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Effect of Humic Acid Foliar Application on Quantitative and Qualitative Yield of Caraway (*Carum carvi* L.) Plant

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Abstract

A field trial was carried out during 2018/2019 and 2019/2020 seasons at the Experimental Farm of Faculty of Agriculture, Assiut University to study the effect of foliar humic acid application at the concentrations of 0 (control), 200 and 400 ppm three times, monthly interval on growth, fruit yield, and essential oil yield and its composition of caraway (*Carum carvi* L.) plant.

The results indicated that humic acid treatments improved the vegetative growth characteristics (plant height, branch number per plant and plant dry weight), fruit measurements (umbel number, 1000-seed weight and seed yield) and essential oil parameters (oil percentage, oil yield and oil constituents) in comparison with control plant (without humic acid). However, a rate of 400 ppm was more effective than the level of 200 ppm in this regard.

Seeds of plants received 400 ppm showed the highest contents of total proein, total carbohydrates, total phenolics, ascorbic acid (vitamin C) and thiamine (vitamin B_1). In contrast, these seeds contained the lowest levels of nitrate and nitrite. These findings were closely correlated with increasing 1000-seed weight showing better quality.

Chemical analysis of caraway leaves cleared that the maximum contents of nitrogen, phosphorus, potassium, and pigment were occurred by humic acid at 400 ppm resulting in significant increases compared to 200 ppm level in most cases. It was found a positive relationship between the highest contents of leaf N, P and K and the improvement of vegetative growth and fruit characteristics, consequently increase of seed production.

The gas liquid chromatography (GLC) analysis of the essential oil showed the presence of two main components, carvone and limonene. The highest carvone (40.58%) and the lowest limonene (13.51%) were obtained by humic acid at 400 ppm, meanwhile the control showed the reverse trend; the lowest carvone (18.86%) and the highest limonene (23.60%). The level of 200 ppm showed intermediate contents. The quality of caraway seeds is considered to correlate with carvone/limonene ratio; the higher ratio expressed as better-quality. Accordingly, the best treatment achieved the highest ratio (3.0). It was observed a direct relationship among the increases of seed yield, essential oil and their qualities.

In addition, there were other components of the volatile oil present in small amounts such as myrcene, fenchone, camphonon,6, carveol, linalool, anethole, estragole and caryophyllen oxide.

It could be recommended to spray caraway plants with humic acid at 400 ppm 3 times, monthly intervals for its superiority via enhancing vegetative growth, improving yield and quality of seeds and essential oil, as well as chemical composition of caraway plants.

Keywords: *Caraway, humic acid, vegetative growth, seed yield, essential oil.*

Introduction

Carawy (*Carum carvi* L.) is one of the important aromatic plants belongs to Apiaceae family. The dried fruit (seeds) contain approximately 1-6% essential oil, with carvone and limonene are the dominant components (Guenther, 1961). Caraway seeds and their essential oil have several medicinal purposes as carminative, mild stomachic and antispasmodic as a tonic in the treatment of digestive disorders. Dried fruits are widely employed for favoring bread, cake confectionery, cheese and kinds of food products (Weiss, 1997).

Humic acid is found to improve the productivity of the aromatic seed crops quantitatively and qualitatively comparing with the chemical fertilizers. The utilization of humic acid as natural nutrients helps to improve yield and quality traits of medicinal and aromatic plants characterized by safe production, besides reducing production costs and environmental pollution without reduction of yield (Gomma and Youssef, 2008; Acimovic *et al*., 2015b; Awad, 2016; Mahmoud *et al*., 2017; El-Banna and Fouda, 2018 and Hassan, 2019).

Many researchers have reported that humic acid recognized as a plant growth promoter by increasing the quality of crop and supply for plant nutrition, enhancing plant growth and development, as well as increasing the quantity of yield due to its essential action on physiological and metabolic processes (Eyheraguibel *et al*., 2008 and Asik *et al*., 2009). The positive effects of humic acid on cell membrane functions by promoting nutrient uptake, respiration, nucleic acid biosynthesis, ion absorption, and enzyme activity as hormone-like substances (Nardi *et al*., 2002).

Therefore the objective of the present work was to investigate the benefit effects of humic acid application on vegetative growth, fruit yield, essential oil content and its composition, as well as some active biochemical constituents and nutrient elements content to achieve safe caraway production.

Materials and Methods

An open field experiment was carried out at the Experimental Farm of Faculty of Agriculture, Assiut University during two continual seasons (2018/19 and 2019/20) to investigate the effects of humic acid on quantitative and qualitative characteristics of caraway (*Carum carvi* L.) plant as a trial to improve its growth and productivity.

