

Chemical studies on adulteration of garlic and onion oils

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-Onion and garlic are considered major vegetable crops in Egypt. Because of the importance of their essential oils in the international trading many trials have been carried out for their adulteration with common adulterants such as; aged oil, maize oil, ethyl alcohol and paraffin oil. Accordingly, these studies were carried out to give sufficient information about the authenticity of such oils. Both onion and garlic oils were mixed with above mentioned adulterants in the concentration of 10, 20 and 30%. A comparative physico-chemical analysis was carried out on the samples of both onion and garlic oils to study the effect of the foregoing adulterants on their physico-chemical properties, which would help to determine the degree of authenticity of such volatile oil. The obtained results could be summarized as follows : Part 1: Onion volatile oil : Physical properties for fresh onion volatile oil included; specific gravity, refractive index, acid number were, 1.0965, 1.5614 and 7.27 respectively whereas, the addition of increment amount of various adulterants caused a proportional decrement in specific gravity, refractive index and acid number with the exception of adulterated samples with aged oil caused an increase in specific gravity and acid number. On the other hand, the solubility in ethanol of adulterated samples with aged onion volatile oil, maize oil and paraffin oil decreased when compared to the solubility of fresh onion volatile oil. On the contrary the solubility of the adulterated samples with ethyl alcohol did not change. Besides, the solubility in organic solvents such as diethyl ether, carbon tetrachloride, n-hexane, benzene and chloroform was the same since, all samples were completely soluble. UV spectra of onion volatile oil, aged onion volatile and adulterated samples with various above mentioned adulterants showed a maximum absorption at 278 nm, whereas upon using the same concentration the absorption intensities differed proportionally according to the concentration of the used adulterant. IR spectrum of onion volatile oil showed different functional groups. The dominant active groups were : trans double bond, C-OH stretching, propyl sulphide, CH₃ (bending), active methylene group, carbonyl group and CH₃-CH₂- alkane. No new bands were detected in the IR spectra of onion volatile oil adulterated with aged onion volatile oil. whereas, the adulterated samples with maize oil caused the appearance of new band at 1740 cm⁻¹ (C=O stretching of aliphatic esters). Moreover, the adulteration with maize oil led to broadening in absorption bands at 910-980 cm⁻¹ (trans double bond) and 2840-3000 cm⁻¹ (-CH₃-stretches). When ethanol was used as adulterant, intensities of absorption bands increased by increasing the amount of ethanol added to onion volatile oil. whereas, samples adulterated with paraffin oil caused the appearance of four new bands at 705, 1125, 1270 and 1730 cm⁻¹ which refer to alkenes, C-O in primary alcohols, C-O-C antisymmetrical stretching and C=O stretching in aliphatic esters, respectively. The previous absorption bands were distinguished when commercial paraffin oil was tested alone. G.L.C. of fresh onion volatile oil showed that the total peak number were 23. Sixteen volatile compounds were identified while seven compounds were unknown. The main identified components could be stated in a descending order ; methyl taurine, methyl propyl trisulphide, undecanal, dipropyl trisulphide and propyl alcohol. The G.L.C. analysis of aged onion volatile oil was the same when compared with the fresh oil. However, these components slightly decreased except propyl alcohol, propyl disulphide propane and methyl propyl trisulphide were increased. The G.L.C. of adulterated samples of onion volatile oil with ethanol indicated that all components decreased as a result of the dilution action of ethanol with the appearance of a single

peak of ethanol located directly after the solvent peak which disappeared upon washing the adulterated samples with saturated solution of sodium chloride followed by a subsequent drying with anhydrous sodium sulphite. Glycerol determinations for pure onion volatile oil samples as well as adulterated samples with maize oil indicated that glycerol could not be detected in the pure sample of onion volatile oil whereas, glycerol increased proportionally with the increasing of maize oil used as adulterant. The qualitative determination of ethanol by iodoform test for the pure onion volatile oil and adulterated samples indicate that no iodoform crystals were formed for the pure onion volatile oil and adulterated samples with aged onion volatile oil, maize oil and paraffin oil. whereas, flat yellow crystals immediately observed in samples of onion volatile oil adulterated with ethyl alcohol. On the other hand, the volumetric and colorimetric quantitative determination of ethanol revealed that the volumetric method was less sensitive when compared to colorimetric method. Also, as expected the ethyl alcohol content increased proportionally upon increasing the amount of ethanol used as adulterant. Paraffin oil was determined quantitatively using thin layer chromatography. Results obtained indicate that the paraffin oil content increased proportionally with increasing the percent of paraffin oil in the adulterated onion volatile oil.

