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Miscellany

Chemical Compositions of Brandies Produced at the Institute Winery of Yamanashi University

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Our Institute has produced wines and brandies of various kinds since 1952. The microbiological and chemical studies on the production of wines have been published, however, no study on the brandy production has ever been reported. Therefore, we analyzed some brandies produced at the Institute Winery in 1962-1966. The chemical

compositions of the brandies are described below.

1. **Brandies used for analyses** The brandies used were classified in accordance with the U.S. standards made by Treasury Department in 1977. In Japan, however, brandy belongs to spirits and there is no further subclassification for brandy.

Classification of brandy	Fruit	Raisin	Fruit	Fruit
Variety of grape	Mixed : Koshu, Delaware, Muscat Bailey A, Black Queen	Unknown : Raisins imported from Greece	Mixed : Koshu, Delaware, Muscat Bailey A, Black Queen, Mills, Kawakami No. 2	Koshu
Year of production	1962	1963	1963	1964
Type of still	Column	Pot	Pot	Pot
Ethanol concentration and volume of the distillate stored in a barrel	51.0% 200 l	45.0% 200 l	45.0% 200 l	45.0% 200 l

* Sapporo Wines Ltd., Katsunuma Winery.

Capacity of a white oak barrel	200 l	200 l	200 l	200 l
Volume of the distillate and year when transferred into 1.8-l glass bottles	107 l 1982	192 l 1982	125 l 1969	93 l 1982
Classification of brandy	Fruit	Fruit	Lees	Fruit
Variety of grape	Delaware (1)	Delaware (2)	Mixed : Koshu, Delaware	Koshu
Year of production	1964	1964	1964	1966
Type of still	Pot	Pot	Column	Pot
Ethanol concentration and volume of the distillate stored in a barrel	45.0% 180 l	50.5% 100 l	45.0% 100 l	50.1% 148 l
Capacity of a white oak barrel	200 l	100 l	200 l	200 l
Volume of the distillate and year when transferred into 1.8-l glass bottles	96 l 1982	64 l 1982	45 l 1982	84 l 1982

2. General analyses General analyses were performed according to the methods, "Methods for Analysis of Musts and Wines"¹⁾ and "Kokuzeichō Shoteibunseki-

hōchūkai."²⁾ Total phenol was determined with the modified automatic analyzer of the flow diagram described by Slinkard and Singleton.³⁾

Samples	Mixed	Raisin	Mixed	Koshu
	1962	1963	1963	1964
Specific gravity	0.954	0.954	0.949	0.957
Ethanol, % by volume	39.2	38.0	41.2	36.8
pH	3.70	3.77	3.91	3.70

Total acid, g/l as acetic acid	1.71	1.03	0.62	1.23
Volatile acids, g/l as acetic acid	1.34	0.86	0.48	0.91
Reducing sugar, g/l as glucose	0.4	0.3	0.4	0.2
Total nitrogen, mg/l	7	15	5	14
Total phenol, mg/l as gallic acid	675	345	405	465
Ash, mg/l	112	32	36	84

Samples	Delaware (1) 1964	Delaware (2) 1964	Lees 1964	Koshu 1966
Specific gravity	0.952	0.952	0.961	0.950
Ethanol, % by volume	39.2	40.3	33.9	40.4
pH	3.64	3.86	3.64	3.67
Total acid, g/l as acetic acid	1.03	0.72	1.54	0.93
Volatile acids, g/l as acetic acid	0.84	0.60	1.34	0.74
Reducing sugar, g/l as glucose	0.4	0.2	0	0.4
Total nitrogen, mg/l	14	12	10	12
Total phenol, mg/l as gallic acid	442	310	435	450
Ash, mg/l	104	60	152	80

3. Gas chromatographic analysis of higher alcohols, acetaldehyde, and ethyl acetate The brandy (2 μ l) was directly injected into a stainless steel column (3mm in diameter and 2m in length) containing 25% PEG 6000 on Shimalite, 60/80 mesh.

The instrument (Shimadzu, Model GC-6A) was operated under the following conditions: injection port, 200°C; flame ionization detector, 200°C; column, linear increase from 70°C to 153°C at 4°C/min; and carrier gas, nitrogen, at 40ml/min.

Samples	Mixed	Raisin	Mixed	Koshu
	1962	1963	1963	1964
Acetaldehyde	28	64	57	23
Ethyl acetate	93	69	49	74
1-Propyl alcohol	13	15	14	12
iso-Butyl alcohol	44	32	22	76
1-Butyl alcohol	trace	trace	trace	0
iso-Amyl alcohol	183	183	106	295
1-Hexyl alcohol	2	2	1	2

Samples	Delaware	Delaware	Lees	Koshu
	(1) 1964	(2) 1964	1964	1966
Acetaldehyde	21	19	20	21
Ethyl acetate	49	43	59	53
1-Propyl alcohol	16	17	16	11
iso-Butyl alcohol	32	38	67	61
1-Butyl alcohol	trace	trace	trace	trace
iso-Amyl alcohol	70	64	155	286
1-Hexyl alcohol	trace	1	2	2

4. Analysis of glucose and fructose by HPLC Glucose and fructose were analyzed with bicinchoninic acid according to the methods described by Sinner and Puls.⁴⁾ The instruments used were Shimadzu pump units, Model LC-4A and Model LC-3A, and a Shimadzu spectrophotometer, Model SPD-1. The sample (10 μ l) was applied to a column of Shimadzu gel SCR-101 N (0.7mm in diameter and 30cm in

length). The sugars were eluted with water at a flow rate of 0.8ml/min and the column temperature was kept at 55°C. The column effluent (0.8ml) was mixed with the bicinchoninic acid reagent⁴⁾ (0.5ml) : a mixture of 13ml of a solution containing CuSO₄·5H₂O (0.34g), 30ml of a solution containing aspartic acid (1.23g) and anhydrous sodium carbonate (1.7g), 1,000ml of a solution containing 2,2'-bicinchoninic acid, disodium salt

(1.5g) and anhydrous sodium carbonate (72 g), and 157 ml of water. The reaction of the sugars with the bicinchoninic acid was carried out in a stainless steel tube (0.3 mm in diameter and 15 m in length) placed in an oven kept at 100°C. The reaction time was about 49 sec. The absorbance at 560 nm was measured after the reaction mixture had been cooled by introducing into a stainless steel tube (0.3 mm in diameter and 2 m in length) placed in running tap water.

