SUMMARY

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The present study was initiated to investigate the potential utilization of by-products of commercial processing of different citrus fruits as processed in food industry plants in Egypt. The present study included the utilization of different components of citrus processing waste for the preparation of various nutrient or substances of high economical value such as essential oils, pectin pomace, fixed oils and nutritious food or feed meal. These four products were prepared by different methods and characterized from the point of their properties as well as chemical compostion. It is believed that preparation of such materials of high quality would improve the economy of processing citrus fruits and would minimize problem of citrus waste treatment and pollution of environment.

Part I. Estimation of amount of by-products of different citrus fruits:

1. Estimation of amount of extracted juice and by-products of pressing the same weight of fresh different citrus fruits indicated that they differed among themselves in amount of juice extracted and amount of total residue, as well as in amount of each component of residue (peel, peel and membrane, flavedo, albedo and seeds).

2. Peels constituted the major part of citrus residue while albedo constituted the second great fraction, where bitter orange showed the highest amount of these parts of by-products.

3. Amount of flavedo was correlated with amount of peel residue and the highest flavedo was obtained for bitter orange.

4. The highest amount of grated peels and pulp which used for extracting pectin pomace, was present in grapefruits.

5. Seeds constituted the least fraction in citrus by-products. Bitter orange and mandarin were the first and second order, respectively, from the point of amount of seeds in by-products.

Part II - Preparation and characterization of citrus peel oils:

Essential oils of different citrus fruits, were extracted from peels of Baladi orange, bitter orange, mandarin and grapefruit using water and steam distillation as well as cold-pressing technique and their physochemical properties and chemical constituents were determined.

6. Amount of essential oils per fresh weight of fruits varied with kind of citrus, however, the highest amount was found in bitter orange (0.68%) Baladi orange, mandarin and grapefruit contained 0.58, 0.45 and 0.36%.

7. Although mandarin had lower amounts of essential oil in fresh weight of fruit, it had the highest content of these oils in the flavedo layer of citrus fruits.

8. Determination of physical properties of essential oils indicated that all citrus peel oils extracted by water and steam distillation had lower values for specific gravity and refractive index, higher optical rotation value, lighter color, and more solubility in alcohols than all of the other citrus oils extracted by cold-pressing technique.

9. Determination of chemical properties of essential oils indicated that all hydrodistilled oils showed a common tendency in lower values of acidity, ester and aldehyde content than all those expressed by cold-pressing, however, the aldehyde/ ester ratio was very high in all oil obtained by water and steam distillation.

10. Gas liquid chromatographic analysis of the distilled oils revealed that ten peaks were separated from oils of mandarin and grapefruit, 8 from bitter orange and only 7 from Baladi orange.

11. Chromatograms of cold-pressed oils of mandarin and grapefruits showed 9 peaks, while that of Baladi orange oil had only 8 peaks.

12. The identified compounds were α-pinene, B-pinene, d-limonene, ocimene, nerol, linalool, citral and linalyl acetate.

13. Four unidentified compounds were present in chromatogram of citrus oil, however, they constituted a very small proportion.

14. Terpene hydrocarbons were the major group of components present in all citrus oils, regardless of method of extraction.

15. GLC analysis indicated that limonene content could be taken as a characteristics for citrus peel oils, where it constituted the highest percentage, amounted about 96.70 and 96.14%, 95.90 and 94.75%, 95.49 and 93.48% in oils of Baladi orange, mandarin and grapefruit extracted by the two methods, respectively.

16. The other identified terpene hydrocarbons were present in a similar distribution pattern in both groups of oils, for example, despite of extraction method, all citrus oils showed higher α-pinene than B-pinene and ocimene was in the smallest amount, except grapefruit oil which exhibited higher ocimene than B-pinene.

It was experimentally impossible to distinguish between d-limonene and myrecene, and it was believed that myrecene could be present in the investigated oils.

17. Numerous oxygenated compounds, alcohols, aldehydes and esters were identified in citrus oils investigated. However, they differed in kind and concentration of each of these compounds.

18. The identified alcohols were nerol and linalool, however, nerol was present in greater proportion than linalool. Alcohols were detected in bitter orange and grapefruits oils extracted by both methods and in cold-pressed orange oil. However, cold-pressed oils contained higher alcohols than distilled oils.

19. The aldehyde compound detected was citral which was present in Baladi orange and grapefruit oils extracted by both methods. However, distilled grapefruit oil had higher citral amount than Baladi orange oil, while both cold-pressed oils had comparable contents.

