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Effect of weed management practices and foliar application of α-Tocopherol on the productivity and oil characteristics of an Egyptian peanut cultivar

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Abstract

This work aimed to study the effect of some weed management practices associated with Giza 6 peanut variety cultivated during the summer season of 2021, on peanut oil characteristics. Also, their effect on the yield and growth parameters of peanut plant and the accompanied weeds was studied. The applied weed management techniques included hand hoeing and Clethodim herbicide treatment, using full and half rates, were done as a post-emergence compared to the untreated control. Foliar application of α-Tocopherol was done as a strategy of fighting stress accompanied to all other treatments and to control. Results showed that applying full rate of Clethodim herbicide + α-Tocopherol caused the most noteworthy diminishing in fresh and dry weights of peanut weeds. While, hoeing + α-Tocopherol gave the highest increasing percentage in most of peanut plant growth parameters as well as seed yield per feddan. The highest oil yield/feddan was also recorded for hoeing+ α-tocopherol treatment. Most of the chemical characteristics (peroxide, iodine and acid values) of peanut oils of the different treatments fulfilled the Codex standard characteristics for peanut oil and were better than that of the untreated control. Fatty acids composition of all peanut oil samples showed its characteristic profile with oleic: linoleic acid ratios ranged from 1.2 – 1.4 which gives peanut oil its healthy and stability advantage. Chloroplast pigments (total carotenoids and chlorophylls) and total Tocopherols contents were positively affected with the different treatments compared to the untreated control. These results assessed the protective action of the foliar application of α-Tocopherol compared to the untreated control. The peanut oil extracted from 50% herbicide + 30 % urea + α-Tocopherol treated seeds was found to have the most improved characteristics including fatty acids composition, chloroplast pigments and total Tocopherol contents. It can be concluded that weed management practices along with foliar application of α-Tocopherol are important measures needed to overcome the bad effects of weeds and proved to enhance the produced oil characteristics and the productivity of peanuts compared to the untreated control.

Keywords: Peanut oil, weed management, Clethodim herbicide, tocopherol, growth parameters.

1. Introduction

Peanut or groundnut (Arachis hypogaea L.) is a major food and oil crop as, in Egypt, it is considered as one of the most critical summer oil crops, where, according to FAO [1], its developed range came to almost 62000 ha, with add up to 199000 tons. Although it is a low-priced commodity and known as poor men's cashew, its seed is a valuable source of nutrients as it contains around 40-55% oil, 25-28% protein, 5% fibres [2]. Besides, peanut seeds are rich in many vitamins like those soluble in fat (A, D, E and K) and those soluble in water (B-Complex and vitamin C). It also contains important essential minerals such as calcium, phosphorus, magnesium, zinc, iron, potassium, copper and selenium [3]. Most of the total peanut world production is used in producing peanut oil, while the remaining amount is utilized in food products. In 2015, peanut oil contributed about 8.7% of the total production of oilseeds by 45 million tons of the total production in the world [4].

Peanut oil is one of the vital edible vegetable oils in the world, due to its high content of nutrients, such as natural vitamin E (Tocopherol), 80% of unsaturated fatty acids...etc that are beneficial in reducing heart diseases and preventing diabetes [5,6].

Peanut crop faces a serious problem of the growth of several weeds adjacent to the shelled nut plants, especially in the primary growth stages, where, after 7 to 10 days of sowing, the seedling emerges. Growing weeds compete for solar radiation, underground space, water, nutrients and hinder pegging causing yield losses as high as 70% [7]. So, during the critical period of crop-weed competition, it is important to keep the crops in a weed-free condition to obtain high yields by selecting an appropriate weed control method depending on the type of the crop and weeds, the equipment available, and the time of

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treatment [8,9]. Kumari et. al. [10] reported that applying good weed control practices at early stages, along with other agricultural measures, promotes vigorous crop growth and inhibit subsequent weed growth. Hoeing or hand weeding is the most costly common weed control strategy due to high cost of labour, therefore using herbicides could be an incredible elective, but it may permit weeds to rise after a period of time. Burke et. al. [11] reported that Clethodim herbicide is registered in peanut to control annual and perennial grasses. Information on the effects of management practices of weeds associated with oilseeds crops on the characteristics and fatty acids composition of the produced oil is considered scarce.

Manaa et. al. [12] reported that environmental stresses caused by biotic and abiotic factors, negatively affect, either directly or indirectly, the productivity and quality of the important crops through the formation of Reactive Oxygen Species (ROS). Herbicides are one of the various environmental factors that cause oxidative stress by an excess accumulation of ROS [13], which may cause damages to the metabolism of the plants due to its high toxicity and may affect oil composition, in oil crops, as one of the most important plant products.

In order to resist oxidative stress conditions, plants possess various antioxidants systems which include nonenzymatic antioxidants such as tocopherols, carotenoids, ascorbic acid and enzymatic antioxidants such as catalases and superoxide dismutases (SOD) enzymes [12]. Applying herbicides stimulates plants to undertake some defensive and protective mechanisms like changing their concentrations of vitamins, including α-Tocopherol and ascorbic acid, which may also affect the produced oil composition. Applying exogenous vitamins is another form of fighting damage caused by herbicides and other environmental stresses. α-Tocopherol is the most effective antioxidant against lipid oxidation [14]. It is mainly located within chloroplast membranes where it protects chlorophyll, quench oxygen radicals and stabilize cell membranes [15].

Sadiq et. al.,[16] reported that improving the oxidative defence system in plants that suffers from stress can take place either by enhancing their internal antioxidants production through plants engineering or by applying exogenous antioxidants like tocopherols. The latter technique is simple to be applied, economical, and efficient, so it is widely investigated. From another point of view, using herbicides at different stages of cultivation, especially the highly lipophilic one, in protecting oil crops from weeds, may results in an easily bio-accumulation of these herbicides in oilseeds and hence will be extracted into the oil during the extraction process [17].

So, this work aimed to study the effect of some weed management practices along with foliar application of α-Tocopherol on the associated weeds, yield and growth parameters of peanut plant and the characteristics and yield of the extracted oil and to detect the presence of herbicides residues in the oil..