Seeds of caraway were obtained from Horticulture Research Institute, Agric. Research Center, Giza, Egypt and sown in a clay soil for two seasons in October 25th 2018 and 2019 in plots 2x1.5 m with three rows at 50 cm apart in each plot and 25 cm between the seed hills within the row. Six weeks after, the thinning was done leaving two seedlings per hill (36 plant/plot). A total of caraway plants was approximately 48000 per feddan. Some physico-chemical properties of field cultivation soil are shown in Table (A). The averages of ambient temperatures ranging between 20 and 35°C, as well as the relative humidity between 70 and 75% in the study area during the period of experimentation. All horticulture practices as irrigation, weeding and fungicides treatment were similarly done whenever needed. No fertilizers and herbicides were supplied to soil.

The potassium humate used in this study having a physical data as follows: appearance (black powders), pH (9-10) and water solubility (>98%). The quarated analysis were as follow: Humic acid 90% and K_2O 10%.

Table A. Physico-chemical properties of the experimental soil.

Physical properties		Chemical properties	
Particle size distribution		Total carbonate (%)	3.10
Clay	44.6	Sulfur (ppm)	195.00
		Phosphorus (mg P/100 gm soil)	2.54
Silt	35.0	Sodium (%)	0.48
		Potassium (meq/100 gm soil)	59.50
Sand	20.4	Calcium (meq/100 gm soil)	18.70
		Chloride (%)	0.86
Soil texture	Clay	Magnesium (meq/100 gm soil)	11.40
		Total nitrogen (%)	0.065
$CaCO_3$ (%)	3.10	pH (suspension of 1:2.5 w/w soil : water)	7.65
		EC dS/m (water extract of 1:5 w/w soil : water)	0.61
Organic matter (%)	1.32	DTPA-Extractable (ppm):	
		Fe	9.7
Field capacity (F.C) %	41.2	Mn	10.3
		Zn	1.2

Humic acid at the concentration of 0 (control), 200 and 400 ppm were applied in aqueous solutions as foliar spray after 60, 90 and 120 days from sowing corresponding February, March and April, respectively, in 2019 and 2020. The foliar spray application was done using air compressed hand sprayer to the point of run-off in the early morning. The untreated plants (control) were sprayed with tap water. Triton B wetting agent was used at a rate 1 ml/l as a surfactant immediately before spraying.

Data recorded

Caraway fruits (seeds) were harvested at full ripeness in May of both seasons. Data were recorded at the end of experiments (27 weeks from sowing) on vegetative characteristics; plant height, number of branches per plant, plant dry weight and root-shoot ratio (was calculated by dividing root dry weight by shoot one), as well as seed measurements (number of umbles per plant, 1000-seed weight, seed yield per plant and per feddan).

Chemical analysis

The chemical constituents of N, P and K contents in leaves, as well as total protein, total carbohydrates, total phenolics, nitrate and nitrite contents in the harvested seed at full ripeness were measured in the dry material. The wet digestion of 0.1 g plant material with sulphuric and perchloric acids was done to determine leaf nutrient elements (N, P and K), as well as nitrogenous compounds (total nitrogen, NO^-_3 and NO^-_2) in seeds according to Baruah and Barthakur (1997). Nitrogen was determined colorimetrically at 400 nm wavelength using the Nessler's reagent method described by Allen (1959). Protein content in seeds was quantified and calculated using the conversion factor of 6.25 based on the assumption that the protein contains 16% nitrogen according to Ranganna (1978). Nitrate (NO^-_3-N) was estimated spectro-photometrically at 410 nm as described by Cataldo *et al.* (1975), as well as nitrite (NO^-_2-N) at 520 nm according to Hesse (1994). Phosphorus was determined colorimetrically at 660 nm using stannous chloride phosphomolibdic-sulphuric acid system according to Jackson (1978). Potassium was determined in the digested solution using Flame-photometer model 52 with acetylene burner according to Jackson (1978). Total carbohydrates in seed was measured colorimetrically by anthrone sulphuric acid method at 630 nm according to Hansen and Moller (1975). Leaf pigments (chlorophyll "a", chlorophyll "b" and carotenoids) contents were measured by spectrophotometer and calculated according to the equations described by Vernon (1960). Total phenolics content was determined spectrophotometrically at 750 nm using a modified Folin-Ciocalteu reagent assay according to Strail *et al.* (2006).

Determination of vitamins

Vitamin C as ascorbic acid was determined in seeds according to Bajaj and Kaur (1981). Assays of thiamine (vitamin B_1) in caraway seeds were carried out using a method described by Rapala-Kozik *et al.* (2008).