20. The identified ester component, linalyl acetate, was found in comparable concentration in the two mandarin oils extracted by both different methods, but not detected in other citrus oils.

21. General comparison of citrus peel oils extracted by the two methods of extraction indicate that distilled oils, with respect to terpene hydrocarbons, had higher total terpenes, d-limonene and ocimene, lower α-pinene and B-pinene

content, except B-pinene in Baladi orange and ∝ -pinene in grapefruit. Concerning the detected oxygenated compounds, both groups of oils had comparable esters, while the distilled oils had higher aldehyde es cially in grapefruit oils and lower alcohols than the corresponding cold-pressed oils.

22. Baladi orange peel oils extracted by both methods were characterized by having higher d-limonene and lower amount of other terpene compared to mandarin and grapefruit oils. Moreover, they contained citral with a slight higher amount in cold-pressed oil than the corresponding one.

23. Mandarin peel oil extracted by both methods were characterized by having the highest content in the small fraction of terpene hydrocarbon (other than limonene) especially ∝ - and B-pinene compared to other citrus oils. Moreover, they contained linalyl acetate at the same proportion in both oils extracted by the two methods which indicates that hydrolysis of esters in both methods was comparable.

24. Grapefruit peel oils were characterized by having the lowest terpene hydrocarbon content, mainly due to lower d-limonene, but also contained the highest ocimene. Moreover, they contained the highest content of oxygenated compounds, especially alcohols and higher aldehyde compared to other citrus oils.

25. Distilled bitter orange oils were characterized by having the highest terpene hydrocarbons, especially d-limonene

compared to other citrus oils. Moreover, alcohols were identified as nerol and linalool in bitter orange oils which made its content in oxygenated compounds higher than that in Baladi orange.

Part III. Characterization of pectin pomace of citrus peel

This part of study investigated the potential of citrus by-products in providing good yield of pectin of good quality. Pectin pomaces were prepared from dried grated peels and membrane (albedo and core or pulp) of Baladi orange and grapefruit as well as dried grated peels of mandarin. Extraction of pectin from dried residues, after their pretreatment is an efficient mean for extending season of pectin manufacture and elimination of rapid changes in yield or characteristics of pectin due to handling of large emounts of fresh wastes produced daily. Moreover, such technique would reduce amounts and, in turn, costs of solvents used in pectin preparation. Dried by-products of orange and grapefruits were extracted by ammonium oxalate solution while that of mandarin by Hcl. The extracted and precipitated pectins were partly purified through washing with alcohol and were characterized from the point of their physical and chemical properties as well as their content in neutral sugar and mineral matter.

26. Chemical analysis of dried starting materials used for pectin preparation indicated that their moisture content

averaged 9.7% which make them suitable for long storage. Dried by-products of Baladi orange and grapefruit exhibited comparable contents in crude protein, ether extract and ash (5.32 and 5.33%, 1.75 and 1.66%, 2.95 and 2.96% of dry weight, respectively). Dried peels of mandarin had higher contents in all these nutrients (6.94, 3.39 and 4.65, respectively). Dried by-products had higher amounts of crude fiber (19.4-31% of dry weight) where grapefruits by-products had highest value and that of mandarin had the lowest one.

27. High amounts of pectic substances (28.21-31.66% on moisture free basis) were present in grapefruit, orange, and mandarin by-products, arranged in decreasing order of abundance. The use of water, 0.75% ammonium oxalate and 1 N Na oH provided a degree of fractionation of pectic substances of citrus pectins where each fraction varied greatly with kind of fruit.

28. Estimation of practical yield of pectin indicate that maximum, yield was obtained upon using grapefruit dried wastes (27.7%). Lower yields were obtained using Baladi orange and mandarin wastes (24.85 and 18% of dry weight). Efficiency of pectin recovery from Baladi orange and grapefruit wasts did not differ (88.1 and 87.5, respectively) which were higher than that calculated with mandarin (77.62).

29. Molecular weights of pectin preparations varied within a small range from 70,213 to 84,042 and with an average value which is higher than that for commercial pectins. Molrecular weight was much higher in pectins of orange than those of mandarin and grapefruit which did not differ greatly (78,723 and 70,213, respectively).

30. In a decreasing order, pectins of orange, mandarin and grapefruit showed variable gelly grades (167,162 and 112, respectively) which also were lower than those of purified commercial pectins. Jelly grade of citrus pectin seemed to depend mainly upon its degree of polymerization of galacturonic acid and hence upon its molecular weight rather than any other pectin characteristics.

