

CHEMICAL STUDIES ON WATERMELON (CITRULLUS VULGARIS)
AND SWEETMELON (CUCUMIS MELO) SEED OILS

Fouad M. El-Shouny

Dept. of Soil Science, Fac. of Agric., Minufiya Univ.,
Shebin El-Kom, Egypt.

دراسات كيميائية على زيت بذور البطيخ والشمام

فؤاد مطاوع الشونى

قسم علوم الأراضى - كلية الزراعة - جامعة المنوفية

ملخص البحث

وجد أن بذور البطيخ والشمام تحتوى على ٢٦,٥% و ٢٤,٣% زيت من الوزن الجاف على التوالى .

وكانت خواص زيت البطيخ كالتالى : رقم التصين : ١٨٩,٩٢ ورقم الحامض : ٥٩ , والعدد اليونى : ١١٩,٣٤ ومعامل الانكسار على درجة ٢٥م^٥ ١,٤٦٦ والكثافة النوعية : ٩١٣ , وكانت نسبة المواد الغير متصبنة ٨١,٨١% .

أما زيت الشمام فكانت خواصه كالتالى : رقم التصين ١٩٤,٥ ورقم الحامض : ٧٢ , والعدد اليونى : ١٢٥,٧ ومعامل الانكسار على درجة ٢٥م^٥ ١,٤٦١ والكثافة النوعية : ٩٢ , وكانت نسبة المواد الغير متصبنة ١,٠٥% .

وقد أظهر التحليل الكروماتوجرافى (TLC) للزيتين تحت الفحص أن الجليسريدات الثلاثية هى المكون الرئيسى فيهما بينما تواجدت الجليسريدات الشائبة والأحادية بتركيزات بسيطة .

وقد أظهر التحليل الكروماتوجرافى الغازى لاسترات الميثايل للزيتين أن نسبة حمض اللينوليك كانت عالية وكانت نسبتها ٥٧,٠٢% و ٦٢,٧٦% فى زيتى البطيخ والشمام على التوالى .

بينما كان حامض البالميك هو أعلى الأحماض الدهنية المشبعة فى كل من الزيتين وكانت نسبته فى زيت البطيخ ١١,٣٥% بينما كانت هذه النسبة ١٠,٠٦% فى زيت الشمام .

ومن ناحية أخرى فقد أظهر التحليل الكروماتوجرافي الغازي للمستيرولات
أن البيتاستوستيرول كان المكون الأساسي للمستيرولات في الزيتين فكانت نسبته
٩٨, ٥٣% في زيت البطيخ بينما كانت نسبته ٨٣, ٩٠% في زيت الشمام.

ABSTRACT

Watermelon and Sweetmelon seeds contained 26.5% and 24.3% oil (dry wt.) respectively. The physico-chemical properties of the oil produced from watermelon were sap. value 189.92, acid value 0.59, iodine value 119.34, refractive index (n^{25}) 1.466, sp. gravity (d^{25}) 0.913 and 0.81% unsaponifiable matters (UNS). Such values were 194.4, 0.72, 125.7, 1.461, 0.92 and 1.05% at the same order when sweetmelon oil was considered.

TLC of lipid classes of the above oils showed that the triglycerides were abundant. While mono- and diglycerides were of minor existence.

GLC of fatty acids of watermelon and sweetmelon revealed the presence of high content of linoleic acid (57.02% and 62.67% respectively).

Palmitic acid was the major saturated fatty acid which contributed 11.35% and 10.06% at the same order.

GLC fractionation of the UNS indicated that B-sitosterol was the major sterol. It was 53.98% in the UNS of watermelon oil and 90.83% when the UNS of the sweetmelon oil was considered. Neither campsterol, nor Δ^7 stigmasterol was detected in the UNS of sweetmelon oil.

INTRODUCTION

Watermelon and sweetmelon are two of the most popular vegetable crops in Egypt. Such crop covered about 20000 feddan as mentioned by Bulletin of Ministry of Agriculture (1983), corresponding to production of about 4000 tons seeds.

Preliminary studies as reported by Nwokolo and Sim (1987), indicated that watermelon seeds are excellant source of dietary oil and are used in human diets in many parts of West Africa.

The high quality of such oils owing to their large quantities of linoleic acid makes them of great importance as an oil source of high potential value as mentioned by Khan et al. (1985).

The high oil contents in watermelon and sweetmelon seeds attracted the attention of Vigo et al. (1973) who found 22.2% and 23.8% oils in them respectively. Also Dutta et al. (1984), stated that watermelon and sweetmelon contained 26.2% and 23.3% oil.