5. Analysis of simple phenolic compounds by HPLC Simple phenolic compounds were analyzed according to the methods described previously.⁵⁾ Each brandy (20 ml) was adjusted to pH 1.0 with dilute HCl. The brandy was extracted twice with an equal volume of ether. The ether layer was evaporated to dryness. The residue was dissolved in 4 ml of 2 N HCl, transferred into a glass test tube with a glass stopper, and heated at 100°C for 1 h with a Taiyo dry thermobath (Model TA-2H).

Samples	Mixed varieties 1962	Raisin 1963	Mixed 1963	Koshu 1964
	(mg/l)			
Glucose	185	181	179	62
Fructose	168	164	161	58

Samples	Delaware (1) 1964	Delaware (2) 1964	Lees 1964	Koshu 1966
	(mg/l)			
Glucose	180	trace	trace	182
Fructose	170	154	trace	168

Samples	Mixed 1962	Raisin 1963	Mixed 1963	Koshu 1964
	(mg/l)			
Gallic acid	7.4	3.9	7.4	9.6
Protocatechuic acid	33.1	0	5.5	0
Caffeic acid	6.7	9.6	0	6.3
p-Coumaric acid	7.8	12.3	0	7.2

Samples	Delaware (1) 1964	Delaware (2) 1964	Lees 1964	Koshu 1966
			(mg/l)	
Gallic acid	4.1	2.8	3.9	6.2
Protocatechuic acid	0	0	5.5	0
Caffeic acid	5.6	10.9	23.5	5.6
p-Coumaric acid	3.4	10.7	15.7	4.4

After cooling, the sample solution was extracted twice with 2 ml of ether. The combined ether layers were evaporated to dryness. The residue obtained was dissolved in aqueous methanol and this solution was used for analysis.

6. Atomic absorption analysis of cations A 25 ml of each brandy was poured into a 50-ml porcelain crucible, evaporated to dryness first on a water bath, then in an oven at 100°C. The crucible with the residue was placed in a muffle furnace (Yamato, Model FM-35) kept at 525°C. After 1 h,

the crucible was removed from the furnace, and water (10 ml) was added into it. The solution was evaporated and heated in the furnace. The ash obtained was dissolved in 10 ml of 6 N HCl and the solution was evaporated on a water bath. The residue was dissolved in 10 ml of 6 N HCl and evaporated to dryness. The residue was dissolved again in an appropriate volume of 6 N HCl. The concentrations of the cations in this solution were determined with a Hitachi atomic absorption spectrophotometer (Model 170-30).

Samples	Mixed 1962	Raisin 1963	Mixed 1963	Koshu 1964
			(mg/l)	
Potassium	87	50	24	45
Sodium	40	42	10	21
Calcium	2	2	3	1
Magnesium	4	3	4	3
Iron	1	0.8	1	2
Copper	0.2	0	0.1	0

Samples	Delaware	Delaware	Lees	Koshu
	(1)	(2)		
	1964	1964	1964	1966
	(mg/l)			
Potassium	43	35	86	44
Sodium	33	8	36	9
Calcium	4	2	6	2
Magnesium	6	3	6	3
Iron	0.7	0.5	0.6	1.6
Copper	0.3	0.2	0.3	0.7

7. Amino acid analysis Each brandy (100ml) was evaporated to dryness and the residue was dissolved in 1ml of water. The sample was filtered through a mem-

brane filter (Gelman, Alpha-45): The filtrate was analyzed according to the method described previously.⁶⁾

Samples	Mixed	Raisin	Mixed	Koshu
	1962	1963	1963	1964
	(mg/l)			
Aspartic acid	0.013	0.040	0.019	0.063
Threonine	trace	0.005	0.011	0.007
Serine	trace	0.023	0.020	0.019
Glutamic acid	trace	0.010	trace	0.013
Proline	1.125	0.033	0.014	0
Glycine	0	0.016	0.012	0.025
Alanine	0.036	0.056	0.039	0.045
Isoleucine	0	0.005	0.006	trace
Leucine	0	0.010	0.012	0.005
Tyrosine	0	trace	0	0
Lysine	0	0	0	0

Samples	Delaware	Delaware	Lees	Koshu
	(1)	(2)		
	1964	1964	1964	1966
	(mg/l)			
Aspartic acid	0.015	0.017	0.020	0.010
Threonine	0.005	trace	0.008	0.003
Serine	0.017	trace	0.023	0.008
Glutamic acid	0.007	0	0	trace
Proline	0.315	0.012	0	0
Glycine	0.011	0.020	0.016	0.004
Alanine	0.061	0	0.108	0.020
Isoleucine	0.006	trace	0.007	0.020
Leucine	0.012	trace	0.012	0
Tyrosine	0.007	0	0	0
Lysine	0.002	0	0	0

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