31. Optical rotation values of citrus pectin ranged between (+216.59° to +232.26°) and correlated with values for AGA, as higher purity pectin induced higher specific rotation value, and also with those for turbidity or appearance and absorbance of 0.2% pectin solution.

32. Although not completely purified, citrus pectin preparations showed lighter color than the two commercial pectins, especially orange and grapefruit pectins which possed whiter color.

33. Although showed variable values, all citrus pectins had higher flow time values than these for two commercial ones.

34. Both appearance and absorbance of 0.2% pectin solutions were strongly correlated to each other as well as to values for AGA content. Solution of grapefruit pectin was more clear in appearance higher in absorption value which compared well with those of commercial pectins. The highest turbidity (moderate turbidity) and lowest absorbance was observed in orange pectin solutions while that of mandarin pectin showed light turbidity properties.

35. Mandarin pectin has slight higher pH than other pectin, probably as a result of method of its extraction using Hcl.

36. Moisture content of citrus pectins ranged between approximately 5.3-8.1% which was not greatly different than that of the commercial slow set pectin (7.8% moisture). However, the other commercial pectin had much lower moisture content (4.4%) which was slightly lower than that of orange pectin (5.3%). Results for moisture content agree with the recommendations of FAO (1978).

37. Ash content in the three citrus pectin preparations ranged from approximately 1.0 to 3.16% of dry matter. Mandarin had the highest content of 3.16% while grapefruit and orange pectins had comparable amount (approximately 1.11

and 1.0% respectively). No great difference in ash content was observed between citrus pectin and slow set commercial pectin (1.46% ash) while low methoxyl pectin had higher amount of ash (4.377%). Ash content of citrus pectin is much lower than those permitted by food laws of many countries especially Germany and Switzerland.

38. The prepared unpurified citrus pectins had remarkable A.G.A. contents which were comparable or even exceeded those of commercial pectins, with the exception of orange pectin (61.67% A.G.A.). Mandarin pectin showed comparable or even slight higher A.G.A. content (69%) than these of commercial ones (66.5 and 67.3%). Grapefruit pectin in particular, had the highest A.G.A. content (77.01%) which was superior than those of commercial ones which indicate that the method of pectin extraction was very successful in such respect and probably any further purification is not necessary as it will increase costs of production.

39. Methoxyl content of citrus pectin preparations lied between approximately 8.5 to 9.1% which were slightly higher than that of slow set commercial pectin while that for low methoxyl commercial pectin was 3.64% methoxyl content. Such methoxyl content classified them as high methoxyl pectins of the hydrogen bonded type gel which render them very usable in jams and fruit jellies and other food uses.

40. Small amount of acetyl group were detected in all citrus pectin preparations which ranged from 0.413 to 0.592% and 50% lower than those present in the two commercial pectins. Data of acetyl content was found to correlate well with those of jelly grade as well as appearance and absorbance of 0.2% pectin solutions rather than those of purity.

41. Data of reducing power (ferricyanide number) of citrus pectins preparations indicated that degree of pectin hydrolysis during their preparation was as low as possible since commercial pectins exhibited much higher values. More reducing power was found in mandarin pectin (3.06) than orange and grapefruit which did not differ greatly in such respect (2.52 and 2.32, respectively) as they were prepared with the same procedure which was different than that for mandarin pectin.

42. Identification of neutral sugars of crude citrus sections was performed using paper chromatography where chromatograms, of sugars liberated upon acid hydrolysis indicated the presence of galacturonic acid, galactose, arabinose and rhamnose in all citrus pectins analyzed. Qualitative estimation of these neutral sugar fractions revealed that quantity of rhamnose were lower than other sugars present.

43. The determination of individual minerals in citrus by-products as well as in prepared crude pectins included the spectrophotometeric determination of phosphorus and atomic absorption spectroscopic methods for sodium, potassium, cupper, zinc, manganese and iron.

44. Data of mineral content of dried citrus waste materials indicated that calcium was the principal element in ash of dried citrus waste materials. Despite of kind of fruit, minerals present in the different ashes were in amounts of decreasing order, Ca, K, Na, Mg, Fe, Mn, Zn Cu and P. Orange dry waste material, in particular, contained Na and Mg, Mn in much lower amount as compared to other citrus. Except for Na, K and P, dried peels of mandarin had higher amounts of most minerals especially Ca and Mg than other citrus materials which was attributed to the higher ash content in mandarin waste material.