Extraction of the essential oil

Essential oil contents of caraway seeds (50 g) were extracted by the hydro-distillation method for two hours according to U.S.P. (1995); essential oil percentage yield per plant and per feddan were calculated.

Analysis of essential oil composition

Gas liquid chromatography (GLC) analysis of caraway essential oil was carried out using gas chromatograph (Hewlett Packard GC. Model 5890) equipped with a flam ionization detector (FID). A fused silica (HP-5MS) capillary column (30 m length, 0.53 mm internal diameter "i.d.", 0.88 mm film thickness) was used for the separation in the GC. The identification of the different constituents was achieved by comparing their retention times with those of the authentic samples according to the methods outlined by Singh *et al.* (2006).

Statistical analysis

The obtained data in both seasons of the study were exposed to analysis of variance as a complete randomized design with five replicates using Statistix 8.1 analytical software, and the means were compared using a least significant difference (L.S.D.) test according to Dowdy and Wearden (1983).

Results and Discussion

Vegetative growth characteristics

Data presented in Table 1 showed that treatments of humic acid foliar application improved plant growth parameters expressed as plant height, number of branches per plant and plant dry weight. Spraying caraway plants with humic acid at 400 ppm was more effective than 200 ppm level resulting in significant increases in these characters compared to control (without humic) which gave the lowest values in both seasons. Meanwhile, humic acid showed insignificant effect on root /shoot ratio. These results are in harmony with those obtained on caraway plant by Gomaa and Youssef (2008), Awad (2016), Mahmoud *et al*. (2017) and Hassan (2019).

The superiority of plant growth with addition of humic acid might be attributed to its vital role in supply the plants major and minor nutrient elements require for promoting plant metabolism and development. It can improve plant growth directly by accelerate the proteosynthesis, and increasing water and nutrient uptake and yields of plants (Panda, 2006). Humic acid is also assumed to increase the chlorophyll content of green plants, and hence can be used to control chlorosis and improve photosynthesis (Nardi *et al*., 2002). The role of humic acid in stimulating plant growth is by the enzyme activation, changes in membrane permeability and the activation of biomass production (Ulukan, 2008). In addition, foliar spray with humic acid reduces the transpiration rate, and this in turn leads to keep high water content in the plant tissues and hence might favor the plant metabolism, the physiological processes, photosynthetic rate and many other important functions that directly affect the plant growth (Tan, 2011). Humic acid can provide protection against some toxic growth inhibiting substances introduced in the soil (Arun, 2002).

Table 1. Growth characteristics of caraway plants as affected by humic acid levels during the two seasons of 2018/19 and 2019/20.

Humic acid (ppm)	Plant height (cm)		Branch No./plant		Whole plant dry weight (g)		Root/shoot ratio	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd
0 (Control)	112.2	97.4	11.9	15.0	22.23	23.00	0.199	0.215
200	113.2	103.6	12.1	15.9	23.98	25.77	0.188	0.197
400	117.4	117.2	13.2	16.9	27.21	28.18	0.179	0.188
L.S.D. 0.05	5.1	5.3	1.2	1.3	4.57	3.76	N.S	N.S

1st: First season 2nd: Second season.

Seed (fruit) yield

Foliar application of humic acid had a significant effect on all seed yield parameters especially at a rate of 400 ppm compared to control in both seasons (Table 2). This increment in spraying caraway plants with humic acid may be due to stimulate plant growth through availability of nutrients for plants which reflected on increasing number of umbels per plant (37.9 in average), weight of 1000 seeds (5.88 g) and seed yield (12.12 g/plant and 582 kg/fed). These results are parallel to the results of Gomaa and Youssef (2008) and Acimovic *et al.* (2015a) on caraway, Sharaf-El-Deen *et al*. (2012) on fennel, Safaei *et al.* (2014) on black cumin, and Beyzi *et al*. (2017) on coriander.

Furthermore, the increase of seed yield per plant and per feddan resulted from humic application could be due to increase in the number of umbels formed by plant and the weight of 1000 seeds. Such effects of humic acid on fruit yield may be attributed to synthesis of metabolites used in fruit formation.

Table 2. Seed (fruit) measurement of caraway as affected by humic acid levels during the two seasons of 2018/19 and 2019/20.

Humic acid (ppm)	Umbel No./plant		1000 seed-weight (g)		Seed yield (g/plant)		Seed yield (kg/fed)	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd
0 (Control)	31.8	26.4	4.61	5.77	7.78	8.09	373.5	388.4
200	33.2	34.5	4.73	6.27	9.70	10.08	465.7	484.0
400	35.8	40.0	5.29	6.46	11.87	12.37	569.8	593.9
L.S.D. 0.05	3.5	5.1	0.36	0.31	1.41	2.06	67.6	93.5

1st: First season 2nd: Second season.

