((Effect of storage periods on peroxides of edible fats and oils))

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Abstract

This experiment was conducted on 15/9/2022 in the laboratories of Al-Fadhel Company in the city of Hilla, after extracting animal fats (tall fat sheep , sheep belly oil, Cow oil and Butterfat) by thermoplastic method, sesame oil by pressing method, and hydrogenated oil from the markets, in stages, to observe the development of the first stage of fat oxidation due to exposure to heat, oxygen, light, and humidity at room temperature, which produces roots Free peroxide assay (PV).As well as the second stage, which produces aldehydes and ketones with a rancid smell, by examining thiobarbituric acid. The results of the peroxide test showed that there was no significant difference, and the peroxide values varied within the Iraqi standard. As for the TBA test.The results showed the influence of the source of oil and fat, so the hydrogenated oil excelled as an indication of its exposure to abnormal storage conditions that led to the beginning of oxidation and the formation of aldehydes and ketones, and immediately after the 15th day it came out of control according to the standard specification, to be followed on the 18th day by the release of free fat and sheep belly fat, due to the high level of unsaturated fatty acids. As the results of the current study showed, the lack of antioxidants, then on the 20th, sesame oil got out of control due to its high content of unsaturated fatty acids. Then, on the 23rd, the bovine fat gets out of control, and the beef fat is the only one that gets out of control. On the 30th, that is, the last two samples that got out of control is the buttock fat and the beef fat.

INTRODUCTION

1-1-PEROXIDE VALUE

Oils and fats are exposed to oxidation during processing and storage, which negatively affects the quality of oil and fat, and thus on human health. Determining the peroxide value (PV) of edible oils is important because it is one of the most used quality standards to controlling fat oxidation. The method of controlling the quality of oil and fat and the scientific basis for estimating the peroxide number is the iodometric interaction and the ability of peroxides in the oil or anointing on separate events of iodine in an amount equivalent to the amount of peroxides, then estimating the individual iodine equivalents using sodium thiosulfate in the presence of starch evidence. The peroxide number is the milliequivalent value of hydrogen peroxide per kilogram of fat. It is considered a standard for oxidized fat, and its examination is an estimate of the degree of oxidation of oil and fat. It depends on the ability of the peroxide to liberate iodine (I_2) from potassium iodide (KI) in icy acid such as acetic acid. Fresh fat has a peroxide number of 10 (MEq) or less. Signs of fatty rancidity appear when the peroxide number is 20-40 (17).

Male et al (16);(7) The measurement of oxidation products in oils and food fats at temperatures that represent the conditions of production and storage, so the results were that there are significant interactions according to the type of oil and fat at 22.5 ° C. The peroxide value (PV), which is a marker for the initial stage of lipid oxidation, increased, and oils and fats remained unstable when heat,

light, and oxygen were available and in the study of peroxide values of sesame oil during deep frying of Indian potato chips and in three batches after each stage of deep frying .The results showed a change in the peroxide values, and there was an increase after the second roasting of the Indian potato chips from 3.9914 (Meq/kg) to 11.9555 (Meq/kg), but after the third frying there was a slight decrease to (11.3095) Meq/kg (12).

The research aims to detect the effect of the source of oils and fats on the oxidation resistance at room temperature to determine the period of their storage to be suitable for consumption

1-2- Thiobarbituric Acid (TBA).

It is the value of the Manold Hyde formed per kilogram of fat or oil. It is one of the most important changes resulting from storage and is considered an index of fat oxidation. It changes color, smell, flavor, nutritional value, and vitamin content as a result of the interaction of unsaturated fatty acids with their double bonds with oxygen to produce peroxides, then aldehydes and ketones with a rancid odor. The value of thiobarbituric acid is affected by the storage period and the amount of antioxidants, which is the method of examining oil or fat that depends on the formation of a red color due to the interaction of the acid with the manoldehyde compound formed in the oxidized fat. (3).

(16) indicated that the oxidized oil as a result of the leakage of heat and air forms volatile aldehydes, and the remaining ones are harmful to the consumer, and this accumulation depends on the oxidation temperature and the type of oil because animal fats contain a small part of (tocopherols). As an antioxidant compared to vegetable oils, the study confirmed the effects of oxidized fats on public health, digestive system safety, immune efficiency, and metabolic oxidation. Therefore, it became important to monitor fat factories and their storage methods. The results of primary oxidation are peroxides, and secondary ones are aldehydes and ketones.

