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https://doi.org/10.5109/24126

出版情報：九州大学大学院農学研究院紀要. 41 (1/2), pp.29-33, 1996-11. Kyushu University
バージョン：
権利関係：

J. Fac. Agr., Kyushu Univ., **40**(1・2), 29-33 (1996)

Organic Acid Profiles in the Juice of Fig Fruits

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(Received July 31, 1996)

To elucidate the organic acid composition and content of fig (*Ficus* carica L.), a gas chromatography was performed for juices of 20 fig varieties. Acetic, butyric, oxalic, malonic, succinic, fumaric, malic and citric acids were consistently detected throughout fruit growth. Citric acid was predominant , followed by malic acid. Propionic and lactic acids werenot detected. Glyoxylic and tartaric acids were detected only in some varieties and in certain stages of fruit growth. Furthermore, a relationship between the titratable acidity and the organic acid composition was discussed.

INTRODUCTION

Literature of fig (*Ficus carica* L.) has been voluminously documented since a long time ago (Condit and Enderud,1956), and almost all well-known fig varieties have been well described (Condit,1955). However, information on organic acids in fig fruits is extremely limited. The presence of citric, acetic, and 'a small quantity' of malic acids has been reported in 'Calimyrna' figs (Nelson,1928). Information on organic acids in fruit products is needed at least for three reasons. First, acidity is sometimes expressed as the quantity of one acid assumed to be the only acid present (citric or malic acids). In this respect, differences in expressing the acidity of fig juice are noticed (Hirai, et *al.*,1964). Second, the level of acid contributes markedly to the flavor of fruits. Differences in the flavor of fruit products are common due in part to differences in sugar and acid content ratios. Third, the level of acidity should apparently be considered in fig breeding programs, as already been suggested in citrus (Cameron and Soost, 1974; Soost and Cameron, 1961) and apple (Nybon, 1959).

The present paper concerns organic acids in the juice of figs at fruit maturity as determined by gas chromatography. Furthermore, changes in organic acid concentrations during fruit growth were monitored.

MATERIALS AND METHODS

Fruits of fig varieties examined were sampled from the trees grown in Kyushu University Farm, Fukuoka, Japan, mostly between August to October 1995; fruits of 'Saint John' were sampled on July 21, 1995. Except 'Black Ischia No. 2', 'Negro Largo No. 2', 'Tanikawa', 'Saint John', 'Negronne', 'King', and 'Royal Vineyard' whose available samples were 14, 6, 15, 15, 16, 4, and 2 fruits, respectively, the samples of the other varieties listed in Table 1 were of 20 fruits. Ten fruits of 'Brown Turkey' and 'Houraishi' (Table 2) were

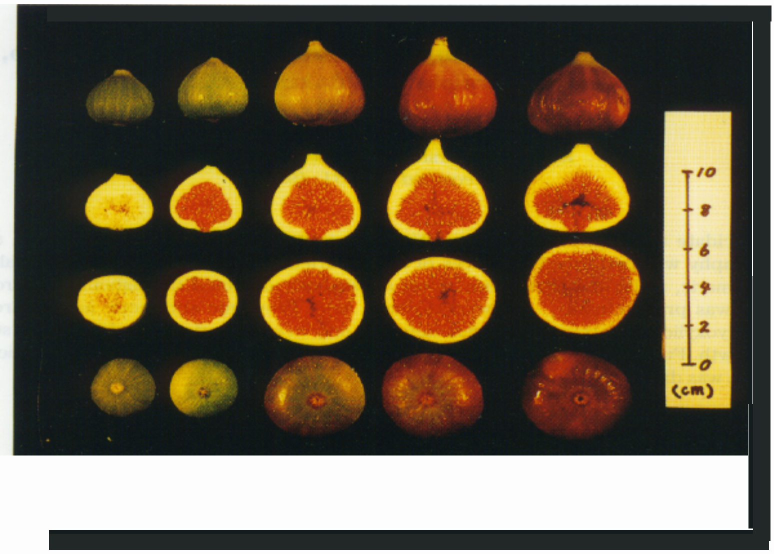

Fig. 1. Fruit-growth stages used on sampling.

Table 1. pH and organic acids[a] in the juice of figs at fruit maturity.