Seed quality in relation to chemical composition

There were significant increases in the chemical composition of caraway seeds including protein, carbohydrate and phenolic contents as the level of applied humic acid raised compared to control in both seasons (Table 3). These components are accumulated in seed tissues at 400 ppm level was much than 200 ppm resulting in 22.6 and 21.5% for total contents of protein and carbohydrates, respectively, as well as total phenlic compounds (2.9 mg/g D.M. as average). In the contrary, the high humic acid rate recorded the lowest concentrations of nitrate and nitrite averaging 652.5 and 75.9 µg/g D.M., respectively.

Numerous researchers revealed that humic acid application play a major role in stimulation the physiology and biochemical quality of seeds. Humic acid as foliar spray proved to be ideal and suitable organic source for better protein synthesis as increased significantly with increasing the rate as mentioned by Eyheraguibel *et al*. (2008) in maize grains, Asik *et al*. (2009) in wheat grains and Vijayakumari *et al*. (2012) on soybean seeds. On caraway, Gomaa and Yousef (2008) and Mahmoud *et al*. (2017) stated that supplied plants with humic acid increased total carbohydrate and phenolic compounds content in seeds. El-Banna and Fouda (2018) reported that seed quality was correlated with high concentration of total nitrogen and reductions of nitrate and nitrite contents in caraway seeds.

Table 3. Chemical composition of caraway seeds as affected by humic acid levels during the two seasons of 2018/19 and 2019/20.

Humic acid (ppm)	Total protein %		Total carbohydrates %		Total phenolics (mg/g D.M)		NO^-_3-N (µg/g D.M.)		NO_2-N (µg/g D.M.)	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
0 (Control)	18.38	19.43	14.33	13.61	1.66	2.33	780	800	110.8	111.8
200	20.35	21.49	17.00	17.51	2.08	2.76	703	720	90.0	90.8
400	21.88	23.25	20.76	22.22	2.51	3.31	645	660	75.5	76.2
L.S.D. 0.05	0.66	1.03	1.21	1.33	0.09	0.14	40	37	5.3	5.4

1st: First season 2nd: Second season.

It is quite clear that humic acid at 400 ppm had a positive influence on filling caraway fruits in high order umbels and this can be the consequence of high contents of total protein, total carbohydrates and other organic compounds, as well as optimal absorptions of essential macro- and micronutrients during periods of fruit formation and ripening to attain their full potential. These results were similar to those obtained by Bewley and Black (1994). Moreover, a general explanation was on the basis of more carbohydrates which closely correlated with a marked increase in vegetation. This specific finding led to increase in photosynthesis activity, consequently producing more photosynthetic products and carbohydrate accumulation. The adaptation of oil production dependent on maintaining high carbohydrates. These observations are supported by the findings of Sangwan *et al*. (2001).

Some workers emphasized that phenolic compounds have important roles in the physiological and biochemical processes of seeds. Among the most significant functions of the phenolics are their accumulation in seeds may be metabolically create an adaptive role by restricting the growth and development of seeds against DNA-damaging storage. Phenolic may act as disease resistance mechanism in seeds, and influence competition among plants by producing toxins such as cinnamate (Vallee and Falchuk, 1993).

As evident from the results of this work, humic acid at 400 ppm showed higher ascorbic acid (vitamin C) and thiamine (vitamin B_1) in caraway seeds by 43 and 39%, respectively over control (Fig. 1). These results corroborate with the findings of Mahmoud *et al*. (2017) on caraway. Other authors declared that humic acid as foliar application increased vitamin C content in pea seeds (Gad *et al*., 2012) and in soybean seeds (Vijayakumari *et al*., 2012) as well as increased thiamine content in peanut seeds (Moraditochaee, 2012) and in wheat grains (Radwan *et al*., 2015).