2. Materials and Methods

2.1. Agricultural weed management practices

Field tests were carried out at the Agribusiness Test Station of National Research Centre, Nubaria, Behira Governorate, Egypt, (scope 30.8667 N, and longitude 31.1667 E) during the summer season of 2021. Clethodim herbicide was used against grasses growing on peanut under field fertigation frame work (trickle water system) condition. Sandy soil was used with pH 7.8, natural matter 1.6%, electric condition (E.C.) 1.04 mmohs/cm, $CaCO_3$ 1.56%, add up to N 0.043%, add up to P 0.022%, and add up to K 0.02%. Plot zone was 15 m^2 (3 m width by 5 m length) containing 5 edges dispersed 60 cm separated. Peanut seed cultivar (Giza 6) was purchased from the Agricultural Research Centre, Giza, Egypt. Seeds were sown in 8thJune , 2021, two seed per hill in consistent dispersed slopes (20 cm separated) on one side of edge.

Weed control treatments were as follows:

1. Unweeded (weeds were allowed to grow with peanut plants) Control.
2. Unweeded (weeds were allowed to grow with peanut plants) Control+ α-Tocopherol.
3. Twice hand hoeing was carried out (20 and 35 days after sowing) + α-Tocopherol.
4. 100% Clethodim herbicide (full rate) + α-Tocopherol.
5. 50% Clethodim herbicide (half rate) + 30 % urea + α-Tocopherol.

Herbicide treatments were sprayed as post-emergence treatment after 30 days of sowing by Clethodim herbicide using knapsack sprayer at water volume of 200 L/fed. Clethodim full rate (100%) was 297.5 g a.i./ha (recommended rate) and 148.75 g a.i./ha for 50% rate. Foliar application of α-Tocopherol (800ppm) was done after 37 days of sowing for all treatments.

Sowing peanut seeds at the rate (35 kg/fed) were in rows (60 cm apart and 20 cm between hills). Immature seeds were collected after 90 days of sowing. Harvest was done on 5thOctober in the season (after 120 days of sowing). Inoculation of peanut seeds was done with the specific rhizobium bacteria inoculants, just before sowing, to fix nitrogen in soil. Mono-super phosphate fertilizer (15.5% P_2O_5) was added at rate of 150 kg/fed during the preparation of seed bed. Potassium sulphate (48% K_2SO_4) was applied at sowing at the rate of 50 kg/fed. Ammonium sulfate (20.6 %N) nitrogen fertilizer was added at a rate of 30 kg N/fed in two equal halves, the first one at sowing, while the second half after 30 days later. After every 3 days, sprinkler irrigation was applied. The recommended agricultural practices for peanut production were followed.

2.1.1. Agronomic measurements:

2.1.1.1 Weeds:

Growing weeds were collected by hand from one square meter in each plot at 7 and 14 weeks after sowing (WAS) and classified into three groups according to Täckholm [18] as follows:

1. Broad-leaved annual weeds.
2. Narrow leaved annual weeds (grasses).
3. Total annual weeds.

Fresh weights of weeds and grasses were recorded and dry weight of each group was also recorded after drying at 70 ºC for 24 hours.

2.1.1.2. Yield components:

To determine yield components (plant height, branches number / plant, plant weight (fresh and dry) g^{-1}, number of pods / plant, pod weight (fresh and dry) g^{-1}, seed yield (Kg/ feddan) and seed index (weight of 100 seeds), ten peanut plants from each plot were taken at harvest.

2.1.1.3. Yield:

To determine seed yield (kg /feddan), harvesting was done for four rows from each plot.

2.2. Peanut oil extraction and oil characteristics evaluation

2.2.1. Determination of oil content and oil extraction.

Oil was extracted by n-hexane from mature peanut seeds using Soxhlet procedure for the determination of oil content as described by AOCS Official Method [19].

For the other evaluations, oil was extracted at room temperature to avoid the effect of high temperature in the soxhlet method. Immature and mature peanut seeds were crushed and n-hexane added to the crushed seeds in sufficient amount and the mixture was then left overnight after stirring for one hour at room temperature (25 ± 3 °C). The mixture of peanut oil and n-hexane (miscella) was filtered and the seeds were soaked again in n-hexane and so on for a total of three times. The combined miscella was filtered through sodium sulphate anhydrous using Whatman filter paper No.1 and then the filtrate was distilled at about 40 °C under vacuum using rotary evaporator. The extracted oil was then stored in dark brown glass bottles at -18 °C until analysis [20].

2.2.2. Calculation of the oil yield (Kg / feddan)

Oil yield (Kg/feddan) for each treatment was calculated according to the following equation:

[Oil content X (seed yield of feddan^{-1})]/ 100

2.2.3. Proximate analysis of the extracted oils

Acid, peroxide and iodine values were determined according to AOCS Official Methods Cd 3d-63, Cd 8b-90 and Cd 1-25 [21] respectively.

2.2.4. Determination of fatty acids composition

Fatty acid methyl esters of peanut oil samples were prepared using a modified trans-methylation method according to AOAC, Official Methods of Analysis [22]. FAMEs were separated on an HP 6890 plus gas chromatography (Hewlett Packard, USA) and the detailed conditions were mentioned in Hamed *et. al.* [23].

2.2.5. Total Tocopherols content

Total Tocopherols content in oil samples was determined by high performance liquid chromatography (HPLC). Agilent 1260 series HPLC was used, where the separation was carried out using Eclipse Plus C18 column (4.6 mm x 100 mm i.d.) at 40°C constant temperature. The mobile phase consisted of methanol: acetonitrile (65:35 v/v) at a flow rate 1 ml/min. The fluorescence detector was monitored at 290 nm excitation and 330 nm emission. The injection volume was 10 µl sample solution.

2.2.6. Determination of total pigments content

Total pigments content was determined according to the method described by Borello and Domenici [24], where chlorophylls' total fraction (C_{Ch_tot}) and carotenoids' total fraction (C_{Ca_tot}) are calculated from the absorbance values at 670 nm (A_{670}) and 470 nm (A_{470}), respectively, and expressed in ppm (mg of pigment in 1 Kg of oil), by using the following equations:

$$C_{Ch\_tot}\ (\text{Total chlorophylls}) = \frac{A_{670} \cdot 10^6}{613 \cdot 100 \cdot d} \quad (1)$$

$$C_{Ca\_tot}\ (\text{Total carotenoids}) = \frac{A_{470} \cdot 10^6}{2000 \cdot 100 \cdot d} \quad (2)$$

Where d = optical path length of the cell (1 cm).