Varieties	pH	Acet	Buty	Oxal	Malo	Succ	Fuma	Glyo[b]	Mali	Tart[b]	Citr	Oxal	Mali +Citr
		(---------------				µmeg⁻¹FW				--------------)	(----	%[c]	----)
Black Ischia No. 2	5.19	0.39	0.13	0.97	0.28	0.26	0.10	-	5.25	-	11.44	5.15	88.73
White Ischia	4.93	0.11	0.08	0.09	0.18	0.10	0.07	-	4.29	-	8.03	0.65	95.22
Juatena	5.67	0.24	0.10	0.06	0.26	0.17	0.25	-	3.26	-	5.69	0.56	89.27
Brunswick	5.41	0.09	0.10	2.56	0.25	0.18	0.12	-	3.10	0.04	5.58	21.25	72.20
Masui Dauphine	5.30	0.19	0.13	0.86	0.24	0.22	0.19	-	6.38	-	10.18	4.70	90.06
Celeste	4.99	0.11	0.05	0.36	0.12	0.08	0.05	-	2.65	0.05	5.61	3.93	91.12
Nagro Largo No. 1	5.39	0.05	0.02	0.04	0.05	0.05	0.01	-	0.81	-	1.76	1.41	91.97
Nagro Largo No. 2	5.34	0.30	0.30	0.41	0.71	0.46	0.30	-	6.58	-	18.28	1.49	90.93
Tanikawa	5.06	0.55	0.37	2.55	0.31	0.19	0.19	0.17	7.51	-	80.3	12.85	78.18
Saint John	5.57	0.86	0.74	5.31	1.20	0.43	0.67	0.54	7.51	-	12.13	18.07	66.82
Negronne	4.88	0.14	0.08	0.28	0.12	0.15	0.06	-	3.18	-	9.85	1.98	94.10
Choer	5.06	0.06	0.05	0.17	0.07	0.07	0.02	0.14	2.25	-	4.94	2.15	92.61
California Black	5.01	0.61	0.38	2.67	0.90	0.69	0.73	-	17.40	4.23	17.11	5.96	77.18
San Pedro Black	5.50	0.11	0.07	0.40	0.14	0.09	0.09	-	2.91	-	2.96	5.97	86.64
King	5.30	0.41	0.57	0.70	0.28	0.16	0.23	-	9.05	-	13.08	2.87	90.41
Violet Sepor No. 1	5.14	0.97	0.93	6.88	0.70	0.39	0.68	-	7.85	0.11	30.81	13.94	78.39
Violet Sepor No. 2	4.97	0.05	0.02	0.14	0.07	0.05	0.05	-	1.27	-	3.41	2.82	92.50
Royal Vineyard	5.46	0.17	0.53	1.77	1.44	0.84	1.19	-	6.86	10.38	20.89	4.01	62.97

[a]In the order of acetic, butyric, oxalic, malonic, succinic, fumaric, glyoxylic, malic, tartaric, and citric acids; [b]Dash, undetected; [c]Per cent of total organic acid detected.

Table 2. Organic acid contents and pH in the juice of ‘Brown Turkey’ and ‘Houraishi’ at different fruit-growth stages”.

Organic acids[b] and pH	Brown Turkey (µme g $^{-1}$FW)					Houraishi (pme g $^{-1}$FW)				
	I	II	III	IV	V	I	II	III	IV	V
Acetic acid	0.28	0.41	0.32	0.33	0.12	0.50	0.67	0.42	0.32	0.09
Butyric acid	0.78	0.98	0.38	0.38	0.08	0.78	0.76	0.41	0.39	0.08
Oxalic acid	6.60	2.78	0.58	3.21	0.32	4.11	3.32	1.94	2.29	0.36
Malonic acid	1.15	2.66	0.38	0.32	0.16	0.81	0.69	0.30	0.30	0.12
Succinic acid	0.24	1.63	0.58	0.51	0.23	0.20	0.26	0.27	0.30	0.11
Fumaric acid	0.40	1.25	0.26	0.29	0.10	0.46	0.41	0.38	0.10	0.04
Glyoxylic acid	2.39					2.71			1.09	
Malic acid	24.20	11.73	12.92	11.08	3.58	21.80	14.73	15.14	11.65	2.11
Tartaric acid								0.56	0.02	
Citric acid	41.26	97.16	37.46	27.46	8.61	35.44	117.80	64.00	56.07	12.12
Total	77.30	118.60	52.87	43.56	13.19	66.79	138.64	83.41	72.53	15.04
pH	4.90	4.33	4.79	4.96	4.95	4.93	4.15	4.05	4.27	4.46
Oxalic acid (%)[c]	8.54	2.35	1.11	7.37	2.42	6.15	2.40	2.32	3.16	2.38
Malic acid (%)	31.31	9.89	24.44	25.44	27.13	32.64	10.63	18.15	16.07	14.02
Citlic acid (%)	53.38	81.92	70.86	63.03	65.26	53.06	84.97	76.73	77.31	80.59
Others (%)	6.77	5.85	3.60	4.16	5.19	8.15	2.01	2.79	3.47	3.00

“See Fig. 1; [b]Dash, undetected; [c]Per cent of total organic acid detected.

sampled at the I-IV stages of fruit growth, but 20 fruits were sampled at the V stage. The fruit-growth stages were determined arbitrarily based on the development of fresh and/or skin colors as shown in Fig. 1. At each sampling date, the fruits were peeled, and the samples were frozen until sampling was completed. About 100g of the sample was weighed, homogenized with added deionized-water, and centrifuged (2,500 rpm for 10 min). The supernatant was brought to a 200 ml volumetric flask by adding water and the centrifugation was repeated three times.