Sao and Potts (1952), mentioned that watermelon seeds contained 19% oil with the following properties, sap. value 192.2, iodine value 127.8, acid value 2.75, ref. index 1.474, sp. gravity 0.921 and 0.86% unsaponifiable matters. In this connection Oyenuga and Fetuga (1975) stated that the physico-chemical properties of watermelon seeds were ref. index 1.468, sp. gravity 0.91, acid value 0.584, iodine value 118.7 and 192.8 for saponification value.

Vigo et al. (1973), mentioned that the unsaturated fatty acid represented 77% and 85% of the total fatty acids in watermelon and sweetmelon oils respectively.

Datta et al. (1984), pointed out that the major fatty acids presented in the oils produced from both watermelon and sweetmelon seeds were linoleic, oleic, palmitic and stearic acid.

The sterol contents of the unsaponifiable matters UNS of the formentioned cultivars were studied by Garg and Nes (1986) who mentioned that Δ^5 avenasterol and Δ^7 were detected in watermelon seeds UNS.

Eisner and Firestone (1963), noticed that B-sitosterol was the major sterol in each of the vegetable oils investigated as it constituted 91% of sterol fraction extracted from olive oil. Itoh et al. (1973), stated that Δ^5 avenasterol and Δ^7 stigmasterol were found in most of 19 vegetable oils.

Since the acute shortage of edible oils is one of the world problems, yet it became more complicated in developing countries. It was though useful to investigate other sources to be as a support for such vital diet.

Therefore, this work aimed to evaluate the oil contents of the seeds of two common cultivars i.e. watermelon (*Citrullus Vulgaris*) and sweetmelon (*Cucumis Melo*) and their composition of fatty acids and sterols.

MATERIAL AND METHODS

The watermelon (*Citrullus Vulgaris*) and sweetmelon (*Cucumis melo*) seeds were purchased as wastes from their fruits consumed locally during the season (1987). The produced seeds were washed and air dried for one week. Such seeds then crushed and soaked in n-hexane and extracted according to Dhoperhwarker and Mead (1961).

Oil content, refractive index, specific gravity, saponification number, iodine value and unsaponifiable matter were determined according to A.O.A.C. methods (1980).

TL-Chromatography:

The nonpolar lipid fraction was cleaned up via silicic acid adsorption chromatography similar to Zaderiowski and Sosulski (1978).

The separation of such nonpolar fraction to its classes was carried out by thin layer chromatography using silica gel G plates 20x20 cm., layer thickness 0.25 mm. using the solvent system : petroleum ether : diethyl ether : acetic acid 80/20/1 v/v/v. The separated spots were visualized on a dried plate by means of iodine vapours.

GLC analysis:

Methyl esters of fatty acids were prepared similar to Seelback and Quackenlush (1957). The composition of fatty acids were achieved by GLC analysis using Pye Unicom gas chromatography, Model 104, fitted with flame ionization detector, the column filled with 10% PEGA on the acid washed diatomate 100-200 mesh. The operating conditions were: N₂ 45 ml/min, H₂ 45 ml/min, detection temperature 220°C, chart speed 2 cm/min.

UNS analysis:

The unsaponifiable matters were separated according to Maia et al. (1976). The ethereal extracts of the UNS were passed over basic copper carbonate for their purification from any traces of free fatty acids as recommended by Capella et al. (1960). The sterol fraction of the unsaponifiable matters of both oils were separated on a florisil column according to Eisner and Firestone (1963). The isolated sterols were fractionated by GLC using the Pye Unicom gas chromatography Model 104 with flame ionization detector. The operating conditions for the GLC determination were, column temperature 270°C, detector temp. 300°C, chart speed 2 min/cm. Identification of sterols was based on comparison of authentic samples analyzed under the same conditions.

RESULTS AND DISCUSSION

The crude oil contents produced from the whole seeds of watermelon and sweetmelon seeds were 26.5% and 24.3% (dry wt.) respectively Table (1). In this connection Vigo et al. (1973) mentioned that the whole seeds of watermelon and sweetmelon contain 22.2% and 23.8% oil respectively. Also Dutta et al. (1984) pointed out that the formentioned values were 26.2% and 23.3% for the two cultivars respectively.

Table (1): Physical and chemical properties of the crude oils extracted from watermelon and sweetmelon seeds.