3- Materials and methods

3-1-Extraction of Plant Oils

3-1-1-Sesame oil extraction

This is according to the method mentioned by (2) by purchasing locally grown raw sesame seeds with a blackish color, cleaning them well, and extracting them by squeezing using an Iranian-made device of the type BEKRDANEH MINI PRESS, where it operates under cold and hot hydraulic pressure, a sample of sesame seeds was placed in the funnel of the device and operated on cold, in order to facilitate squeezing sesame seeds because they are oily seeds with a high oil content.Then the oil drips with the impurities of a black color. As for the residue of the cake, it is isolated by the device. Then we leave the oil for about six hours to filter to get rid of the impurities, to get a bright yellow oil with a purity rate of 36.70%

3-2 - Animal fat extraction

3-2-1- Extraction of cow fat

Extraction of cow fat by the thermal amniocentesis method mentioned by (9);(14) by preparing cow fat, washing it and cutting it in the form of small cubes as in Appendix (2) to increase the surface area for exposure to heat by placing it in a pot over a very low heat. With continuous stirring and monitoring until the pieces of grease turn brown, indicating that they have exhausted the fatty substance and the fatty medium turns into a semi-clear medium, then it is left to cool and filter, and it has a purity rate of 75%.

3-2-2 Extraction of sheep belly oil

Extraction of sheep belly fat using the thermoplastic method mentioned by (9);(14) where the sheep belly fat was prepared and cut to be placed in a pot on a slow cooker until the pieces of fat browned with continuous stirring and monitoring and left to cool as in Appendix (3)Then it is filtered through a glass container to keep it at a purity rate of (77.77%), which is the highest percentage of filtration among oils

and fats. Belly fat hardens after an hour and a quarter of its filtration to be white in color, less dense and slightly less solid than cow fat.

3-2-3- Tall fat sheep

The tall fat was prepared and cut into cubes and placed in a pot on a low heat until the pieces of the mechanism browned with continuous stirring and monitoring by the method called thermal conductivity mentioned before(9);(14) Then it is left to cool and filtered in a bottle with a net content of 61%. Tall fat does not freeze at room temperature until it is kept in the refrigerator to harden and be of white color and clear flavor.

3-2-4- Extraction of milk fat (Butterfat)

This is done by the method mentioned by (9);(14) The method of thermal sautéing is to prepare the amount of butter to be placed on a low heat until the milk residue (the sediment of clarified butter is a by-product rich in fat) separates with the butter and is left to cool.It is filtered as in Appendix (4) to separate the amount of milk to obtain the free, filtered fat in a bright and bright turmeric yellow color with a net clearance of 52.97%. It has a distinctive flavor that is considered the first among animal fats. It also does not freeze at room temperature, after it is kept in the refrigerator.

3-3- Peroxide Value (p.v) Calculation

This is according to the method mentioned by (8) and depends on the co-oxidation by adding the ferrous ion Fe (II) ferrous and due to the presence of peroxide in the oil and fat sample to turn into the Fe (III) ferric ion and form a complex Fe (III) - thiocyanate with a light red color , which is read at 500 nm using a spectrophotometer.

Method of work: by preparing the six samples and melting the animal fat and hydrogenated oil samples with the liquid sesame oil sample. Then (10) mg (fat or oil) was withdrawn in half ml ethanol, then 50 µL of ammonium thiocyanate was added, followed by 50 µL of Fe (II) solution after 10 minutes.The absorbance was measured at 500 nm using a UV-VIS spectrophotometer. The (competent) plank contains all reagents except lipids. PV is expressed as: Meq/kg Meq O2 / Kg fat using the formula:

$$\text{Peroxide Value (PV)} = \frac{Abs}{55.84 \times w} \times \frac{1}{b} \text{ [mEq}$$

w - fat weight (g) / *Abs* – absorbance / 55.84 - atomic weight of Fe^{3+}

b - the slope of the Fe (III) calibration curve. **0.0254**

3-4- Calculation of Thiobarbituric Acid (TBA)

It is the measurement of the concentration of malondialdehyde (MDA) using a thiobarbituric acid reagent to measure the amount of malondialdehyde as an indicator of the final lipid oxidation product according to the method (1) modified by (17).