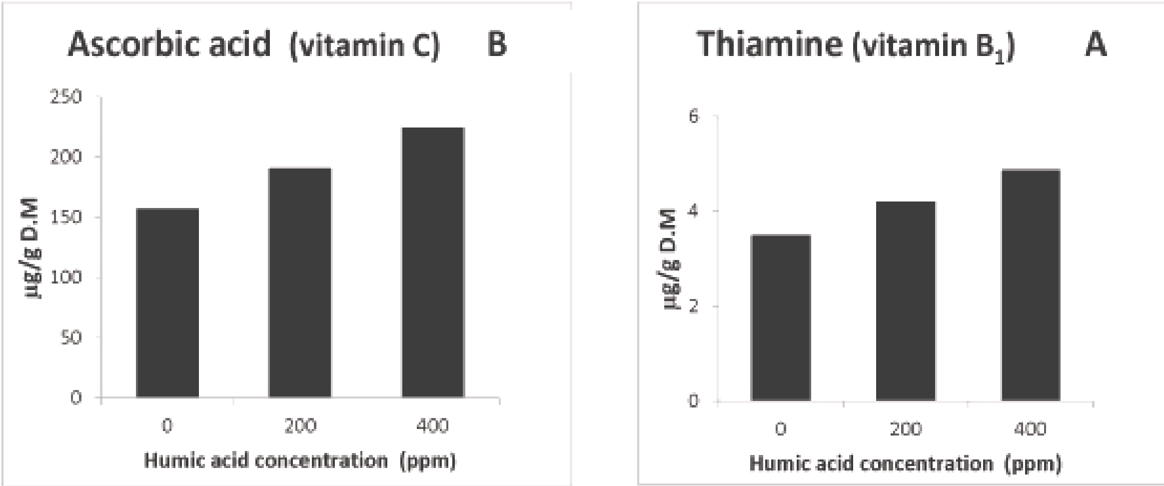

Fig. 1. Effect of humic acid levels on ascorbic acid and thiamine contents in Caraway seeds.

These increases of both vitamins could be related to the stimulative effects of humic acid on the adequate nutritional status that is essential for maintaining the optimal activities of all physiological processes. Thus, humic acid at 400 ppm proved to be more sufficiently active to absorb the amounts of nutrient elements at adequate levels reflected genetically controlled enhancement in mechanism of mineral nutrition which were obviously in close relationship to the best growth of caraway plans. It is also necessary for chlorophyll synthesis, carbohydrate formation since it combines with protein to promote endogenous hormones synthesis, whereas the positive association exists among them to metabolically create beneficial effects or regulate possibly both vitamins content in caraway seeds. These observations are in agreement with the opinions of many authors applied humic acid (Juárez *et al*., 2011; Chamani *et al*., 2015 and Mahmoud *et al*., 2017).

On the other hand, the biosynthesis of both vitamins were correlated with the regulation of the metabolism of soluble carbohydrate (Golda *et al*., 2004), increased energy generation for the synthesis of proteins (Belanger *et al*., 1995), acceleration of DNA synthesis (Ajjawi *et al*., 2007), increased endogenous hormones levels of IAA and GA, and decreased ABA (Raschke *et al*., 2007) and activities of antioxidant enzymes (Rapala-Kozik *et al*., 2008), as well as play specialized roles against DNA damage or pathogen attack (Ahn *et al*., 2005).

Essential oil content

Studying essential oil (Table 4), it was obvious that humic acid at 200 and 400 ppm had a positive effect on oil formation whereas the higher level markedly greater than the lower one resulting in significant increases in oil percentage and yield in comparison with a rate of 200 ppm or control in both seasons. The highest percentage and yield obtained by foliar humic acid application at 400 ppm were 3.29 and 3.46%, 0.40 and 45 ml/plant and 19.16 and 21.68 l/fed as average for the first and second seasons, respectively. These results are in conformity with those reported by Gomaa and Youssef (2008), Acimovic *et al*. (2015b), Awad (2016) and Mahmoud *et al*. (2017) on caraway.

The beneficial effect of humic acid on essential oil formation due to the direct function of humic acid on solubilization and transport of nutrient elements which enhance the vegetative growth characteristics and play an important role in synthesis of plant constituents such as essential oil. The sufficient availability of these elements might be led to higher seed yield and consequently higher essential oil yield as mentioned by Parry (1985).

In this concern, Sangwan *et al*. (2001) concluded that the production of essential oil not only depends upon the metabolic state and present developmental differentiation programme of the synthesizing tissue, but also highly integrated with the physiology of the whole plant. Besides, the oil productivity is friendly to ecophysiological, environmental and other factors. All these aspects of the modulation of essential oil production must be taken into consideration.

Table 4. Essential oil productivity of caraway seeds as affected by humic acid levels during the two seasons of 2018/19 and 2019/20.

Humic acid (ppm)	Essential oil %		Essential oil yield (ml/plant)		Essential oil yield (l/fed)	
	1st	2nd	1st	2nd	1st	2nd
0 (Control)	2.51	2.70	0.20	0.23	9.56	10.90
200	2.90	3.08	0.29	0.33	13.77	15.84
400	3.29	3.46	0.40	0.45	19.16	21.68
L.S.D. 0.05	0.20	0.51	0.05	0.16	2.33	6.09

1st: First season 2nd: Second season.