Properties	Watermelon	Sweethmelon
Oil percent	26.5%	24.3%
Refractive index $n^{(25)}$	1.466	1.461
Specific gravity $d^{(25)}$	0.913	0.92
Acid value	0.59	0.72
Iodine value	119.34	125.7
Saponification value	189.92	194.5
Unaponifiable matters	0.81	1.05

The physical and chemical properties of the crude oils extracted from seeds of the above cultivars are presented in Table (1). The iodine numbers of the two oils were 119.34 and 125.70 respectively, thus, these oils could be categorized as semi-drying oils. The low acid values 0.59 and 0.72 of such oils could be used as indication for their stability to lipid deterioration.

Saponification value, refractive index, specific gavity and unaponifiable matters of sweetmelon seed oil showed the following value 194.5, 1.461, 0.920 and 1.05% respectively. Such values were 189.92, 1.466, 0.913 and 0.81% at the same order on using watermelon seed oil. These results are in accordance with those reported by Sao and Potts (1952) who mentioned that the characteristic of watermelon seed oil were ref. index 1.471, sap. value 192.8, iodine value 127.8, specific gravity 0.9216, and 0.86% unaponifiable matter.

The fractionation of the nonpolar fraction of both oils Fig.(1) revealed the presence of the major components existed in other edible oils such as cotton seed oil (B) and corn oil (D) migrated on the same chromatogram.

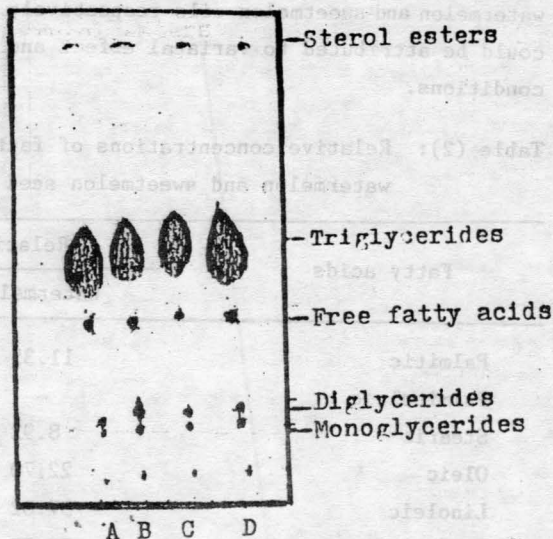


Fig. (1): TLC chromatogram of oil samples of

- | | |
|----------------|------------|
| (A) Watermelon | (B) Cotton |
| (C) Sweetmelon | (D) Corn |

It is worthy to notice that triglycerides fraction was predominant in such nonpolar fraction while monoglycerides were of minor existence.

The relative concentrations of the corresponding fatty acids are presented in Table (2). The separated fatty acids were identified with the aid of authentic samples under similar conditions. Such presentation show that the unsaturated fatty acids contributed the major components (79.72% and 81.36%) in watermelon and sweetmelon seed oils respectively. Linoleic acid was the major unsaturated fatty acid presented in both oils (57.02 and 62.67%) respectively. In this connection Vigo *et al.* (1973) mentioned that the unsaturated

fatty acids represented (77% and 85%) of the total fatty acids in watermelon and sweetmelon oils respectively. However, such variations could be attributed to variatal effect and other environmental conditions.

Table (2): Relative concentrations of fatty acids composition of watermelon and sweetmelon seed oils calculated from GLC.

Fatty acids	Relative concentration %	
	Watermelon	Sweetmelon
Palmitic	11.35	10.70
Palmitoleic	-	1.26
Stearic	8.92	7.93
Oleic	22.70	17.43
Linoleic	57.02	62.67
Total unsaturated	79.72	81.36
Total saturated	20.27	18.63

The saturated fatty acids constituted the minor fractions (20.27% and 18.63%) of which palmitic was the predominated (11.35 and 10.70%) in watermelon and sweetmelon seed oil respectively. Such results were in agreement with Dutta *et al.* (1984).

It is interest to notice that palmitoleic acid was identified (1.26%) in sweetmelon seed oil, while it was undetectable in watermelon seed oil.

The sterol fraction isolated from watermelon and sweetmelon oils analyzed by GLC were identified according to a standard samples separated under the same conditions.

Table (3): The sterol constituents of the UNS of watermelon and sweetmelon seed oils.

Identification	Watermelon	Sweetmelon
	%	%
Campesterol	6.24	-
B-sitosterol	53.98	90.83
Δ^5 avenasterol	24.78	9.17
Δ^7 stigmasterol	14.99	-

The data in Table (3) indicated that B-sitosterol was the predominant sterol which represents (52.97% and 90.83%) of the unsaponifiable matters of both oils respectively.