Total pigments gain (%) was calculated according to the following equation:

((Total pigments content of a treatment - Total pigment content of untreated control) / Total pigment content of untreated control)) *100

2.2.7. Determination of Clethodim residues in the extracted oil

Extraction and clean-up: Modified QuECHERS extraction method followed by HPLC chromatographic separation was used for the determination of Clethodim residues according to He *et al.* [25] method with slight modifications. Five grams of peanut oil sample was weighed into a 50-mL polypropylene centrifuge tube and then 5 mL of water were added, followed by 10 mL of acetonitrile and then the mixture was vigorously shaken for 1 min. Four grams of Na Cl were then added into the tube with vigorous shaking, then centrifugation was done at 5000 rpm for 5min. Then 6.5 ml of the supernatant was transferred into a centrifuge tube containing 150 mg PSA + 150 mg C18. The tube was shaked for1 min by vortex and centrifuged at 5000 rpm for 5 min. Supernatants were collected and filtered through 0.22

µm polytetrafluoroethylene (PTFE) filters (Millipore, USA) into 2 ml clear vials.

HPLC separation conditions for Clethodim: separation was done on a Hewlett Packard (HP series 1100) HPLC, Quaternary pump model (G 1314A) monitored at 217 nm. An ODS-Hypersil 5 µm (20 cm X 4.6 mm i.d.) column was used and the temperature was 40 °C. The residues were eluted isocratically with acetonitrile : water (80: 20 v/v). A 20 µl injected at a flow rate of 1.0 ml/min.

2.3. Statistical analysis

Obtained data were subjected to analysis of variance (ANOVA) applied to separate the means using Co-Stat 4.11 software according to Snedecor and Cochran [26]. Probability values of less than 5% ($p < 0.05$), were considered to be significant.

3. Results and discussion

3.1. Weed management

The weeds within the exploratory location were Field Sandbur (*Cenchrus Ciliaris L.*) and Bermuda grass (*Cynodon dactylon L.*) as grasses and Purslane (*Portulaca oleracea L.*) and Jungle Rice (*Echinochloa colonum L.*) as broad leaved weeds (Table 1). In terms of biomass, grasses were the most noteworthy either in fresh or dry biomass gathered. The highest biomass of both grasses and broad leaved weeds was recorded within the control treated with α-Tocopherol, while the lowest one being within the group treated with the full rate of herbicide + α-Tocopherol (Table 1). α-Tocopherol was applied by a rate of 800 ppm according to a previous work done by Talaat *et. al.* [27]to help the plant in fighting oxidative stress caused by applying the herbicide which in turn improves its growth and yield. Results in Table (1) show that applying α-tocopherol to the control caused an increase in the fresh and dry weights of the total weeds in comparison to the untreated control which means that α-tocopherol enhanced the growth of these weeds.

Mechanical control by hand hoeing for two times reduced significantly the dry weight of weeds at 14 WAS (Table 1) which was in accordance with the findings of El-Deek *et al.* [28]. Clethodim herbicide proved to control a number of distinctive weed species in peanut and other field crops [29]. Information in Table (1) revealed that Clethodim herbicide, as post-emergence treatment at prescribed rate, initiated the most elevated impact on number of total weeds. Applying full rate (100%) of Clethodim herbicide with α-tocopherol caused the most noteworthy lessening in dry weight of peanut weeds compared to all other treatments as shown in Table (1). The rate diminishment of fresh weight biomass values recorded 25% and 47% of the broad leaved and grasses individually after development compared to untreated control. While applying the herbicide by a half rate of 148.75 g a.i./ha gave a rate lessening value of 3% and 30% for broad leaved and grasses respectively.

Also, results in Table (1) show that there were significant differences, in all fresh and dry weights of different weeds associated with peanut crop, between hoeing treatment with α-tocopherol, Clethodim herbicide (full rate) with α-Tocopherol, Clethodim herbicide (50% rate) half rate + urea with α-Tocopherol. Mixing 30% urea with the 50% rate of Clethodim herbicide diminished the total weed mass up to 19 % either for fresh or dry weights compared to un-weeded trial (Table 1).

Table (2) shows the growth parameters of all treated peanut plants. Results showed that all treatments increased significantly all the growth parameters of peanut compared to the untreated control. The highest increasing percentage in most of the growth parameters was resulted from hoeing with α-Tocopherol followed by full rate of Clethodim herbicide with α-Tocopherol, whereas the lowest percentage was recorded with half rate Clethodim herbicide as a post emergence. The above results are in agreement to those of Kumar *et al.* [30].

Regarding the data of seed yield per feddan, Table (2) revealed that all treatments increased the seed yield per feddan, where hand hoeing with α-Tocopherol treatment gave the highest yield, while the lowest yield was recorded for the untreated control. The decreasing order of all treatments with significant differences (Table 2) was hand hoeing + α-Tocopherol > Clethodim herbicide full rate + α-Tocopherol > Clethodim herbicide (half rate) + urea + α-Tocopherol > control+ α-Tocopherol. A previous work done by Abouziena *et. al.* [31] showed that using full rat of Clethodim herbicide only gave seed yield of 1600 Kg /feddan, while in our work using α-Tocopherol along with the full rate of Clethodim increased seed yield up to 3040 Kg /feddan.

El-Deek *et al.* [28] reported that hand hoeing treatment gave the best peanut yield. Also applying α-Tocopherol to the control significantly increased all growth parameters of peanut plant compared to the untreated control. Our results agreed with those of Soltani *et al.* [32] who stated that applying vitamin E (α-Tocopherol) to leaves promotes the yield and growth of plants especially under stress conditions. Also, Rahmawati and Damanik [33] investigated foliar spray of α-Tocopherol at a rate of 500 mg L^{-1} in soybean under salt stress. It increased significantly the dry weight of root and shoot, branches number, chlorophyll contents, and total soluble proteins.

