fe* D.W.B*** | Cd* W.W.B | Cd* D.W.B | Pb* W.W.B | Pb* D.W.B |
|---|---|---|---|---|---|---|---|---|
| Market samples: | | | | | | | | |
| 1 | + Hem. | $80.12 \pm 0.76^{a}$ | $3.18 \pm 0.05^{e}$ | $16.10 \pm 0.30^{d}$ | $0.44 \pm 0.01^{c}$ | $2.22 \pm 0.06^{a}$ | $1.76 \pm 0.05^{de}$ | $8.92 \pm 0.26^{a}$ |
| 2 | + Nig. | $64.10 \pm 0.38^{f}$ | $18.06 \pm 0.16^{a}$ | $50.32 \pm 0.47^{a}$ | $0.81 \pm 0.04^{a}$ | $2.25 \pm 0.11^{a}$ | $3.09 \pm 0.05^{a}$ | $8.61 \pm 0.30^{ab}$ |
| 3 | + Hem. | $72.35 \pm 0.61^{bc}$ | $4.65 \pm 0.06^{d}$ | $16.80 \pm 0.22^{d}$ | $0.55 \pm 0.02^{bc}$ | $1.98 \pm 0.07^{cd}$ | $2.22 \pm 0.06^{c}$ | $8.00 \pm 0.22^{bc}$ |
| 4 | + Hem. | $70.28 \pm 0.48^{cde}$ | $5.83 \pm 0.10^{c}$ | $19.61 \pm 0.35^{c}$ | $0.62 \pm 0.01^{b}$ | $2.06 \pm 0.03^{bc}$ | $2.43 \pm 0.11^{b}$ | $8.16 \pm 0.40^{bc}$ |
| 5 | Nat. | $73.16 \pm 0.35^{b}$ | $2.71 \pm 0.06^{f}$ | $10.10 \pm 0.21^{e}$ | $0.32 \pm 0.01^{d}$ | $1.20 \pm 0.05^{e}$ | $1.37 \pm 0.09^{f}$ | $5.11 \pm 0.33^{d}$ |
| 6 | + Nig. | $70.28 \pm 0.57^{cde}$ | $8.80 \pm 0.05^{b}$ | $29.60 \pm 0.18^{b}$ | $0.62 \pm 0.03^{b}$ | $2.10 \pm 0.10^{ab}$ | $2.37 \pm 0.08^{b}$ | $7.69 \pm 0.28^{c}$ |
| Lab. samples: | | | | | | | | |
| 7 $Na_2CO_3$ (3%) [A] | — | $68.65 \pm 0.28^{e}$ | $2.38 \pm 0.03^{f}$ | $7.60 \pm 0.11^{f}$ | $0.35 \pm 0.01^{d}$ | $1.10 \pm 0.04^{e}$ | $0.99 \pm 0.05^{g}$ | $3.17 \pm 0.19^{e}$ |
| 8 $Na_2CO_3$ (3%) [B] | — | $69.13 \pm 0.40^{e}$ | $2.19 \pm 0.05^{f}$ | $7.11 \pm 0.19^{f}$ | $0.35 \pm 0.02^{d}$ | $1.12 \pm 0.07^{e}$ | $0.96 \pm 0.03^{g}$ | $3.11 \pm 0.11^{e}$ |
| 9 Nat. blackened | Control | $71.49 \pm 0.71^{bcd}$ | $1.76 \pm 0.16^{f}$ | $5.95 \pm 0.16^{f}$ | $0.32 \pm 0.01^{d}$ | $1.10 \pm 0.03^{e}$ | $0.94 \pm 0.04^{g}$ | $3.20 \pm 0.13^{e}$ |
| 10 | + Nig. | $69.95 \pm 0.66^{de}$ | $5.46 \pm 0.07^{c}$ | $17.60 \pm 0.25^{d}$ | $0.58 \pm 0.03^{b}$ | $1.86 \pm 0.09^{cd}$ | $1.66 \pm 0.07^{e}$ | $5.34 \pm 0.22^{d}$ |
| 11 | + Hem | $68.28 \pm 0.43^{e}$ | $5.36 \pm 0.11^{c}$ | $16.90 \pm 0.39^{d}$ | $0.57 \pm 0.02^{b}$ | $1.80 \pm 0.05^{d}$ | $1.81 \pm 0.06^{d}$ | $5.71 \pm 0.20^{d}$ |

*As mg/100 g. **W.W.B = Wet Weight Basis. ***D.W.B = Dry Weight Basis.
+ Means ± standard error in a column not sharing the same letter are significantly different at $P < 0.01$

B olives treated with 5% $Na_2CO_3$ and those treated with 2% KOH or NaOH, either as a sole alkali or mixed with 2% $Na_2CO_3$. This effect was not obvious for grade A olives.

In general, the penetrometer reading for grade-A fresh olives (mature) was greater (softer) than those for the corresponding grade B olives. However, treatment with alkalis gave a less pronounced effect on texture of grade-A olives than grade-B ones. Treatment of olives with $Ca(OH)_2$ resulted in the lowest penetrometer readings. This was true for both olive grades investigated in the present study.

### Detection of artificial dyes, moisture and heavy metals

The market samples investigated in the present study were those with the dark black colour (five samples) and a naturally darkened sample as control. As can be seen from Table 11, three samples were positive for hematin while the other two samples were positive for nigrosine. It is obvious that Egyptian consumers usually prefer the dark black olives regardless of darkening process. This can be attributed to the fact that the majority of consumers, especially those of low-income, know little about the hazards of artificial darkening methods of olives.

In general, market samples possessed significantly higher moisture contents than the laboratory-made samples treated with $Na_2CO_3$. Nevertheless, it was clear that the market samples, with an exception of the naturally blackened sample, contain significantly higher concentrations of heavy metals determined in the present study (iron, cadmium and lead). Iron contents of market samples that were artificially darkened hold 3- to 8-fold the iron concentrations of their counterparts belonging to natural types and samples blackened with $Na_2CO_3$. Moreover, the former samples had 2-fold and from 2-3 fold concentrations of cadmium and lead, respectively, as compared to the latter samples (Table 11). Such data confirm contamination with heavy metals of artificial dyes and commercial alkalis usually used by small processors in Egypt. Of course, this doubles the hazardous effects of artificial dyes that are usually used by some black olive producers in Egypt to make their olives more attractive to the consumer.

In the light of data presented here, it can be concluded that the darkening of olives applied by small processors is a hazardous process. This is due to utilization of artificial dyes and/or low grade commercial chemicals which are commonly contaminated with heavy metals. The present work indicates that applying food grade $Na_2CO_3$ in the darkening process produces most acceptable darkened olives.

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