Essential oil constituents

There were 38 compounds determined in caraway essential oil (Table 5), among them there were two main components, carvone and limonene, whose mixture in this experiment constituted from 42.46 to 54.09 of total oil composition. The highest percentage of carvonene + limonene mixture was resulted from humic acid at a concentrate of 400 ppm (54.09%) followed by 200 ppm level (46.39%), meanwhile the lowest percentage of the mixture was obtained by control (42.46%). Whereas, humic acid at 400 ppm increased carvone and decreased limonene percentages in caraway essential oil, contrast to this the control. These results are in agreement with those reported on caraway oil by Acimovic *et al*. (2014) and Mahmoud *et al*. (2017). Furthermore, GLC analyses for all components showed the presence of myrcene, fenchone camphonone, 6, carveol, linalool, anethole, astragole, caryophyllene oxide and others were present in small amounts in the seeds volatile oil. Similar results were obtained by Diab (2007) and El-Tarawy *et al*. (2017).

Table 5. Essential oil constituents (%) and carvone/limonene ratio in caraway seeds as affected by humic acid levels during 2019/2020 season.

Compound (%)	R.T. (min.)	Humic acid levels (p.p.m.)		
		0 (control)	200	400
A-pinene	4.74	0.09	0.15	0.67
Bicycle (3-1,3) hexane	5.59	1.14	0.86	0.25
Myrcene	6.02	1.19	2.01	4.56
Limonene	7.00	23.60	20.90	13.51
Fenchone	8.47	1.38	2.66	6.22
Cyclohexene-1-01	9.37	1.57	2.65	3.36
trans-limonene oxide	9.84	4.60	2.57	1.33
Camphonone,6-	10.56	0.42	0.31	0.22
Cyclohexene-1-Menthone	11.54	0.69	1.40	2.78
cis-Dihydro carvone	11.68	0.77	2.75	3.63
Carveol	12.13	0.36	0.41	0.46
Carvone	12.99	18.86	25.49	40.58
Cyclohexene-1-one	13.59	2.63	5.27	8.90
Octadienal,3,7-dimethyl	13.93	0.36	0.50	1.03
Cyclohexene-1-carboxal	14.04	1.29	1.48	1.64
Anethole	14.20	0.21	0.24	1.08
Estragole	14.21	0.24	1.67	1.85
Trimethlbicyclo	14.42	0.35	0.18	0.13
p-Mentha-1,8-dien	14.47	0.94	0.35	0.25
(35,6R)-3-Hydroperoxy	14.68	2.19	1.06	0.44
α-Farnesene	15.25	0.50	0.28	0.14
1,2-cyclohexanediol	15.44	1.03	0.83	0.67
Bicyclohexyl-2-one	16.27	2.22	0.18	0.06
Naphthol	17.24	0.43	0.26	0.25
Caryophyllene oxide	17.45	0.58	0.14	0.12
Benzene,1,4-dimethoxy-2-methyl	17.58	7.84	3.78	1.48
Humulene	18.29	0.16	0.24	0.32
Cyclodecadiene	18.99	0.63	0.48	0.18
Naphthalene	19.11	0.51	0.38	0.27
α-Selinene	19.33	0.43	0.52	0.62
Germacrene A	19.57	0.74	0.64	0.57
Isoaromadendrene	21.03	0.20	0.12	0.07
Salvial-4 (14)-En-1-one	21.68	0.42	0.54	0.33
Aromadendrene oxid	22.90	0.18	0.20	0.24
Neointermedol	23.07	0.49	0.16	0.17
Trans-Longipinocarveol	24.56	0.00	0.11	0.12
Hexadecanoic acid	39.10	1.72	0.00	0.00
Linalool	39.30	1.72	0.00	0.00
Other minor components (%)		2.38	1.37	0.74
Carvone+Limonene mixture (%)		42.46	46.39	54.09
Carvone/Limonene ratio		0.80	1.22	3.00

R.T.-retention time values are mean of three replicates.

Interestingly, there is evidence that biosynthesis of carvon and limonene occurs via the same pathway. This implies that limonene in both an intermediate in the biosynthesis of carvone, as well as the end product (Bouwmeester *et al*., 1995). As shown in Table 5, humic acid at 400 ppm showed the dominant compound in caraway essential oil is carvon (40.58%) and the lowest limonene content (13.51%). These findings indicated that humic acid which would in turn favour formation of carvone to formation limonene. These results support previous observations (Acimovic *et al*., 2015b and Awad, 2016). These authors postulated that humic acid can change plant behavior regarding the biosynthesis of bioactive compounds whereas induced an increase in the carvone proportion and decrease in limonene proportion, but did not affect the chemotype of caraway essential oil.