Table (1): Effect of different weed control treatments and α-Tocopherol on the fresh and dry weights of different weeds associated with peanut crop

Treatment	Fresh weight (gm) of different weeds							Dry weight (gm) of different weeds						
	Broad leaved weeds			Grasses				Broad leaved weeds			Grasses			
	Purslane	Jungle Rice	Total	Field Sandbur	Bermudagrass	Total	Total weeds	Purslane	Jungle Rice	Total	Field Sandbur	Bermudagrass	Total	Total weeds
Control	250.0^{b}	298.0^{b}	548	432.0^{b}	307.0^{b}	739	1287	52.1^{b}	51.4^{b}	103.5	73.2^{b}	95.9^{b}	169.1	272.6
Control + α-Tocopherol	287.0^{a}	413.0^{a}	700	558.0^{a}	380.3^{a}	938	1638	59.8^{a}	71.2^{a}	131.0	94.6^{a}	118.9^{a}	213.5	344.5
Hoeing + α-Tocopherol	194.0^{e}	267.0^{c}	461	389.0^{c}	268.0^{bc}	657	1118	40.4^{e}	46.0^{c}	86.4	65.9^{c}	74.1^{c}	140.0	226.4
100% Clethodim + α-Tocopherol	215.0^{d}	194.0^{d}	409	197.0^{e}	192.0^{d}	389	798	44.8^{d}	33.4^{d}	78.2	33.4^{e}	60.0^{c}	93.4	171.6
50% Clethodim+ 30 % urea + α-Tocopherol	234.0^{c}	296.0^{bc}	530	281.0^{d}	236.0^{c}	517	1047	48.8^{c}	51.0^{bc}	99.8	47.6^{d}	73.8^{c}	141.4	221.2

Data were statistically analyzed by ANOVA using Co-Stat 4.11software. Duncan's multiple range test was used to determine statistically significant differences among means at $p < 0.05$. Different symbols within the same column indicate significant difference.

Table (2): Effect of different weed control treatments and α-Tocopherol on yield and yield components of peanut plant.

Treatment	Plant height (cm)	fresh weight of Plant (gm)	dry weight of Plant (gm)	No. of branches	No. of pods	Fresh weight of pods (gm)	Dry weight of pods (gm)	weight of100 seed (gm)	seed yield of Feddan^{-1} (kg)
Control	34.3^{c}	152.4^{b}	22.1^{b}	12.2^{b}	23.3^{b}	45.5^{c}	28.8^{b}	66^{d}	1518^{e}
Control + α-Tocopherol	51.0^{b}	299.4^{a}	43.4^{a}	13.5^{a}	25.7^{b}	59.7^{c}	28.0^{b}	75^{c}	1950^{d}
Hoeing + α-Tocopherol	58.0^{a}	400.2^{a}	58.0^{a}	14.2^{a}	39.3^{a}	98.3^{a}	56.5^{a}	85^{a}	3315^{a}
100% Clethodim + α-Tocopherol	61.5^{a}	376.1^{a}	59.4^{a}	14.2^{a}	37.5^{a}	80.7^{b}	43.3^{a}	80^{b}	3040^{b}
50% Clethodim + 30 % urea + α-Tocopherol	57.7^{a}	341.5^{a}	49.5^{a}	12.0^{b}	39.3^{a}	78.0^{b}	44.6^{a}	83^{ab}	2822^{c}

Data were statistically analyzed by ANOVA using Co-Stat 4.11software. Duncan's multiple range test was used to determine statistically significant differences among means at $p < 0.05$. Different symbols within the same column indicate significant difference

3.2. Characteristics of the extracted peanut oil

Oil content, peroxide, acid and iodine values were determined in the mature seeds and its extracted oil, which is the final product, while the progress of formation of fatty acids, pigments and total Tochopherols were monitored in the oils of immature and mature seeds.

3.2.1. Oil content

Table (3) shows the oil content percentages of the mature peanut seeds collected after harvesting for all treatments. It can be noticed that the oil contents of all treatments were higher than that of the untreated control, except for 100% Clethodim herbicide +α-Tocopherol treatment, whereas hand hoeing combined with α-Tocopherol treatment gave the highest oil content (45.18 %) as well as the highest oil yield per feddan (1497.72 kg/feddan) which was in accordance with the results of Table (2) as this treatment gave the highest seed yield per feddan. On the other hand, although that the treatment with the full rate herbicide combined with α-Tocopherol gave the lowest oil content (41.74%), which may be due to herbicide stress, it came second in oil yield per feddan (1268.9 kg) which is attributed to its high seed yield per feddan which was 3040 Kg / feddan. So, the increasing order of oil yield/feddan for all treatments was untreated control< control + α-Tocopherol< 50 % Clethodim + 30 % urea + α-Tocopherol< 100% Clethodim + α-Tocopherol< hoeing + α-Tocopherol where the untreated control gave the lowest yield. This means that applying α-Tocopherol along with the weed managements practices enhanced the oil yield per feddan.

Table (3): Oil content of mature peanut seeds

Treatment	Oil content (%)	Oil Yield (Kg/Feddan)
Control	42.75[d]	648.95
Control + α-Tocopherol	44.38[b]	865.41
Hoeing + α-Tocopherol	45.18[a]	1497.72
100% Clethodim + α-Tocopherol	41.74[e]	1268.9
50% Clethodim + 30 % urea + α-Tocopherol	43.09[c]	1216

Data were statistically analyzed by ANOVA using Co-Stat 4.11software. Duncan's multiple range test was used to determine statistically significant differences among means at $p < 0.05$. Different symbols within the same column indicate significant difference.

3.2.2. Peroxide value (PV)

Peroxide value (PV) points out to the oxidative stability of the oil. Therefore, a high PV of oil is an indicator to a weak oil resistance towards oxidation and it is a signal of deterioration level.Table (4) indicates that PVs of all oils obtained from all treatments are low with little differences. It ranged from 0.78 to 1.45 meq O_2/kg oil which agreed with the Codex Standard [34] who stated that the acceptable range for most cold pressed vegetable oils <10 meq O_2/kg oil.The least PV (0.78meq. O_2/kg oil) was recorded for 50 % Clethodim + 30 % urea + α-Tocopherol trial. The stress caused by using full rate herbicide may results in a slight increase in PV (1.42meq O_2/kg) over that of control (1.14meq O_2/kg). But, using α-Tocopherol may helped to resist the stress and inhibited PV from more rising.

3.2.3. Iodine value (IV)

Unsaturation degree of an oil could be defined by determining its iodine number and hence it gives an idea about its susceptibility to oxidation. So, as the degree of unsaturation increases, the iodine value increase and its oxidizability increase and vice versa. As shown in Table (4), either control sample (without any treatments) or all other treatments were in the IV range (91.10-95.14g I_2/100g oil).Also, it can be noticed from Table (4) that the oil extracted from peanuts treated by hand hoeing + α-Tocopherol had the highest IV (95.14 I_2 g/100g oil), while when peanut treated with 50 % Clethodim + 30 % urea + α-Tocopherol, it was 91.10 I_2 g/100g oil. Carrin and Carelli [35] reported that the characteristic range of IV of crude peanut oil (86-107 g I_2 /100g) is close to olive oil IV (75–94g I_2 /100g) and lower than that of soybean oil (120–143g I2 /100g), which indicates more stability.