Part II. Garlic volatile oil : The physical properties for garlic volatile oil included specific gravity, refractive index, optical rotation and acid number were 1.0770, 1.5665, 0.0 and 0.88, respectively. The addition of increment amount of various adulterants caused a proportional decrement in specific gravity, refractive index and acid number whereas, the adulteration with aged oil caused an increase in acid number. On the other hand, the solubility in ethanol of aged garlic volatile oil and adulterated samples with. aged garlic volatile oil, maize oil and paraffin oil was less : than that of the solubility of fresh garlic volatile oil, on contrary the solubility of the adulterated samples with ethyl alcohol had not been affected. Besides the solubility of garlic volatile oil samples in organic solvent such as; diethyl ether, carbon tetra chloride, n-hexane, benzene and chloroform was the same since all samples were completely soluble. UV spectrum of garlic volatile oil, aged garlic volatile oil and adulterated samples with various adulterants showed a maximum absorption at 278 nm. whereas, upon using the same concentration the absorption rate differed proportionally according to the concentration of the used adulterant. IR spectrum of garlic volatile oil showed active groups, the dominant active groups were: $-(CH_2)_n$ -rock, trans double bond, C-O stretching in primary alcohol, alkenes, CH_3 -stretching and C-H stretching. No significant changes in intensities of absorption band were observed when aged garlic volatile oil were incorporated with fresh garlic volatile oil. whereas, the adulterated samples with maize oil caused the appearance of four new absorption band, at 1090 cm^{-1} (C=O in primary alcohol), 1460 cm^{-1} (OH bending in carboxylic acid), 1740 cm^{-1} (C=O stretching in aliphatic esters) and 3455 cm^{-1} (bonded OH) which are distinguished for maize oil. As for the use of ethanol as adulterant the intensities of absorption bands increased by increasing the amount of ethanol added to the garlic volatile oil. The samples adulterated with paraffin oil caused an appearance of four bands at 700 , 1120 , 1460 and 1725 cm^{-1} which referred to alkenes, C-O in primary alcohol, OH bending in carboxylic acids and C=O stretching in aliphatic esters, respectively. The previous absorption bands are distinguished to the use of commercial paraffin oil. G.L.C. of fresh garlic volatile oil show that the total peak number were 25. Thirteen volatile compounds were identified while 12 compounds were unknown- The main identified components could be stated in a descending order; diallyl thiophene, dimethyl thiophene, 2-propenyl-2-propane thio-sulphonate, diallyl - trisulphide and dipropyl trisulphide. As for aged garlic volatile oil no new components appeared, whereas, all the components decreased except dimethyl thiophene increased. Glycerol determination for pure garlic volatile oil as well as adulterated samples with maize oil had the same trend as mentioned before in the results of onion volatile oil.

- 181 - The qualitative determination of ethanol by iodoform test for the pure garlic volatile oil and adulterated samples indicate that no iodoform crystals were formed for the pure garlic volatile oil and adulterated samples with aged garlic volatile oil, maize oil and paraffin oil, whereas, flat yellow crystals immediately observed in the adulterated samples with ethyl alcohol. On the other hand, the ethanol determination by volumetric and colourimetric methods had the same pattern as mentioned before in the results of onion volatile oil. The determination of paraffin oil using TLC technique indicated that paraffin oil content increased proportionally with increasing the amount of paraffin oil in adulterated samples. Conclusively, it seems that the most important

determination which could be used to detect adulteration of both onion as well as garlic volatile oils are; solubility, in ethyl alcohol, specific gravity, refractive index, acid number, iodoform test and U.V. spectrum which could be considered as a presumptive test, whereas, quantitative determination of alcohol volumetrically and colourimetrically, glycerol by periodic acid oxidation, paraffin oil by T.L.C., G.L.C. and LR could be considered as affirmative tests for the discovery of adulteration practices.