Such results were also mentioned by Eisner and Firestone (1963) who indicated that B-sitosterol was the major sterol in each of the vegetable oils investigated as it constitute 91% of sterol fraction extracted from olive oil. Also El-Tahawi *et al.* (1979) reported that B-sitosterol was the major phytosterols in the fennel fixed oil. Such results were also reported by Maia *et al.* (1976) for the sterols composition of cashew nut oil.

It is worthy to indicate that neither campesterol nor Δ^7 stigmasterol was detected in sweetmelon UNS which could be considered specific for such oil. In this respect La croix (1970) and Gutfinger and Letan (1973) reported that the contents of the UNS of the oils were quite specific for each and could be used for their identification or any additives if present. Gutfinger and Letan (1974) indicated that the soybean, cotton seed and olive oils differed in their contents of total unsaponifiables.

REFERENCES

- A.O.A.C. (1980). Official method of analysis. Association of official Agriculture chemists. Washington, D.C.
- Capella, P.G., G.S. Zotti, A. Ricca, A.F. Valentini and G. Jacini (1960). Chromatography on Silicic acid of the unsaponifiable matter of fats. J. Am. Oil Chem. Soc. 37, 564.
- Dhoppershwarker, G.A. and J.F. Mead (1961). Role of oleic acid in the metabolism of essential fatty acids. J. Am. Oil Chem. Soc., 28, 297.
- Dutta, J., S. Sondip, P. Prasanta (1984). Seed-fats of some cucurbita. Yield, fatty acid composition, positional distribution of fatty acids in triglycerides and triglycerides composition. Trans. Bore. Res. Inst. Calcutta 47 2: 111-119.
- Eisner, J. and Firestone, D. (1963). Gas chromatography of unsaponifiable matter II. Identification of vegetable oils by their sterols. J. Assoc. Offic. Agric. Chemist's 46 No.3 : 542-550.
- El-Tahawi, B.S., N. El-Shahat and H.A. El-Naggar (1979). Chromatographic studies on fennel fixed oil. Ann. Agric. Ain Shams Univ. Res. Bull. No. 1060, Cairo, Egypt.
- Garg, V.K. and W.R. Nes (1986). Occurrence of sterols in plants producing predominantly sterols: Studies on the sterol composition of six cucurbitaceae seeds. Phytochemistry, 25 11: 295-7.
- Gutfinger, T. and A. Letan (1973). Detection of adulteration of Almond oil with Apricot oil through determination of Tocopherols. J. Agr. Food Chem. Vol. 21 No. 6, 1120.
- Gutfinger, T. and A. Letan (1974). Unsaponifiable in several vegetable oils, Lipids 9: 658.
- Itoh, I., T. Tanura and Matsumoto (1973). Sterol composition of 19 vegetable oils. J. Am. Oil Chem. Soc. 50: 122-125.
- Khan, S.A., D.K. Muhammad, M.J. Iqbal and K. Bhatti (1985). The fatty acid of indigenous resources for possible industrial application part investigation of the species of cucurbitaceae family. Pak. J. Sci. Ind. Res., 28(1):27-30.
- La croix, D.E. (1970). Collaborative study of the Extraction of plant sterols from Adulterated Butter oil using a Digiton-Impregnated celite column. J. Assoc. Offic. Anal. Chemists 53: 535.
- Maia, G.A., W.H. Brown, F.M. Whiting and J.W. Stull (1976). Cashew nut unsaponifiable matter. J. Food Science 41(1): 190-4.
- Nwokolo, E. and J.S. Sim (1987). Nutritional assessment of defatted oil meals of melon (*Colocynthis citrullus* L.) and fluted pumpkin (*Telfaria occidentalis* Hook) by chick assay. J. Soc. Food Agric., 38, 237.

- Oyenuga, V.A. and B.L. Fetuga (1975). Some aspects of the Bio-chemistry and nutritive value of the watermelon seed *Citrullus vulgaris*, *shrad. J. Sci. Fd. Agri.*, 26:843-854.
- Sao Chung, M.T. and W.M. Potts (1952). The analysis and characterization of the oil from the seed of *Citrullus vulgaris*. *J. Am. Oil Chem. Soc.*, 29, 444.
- Seelback, C.W. and F.W. Quackenlush (1957). Thermal diffusion fraction : Oils and fats and some derivatives. *J. Am. Oil Chem. Soc.* 34, 603.
- Vigo, M.S., M.H. Bertani and P. Cattaneo (1973). Seeds of Argentinian *cucurbitaceae* II. Chemical composition of seed and seed oils from watermelon, vegetable sponge. *An. Asoc. Quin. Argent*, 61(3): 121-3.
- Zadernouski, R. and F. Sosulski (1978). Composition of total lipids in Rape seed. *J. Am. Oil Chem. Soc.* 55, 870.