CHEMICAL CHANGES THAT OCCUR DURING STORAGE OF BITTER ORANGE PEEL OIL

By

Ez - Eldin A. Shereef

B. Sc. (Agric)

University of Ain Shams , (1966)

THESIS

Submitted in Partial Fulfilment for the Degree of

M. Sc.

IN

AGRICULTURAL CHEMISTRY

Faculty of Agriculture

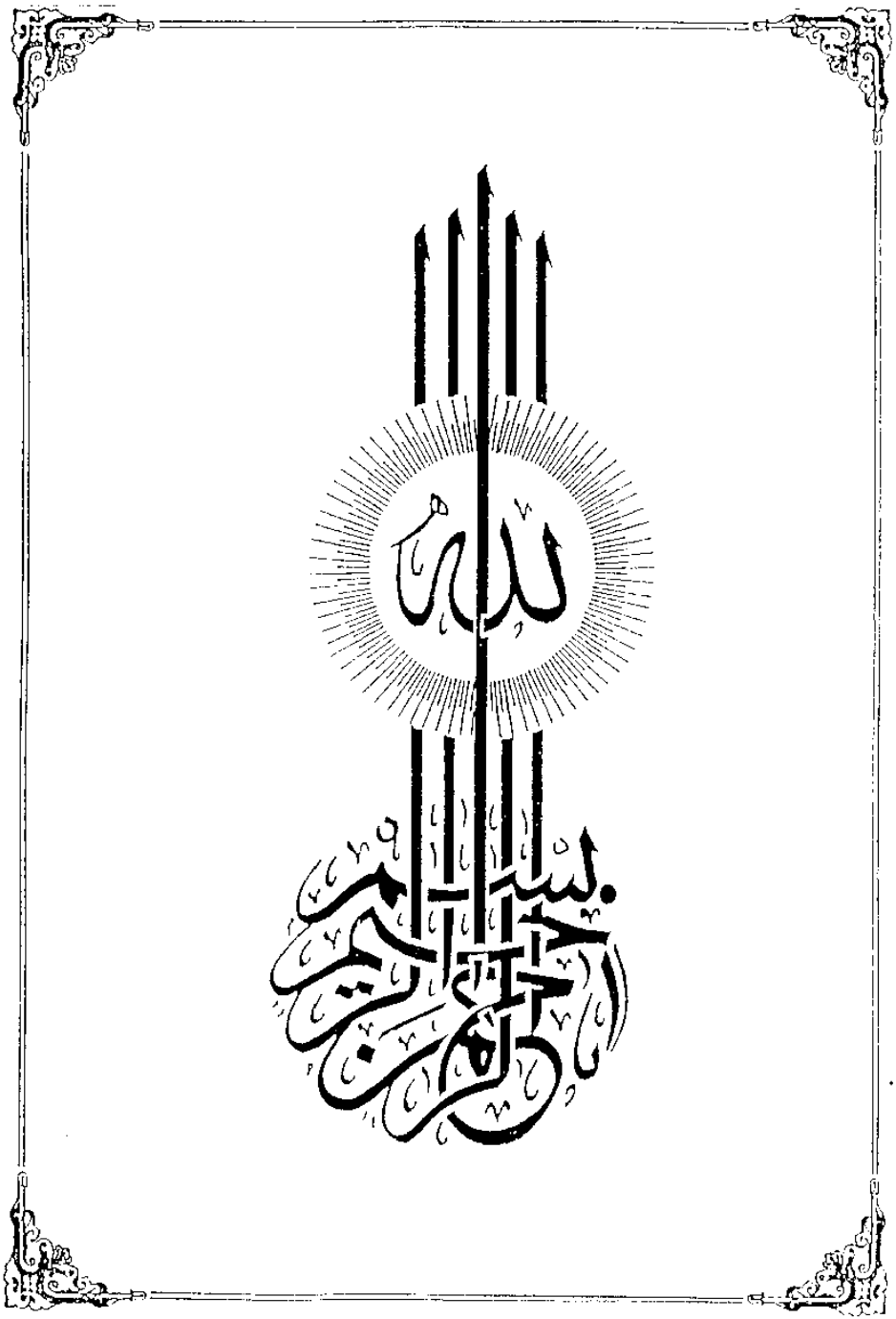
University of Ain - Shams . Cairo A. R. E.