Solutions: Use thiobarbituric acid reagent (prepared by dissolving 250 gm of thiobarbituric powder in a volumetric vial of 100ml capacity. The volumetric vial contains 50ml distilled water and half ml concentrated hydrochloric acid 10g and acetic acid trichloride Complete the volume to the mark. The components were dissolved using an ultrasonic device. This detector is suitable for one week only. It is preferable to prepare it in real time. Method of work: The samples of oils and fats were prepared and the hardened samples were dissolved. We take 0.5 ml and add 0.5 ml ethanol. Then add 2 ml of thiobarbituric acid reagent prepared from the American company (SIGMA), shake the tube well, then put the results in a boiling water bath for 30 minutes to complete the reaction. After completing the incubation period, the samples were left at room temperature to cool.The absorbance of the resulting colored solutions was measured using a spectrophotometer at a wavelength of 500 nm. The control treatment (plank) was prepared with the same steps above, except for the step of adding oil or fat. If it was replaced by ethanol, the value of thiobarbituric acid (TBA)

was calculated according to the following equation:

TBAR value (Meq/kg) = [50 × (A-B)]/m (1),

A = test tube absorbance

B = absorbance of the efficient solution (Planck). M = model weight

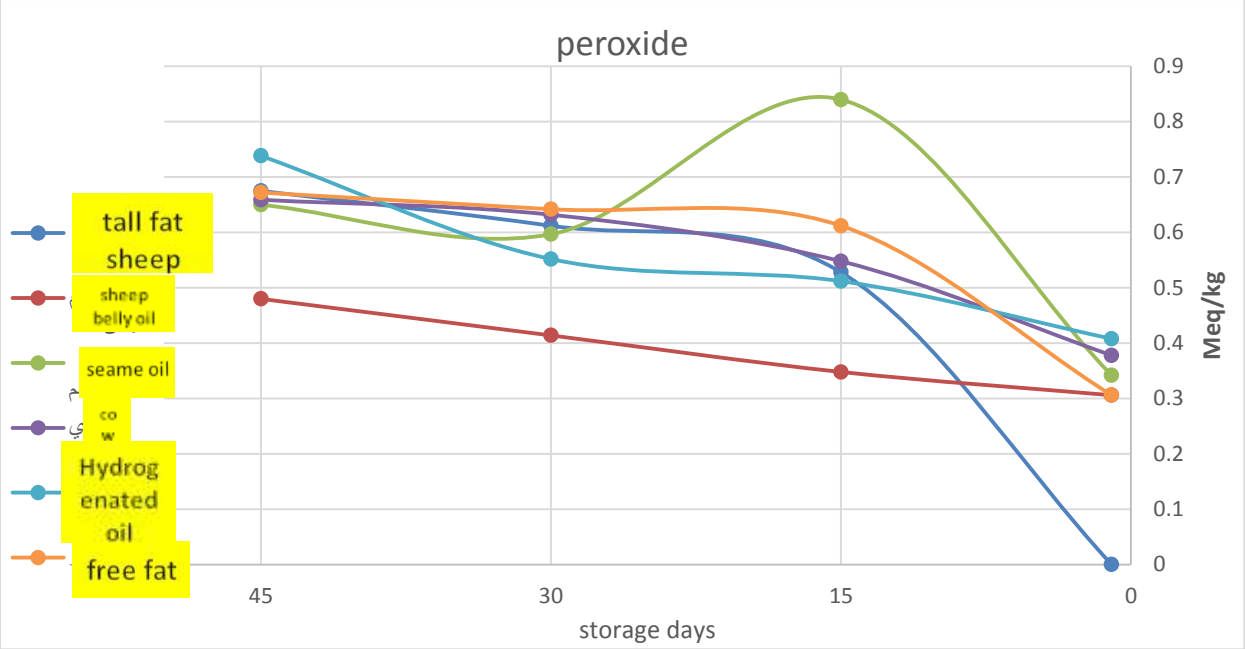
4. Results and Discussion

4-1- Peroxide number

The results of the peroxide test of the oils and fats samples under the current study, as shown in Figure (1-4)and Table (1-4), showed the effect of the source of oil and fat on the peroxide values on the first day. The percentages were simple, since the oil and fat were newly extracted. However, the fat of the stomach was excelled on peroxide value of 0.42 Meq/ kg and the lowest peroxide value was for sheep belly fat and ghee fat, the rest of the peroxide was equal to 0.306 Meq/ kg, and the hydrogenated oil values. beef fat and sesame oil were (0.408, 0.378, 0.342) Meq/kg, respectively. On day 15, sesame oil had a peroxide value of 0.84 