2.2.3. Acid value (AV)

The detection of free fatty acid in oil indicates the possible hydrolytic decay of the oil, and was used to assure itsedibility and quality.According to Codex Standard [34], the allowed level of free fatty acids in cold pressed oils should be no higher than 4 mg KOH/goil. As presented in Table (4), acid value (AV) of all samples ranged from 0.14 – 0.47 (mg KOH/g oil). All AV's fulfil within the recommended range (Table 4), where the lowest AV was recorded for control + α-Tocopherol while highest AV was recorded for the oil extracted from the untreated control (0.47mg KOH/g oil). This indicates that weed management treatment and + α-Tocopherol protected the oil from hydrolysis and preserved to some extent the fatty acids.

Overall, Table (4) shows that the oil of50 % Clethodim + 30 % urea + α-Tocopherol treatment had low PV, IV and AV which indicates high stability compared to untreated control. In addition, all chemical characteristics of peanut oil showed no deviation from the Codex Standard values [34] which was also agreed with the results of Akhtar *et. al.* [36]. Also our results may indicate that the foliar application of α-tocopherol along with weed management practices may enhanced the chemical properties, compared to those of the untreated control.

3.2.4. Fatty acids composition of peanut oils extracted from the different treatments of immature and mature peanuts

Fatty acids composition of peanut oils was monitored in immature (Table 5) and mature (Table 6) seeds of the different trials to investigate their treatment effect. In general, Tables 5&6 shows that the major unsaturated fatty acids in all peanut oil samples are oleic (C18:1) and linoleic (C18:2) acids while palmitic (C16:0) acid is the major saturated fatty acid. Stearic (C18:0), arachidic (C20:0), eicosenoic (C20:1), behenic (C22:0), and lignoceric (C24:0) acids occur in minor proportions which was in agreement with the results of Carrin and Carelli [35]. In spite of the presence of statistically significant differences ($p \leq 0.05$) between most of the samples in Tables 5&6, ranges of all saturated and unsaturated fatty acids fell within the reported peanut fatty acid profile [37,38].

Table (5) demonstrates the fatty acid composition of the oils extracted from the immature peanut seeds, where oleic acid predominates, but it could be noticed that the lowest oleic acid% (ω9) (43.30%) was recorded for the untreated control sample, while the highest percentage (46.94%) was recorded for the oil of 50% herbicide + 30 % urea + α-Tocopherol treated seeds. On the other hand, the highest linoleic % (ω6) (35.26%) was recorded for the oil of Hoeing + α-Tocopherol sample and the lowest (33.14%) was for the oil of 50% herbicide + 30 % urea + α-Tocopherol treated seeds. The highest recorded total unsaturated fatty acids (TUSF) was for the oil sample of 50% Clethodim+ 30 % urea + α-Tocopherol treatment. While the lowest TUSF % and the highest total saturated fatty acids % (TSF) was for the untreated control. Different conditions can affect the fatty acids

composition of peanut oil like the genotype, seed maturity, climatic conditions, growth location, and interactions between these factors [39]. Carrin and Carelli [35] reported that seed maturity causes an increase in oleic acid % and a decrease in linoleic acid %. By comparing Table (5) (immature seeds) with Table (6), which shows the fatty acids composition of mature seeds of all treatments, it could be noticed that after maturity oleic acid increased while linoleic acid decreased for all samples of the different treatments. Our results were in agreement with those of Hinds [40] who found that the percentage of oleic acid increased, while that of palmitic and linoleic acids decreased during the different stages of seeds maturation. The highest recorded percentage of oleic acid (ω9) (47.47%) in mature seeds (Table 6) was for the oil of 50% Clethodim + 30 % urea + α-Tocopherol, while the highest recorded percentage of linoleic acid (34.36%) was for the sample of Hoeing + α-Tocopherol. This may give an indication that both foliar application of α-Tocopherol and weed management practices enhanced and protected, to some extent, the formation of USFA whether mono or poly. This could be confirmed by the lowest percentage of total unsaturated fatty acids which was recorded for the untreated control (80.10 %)

Table (4): Chemical characteristics of peanut oil samples extracted from mature peanut seeds

Treatment	Peroxide value ($meqO_2$/Kg Oil)	Iodine value (I_2 g/100g Oil)	Acid value (mg KOH/g oil)
Control	1.14^{d}	94.08^{c}	0.47^{a}
Control + α-Tocopherol	1.45^{a}	93.32^{d}	0.14^{e}
Hoeing + α-Tocopherol	1.20^{c}	95.14^{a}	0.17^{d}
100% herbicide + α-Tocopherol	1.42^{b}	94.83^{b}	0.34^{b}
50% herbicide + 30 % urea + α-Tocopherol	0.78^{e}	91.10^{e}	0.28^{c}

Data were statistically analyzed by ANOVA using Co-Stat 4.11 software. Duncan's multiple range test was used to determine statistically significant differences among means at $p < 0.05$. Different symbols within the same column indicate significant difference..

Table (5): Fatty acids composition of peanut oil samples extracted from immature peanut seeds

Fatty acids (%)	Treatment				
	Control	Control + α-Tocopherol	Hoeing + α-Tocopherol	100%herbicide + α-Tocopherol	50% herbicide + 30 % urea + α-Tocopherol
Palmitic acid (C16:0)	12.53^{b}	12.63^{a}	12.00^{d}	12.60^{b}	12.12^{c}
Palmitoleic acid (C16:1)	0.65^{a}	0.59^{b}	00^{d}	0.40^{c}	00^{d}
Stearic acid (C18:0)	2.5^{a}	2.35^{b}	2.30^{b}	2.13^{d}	2.20^{c}
Oleic acid (C18:1)(ω9)	43.30^{a}	44.02^{b}	43.85^{c}	44.50^{d}	46.94^{e}
Linoleic acid (C18:2)(ω6)	33.62^{b}	33.26^{d}	35.26^{a}	33.51^{c}	33.14^{e}
Arachidic acid (C20:0)	1.19^{a}	1.09^{b}	0.90^{c}	0.59^{d}	0.13^{e}
Eicosenoic acid(C20:1)	1.32^{a}	1.22^{c}	1.24^{b}	1.23^{bc}	1.22^{c}
Behenic acid (C22:0)	3.71^{a}	3.14^{d}	3.03^{e}	3.30^{c}	3.34^{b}
Lignoceric acid (C24:0)	1.19^{d}	1.71^{b}	1.41^{c}	1.74^{a}	0.91^{e}
TSF*	23.12	20.92	19.64	20.36	18.7
TUSF**	78.89	79.09	80.35	79.64	81.3
US/S***	3.41	3.78	4.09	3.91	4.35
Oleic/Linoleic	1.29	1.32	1.24	1.33	1.42