The overall quality of caraway seeds is considered to correlate with the content of essential oil and its carvone/limonene (C/L) ratio; the higher ratio expressed as better-quality (Kallio *et al*., 1994). Humic acid at 400 ppm achieved the highest C/L ratio (3.0). Therefore, it can be concluded that caraway tested under humic acid application belongs to cravone chemotype. In contrast, the control showed the lowest C/L ratio (0.8), this indicated that the quality of essential oil was poor. However, humic acid at 200 ppm resulted in intermediate ratio (1.22).

Leaf nutrients and pigments

Data presented in Table 6 indicated that treatments of humic acid foliar application had a significant effect on leaf contents of nitrogen, phosphorus and potassium compared to control in both seasons. However, a rate of 400 ppm was more effective resulting in significantly higher concentrations of these nutrient elements than a level of 200 ppm. These results are coordination with the findings of Gomaa and Youssef (2008), Awad (2016), Mahmoud *et al*. (2017), El-Banna and Fouda (2018) and Hassan (2019) on caraway.

In this scenario, Stevenson (1994) reported that the interpretation of all molecular weights of humic acid can be absorbed and show evidence that the uptake is dependent on the active component of transport. Aiken *et al*. (1985) demonstrated that the effects of humic acid on ion uptake appear to be more or less selective and variable, in relation to their concentration and to the pH of the medium. Chen *et al*. (2004) stated that the effects of humic acid on ion absorption by plant roots are not easily explainable. It is possible that thumic acid exert several effects on plant functions and some of these may result, directly or indirectly, in a modulation of ion uptake.

Table 6. Leaf nutrients and pigments as affected by humic acid levels during the two seasons of 2018/19 and 2019/20.

Humic acid (ppm)	Nitrogen %		Phosphorus %		Potassium %		Chlorophyll "a" (mg/g)		Chlorophyll "b" (mg/g)		Carotenoids (mg/g)	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
0 (Control)	2.54	2.59	0.351	0.354	2.62	2.60	1.246	1.343	0.351	0.430	0.363	0.354
200	2.82	2.88	0.373	0.392	2.90	2.92	1.451	1.495	0.381	0.477	0.406	0.381
400	3.03	3.11	0.419	0.431	3.19	3.35	1.792	1.835	0.459	0.593	0.464	0.445
L.S.D. 0.05	0.14	0.14	0.018	0.006	0.15	0.13	0.256	0.295	0.088	0.129	0.051	0.074

1st: First season 2nd: Second season.

Concerning leaf pigments, it was observed that humic acid treatments significantly increased chlorophyll "a", chlorophyll "b" and carotenoids compared to control in both seasons (Table 6). However, a level of 400 ppm was significantly higher than a rate of 200 ppm in relation to leaf pigments in most cases. These results coincided with Gomaa and Youssef (2008), Mahmoud *et al.* (2017) and Hassan (2019) on caraway.

As evident from the results discussed above, findings presented the most pronounced treatment (400 ppm) was more sufficiently active to absorb the amount of such nutrient elements at adequate levels and translocated them towards the leaves as a site of accumulation resulted in the highest contents which were obviously in close relationship to the best growth that reflected on increasing leaf pigments content. The synthesis of chlorophyll is closely associated with the highest nitrogen content. Thomas *et al.* (2003) revealed that the production of leaf pigments was reduced in many plants when nitrogen is laking. An early and dramatic symptom of nitrogen deficiency is a general yellowing of leaves or chlorosis, due to an inhibition of chlorophyll synthesis.

It is interesting to note positive relationships among leaf pigments, carbohydrate accumulation and protein content in caraway seeds. Chlorophyll is a limited factor for the photosynthesis which take place in leaves, an increase in chlorophyll content was associated with increasing in carbohydrates synthesis as mentioned by Gibson (2005). Furthermore, nitrogen is expected from its major role as a constituents of protein and many coenzymes and interference with protein synthesis and hence with growth. The resulting slow-down of photosynthesis causes a nitrogen deficient to lake not only essential amino acids, but also the machinery for synthesis of necessary carbohydrates. A reduction of nitrogen in leaves causes photosynthesis fails to keep pace and a depletion of carbohydrates (Rajan, 2003).

