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Constituents of the DRIED TOMATO FRUITS (*Lycopersicon esculentum, Mi Soo*)

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건조 토마토의 성분조성에 관하여

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Abstract

For surveying of constituents concerning the flavor of the dried tomato fruits, nonvolatile components such as minerals, sugars, free amino acids, nucleotides and lipids were analyzed and determined.

Potassium, calcium and phosphorus were the major constituents of ashes, but trace amounts of cadmium and lead were determined.

Glucose and fructose were the major constituents in sugars, and the latter slightly showed higher value than the former.

The content of total free amino acids was 8322.5mg%, and that of the major components such as asparagine, aspartic acid, urea, glutamic acid, ß-alanine and γ-aminobuthyric acid showed 58.01% to the total amount.

The nucleotides were composed of CMP, UMP, GMP and IMP, and CMP among them showed the highest value as about 58.07% to the total amount. On the other hand, IMP showed the lowest one.

The major components of the total fatty acids from the saponifiable fraction in the lipids were $C_{18:2}$, $C_{18:1}$ and $C_{16:0}$, and those of the total sterols from unsaponifiable one were stigmasterol and ß-sitosterol.

요 약

건조 토마토의 향미성분과 관련있는 성분조성을 알고자 무기질, 당, 유리형 아미노산, 핵산 및 지질등의 불휘발성 성분을 분석 정량하였다.

회분의 주요성분은 칼륨, 칼슘 및 인이며, 카드뮴과 납은 극소량함유 되었고, 당류에서는 glucose와 fructose가 주성분이었으며, fructose가 glucose보다 약간 함량이 높았다.

총 유리 아미노산의 함량은 8322.5mg%이였고, 주요 아미노산은 asparagine, aspartic acid, urea, glutamic acid, β-alanine 및 γ-aminobutyric acid로서, 총 유리 아미노산의 58.01%를 차지하였다.

핵산과 관계되는 물질은 CMP, UMP, GMP 및 IMP였으며, 이중 CMP가 전체의 약 58.07%로서 가장 함량이 높았고, IMP가 가장 낮은 함량을 보였다.

총지질로 부터 얻어진 검화물 중의 지방산의 주성분은 $C_{18:2}$, $C_{18:1}$, $C_{16:0}$이었으며, 불검화물중의 주요성분은 stigmasterol 및 β-sitosterol 이었다.

Introduction

The tomato fruits which belong to Solanceae family are used commonly for eating rawly or processing with their characteristic flavors. By improvement and westernization of our eating habits, the tomato fruits for home consumption annually shows a tendency to increase. Scientific researches on the improvements of their varieties and cultural methods were excellently accomplished with the possibility of their production year after year. The tomato fruits are intrinsically valuable one from food processing and nutritional points of view, so that the authors reported on the changes of vitamin C, free amino acids and volatile components concerning the flavors during artificial ripening or processing up to the present[1~6].

On the other hand, although many researches on individual component concerning tomato flavors were reported by many investigators until now, the reports on their several components which exert a favorable influence upon them at one stroke, were seldom shown. On the basis of several reasons described above, the authors attempted to survey the contents of nonvolatile components such as minerals, sugars, free amino acids, nucleotides and lipids of a tomato variety, *Mi Soo*, which grew in a vinyl plastic hothouse.

Materials and Methods

Materials

Eating tomato variety, *Mi Soo*, which were harvested with fully ripened in a vinyl plastic hothouse of a farmhouse in Pusan, Korea, in 1983, were used as sample. These were washed with running water and treated with superheated steam for 3 minutes. In addition to such treatment, these were dried in the sunlight and in oven at 40℃ for 2 days, respectively. Finally these were stored in vacuum desiccator till using for experiment. The cultivated procedure of the tomato fruits used as sample in this work was listed in Table 1.

Determination of Chemical Compositions

Moisture was determined by oven drying method at 105~110℃ under atmospheric pressure. Crude ash, crude lipid, crude protein and crude fiber were measured by A.O.A.C methods, respectively[7]. Pure protein precipitated by Barnstein's method[8] was determined with the same method as in crude protein. The glucose content of which the total sugar was

Table 1. The Cultivated Procedure of the Tomato Fruits for Sample used in Experiment

Variety	*Mi Soo* (Eating Tomato)
Method of Cultivation	In a Vinyl Plastic Hothouse
Initial Manure	Compost and Artificial Manure
Sowing Date	November 7th, 1982
Date of First Transplantation	November 24th, 1982
Date of Second Transplantation	December 12th, 1982
Date of Formality	January 25th, 1983
Blooming Date	February 10th, 1983
Facilitated Reagent	Blossom Set and Sucrose
Date of Fructification	February 15th, 1983
Date of Harvest	April 20th, 1983

converted from the carbohydrate by hydrochloric acid hydrolysis, was calculated by Somogyi-Nelson's method[9].