TSF* = Total Saturated Fatty Acids; TUSF**= Total Unsaturated Fatty Acids; US/S***= Total Unsaturated Fatty Acids / Total Saturated Fatty Acids. Data were statistically analyzed by ANOVA using Co-Stat 4.11 software. Duncan's multiple range test was used to determine statistically significant differences among means at $p < 0.05$. Different symbols within the same raw indicate significant difference

Oleic/linoleic (O/L) acid ratio is considered to be a good stability index toward oxidative deterioration during storage and hence predicting the shelf life of oils. High ratios indicate longer shelf life because linoleic acid (with two double bonds) is more susceptible to oxidative rancidity than oleic acid (with one double bond) [37]. Misuna *et al.* [41] examined oleic/ linoleic ratios in eight commercial peanut varieties in Thailand and found it between 1.2 and 3.8, while among 108 lines from the US peanut collection the O/L ratio varied between 1.1 and 3.2 [42]. Results obtained in Tables (5&6) for oils extracted from immature and mature seeds (O/L ratio 1.2–1.45) were in consistence with all of these reports. Escobedo *et al.* [37] attributed such differences to the variation in location, cultivar, soil and climatic conditions. Also, Carrin and Carelli [35] mentioned that much attention has been directed to the important role of O/L ratio and iodine value (IV) in controlling product's shelf life. Highly enhanced oil shelf life is attributed to high O/L ratio and low IV. This was accomplished in the oil sample of 50% Clethodim + 30 % urea + α-Tocopherol treatment which showed the highest O/L ratio (Tables 5&6) and the lowest IV (Table 4), indicating high oxidative stability, compared to the untreated control. Also, by comparing Table 5 with Table 6, it could be noticed that O/L ratios increased from immaturity to maturity for all treatments, which was in agreement with Pattee [39] who reported that O/L ratio increases with seed maturity. Table (6) revealed that the untreated control sample had the lowest O/L ratio compared to other treated samples, except for the oil sample of Hoeing + α-Tocopherol which contains the highest percentage of linoleic acid. From the health point of view, Kriss-Etherton, *et. al.* [43] reported that consumption of peanut oil has beneficial effects in preventing coronary heart disease, which may be attributed to its relatively high contents of oleic and linoleic acids, in addition to the other bioactive components of the seed. Many other studies assessed the peanut efficiency in decreasing cholesterol levels, platelet aggregation and inflammatory markers [44]. Also, an increased level of oleic/linoleic ratio of plasma LDL, by high ingestion of oleic acid, is associated with a decrease in the oxidative stress biomarkers [44].

Table (6): Fatty acid composition of peanut oil samples extracted from mature peanut seeds

Fatty acids (%)	Treatment				
	Control	Control + α-Tocopherol	Hoeing + α-Tocopherol	100% herbicide + α-Tocopherol	50% herbicide + 30 % urea + α-Tocopherol
Palmitic acid (C16:0)	12.49^{a}	12.11^{d}	12.22^{b}	12.18^{c}	11.07^{d}
Palmitooleic acid (C16:1)	0.28^{d}	0.62^{a}	0.29^{d}	0.37^{c}	0.48^{b}
Stearic acid (C18:0)	2.90^{a}	3.00^{a}	1.8^{b}	1.5^{c}	1.9^{b}
Oleic acid (C18:1)(ω9)	45.74^{c}	46.01^{e}	45.29^{d}	46.68^{b}	47.47^{a}
Linoleic acid (C18:2)(ω6)	32.96^{c}	32.50^{d}	34.36^{a}	32.98^{b}	32.70^{d}
Arachidic acid (C20:0)	0.39^{e}	0.43^{d}	0.47^{c}	0.60^{b}	0.87^{a}
Eicosenoic acid(C20:1)	1.12^{d}	1.16^{c}	1.10^{e}	1.26^{a}	1.18^{b}
Behenic acid (C22:0)	2.94^{e}	3.04^{d}	3.23^{c}	3.78^{a}	3.34^{b}
Lignoceric acid(C24:0)	1.18^{b}	1.13^{c}	1.25^{a}	0.66^{e}	1.00^{d}
TSF*	19.9	19.71	18.97	18.71	18.18
TUSF**	80.10	80.29	81.04	81.29	81.83
US/S***	4.03	4.07	4.27	4.34	4.50
Oleic/Linoleic	1.39	1.42	1.32	1.42	1.45

TSF* = Total Saturated Fatty Acids; TUSF**= Total Unsaturated Fatty Acids; US/S***= Total Unsaturated Fatty Acids / Total Saturated Fatty Acids. Data were statistically analyzed by ANOVA using Co-Stat 4.11 software. Duncan's multiple range test was used to determine statistically significant differences among means at $p < 0.05$. Different symbols within the same raw indicate significant difference.

3.2.5. Effect of different treatments on chloroplast pigments content.

Chloroplast pigments are the compounds responsible for the oil color and each oil has its own characteristic color referred to its pigments content which includes naturally occurring polyphenolic pigments, gossypol, chlorophyll and carotenoids. Chloroplast pigments have been postulated to act as protectors, capturing free radicals similar to α-tocopherol [45]. Carrin and carelli [35] reported that peanut oil contains low concentration of β-carotene (0.1mg/Kg) and chlorophylls (1.4-1.6 mg/Kg) compared to those in soybean oil. Figure (1) shows pigments (A: total chlorophyll and B: total carotenoids) contents of the oils extracted from immature and mature peanut seeds. One can clearly notice the negative effects of infested weeds on pigments content in the extracted oil of the untreated control. As shown in Figure (1 A&B), the extracted oils of most of the treated seeds contains more pigments than the untreated control. Figure (1A) shows that maturity increased the content of total chlorophyll in the extracted oils of all samples. Also it could be noticed that weed management practices along with α-Tocopherol application enhanced the formation of chlorophyll in almost all of the extracted oils from mature seeds especially in the oil extracted from the seeds treated with 50% herbicide + 30 % urea + α-Tocopherol. Regarding total carotenoids content, Figure (1B), it is clear that it decreased after maturity for most oil samples. It is also clear that carotenoides contents of all treated samples were higher than that of the untreated control sample whether in the immature or mature stages. After maturation of peanuts, a color lightening of the oil was noticed. This change in color could be useful method to assess maturity, but other factors like water stress and curing rate were affecting peanut oil color in addition to maturity. Our results agreed with those of Pattee [39] who reported that ß-carotene and lutein are the responsible pigments for the light yellow color of peanut oil.

