

FATTY ACIDS OF INDIGENOUS RESOURCES FOR POSSIBLE INDUSTRIAL APPLICATIONS

Part V : Investigation on the Commercial Species of Rutaceae

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Abstract. Seed oils from the commercially grown varieties of the citrus fruit in Pakistan have been analyzed for their fatty acid compositions. The oils of *Citrus sinensis* L., *Citrus reticulata* and *Citrus paradisi* respectively contain 14 : 0 ; 0.083, 0.0 and 0.32, 16 : 0 ; 38.26, 13.4 and 32.62, 16 : 1 ; 4.43, 0.0 and 0.0, 18 : 0 ; 6.24, 19.8 and 2.53, 18 : 1 ; 34.88, 13.3 and 31.74, 18 : 2 ; 14.4, 52.7 and 29.25, 18 : 3 ; 0.0 traces and 3.46% acids in their glycerides. The amount of the oil is available estimated at 3,200 tons/annum.

The various varieties of citrus constitute one of the foremost fruit crops of Pakistan. Utilization of the fruit on industrial scale results in the accumulation of considerable quantities of wastes, such as peel, pulp and seed. According to one survey, the annual production of the fruits in the Pakistan in 1968-69 stood at 484, 845 tons.¹ The amount of seed in the citrus fruit grown in different parts of the world has been reported in the literature^{2,3} and it varies from 2 to 9.5%. In the present studies, it has been found that "malta" ("mosambi") contained 0.8%, kinnow 2.3%, grapefruit 2.2%, and lemon 2.8% seed. Thus on the average these citrus fruits contain about 2% seeds and, therefore, on the basis of total production of the citrus fruit (4,84, 845 tons), the amount of seed theoretically available in the country is 9696.9 tons.

In continuation of our general efforts for developing new local sources of oils,⁴⁻⁷ we now have examined the seeds from *Citrus reticulata* (kinnow), *Citrus sinensis* L. ("malta") and *Citrus paradisi* ("chokotara") (N. O. Rutaceae) for oil contents and fatty acid compositions.

Materials and Methods

Citrus Seeds : (i) *For Solvent Extraction.* The fruits of *C. reticulata*, *C. sinensis* L. and *C. paradisi* were purchased from the local market and their seeds were hand-picked from the pulp after extraction of the juice. These seeds were washed with water and dried in shade at room temperature (18-20°).

(ii) *For Expression.* The seeds of the citrus varieties were obtained through courtesy of a local fruit processing plant.

Extraction of oils : (i) *By Solvent.* The seeds were crushed in a pestle and mortar and then extracted five times with cold *n*-hexane. The extracts were combined, filtered, dried over anhydrous sodium sulphate and freed from the solvent under reduced pressure by distillation so that the oil was obtained as a residue.

(ii) *By Expression.* The seeds were pressed in a Japanese mechanical expeller (Hander Model 510). The oil so obtained was dried over anhydrous sodium sulphate, filtered and used for further studies.

Examination of the Oil. The yields of the oils as well as their physical and chemical values as determined by the standard procedures,⁸ are recorded in Table 1.

TABLE 1. PERCENT YIELD AND PHYSICAL AND CHEMICAL VALUES OF THE SEED OILS OF CITRUS FRUITS

Yields and values	<i>C. sinensis</i> L.	<i>C. reticulata</i>	<i>C. paradisi</i>
Yield (%)	32.6	32.40	36.38
Refractive index Abb's	1.4660 at 26°	1.4680 at 24°	1.4660 at 24°
Acid value	0.24	0.25	0.15
Iodine value (Wij)	94.21	98.83	82.74
Saponification value	184.91	172.49	171.9
Thiocyanogen value	52.7	57.38	—
Unsaponifiable matter (%)	0.7	0.52	—

Analysis of the Constituent Fatty Acids of the Oils. The oil (5.0 g) was saponified by refluxing with 0.5 N alcoholic KOH (50 ml) for 4 hr. The

unsaponifiable matter was removed by extraction of the cooled soap solution with ether (100 ml × 5). The soap solution was then acidified with 4N H₂SO₄ and the liberated fatty acids were removed in ether, dried and freed from the solvent. They were finally converted into their methyl esters.⁹ The esters were analyzed by GLC on a polyethylene glycol succinate column (9' × 1/8" copper column) at 198° using hydrogen flame ionization detector in a phase-Sep GLC machine. The identity and the percentage composition of the constituent fatty acids were determined from the retention times and the peak areas of their methyl esters, separately and are reported in Table 2.

TABLE 2. PERCENTAGE COMPOSITION OF THE FATTY ACIDS OF THE OILS OF *C. SINENSIS* L., *C. RETICULATA* AND *C. PARADISI* SEEDS.

Fatty acids	Varieties		
	<i>C. sinensis</i> L.	<i>C. reticulata</i>	<i>C. paradisi</i>
14 : 0	0.83	—	0.32
16 : 0	38.26	13.4	32.62
18 : 0	6.24	19.8	2.53
16 : 1	4.43	—	—
18 : 1	34.88	13.3	31.74
18 : 2	14.4	52.7	29.25
18.3	—	Traces	3.46
Total			
Total saturated acids	45.33	33.2	35.47
Total unsaturated acids	53.71	66.0	64.45

Discussion

Citrus fruits are processed by a number of factories in Pakistan for use in various food and beverage preparations. Consequently, a large quantity of seeds are available as a waste or by-product at all such citrus fruit processing plants. As a result of the present findings it is proposed that these seeds be utilized for the recovery of oil. Both expression as well as solvent extraction can be employed for this purpose. On an average, expression can yield 23% and solvent extraction 33% of good quality oil that can either be used for soap making

or for edible purposes. Although the amount of the oil is minor, yet it is considered helpful in view of the fact that Pakistan had to import about 0.2 million tons of oils for edible purposes alone during 1974-75. Compared to some other unconventional sources that have been highlighted previously, citrus seeds can be easily collected at the site of the citrus fruits processing factories. Also, from an examination of the composition of oils, as obtained from the various commercially grown citrus fruits in Pakistan, it is evident that they can be a very good source of palmitic acid. The significance of this finding can be realized from the fact that so far there has been discovered no economical source of palmitic acid in Pakistan. *C. sinensis* L. is particularly rich with regard to this acid and it is also grown quite extensively in the country.

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