Determination of Nonprotein-Nitrogeneous Compounds

5g of dried sample was extracted by refluxing with 80% ethanol for 20 mins in water bath, and then protein in extract precipitated by using such deproteinizing agents as TCA and SSA. The extracts obtained by such treatment were used for determination of Extractive-N, Free amino acid-N[10], and Ammonia-N[11]. In order to determine Amide-N[11] and Peptide-N[10], the extracts were hydrolyzed by 2N HCl for 3 hrs and 6N HCl for 24 hrs, respectively. The content of Amide-N was calculated by the difference of Ammonia-N between before and after of hydrolysis. That of Peptide-N was calculated by the difference of Free amino acid-N between before and after of hydrolysis.

Determination of Free Amino Acids

The extracts for nonprotein-nitrogeneous compound analysis prepared by method described above were demineralized through Amberlite cation and anion column chromatography. Free amino acids were analyzed by the method for physiological fluid analysis using 835~50 automatic amino acid analyzer. The lithium citrate buffer solution systems, such as pH 3.0, 3.7, 3.3, 4.1 and 7.0 were used as the eluents.

Determination of alkalinity and acidity[12]

Alkalinity of which the ash solution was prepared in the ordinary way was determined by 0.1N NaOH titration method under the presence of phenolphthalein as indicator. Acidity in which acidic solution was obtained from the ash solution passing through cation column was measured by the same method as in alkalinity.

Determination of minerals

Minerals prepared by dry and wet combustion method were analyzed by atomic absorption spectrometry (Perkin-Elmer 2380). Phosphorous was determined by only molybden blue colorimetry.

Determination of nucleotides

The nucleotides which were extracted with 10% cooled perchloric acid in the ordinary method, were analyzed by HPLC equipped with Bondapak C-18 column.

Determination of total fatty acids and sterols

Crude lipid was extracted with diethyl ether at room temperature for 48 hrs in the shaking incubator. After removing solvent by vacuum rotary evaporator, crude lipid dissolved in a mixed solvents of chloroform-methanol (2:1) and then was purified and decolorized by Folch's[13] and Ueda's[14] method, respectively. After saponification of purified lipid by 10% KOH in 90% ethanol, it was fractionized to saponifiable and unsaponifiable materials by ordinary method. The former was methylated with 1% p-toluenesulfonic acid in methanol, and the latter was purified by TLC in the same method as described in the previous paper before the use of GLC and GLC-MS analysis[15].

Results and Discussion

Chemical Compositions

The chemical compositions of the dried tomato fruits which were analyzed by the methods mentioned above, were listed in Table 2. To show the highest content among these was the total sugar. The contents of the remainder except this were decreased in the order of moisture, crude protein, crude fiber, crude ash and crude lipid. Such tendency as this would be similar to the results of reports from many investigators engaged in the study of the tomato fruits[16~18].

Table 2. Chemical Compositions and Calorie Content of the Dried Tomato Fruits(*g*/100*g* of Dry Weight Basis)

Compositions	Contents(%)
Moisture	11.81
Crude Lipid	2.38
Crude Protein	10.27
(Pure Protein)	(4.39)
Crude Ash	8.34
Crude Fiber	9.16
Total Sugar	41.02
Calorie (Kcal)	226.58

Since the total sugar content was equivalent to some 58% of the total content except that of moisture in the dried tomato fruits, it would have an important effect on their taste. On the other hand, the remainder would also be more or less effective in them.

Calorie content calculated from the value of which Energieträger was multiplied by Atwater's coefficient fit for each, showed 226.58 Kcal per 100*g* of sample. The major calorie source would originate from the total sugar. Such tendency as this would have something in common with all vegetable foods.