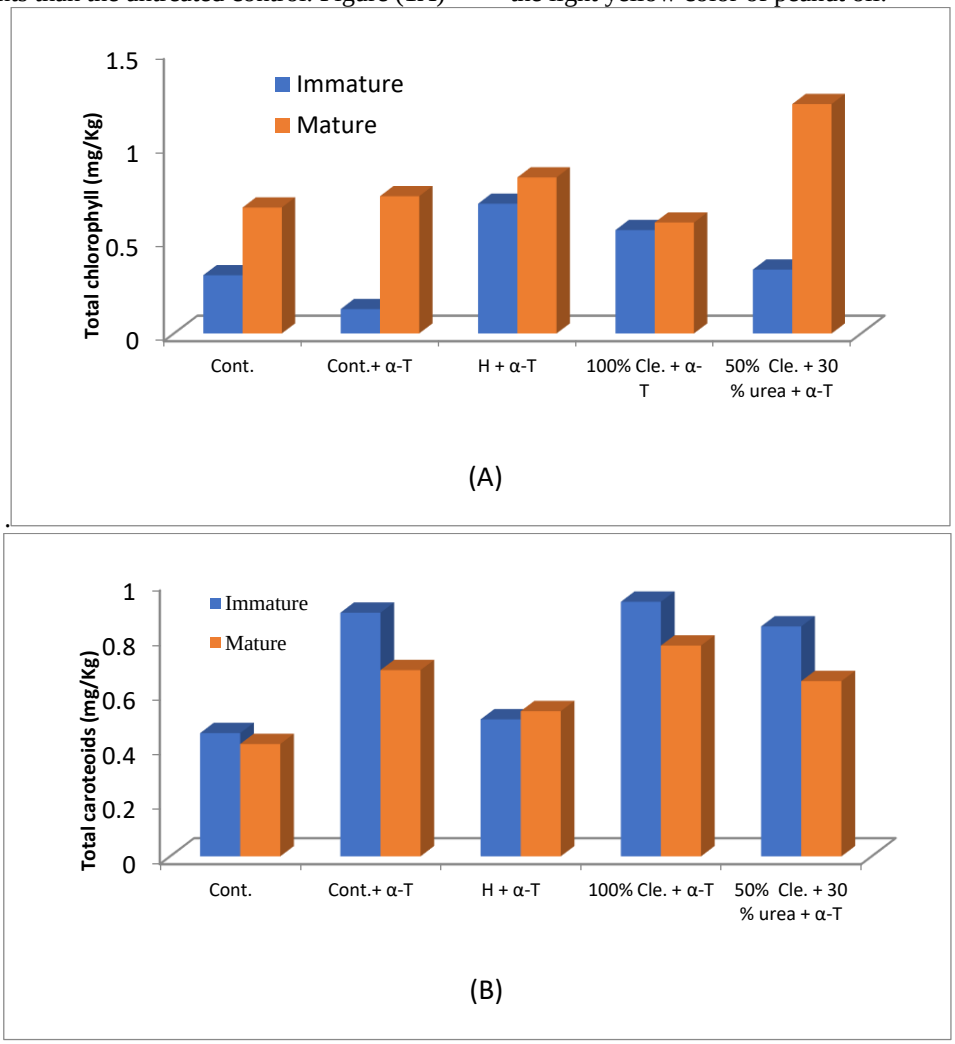

Figure (1): Chloroplast pigments (A: total chlorophyll and B: total carotenoids) contents of peanut oil extracted from the immature and mature treated seeds.

(Cont. = Control, Cont. + α-T = Control + α-Tocopherol, H+ α-T= Hoeing + α-Tocopherol, 100% Cle. + α-T =100% Clethodim + α-Tocopherol, 50% Cle. +30 % urea+ α-T = 50% Clethodim + 30 % urea + α-Tocopherol)

Table (7) shows that total pigments content measured in the oil of the immature and mature seeds and the gain percentage of total pigments increased by the different weed management practices and fighting stress with foliar application of α-Tocopherol compared to the untreated control. All treatments showed pigments gain compared to the untreated control. Regarding mature oil samples, the maximum gain was for the oil of 50% herbicide + 30 % urea + α-Tocopherol mature treated seeds (72.22%), whereas, for immature oil samples, full rate herbicide + α-tocopherol showed the highest total pigment gain (94.74%). Also, an increase in pigments content in the extracted oil of control + α-Tocopherol by 34.21% for immature seeds and by 30.56% for mature seeds more than the untreated control was noticed which may attributed to the effect of α-Tocopherol. For mature seeds, combination between full rate herbicide with α-tocopherol gave total pigments increase by 25.93% similar to that of the combination of α-tocopherol with hand hoeing.

3.2.6. Effect of different treatments on total Tocopherols content.

Tocopherols are naturally occurring lipophilic antioxidants belonging to the vitamin E family. Lipid peroxidation is inhibited in foods by these antioxidants through stabilization of hydroperoxids and other free radicals. Carrin and Carelli [35] reported that peanut oil contains four types of tocopherols: α, β, γ and δ, where α –tocopherol present in a range of 48–373 mg/kg, 0–140 mg/kg for β-tocopherol, 88–389mg/kg for γ-tocopherol, 0–22 mg/kg for delta-tocopherol and 130 to 1300 mg/kg for total tocopherol content [34]. Pattee [39] mentioned that various factors can affect Tocopherol concentration in the oil such as variety, production location, maturity, temperature of seed storage and oil processing steps. Hashim *et. al.* [46] found a significant differences within Tocopherol profile of peanut cultivars during its maturity stages. Oilseeds contain high Tocopherol levels more than that in the photosynthetic apparatus, as α –Tocopherol provides protection against oxidative stress during oilseeds germination [47].