45. Analysis of mineral content of pectins indicated that crude citrus pectins kept much of elements originally present in their starting materials although each individual pectin differed from the others in extent of such trend. Citrus pectins as well as commercial ones showed a great variation in amounts of each individual element, especially Ca and Mg. All citrus pectins have the trend of having calcium as the dominant element among inorganic ions bonded to pectin where it was present in higher concentrations

compared to others. Magnesium ranked the second, from the point of abundance, in mandarin pectins and the third in pectins of orange and grapefruit. The contents of Mg were approximately equal in orange and grapefruit pectins. Except for Ca, Mg and Na, all citrus pectin preparations had lower amounts of other minerals. The commercial pectins had the same trend, however, they contained K, in addition to Ca, Na, Mg, in higher amounts.

46. Mineral contents of all citrus pectins were found within the range found for many American commercial pectin as well as those of Europes a finding, which indicates that they could be safely used in different edible foods.

47. The aformentioned data would indicate the suitability of the adopted simple methods for extraction and preparation of pectin from dried residue of citrus in providing pectin in reasonable yield and of good physical and chemical characteristics and suitable from safely, technological and economic points of view. Costs of production could be reduced greatly as any further purification seems to be unnecessary as indicated data of acetyl and AGA content. About 500 kg of pectin could be produced daily from by-products of single plant processing citrus fruits, which would produce as much as 11 ton/day of residues. Such amount of pectin production would improve economy of citrus

manufacture as save much of hard currency used for importing pectin storage of pectin in Egyptian market.

Part IV. Characterization of citrus seed oils:

Citrus seed oils were obtained from seed meals of Baladi orange, bitter orange and mandarin, using solvent extraction and yield of oil was determined. The recovered oils were compared from the point of the physiochemical properties and these composition of fatty acid and unsaponifiable matter.

48. Seeds constituted variable proportion in their respective fruit processing residues and ranged from 3.4 to 10.5% of the total by-products, with bitter orange having the highest amount of seeds.

49. Chemical analysis indicated that different citrus seeds had comparable moisture but variable ether extract content where oil constituted 38.19, 36.0 and 27.02% of dry weight of seeds of bitter orange, Baladi orange and mandarin, respectively.

50. Refractive index, acid and peroxide number values showed a range of 1.4667 to 1.4692, 1.29 to 2.55 and 6.31 to 11.69 respectively, in oils of citrus seeds with mandarin seed oil having the highest values compared to others.

51. Oils of different citrus seeds showed comparable values for iodine and saponification number which averaged 96.70 and 201, respectively.

52. Although differed in amount present in each oil, oils of citrus seeds were found to contain unsaponifiable matter of less than 1%.

53. The major fatty acids detected by gas chromatographic analysis, in order of decreasing abundance, were linoleic, palmitic, oleic, linolenic and stearic acids. Small amounts of myristic, caprylic, pentadecenoic, palmitoleic and margaric acids were also detected.

54. All citrus seed oils had similar trend of higher unsaturated fatty acids and lower saturated fatty acids. However, they differed among themselves with respect to total amount of these two groups as well as in the percentage contribution of each individual unsaturated and saturated fatty acids.

55. In all citrus seed oils, the main unsaturated fatty acid was linoleic, while palmitic was the main saturated fatty acid.

56. Baladi orange seed oil had the highest amount of total unsaturated fatty acids (74.15%), due to its

higher linoleic (50.12%), and the lowest total saturated fatty acids (25.73), due to the reduced palmitic acid content, compared with other citrus seed oils.

57. Bitter orange seed oil showed the highest amount of total saturated fatty acids (36.29%), due to its higher content of each individual saturated fatty acid and showed the lowest content in total unsaturated fatty acids (63.47%).

58. Mandarin seed oil lied in between the other two seed oils in respect with amount of total unsaturated and saturated fatty acids. However, it had the highest content in oleic acid (25.66%) compared to others.

59. Analysis of fatty acids of citrus seed oils provided an evidence that they could be classed among the oleic/linoleic group of the high unsaturated fatty acids, thus resembling cotton seed, corn and sunflower seed oils.

60. GLC chromatograms of unsaponifiable matter of citrus seed oils indicated the presence of 33 peaks in that for bitter orange, 31 peak in that for mandarin and 27 peaks in that for Baladi orange seed oil of which only 18 compounds were identified. However, unknown compounds constituted 4.29, 7.72 and 18.56% of total unsaponifiable

matter in oils of bitter, Baladi orange and mandarin seeds, respectively.