Nonprotein-Nitrogeneous Compounds

The results of nonprotein-nitrogeneous compounds analysis were given in Table 3. The extractive nitrogen content determined by Semimicro Kjeldahl method was 854.4*mg*% per 100*g* of the dried tomato fruits. The free amino acid nitrogen content measured by modified cadmium-ninhydrin colorimetry[10] was 451.9*mg*%. The peptide nitrogen content calculated with the difference of free amino acid nitrogen increment before and after hydrolysis was 200.4*mg*%. The nitrogen content liberated from amide amino acids, such as Gln and Asn, was 99.5*mg*%. The ammonia nitrogen content showed

Table 3. Nonprotein-Nitrogeneous Compound Compositions of the Dried Tomato Fruits (*mg*/100*g* of Dry Weight Basis)

Compositions	Contents (*mg*%)
Extractive-N	854.4
Free Amino Acid-N	451.9
Amide-N	99.5
Ammonia-N	92.5
Peptide-N	200.4
Others	60.7

92.5mg% of the lowest value among these. The remainer content originated from nonprotein-nitrogeneous compound, such as the nucleotides and so forth, was 60.7mg%. However, these would have an important effect on the taste. Free amino acid nitrogen among these showed the highest value, so that it would also immensely take part in the taste.

Free Amino Acids

The free amino acid composition measured by automatic amino acid analyzer using the method for physiological fluid analysis was given in Table 4. The main constituents indicating over 10% as percentage by content to the total amino acid amounts in the extracts for nonprotein-nitrogeneous compound analysis, were composed of Asn, Asp and urea. The contents of individual amino acids, such as Glu, β-Ala, γ-ABA, NH_2EtOH, Ser, p-Ser and Phe, ranged from 5% to 9%. Hyp, Pro, Cys and so forth were only detected in the trace amounts. On the other hand, the percentages of acidic, neutural, amide, aromatic, sulfur containing, basic and heterocyclic amino acids to the total amounts were 20.1%, 29.55%, 16.33%, 8.26%, 1.23%, 0% and 0.93%, respectively, and then the others were 23.6%.

Table 4. Free Amino Acid Compositions of the Dried Tomato Fruits (mg/100g of Dry Weight Basis)

Compositions	Contents (mg%)	% to Total Amino Acids
Phosphoserine	489.3	5.88
Taurine	trace	—
Phosphoethanolamine	552.6	6.64
Urea	843.9	10.14
Aspartic acid	953.5	11.46
Hydroxyproline	trace	—
Threonine	183.3	2.20
Serine	551.1	6.62
Asparagine	1,175.0	14.12
Glutamic acid	719.2	8.64
Glutamine	183.7	2.21
Proline	trace	—
Glycine	trace	—
Alanine	271.9	3.27
Valine	134.0	1.61
Cysteine	trace	—
Methionine	102.4	1.23
Isoleucine	104.8	1.26
Leucine	156.8	1.88
Tyrosine	210.2	2.53
Phenylalanine	476.9	5.73
β-Alanine	568.5	6.83
γ-Aminobutyric acid	567.9	6.82
Tryptophane	trace	—
Lysine	trace	—
Histidine	77.5	0.93
Arginine	trace	—
Total	8,322.5	100.00

It is well known that free amino acids are not only vitally concerned with the taste[19,20] and nonenzymetic browning[5], but also precursor of volatile components[21]. Natural free amino acids exist in D and L form, but the latter is occupied by an overwhelming majority. Either D or L would make a considerable difference in the taste. The taste of natural free amino acids would be classified into four categories, such as sweet, bitter, delicious and tasteless.

Glu, representative of a delicious taste, showed 719.2mg% of the comparative high value. It is generally agreed that Glu is an important amino acid of the ripened tomato fruits in the various reports[22]. It would have some important effect on the quality of the ripened tomato fruits.

It was general tendency that Thr and Ser exhibiting sweet taste were present in approximately equal amounts, but the value of the former was considerably lower than that of the latter. It would solely be due to the difference in variety or the method of cultivation or soil circumstances and so forth.

While, Arg having a taste of slight bitterness was generally present at some high concentration in the ripened tomato fruits[22,23], it was at undetectable one. It is probably due to some reasons mentioned above. Though it was solely the basal constituent of a bitter taste, it would play an important role as an enhancement in a mixture of free amino acids. The nonproteineous amino acids such as phosphoserine, phosphoethanolamine and urea, would also be considered to play an important role as well as the other amino acids in the taste of the dried tomato fruits.

Sugars and Sugar Alcohol

The results of sugar analysis determined by comparing each peak component on HPLC chromatogram to retention time and concentration of authentic specimen were listed in Table 5. As shown in Table 5, the contents

Table 5. Sugar and Sugar Alcohol Compositions of the Dried Tomato Fruits(mg/100g of Dry Weight Basis)

Compounds	Contents(mg%)
Maltose	4,629.6
Glucose	7,138.5
Fructose	7,858.5
Mannitol	147.0

of maltose, glucose, fructose and mannitol were 4629.6mg%, 7138.5mg%, 7858.5mg% and 147.0mg%, respectively. Those of glucose and fructose were present in approximately equal amounts with a slight preponderance of the latter. This result would be similar to that of the paper from De Bruyn et al[24].