Sample and standard preparations for gas chromatography, gas chromatographic determination of organic acids, including the calculation of organic acid concentrations, followed the method described previously (Widodo, et *al.*,1995). Twelve organic acids (in the order of elution on the chromatogram : acetic, propionic, butyric, lactic, oxalic, malonic, succinic, fumaric, glyoxylic, malic, tartaric, and citric acids) were used as standards. The sample (10 μl) was injected at an initial temperature of 55˚C, let it run for 5 min, then programmed for 4°C min^{-1}, up to a final temperature of 230°C.

RESULTS AND DISCUSSION

Of twelve organic acid standards used, eight organic acids (acetic, butyric, oxalic, malonic, succinic, fumaric, malic, and citric acids) were consistently detected in the juice of all fig varieties investigated (Tables 1 and 2). Propionic and lactic acids were not detected. Glyoxylic and tartaric acids were detected only in some varieties, and they were detected only in certain stages of fruit growth (Table 2). The appearance and disappearance of tartaric acid in balance with malic acid in certain seasons of grape fruit growth (Ranson,1965) and an oxidation of glyoxylic acid by glycolate oxidase and oxygen to produce oxalic acid (Seip, et *al.*,1993) have been suggested which may result in the disappearance of tartaric and glyoxylic acids. By calculating the data of Eheart and Mason (1967) and Widdowson and McCance(1935), immature and mature fig fruits (unspecified varieties) contained 55.0 and 4.7 μ me citrate g^{-1} FW by a titration with NaOH, respectively, which fall within our results. Using the method of lead precipitation, Nelson (1928) reported 4.50 μ me acetate g^{-1} FW and 49.97 μ me citrate g^{-1} FW in 'Adriatic' figs, and 4.33 μ me acetate g^{-1} FW, 54.69 μ me citrate g^{-1} FW and 'a small quantity' of malate in normal 'Calimyrna' figs, which are higher than our data. Differences in varieties, methods, environmental and cultural conditions should, however, be considered in making such comparisons.

The results in this present study show that citric acid is the commonly predominant organic acid found in fig juice, which is in agreement with the present pattern of organic acid accumulation in fig (Ulrich, 1970). Therefore, the level of acidity, or better titratable acidity, of fig fruits should be expressed as citric acid, not as malic acid (Hirai, *et al.,* 1964).

Except for 'Violet Sepor No. 1' and 'Saint John' (Table 1), oxalic acid concentration in fig juice at fruit maturity was significantly lower than that in the flavedo of Japanese acid citrus (3.00-5.90 μ me g^{-1} FW) (Widodo, *et al.,* 1995). Tables 1 and 2 show that the sum of malic and citric acids r&presents mostly more than 80% of the total organic acid detected. However, one cannot assume that the acidity of fig juice is largely of free acidity. With a pH of 4 or even more, which is common in fig juice (Table 1 and 2), a significant portion of organic acids in combined forms as their salts should apparently exist. Significant differences among fig varieties with respect to fruit K, Ca and Mg contents have been reported (Aksoy and Akyuz,1993) which may reflect in differences in the level of combined acids among fig varieties. Unfortunately, the content of combined acid (as a difference between total and free acidities) in fig juice has not yet been reported to be used as a reference for deciding whether or not determining the content of combined acid with a titration is necessary. High portions of oxalic acid in the juice of 'Brunswick' (21.25%), 'Tanikawa' (12.85%), 'Saint John' (18.07%) and 'Violet Sepor No. 1' (13.94%) (Table 1) suggest, however, that not only free acidity, but also combined acid should seemingly be determined in expressing the level of acidity of fig juice.

Changes in organic acid concentrations during fruit growth are shown in Table 2. Malic and citric acids, both as concentration and percent of total detected organic acid, predominated up to maturity. These results confirm those presented in Table 1. Therefore, changes in organic acid in fig juice seem to be affected greatly by changes in both acids. Table 2 shows that there was an initial rise in the acidity on the second sampling of both 'Brown Turkey' and 'Houraishi', followed by a declining acidity up to maturity. An initial rise of acidity has been reported in developing fig cv. 'Rampelina', apple, grape, peach, and mango, but not in banana (Barnell, 1940). In this study, this initial increase was clearly due to an increase in critic acid content. The results indicate also that the level of acidity in immature fig fruits might be higher than that in the flavedo of mature fruits of several acid citrus ('Hanayu', 'Daidai' and 'Lisbon' lemon were 25.17, 38.35 and 34.71 μ me g^{-1} FW) (Widodo, et *al.*, 1995).

ACKNOWLEDGEMENT

A technical assistant of Mr. T. Kataoka during extraction and esterification of organic acids is highly appreciated.

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