61. Total hydrocarbons constituted a range of 53.4-65.4% of total components with Baladi orange seed oil having the highest margin while mandarin and bitter orange oils had comparable content of an average of 53.5%. The major hydrocarbon compound in all oils was n-tricosane (C_{23}).

62. Expressed in terms of peak area, sterols were present in proportion of 34.6-46.6% of the total unsaponifiable matter of citrus seed oil.

63. Sterols were fractionated into four main constituents which were, in order of decreasing abundance B-sitosterol, campsterol, stigmasterol and cholesterol. B-sitosterol was the major sterol compound amounting 93.9, 88.5 and 91.4% of total sterols separated from oils of Baladi, bitter orange and mandarin seeds, respectively. Cholesterol was only detected, but a very small proportion (0.9% of total sterols), in oil of bitter orange seeds.

64. All data collected in the present study lead to conclude that the potential tonnage of oil available from citrus seeds left after citrus processing is great and that citrus

seed oils could be considered edible ones, and its rather high linoleic acid content, similar to corn and sunflower oils adovocate it as suitable dietary fat. Moreover, they may serve as a potential in drying oil industries.

65. Based on data of daily production of wastes from single plant for citrus processing (Kaha Factory) one would expect that 133 kg of seed oil could be produced daily having in mind that 11 ton/day of citrus wastes are produced daily which contain 887 kg seeds of 15% crude oil content. Citrus seed oil could contribute to edible oil production of Egypt which suffers from its shortage.

Part V. Characterization of citrus seed meal:

This part include the investigation of chemical composition, mineral matter content and general protein classes of different citrus seed meals (whole, dehulled and defatted meals) prepared to provide high protein and nutritious edible materials to be used as food or feed. Air dried seeds of Baladi orange, mandarin, bitter orange and grapefruit served as starting raw materials for such products which were then analysed.

66. Amount of seeds present in by-products varied with kind of fruit and represented 6.8, 45, 2.4 and 0.53% of fresh weight of bitter orange, mandarin, Baladi orange and grapefruits, respectively. Seeds had comparable moisture

content. Kernels constituted 69-72.76% while hulls formed 27.24 - 31% of seed weight.

67. Chemical analysis of whole seed meals indicated that crude oil was the major component (36- 38.19% of dry weight) and crude protein was in the second order from the point of amount as well as importance (11.83-16.22%). Total carbohydrates, crude fiber and ash ranged 12.88-27.03%, 11.91-15.87% and 2.24-3.08%,respectively.

68. Dehulled seed meals or kernels had higher ether extract, crude protein and ash content, but lower crude fiber content than whole seed meals.

69. Hulls contained higher amounts of crude fiber, fair amount of crude protein and ash and low oil content.

70. Removal of fixed oils from seed-press cake resulted in increasing concentration of other nutrients such as protein (15.33-18.76%) and ash (3.24-4.18%), and reduced moisture content on these defatted meals.

71. Minerals analysed in whole meals,arranged in decreasing order of abundance, were K, Ca, Na, Mg, Zn, Mn, Cu and P. Seed kernels and hulls exhibited the same order of mineral concentration. Although the three citrus seed did not differ in general order of mineral distribution they

varied greatly with regard to concentration of each individual element analysed. Mineral element content of Baladi orange and mandarin seeds were almost higher than those of bitter orange seed. Data of mineral analysis correlated with those of ash content.

72. Data indicated that consumption of as little as 100 g.from each citrus meal would satisfy the daily recommended allowance and requirements for humans established by NAS (1974) and FAO (1974) for Ca, Mg, Mn and about 250-300 g. is sufficient to provide the daily requirements of zinc (6 mg/day).

73. The classical Osborne classification of unheated proteins of unfatted meal into general classes on the basis of solubility indicated that the majority of soluble proteins were globulins (26.33-43.74%). Albumins constituted the second major class (18.19-24.04%). Glutelins were the third major class (8.98-30.37%),while prolamines constituted the smallest protein class (0.1-4.72%).

74. Data of protein fractionation indicated that nearly 75% of proteins of citrus seeds are readily extractable and only 23-25% of protein were found unsolubilized.

75. Results of this part indicate that possible nutritious meals of high protein content could be prepared in

different forms from citrus seeds (whole, dehulled, defatted seed meals) according to processing facilities in the citrus manufacture plant. About 887 kg of whole seed meals or 754 kg of either dehulled or defatted meals would be obtained from by-products of citrus (11 ton/day) processed in Kaha Company, Egypt, in every day of the season.