Since the sugar is familiar to us as sweet constituent in daily life, it is used much for sweetenings. For such a background, studies on the relationship between the chemical structure of sugar and sweetness have been carried out by many investigators for a long time[25~28]. Relative sweetness of sugar would be considerably dependent on the amounts of low-molecular-weight monosaccharides present, the concentration of solids, the temperature at which they are used, and on other substances such as free amino acids and so forth resulting from the extracting procedure, which may be coexisted. All of sugar and sugar alcohol analyzed in the present work exhibited a sweet taste, so that these would solely or complexly play an important role in a flavor of the ripened tomato fruits.

Alkalinity and Acidity

As shown in Table 6, alkalinity and acidity

Table 6. Alkalinity and Acidity in the Dried Tomato Fruits

Alkalinity	Acidity
45.84	−16.33

were 45.84 and -16.33, respectively. It is well known that alkalinity is dependent on the contents of alkaline metals, such as Na, K, Ca, Mg and so forth in foods, and then acidity is decided by the contents of S, P, Cl and so forth. Since alkalinity of the dried tomato fruits showed higher value than acidity, it would be regarded as alkaline food. This tendency would be a common feature in analysis result of fruits and vegetables. On the other hand, it would become an important source of alkaline metals to us.

Minerals

Analysis result on the mineral constituents was listed in Table 7. As a result shown in Table 7, K, P and Ca were the major mineral constituents in both samples which were prepared by wet and dry combustion method. It was a thing of especial importance that K approximately showed about 79% to total mineral content. Heavy metal contents such as Cd, Cu, Mn, Pb and Zn which cause a great trouble in the food sanitation aspects, were the minor elements in them.

In the case of human body fluid, minerals

Table 7. Mineral Compositions of the Dried Tomato Fruits (mg/100g of Dry Weight Basis)

Minerals	Contents (mg%)		
	1	2	3
Cadmium	0.09	0.04	0.065
Copper	0.03	0.05	0.04
Manganese	0.96	1.61	1.285
Lead	0.03	0.05	0.04
Zinc	2.25	2.59	2.42
Iron	2.93	1.83	2.38
Magnesium	6.34	5.50	5.92
Calcium	161.92	225.84	193.88
Vanadium	0.02	0.01	0.015
Potassium	2,265.67	2,603.50	2,434.59
Phosphorus*	415.43	465.11	440.28

1: From Dry Combustion Method
2: From Wet Combustion Method
3: Average between 1 and 2
*: Determined by Molybden Blue Colorimetry

have some physiologically important functions in control of acid-base balance, muscular movement, nerve operation, osmotic pressure and activity of which enzymes take part in nutrient metabolism. In addition to these, minerals would have some important effect on the sense of taste. According to the opinion proposed by Shallenberger et al[29], it seems that hydrate and complex salt of a certain inorganic compound would have a sweet taste in a moderate concentration being at the rate of dilution. For such a background of useful information, the major or minor mineral constituents would be more or less effective to the taste of ripened tomato fruits.

Nucleotides

The nucleotide content of dried tomato fruits determined by HPLC, was given in Table 8. As a result in Table 8, nucleotides were composed of four constituents, such as CMP, UMP, GMP and IMP. Their contents were 21.5mg%, 9.0mg%, 6.5mg% and 0.0265mg%, respectively. Nucleotides of pyrimidine base showed higher content than those of purine base.

Table 8. Nucleotide Compositions of the Dried Tomato Fruits (mg/100g of Dry Weight Basis)

Nucleotides	Contents (mg%)
CMP	21.5
UMP	9.0
GMP	6.5
IMP	0.0265

A detailed study on the flavor potentiator originated from nucleotides having inosinic acid as the main constituents, began with Kuninaka as leader in the 1950's. Putting all accounts together, nucleotides or their derivatives, such as GMP and IMP involving purine base, would have a delicious taste. But all of them originated from the derivatives, such as CMP and UMP involving pyrimidine base, would not have a good opportunity for a delicious taste. In the case of IMP and GMP, these would enhance the flavor potentiating activity of the ripened tomato fruits in the existence of flavor potentiator, such as Glu.