Generally, it could be concluded that foliar application of humic acid three times after sowing at a rate of 400 ppm was generally superior as a result of nutritious balance which closely reflected on highly seed yield and essential oil production with better-quality (high carvone and low limonene contents. In addition, improvement in the bioactive phytochemicals in the fruits including proteins, carbohydrates, phenols, ascorbic acid (vitamin C) and thiamine (vitamin B_1); they are active constituents as antioxidants which were consistently greater, but accompanied with decreasing in nitrate and nitrite contents that produce high quality of caraway seeds. They were established efficiency on safety manner suitable for marketing and more economic, as well as umpolluted environment.

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تأثير الرش الورقي بحمض الهيوميك علي كمية ونوعية محصول نبات الكراوية

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الملخص:

أجريت تجربة حقلية خلال موسمي ٢٠١٨/٢٠١٩، ٢٠١٩/٢٠٢٠ بالمزرعة التجريبية بكلية الزراعة– جامعة أسيوط لدراسة تأثير الرش الورقي بحمض الهيوميك ثلاث مرات بفاصل شهر بتركيزات صفر (كنترول)، ٢٠٠ و ٤٠٠ جزء في المليون علي النمو ومحصول البذرة والزيت الطيار ومكوناته الأساسية وبعض المكونات الكيميائية للبذور والأوراق لنبات الكراوية.

وتتلخص أهم النتائج فيما يلي:

- حسنت معاملتي حمض الهيوميك مواصفات النمو الخضرية (أرتفاع النبات، عدد الفروع بالنبات والوزن الجاف للنبات) وأيضاً المواصفات الثمرية (عدد النورات، وزن ١٠٠٠ بذرة ومحصول البذرة بالنبات وبالفدان)، وكذلك مواصفات الزيت الطيار (النسبة المئوية للزيت، محصول الزيت بالنبات وبالفدان) بالمقارنة بالكنترول.
- أظهرت معاملة حمض الهيوميك بتركيز ٤٠٠ جزء في المليون تأثيراً جوهرياً بمقارنتها بتركيز ٢٠٠ جزء في المليون في معظم القياسات المدروسة.
- أحتوت البذور الناتجة من المعاملة بتركيز ٤٠٠ جزء في المليون أعلي التركيزات من البروتين، الكربوهيدرات الكلية، الفينولات الكلية، حمض الأسكوربيك (فيتامين C) والثيامين (فيتامين B_1)، بينما أظهرت أقل المحتويات من النترات والنيتريت. وقد أرتبطت هذه النتائج بشدة بزيادة وزن البذور وجودتها.
- أوضح التحليل الكيماوي لأوراق الكراوية أن المعاملة بتركيز ٤٠٠ جزء في المليون أظهرت تأثيراً ملحوظاً في زيادة محتواها من النيتروجين، الفوسفور، البوتاسيوم والصبغات حيث كانت الزيادة معنوية بالمقارنة بتركيز ٢٠٠ جزء في المليون في معظم الحالات. وكان هناك علاقة وثيقة بين زيادة محتوي هذه العناصر بالأوراق وتحسين مواصفات النمو الخضرية والثمرية وبالتالي زيادة الإنتاج.
- أظهرت نتائج التحليل بجهاز (GLC) للزيت الطيار لبذور الكراوية أن المكونان الرئيسيان هما الكارفون والليمونين حيث أعطت المعاملة بتركيز ٤٠٠ جزء في المليون أعلي نسبة مئوية للكارفون (٤٠,٥٨%) وأقل نسبة من الليمونين (١٣,٥١%)، بينما معاملة المقارنة أظهرت عكس ذلك أي أقل نسبة من الكارفون (١٨,٨٦%) وأعلي نسبة من الليمونين (٢٣,٦٠%)، بينما المعاملة بتركيز ٢٠٠ جزء في المليون أظهرت نسب وسطية في هذا الصدد.
- مما سبق يتضح أن ارتفاع نسبة كارفون/ليمونين (٣,٠) نتجت من المعاملة بتركيز ٤٠٠ جزء في المليون ويدل ذلك علي جودة الزيت الطيار حيث تزداد الجودة بزيادة هذه النسبة، وكانت هناك علاقة مباشرة بين زيادة إنتاج كل من البذور والزيت الطيار وجودتهما.
- أظهرت نتائج تحليل الزيت أيضاً كميات قليلة من كل من:

Myrcene, Fenchone, Camphonone, 6, Carveol, Linalool, Anethole, Estragole and Caryophyllene oxide.

- بناء علي نتائج هذه الدراسة فإنه يوصي برش نباتات الكراوية بحمض الهيوميك بتركيز ٤٠٠ جزء في المليون ٣ مرات بفاصل شهر لإنتاج أفضل جودة للنمو الخضري ومحصول البذرة والزيت الطيار والمحتوي الكيماوي لنباتات الكراوية.