Meq/kg. eq/kg and ghee fat values, beef fat and hydrogenated oil were (0.612, 0.548, 0.528, 0.512) Meq/kg, respectively, and on day 30, the ghee fat was excelled on the peroxide value of 0.642 Meq/kg, and the lowest peroxide value was for sheep belly fat with a value of 0.414 Meq/kg. tail fat, sesame oil, and hydrogenated oil were (0.552,0.596,0.612,0.632) Meq/kg.

Table (1-4) Peroxide values (Meq/kg.) for testing oils and fats samples Within the storage period of 45 days

No.	type of fat	On the first day	after 15 days	after 30 days	after 45 days
1	tail fat	.0.42	0.528	0.612	0.675
2	Sheep belly fat	0.306	0.348	0.414	0.480
3	Sesame oil	0.342	0.84	0.596	0.650
4	beef	0.378	0.548	0.632	0.659
5	hydrogenated	0.408	0.512	0.552	0.7384
6	ghee fat	0.306	0.612	0.642	0.672



Figure(1-4) Graph of peroxide values

On day 45, hydrogenated oil was excelled with a peroxide value of 0.738 Meq/kg, and the least peroxide value was for sheep belly fat 0.480 Meq/kg. As for tail fat, ghee fat, beef fat, and sesame oil (0.650, 0.659, 0.672, 0.675), the value was 0.650 Meq/kg. fat . Ozeet is considered a standard of oxidation and depends on the state of saturation of fatty acids and storage conditions such as temperature, oxygen availability, moisture content and the amount of antioxidants Vitamin E (tocopherol). The peroxide of sesame oil decreased after day 15 and its stability until day 45 due to the presence of antioxidants and a slight increase in the peroxide value of beef fat after one day 15 and its stability until day 45 is due to the presence of saturated fatty acids .This applies to other animal fats such as ghee fat, sheep belly fat and beef fat, and this was confirmed by the examinations of our current study. As for the hydrogenated oil, it started with a slight increase until the 30th day, to outperform oils and fats on the 45th day due to storage and transportation conditions, and this was confirmed by examining the current study, but the fats did not come out of Standard specification (5); (13); (8). Fats is more predispose for oxidation and this proved by (16).