Regarding our results, Figure (2) shows total Tocopherols content of peanut oils extracted from the immature and mature seeds. It is clear that total Tocopherols content increased with maturity for all treated and untreated oil samples. Consequently, it could be noticed that all treatments caused an increase in total Tocopherols content in oils of mature peanuts more than the untreated control. The highest total Tocopherols content was recorded for the oil extracted from 100% Clethodim + α-Tocopherol treated mature or immature seeds. Although foliar application of Clethodim herbicide as weed management practice is considered to be a successful way to fight weeds, it is also considered as one of the strong stress factors that could negatively affect the plant. Among our treatments, applying 100 % Clethodim herbicide is the most stress causing treatment to the plant. So, according to Manaa *et. al.* [12], the stress caused by herbicide treatment, stimulates plants to perform some defensive and protective mechanisms which include changes in its content of vitamins (like α-tocopherol and ascorbic acid) which was in agreement with our results. Also, Kanwischer *et. al.* [48] clarified that *Arabidopsis* plants exposed to intense light stress contains an increased levels of antioxidant by many folds.

Sadiq *et. al.* [16] mentioned that during stress conditions, one α-Tocopherl molecule can efficiently nullify about 120 singlet oxygen species, by which a single electron from Tocopherol chromonol ring is donated to free oxidative species such as LOO− to form LOOH and Tocopherol itself is converted to a Tocopheroxy radical that can be recycled again into α-Tocpherol by reacting with other antioxidants such as ascorbate and glutathione. Also, Szarka et al. [49] reported that, under the increasing stress in plants, that cause tocopherol deterioration, further synthesis of tocopherol occurs in a chain reaction. Applying exogenous vitamins have been studied as a way to resist damage generated by herbicidal treatment and other forms of environmental stresses. This approach is common these days, especially exogenous application of non-enzymatic antioxidants to minimize the harmful effects of abiotic stresses on plants [16].

Table (7): Total pigments (mg/Kg) of peanut oil extracted from mature seeds

Treatment	Immature seeds		Mature seeds	
	Total Pigments content (mg/Kg)	Total pigments gain (%) compared to control	Total Pigments content (mg/Kg)	Total pigments gain (%) compared to control
Control	0.76	-----	1.08	-----
Control + α-Tocopherol	1.02	34.21	1.41	30.56
Hoeing + α-Tocopherol	1.19	56.58	1.36	25.93
100% Clethodim + α-Tocopherol	1.48	94.74	1.36	25.93
50% Clethodim + 30 % urea + α-Tocopherol**	1.18	55.26	1.86	72.22

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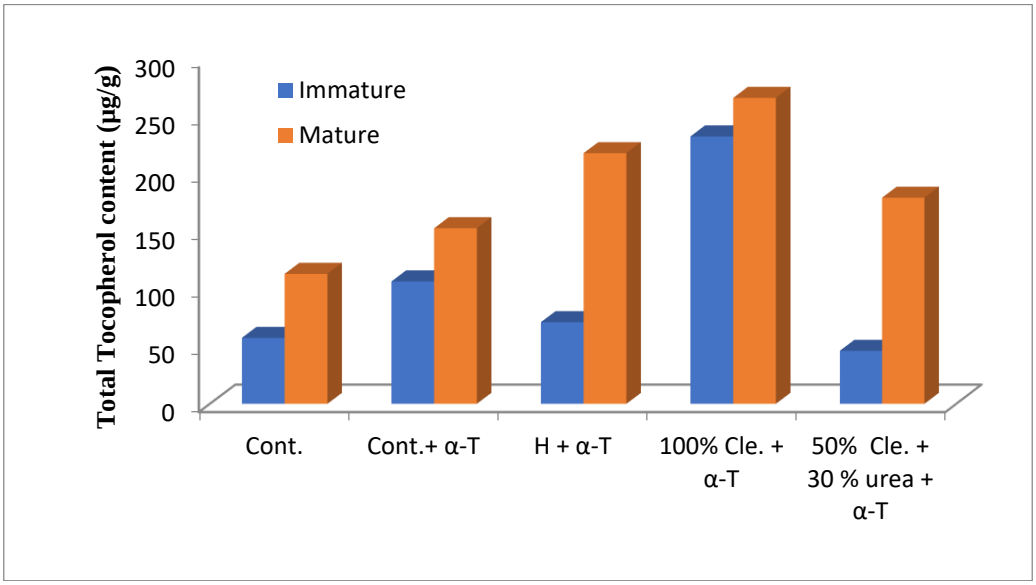

Figure (2): Total tocopherol contents of peanut oil extracted from the immature and mature treated seeds. (Cont. = Control, Cont. + α-T = Control + α-Tocopherol, H+ α-T= Hoeing + α-Tocopherol, 100% Cle. + α-T =100% Clethodim + α-Tocopherol, 50% Cle. +30 % urea+ α-T = 50% Clethodim + 30 % urea + α-Tocopherol)

3.3. Determination of Clethodim residues in peanut oil:

Obtained results revealed that no Clethodim residues were detected in all peanut oil samples. This may be referred to: 1) this herbicide was applied early (after 30 days of planting) so their residues disappeared by the time elapsed; 2) the extraction process of oil from peanut seeds [50].So, peanut oil could be safely used at any time after extraction from seeds.

4. Conclusion

Weed management practices positively affected the characteristics of peanut oil compared to the untreated control. The oil sample extracted from50% herbicide + 30 % urea + α-Tocopherol treated seeds showed the most enhanced characteristics, where it had the lowest peroxide, iodine and low acid values, The highest content of oleic acid and TUSF, the highest O/L ratio, the highest gain of total pigments content compared to untreated control and a considerable amount of total tocopherols. In general, all treatments enhanced the productivity of peanut oil and its characteristics in different manners. On the other hand, weed control protocols managed to decrease the growth of the associated weeds and grasses and increased all of the growth parameters of peanut plant compared to the untreated control. The most increased peanut productivity was achieved by using Hoeing + α-Tocopherol followed by100% Clethodim + α-Tocopherol treatments. As a conclusion, it is highly recommended to perform weed management protocols as they proved to positively affect not only the yield and the growth of the crop but also the characteristics of its main products especially vegetable oils.

5. Conflict of Interest

The authors declare no conflict of interest.

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