Total Fatty Acids

Total fatty acid composition of saponifiable

Table 9. Total Fatty Acid Compositions of Saponifiable Material fractionated from Lipids of the Dried Tomato Fruits (Peak Area %)

Fatty Acid	Peak Area	% to Total Peak Area	Method of Identification	
			GC	GC-MS
$C_{12:0}$	0.04	0.05	*	*
$C_{13:0}$	0.001	0.001	*	*
$C_{14:0}$	0.11	0.15	*	*
$C_{15:0}$	0.01	0.02	*	*
$C_{16:0}$	11.98	16.3	*	*
$C_{16:1}$	0.22	0.3	*	*
$C_{17:0}$	0.07	0.1	*	*
$C_{17:1}$	0.07	0.1	*	*
$C_{18:0}$	3.23	4.4	*	*
$C_{18:1}$	17.71	24.1	*	*
$C_{18:2}$	37.04	50.4	*	*
$C_{18:3}$	4.19	5.7	*	*
$C_{19:0}$	0.004	0.005	*	*
$C_{20:0}$	0.22	0.3	*	*
$C_{20:1}$	0.059	0.08	*	*
Total	74.95	102.00		

material obtained from the purified lipids of the dried tomato fruits, was shown in Table 9. Whole methyl esters of which fatty acids were listed in Table 9, were fully identified by comparing with the retention times and mass spectra of authentic specimen. These characteristically showed the ionized fragmentations originating from McLafferty's rearrangement and β-clavage on their mass spectra. Total fatty acid composition was mainly composed of $C_{18:2}$, $C_{18:1}$, $C_{16:0}$, $C_{18:3}$ and $C_{18:0}$, and its contents were 50.4%, 24.1%, 16.3%, 5.7% and 4.4% to total peak area, respectively. This tendency would be commonly observed in vegetable oil. On the other hand, tomato fruit oil may be a good source of essential fatty acid for us. Since total fatty acids analyzed in this work originated from neutral lipids, glycolipids and phospholipids, we could never clearly say the relation between these and the sence of taste in the ripened tomato fruits. In order to examine closely a correlation between these and the sense of taste, we should make more exhaustive study of this question from now on.

Total Sterols

Total sterol composition of unsaponifiable material fragmented from the purified tomato fruit oil after saponification was investigated by GLC technique, and the result was listed in Table 10. Whole sterol constituents also obtained the information enough for the identification by GLC-MS technique. Cholesterol showed the predominant characteristics of the cleavage patterns at m/e (%) 386 (M^+, 100), 371 (M^+—CH_3, 12), 368 (M^+—H_2O, 20), 353 (M^+—H_2O-CH_3, 10), 329 (M^+—C_3H_4—OH, 1), 328 (M^+—C_3H_4—H_2O, 1), 301 (M^+—H_2O—C_5H_7, 16), 275 (M^+—H_2O—C_7H_9, 22), 273 (M^+—side chain, 9), 271 (M^+—side chain—2H, 2), 255 (M^+—side chain—H_2O, 8), 231 (M^+—side chain—C_3H_6, 6), 229 (M^+—side chain—C_2H_3—OH, 3), 213 (M^+—side chain—C_3H_6—H_2O, 9) and so forth. This is well known to be a zoosterol, but it would be synthesized by the biosynthetic pathways dissimilar to Goodwin et al's proposition[30].

Table 10. Total Sterol Compositions of Unsaponifiable Material fractionated from Lipids of the Dried Tomato Fruits (Peak Area %)

Peak No.	Sterols	Peak Area	% to Total Peak Area	Method of Identification	
				GC	GC-MS
1	Unknown	0.3	1.366		
2	Unknown	0.04	0.182		
3	Unknown	0.04	0.182		
4	Unknown	0.15	0.683		
5	Cholesterol	0.78	3.552	*	*
6	Campesterol	1.56	7.104	*	*
7	Stigmasterol	10.53	47.951	*	*
8	ß-Sitosterol	7.36	33.515	*	*
9	$\triangle^5$-Avenasterol	0.72	3.279	*	*
10	$\triangle^7$-Stigmastenol	0.3	1.366	*	*
11	$\triangle^7$-Avenasterol	0.18	0.820	*	*
Total		21.96	100		

The remainder except cholesterol showed their predominant characteristics of all the same cleavage patterns as in the reference[31]. These would follow the same biosynthetic pathways as proposed by Goodwin et al. It would originate from free sterols, steryl esters and acylated steryl glycosides, so that we could never clearly say the relation between these and the sense of taste in the ripened tomato fruits. For one reason or another, we should make a more detailed study on the substances closely related with sterols. However, these would play an important role in a good appetite because these are the chemical components of lipids in the ripened tomato fruits.

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