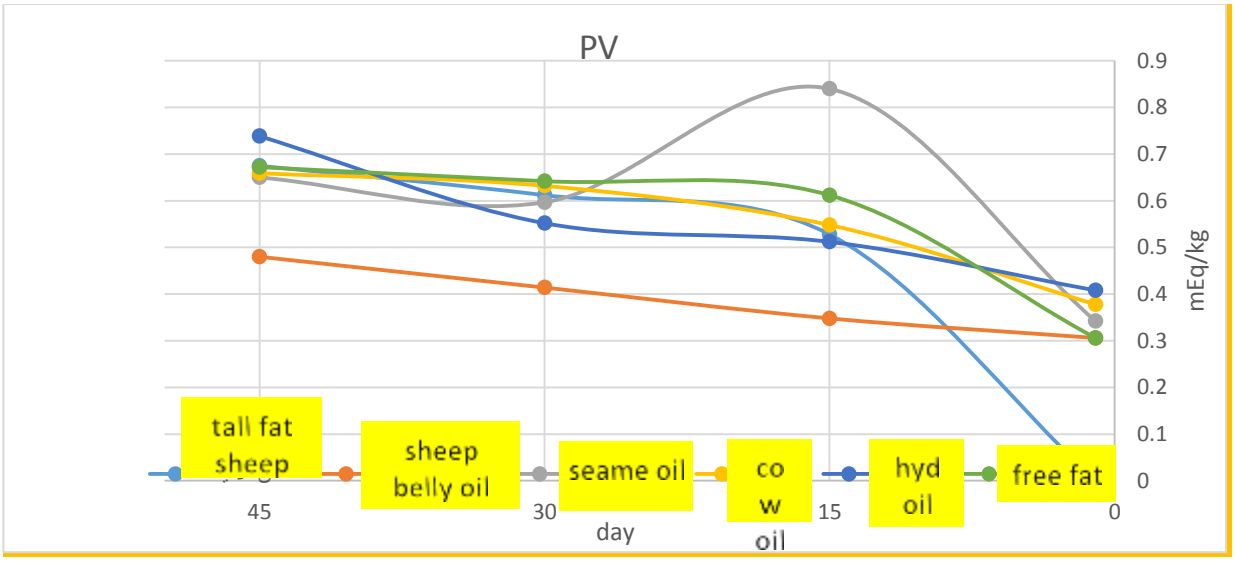


Figure (1-4) Graph of peroxide values (Meq/kg.) for testing oils and fats samples Within the storage period of 45 days

4-2- thiobarbituric acid (TBD)

The results of the thiobarbituric acid test for the oils and fats samples under the current study, as shown in Figure (2-4) and Table (2-4), showed the effect of the oil and fat source on the TBA values on the first day, there were simple percentages of thiobarbituric acid, but the highest value was for ghee fat 0.092 monodehyde / kg, and this is evident in the graph. The lowest acid value was 0.01 monaldehyde / kg for tail fat, while the values for sesame oil, beef fat, sheep belly fat and hydrogenated oil were (0.011, 0.029, 0.043, 0.052) monaldehyde / kg .The acid values were simple, due to the presence of antioxidants such as vitamin E, which prevent oxidation. Freshly extracted oils and fats have not yet been exposed to heat, humidity, and oxygen, so the oxidation products, aldehydes and ketones, decrease, so the acid values are low.

Table (2-4) Thiobarbituric acid tests for oils and fats Within the storage period of 45 days

No.	type of fat	On the first day	after 15 days	after 30 days	after 45 days
1	tail fat	0.01	0.0762	0.1984	0.6326
2	Sheep belly fat	0.0295	0.175	0.32	0.3616
3	Sesame oil	0.0526	0.084	0.4672	0.568
4	beef	0.04322	0.0734	0.354	0.497
5	hydrogenated	0.01154	0.199	00.5616	0.6848
6	ghee fat	0.0929	0.1237	0.696	0.8304