1973

Approved by

Committee in charge

Date: / /1973



INTRODUCTION

The essential oil industry which started in Egypt some fourty years ago is still considered in its infancy in comparison with other flourishing industries in this country. Such an awkward situation attracted the attention of several authorities to investigate the problem very thoroughly. Therefore, several reports were submitted concerning the agricultural and industrial requirements which could eventually lead to a rapid and successful development of such a vital industry.

The environmental conditions prevailing in Egypt are highly favorable for cultivation of aromatic plants. Most of the reliable data on the agricultural requirements of such plants could be traced to the Experimental Station at Elkanater, Department of Medicinal plants and Essential oils, Ministry of Agriculture, and the Medicinal and aromatic plants unit, National Research Centre. The expansion in cultivation, production, industrialization and exportation of some aromatic plants and their products could serve a great deal as a main source of national income specially hard currency.

The area cultivated with bitter orange plants in Egypt during the last 10 years is about three hundred acres (1). The tree is mainly used as a root stock

because of its great resistance to gummosis, a disease which attacks citrus trees. Such an area is undoubtedly insignificant in comparison with other Mediterranean countries.

Lotfy (2) stated that the World production of essential oils in general is approximately 100 million pounds while the Egyptian production represents 0.25% of that amount. It should be stated that the lack of standard specifications for such oils should enhance the authorities to come up with a quality control program on such a product to maintain a high reputation for Egyptian oils in foreign markets.

The economical value of the various types of bitter orange oils is well known abroad, the oil isolated from the peels of fruits besides those distilled from the flowers and/or leaves have attained great importance as flavoring agents in candies, gelatin deserts, puddings, chewing gums and medicinal products besides their use in making perfumes, cosmetics and scenting soaps. The peel is known to be richer than the juice in its vitamin C content and subsequently the residue after distillation of alcohol from fermented peels could serve as a source of vitamin C. (3).

The expansion in the cultivated area with citrus trees and the improvement and the development of citrus canning industry in the Arab Republic of Egypt could initiate other major and subsidiary industries which involve the use of peels, leaves and flowers for extracting essential oils and other valuable products such as vitamins, alcohols and the fixed oil. The continuous demand for Egyptian bitter orange oil points to the importance of such products and requires a thorough investigation of the situation of bitter orange oil in the Arab Republic of Egypt to increase both the quantity and quality of the products needed for local and foreign consumption.

The agricultural and chemical data or the local variety of bitter or sour orange is quite insufficient, and very little work, if any, was done on the characteristics of the oils obtained from the leaves, peels, flowers and seed oil. In fact, previous work on bitter orange was limited to the determination of the physical and chemical properties of absolute Neroli oil and petitgrain bigrade oil, the keeping quality of these oils and their antimicrobial effect (4).

The present investigation is mainly concerned with the chemical changes that occur during storage of bitter

orange peel oil subjected to different storage conditions. Determinations of the physical and chemical properties were also carried out and the validity of the analytical procedures used in the various determinations of bitter orange peel oil was also criticized.

The various points which were subjected to a thorough investigation in this dissertation fall under the following main headings:

a. The physical and chemical properties of bitter orange peel oil.

b. The important factors affecting storage of bitter orange peel oil, which include air, temperature, moisture and light, were examined under the following headings:

(1) Effect of storage temperature (30 and 58°C.) in the presence of air and light for 90 days.

(2) Effect of moisture (1% v/v) at 30 and 58°C. in the presence of air and light for 90 days.

(3) Effect of light at 30°C. in the presence of air for 90 days.

(4) Storage of bitter orange peel oil at 5 ± 2°C. in the absence of air, moisture and light for 600 days.

(5) Storage of bitter orange peel oil at room temperature in the presence of air and light for 600 days.

c) Storage of bitter orange peel oil at high temperature (45 ± 5°C.) in the presence and absence of air for a comparatively short period.

[illegible]

[illegible] belongs to the family Rutaceae ([illegible]). [illegible] local variety of bitter orange in the Arab Republic of [illegible] is commonly known as "Naring" (6).

Various organs of bitter orange tree are used to obtain oils which differ in their properties, methods of isolation, chemical constituents and economical value. It seems rather logical to present the information concerning each type of oil under a separate title, while the various points of interest pertinent to each type of oil are presented under separate subheadings.