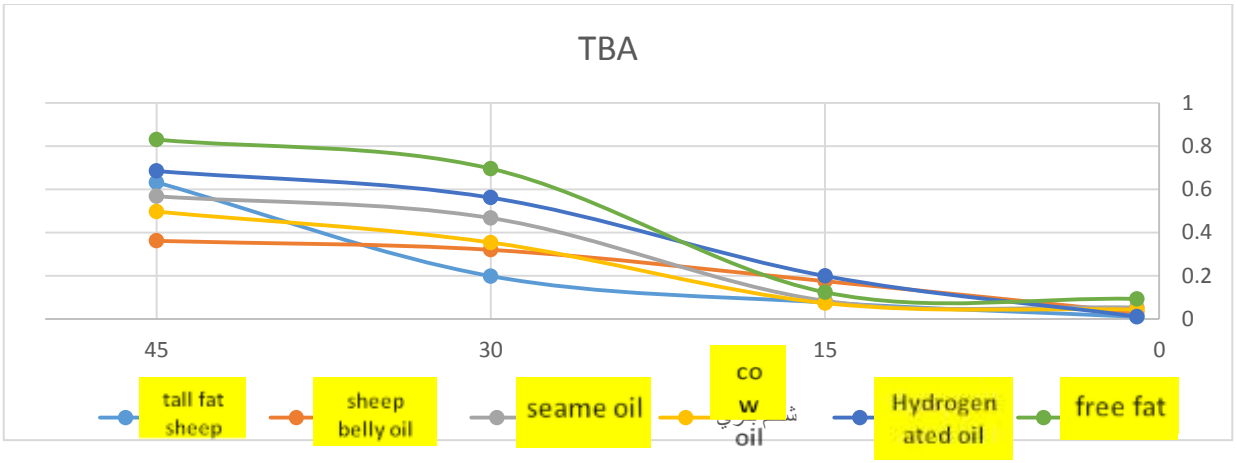


Figure (2-4)graph of thiobarbituric acid values

On the 15th day, hydrogenated oil surpassed the TBA value, which was 0.199 monodehyde / kg, and the lowest TBA value for bovine fat was 0.073 monaldehyde / kg, sheep belly fat, ghee fat, sesame oil, and tail fat (0.076, 0.084, 0.1237, 0.175) (monaldehyde / kg, respectively).The hydrogenated oil excelled as an indication of its exposure to unnatural storage conditions that led to the beginning of oxidation and the formation of aldehydes and ketones, and immediately after the 15th day it was out of control according to the standard specification, to be followed on the 18th by the release of ghee fat and sheep belly fat, due to the high level of unsaturated fatty acids. As the results of the current study showed and the absence of antioxidants, then on the 20th day the sesame oil got out of control due to its high content of unsaturated fatty acids, then on the 23rd the beef fat got out of control and the buttock fat is the only one out of control on the 30th day, i.e. the last two samples that got out of control is the buttock fat and beef fat because it contains saturated fatty acids .Thiobarbituric acid rises due to the oxidation of fats for the aforementioned reasons to produce peroxides, aldehydes and ketones (4). The accuracy percentage of the PV peroxide test for oils and fats is (80-90)% and TBA is 100%. Therefore, the results of the TBA examination depend on what happened in the current study, and that the TBA examination proved that the oil or fat samples were out of control according to the standard specification, while the peroxide examination did not prove it(10). This is consistent with (15) found that oils,saturated fats are resistant to oxidation then monosaturation then un saturated fats

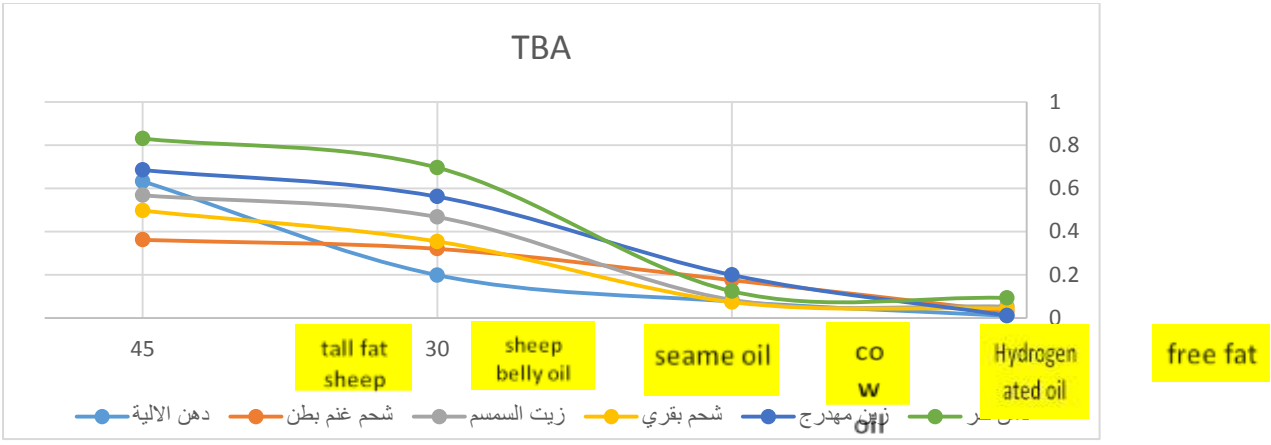


Figure (4-2) Graph of thiobarbituric acid values

5- Conclusion.

Animal fats are accused of being harmful fats, but they have been shown through research to have a longer storage period than oils because they contain higher levels of saturated fatty acids that are resistant to oxidation, despite what was confirmed by Winkler–Moser et al (2020) that unrefined fats are more susceptible to oxidation. but the worst is hydrogenated oil and hydrogenated vegetable oils. It is widely used in the manufacture of various foodstuffs such as cakes, biscuits, fried potatoes and in many fast foods due to its long shelf life. However, vegetable edible oils such as sesame oil contain natural antioxidants that suppress oxidation and radical reactions. (6) .This is consistent with the findings of (11)The damage of hydrogenated fats to the health of the skin, making it more vulnerable to ultraviolet radiation (UVR), which leads to aging and skin cancer. It causes obsessive-like behavior and oxidative damage to the brains of mice, so the study recommends food safety authorities and psychiatric experts to pay attention to such serious health damage.

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