The volatile oils isolated from the leaves, fruit peels and flowers of bitter orange differ widely in their chemical composition; the physical and chemical properties of each type of oil may vary according to origin, season, environmental conditions and methods of isolation. The different types of oils obtained from bitter orange tree possess an odor different from that of sweet orange (7).

The four different types of bitter orange oil are the volatile oil from the leaves (oil of petitgrain bigrade), the volatile oil from the fruit (bitter orange peel oil), the volatile oil from the flowers (oil of neroli bigrade) and the non volatile oil from the seeds of bitter orange fruit.

(1) Bitter Orange Peel Oil

a) Isolation:

Bitter orange peel oil is usually isolated by methods that differ from one country to another and it is undoubtedly different from the procedures employed to separate other types of oils. Some years ago, the principal method of expressing the essential oil from orange peel in California (8) involved crushing the whole fruit between heavy stainless steel cylinders and separating the essential oil from the juice by centrifuging; such a method is rarely employed at the present time, because it yields a somewhat inferior oil in both quality and quantity.

In Spain, the orange oil was produced until 1945 by a process based essentially upon the removal by rasping of the flavedo from the peel of the fruit followed by application of a hydraulic press on the removed flavedo.

This process gave the Spanish orange oil its particular characteristics (high wax content, reddish color, long lasting odor, etc.) which differ from all other types of orange oil. The new process currently used on a large scale in Spain involves puncturing the oil glands with a moving needle while the fruit rotates rapidly on a horizontal spindle, the resulting oil possesses different characteristics

and of much superior quality (9).

This type of oil is not produced on a commercial scale in the Arab Republic of Egypt although the necessary material is quite available at Edfina and Kaha Factories where large quantities of orange peel represent one of the main by-products of such industries.

b) Physical and chemical properties:

Bitter orange peel oil is a volatile oil, orange yellow to brown in color with a very strong odor of sour orange. The physical and chemical properties of this oil were determined abroad by several investigators 10, 11, 12, 13, 14 and 15) who pointed out the similarity to sweet orange oil, but it had a lower optical rotation. Table (1) illustrates the physical and chemical properties of sweet orange peel oil and bitter orange peel oil (11, 12). The data on the physical and chemical properties of bitter orange peel oil is quite scarce in comparison with that reported for sweet orange peel oil.

c) Chemical composition:

The chemical composition of bitter orange peel oil resembles that of sweet orange oil except for the high boiling constituents, responsible for its bitter taste, which appear in the evaporation residue. The chemical

Table (1): The physical and chemical constants of sweet orange peel oil and bitter orange peel oil.

Property	Bitter orange peel oil	Sweet orange peel oil
density	0.852 to 0.857	0.848 to 0.853
specific rotation (25°C)	+ 89° to + 94°	+ 95° to + 98°
refractive index (20°C)	1.473 to 1.476	1.473 to 1.475
Aldehyde content	about 1%	1.3 to 2.7%
Residue after evaporation	3 to 5%	1.5 to 4.2%

composition was elucidated by Igolen and Sontag (14), Bohme and Pietsh (16) who established the presence of the following components:

Phenols	0.09%	Hesperitin (?). A solid phenol "not identified"
Free acids	0.05%	Formic, Acetic, Pelargonic, Cinnamic.
Terpenes	92.00%	d-limonene.
Sesquiterpenes	0.03%	"not identified"
Aldehydes	0.78%	Nonanal, Decanal, Dodecanel.
Free alcohols	0.37%	Linalool, Terpineol.
Esters	2.10%	Linalyl acetate (1% of the oil); Decyl pelargonate. Neryl, Geranyl and Citronellyl acetate.

Igolen and Sontage (14) stated that the optical rotation of bitter orange peel oil varied from + 90° to + 97° and they identified the hydrocarbon. d-limonene (Chart I) as the main constituent of the oil.

The esters were calculated as acetate of linalyl, neryl, geranyl, citronellyl (Chart I) and decyl pelargonate, the alcoholic radical of these esters was identified by Igolen and Sontag (14). Decyl alcohol and pelargonic acid (Chart I), which predominate in all ester fractions; were present probably in the ester form decyl pelargonate.