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Chemical and Spectral Characterization of Color and Phenolic Compounds Including Anthocyanins in Red Table Wines Made from Grapes Grown in Thailand

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Nineteen red wines were made from grapes of 11 varieties grown in a vineyard in Bangkok,Thailand, and various components concerning color and pigments in the red wines were analyzed. Total phenol, flavonoid, and non-flavonoid phenol were, respectively, between 479 and 4,950mg/l with an average of 1,723 mg/l; between 418 and 4,385mg/l with an average of 1,273mg/l; and between 155 and 1,775 mg/l with an average of 453mg/l. Caftaric and coutaric acid contents were, respectively, between 4 and 129mg/l with an average of 41mg/l, and between a trace to 56mg/l with an average of 16mg/l. The absorbance of the wines at 520 nm was between 0.55 and 9.80 with an average of 2.92, and the wine color at pH<1 was between 1.37 and 28.15 with an average of 8.93. The percentage of absorbance at 520 nm for the contribution of polymeric pigments to the wine color was found to vary from 12 to 89%, and tended to increase with an increase in the age of the wine of the same grape variety, and non-colored anthocyanins constituted the greater part of the total anthocyanins. However the age at which each wine reached a peak with respect to quality varied with variety.

Of the 19 red wines made, 15 were considered young based on the "chemical index" of the ratio of polymeric pigment color to wine color in acid and used for statistical analysis among the parameters of color and pigments. There was an apparent relation between wine color and color density, and between wine color (color density) and polymeric pigment color, anthocyanin color,and ionized anthocyanins. Also there were considerable or significant correlations between the sum of major cations becoming bivalent ions present in the wines and the wine color, color density, polymeric pigment color, anthocyanin color, and ionized anthocyanins; and between non-flavonoid phenol and wine color and color density.

The weather conditions in Thailand (tropical) are very different from those in the good quality wine grape-growing areas (cool to moderately cool and dry) of the world. The average annual air temperature, relative humidity, and rainfall in 1981 to 1990 in Bangkok were 28.4℃, 73%, and 1,442 mm (1,2), respectively. Thus Thailand is faced with climatic problems in the production of good quality grapes and wine.

High humidity and high air temperature generally result in the production of grapes of low acidity (3–12), high pH, low sugar(12–14), and low aroma substances (14–17) owing to the destruction of organic acids by active respiration at high temperature, or to a dilution of the juice in the grapes through water absorption, or perhaps to the infection of vines by viruses present in conditions of high humidity. In order to establish a vinification method of producing good quality wines from such grapes, special winemaking practices are required. For example, grape acids such as tartaric or malicacid and/or sugar are added to Thai grape must in order to adjust the acidity and degree Brix (°Brix) to proper concentrations before fermentation. On the other hand, generally, the grape must is never ameliorated with phenolic or color substances because this is legally prohibited. Therefore, the quality of red wines, especially with respect to astringency, bitterness, and color, directly and truly reflects the composition of the phenolic compounds including anthocyanin pigments, of the grapes used. As far as we know, there have been few reports on the color and pigments of wines made from grapes grown in Thailand.

One of the most clearly demonstrated effects of climate on the composition of grapes is that of temperature on berry color, as described by Singleton and Esau (15). They also showed that under a climate warm enough to mature grapes satisfactorily, the cooler the region or season the more anthocyanin pigment is produced in the grape skin. Singleton (18) found that the tannin content of skins increases during ripening at about the same rate as the color does. Also, from the average data on red wines of five *Vitis vinifera* varieties, Amerine and Winkler (19,20) suggested that a very cool region in California was too cool for maximum color or tannin development in the grape varieties, whereas a warm or very warm region might be too warm. They thus concluded that climate seemed clearly important for color and tannin.

Winkler and Amerine (21) and Amerine et al. (22) showed the necessity of applying the C.I.E. (Commission Internationale de l'Eclairage) tristimulus method to define wine color. The Office Internationale de la Vigne et du Vin also chose the tristimulus method in order to standardize wine color (23). However, the tristimulus values give no information about the composition of wine color.

Sudraud (24) determined the absorption spectra of wines, and found that the sum (color density) and ratio (hue) of absorbancies at 420 and 520 nm in a series of aged wines from the same sources gave direct and useful information on wine age. He found age to be related to the ratio of absorbancies at 420 and 520 nm, with young wines having a ratio of about 0.7 and a wine more than 50 years old having a ratio of 1.7; however, this also gives little information on the composition of wine color.

Somers and Evans (25,26) and Jackson et al. (27) studied correlations among various color parameters in young wines of the same variety and the same region. The former (25) showed that there was a significant correlation between color densities and the degree of ionization of anthocyanins in 32 current vintages of two varieties in 1972, but no relation between color density and anthocyanin content. They proposed two spectral indices of "chemical age", derived from the increase in polymeric pigments with aging, in order to observe aging changes in the composition of wine color. The two indices show the ratio of polymeric pigments to total anthocyanins measured at the wine pH, and the ratio of polymeric pigments to total anthocyanins at $pH<1.0$. Their young wines aged about 8 months had ratios of 0.1–0.5 for the former index, and 0.02–0.2 for the latter. A progressive increase in each ratio during aging is expected. Jackson et al. (27) found that there were linear correlations between overall quality and various color parameters and among several parameters in 15 young Beaujolais red wines from the 1974 and 1975 vintages. However, these analyses were conducted in the range of young red wines of the same variety, produced in a small region and in the same year.

During the spectral studies of Thai red wines, it was found that there were significant correlations with various parameters of color and pigments among young and aged wines of different vintages made from different grape varieties. This paper aims to characterize Thai red table wines on the basis of chemical and spectral analyses of color and phenolic compounds, including anthocyanins, and to elucidate the correlations in the parameters of color and pigment among 19 red table wines made from grapes of 11 varieties harvested for 5 years from 1986 to 1990 in Thailand.

MATERIALS AND METHODS

Grapes Eleven Thai grapes, Muscat Hamburg, PP, Troia, Exotic, Cardinal, Black Queen, Ruby Seedless, Beauty Seedless, Kyoho, Pinot noir, and Pinot munier were obtained from a vineyard of the Kampangsan Campus, Kasetsart University, Thailand. In addition, White Malaga, Cardinal, Muscat Hamburg, and Black Queen grapes grown in the Bangkok area were purchased from a fruit market in Bangkok in March, 1990. All the Thai grapes other than two varieties, Black Queen (Bailey X Golden Queen) and Kyoho (Ishihara Wase X Centennial), are *Vitis vinifera*.

Vinification Vinification was carried out at the Institute of Enology and Viticulture, Yamanashi University, Kofu (4 wines) and the Institute of Food Research and Product Development, Kasetsart University, Bangkok (11 wines).

The grapes (5 to 20kg for each wine made) were destemmed and crushed on a wire net by hand.

Potassium metabisulfite was added to the must obtained to give a concentration of 150mg (as SO_2) / *l*. Sugar was added to give a concentration of 23°Brix. Tartaric acid was added so that the final total acidity of the must would be about 0.55 to 0.60%.

The must (6 to 13 *l*) was inoculated with *Saccharomyces cerevisiae* W3 (28) in Yamanashi University and with an active dry yeast (Lalvin Kl (V−1116), *S. cerevisiae*) in Kasetsart University. Fermentation was carried out in 10− or 20−*l* plastic tanks at 15℃ in Yamanashi University, and between 20 and 22 ℃ in Kasetsart University. When the Brix in the must dropped to about two−thirds of the original Brix, the fermening must was pressed with a small, hand−operated basket press made of oak wood at Yamanashi University. At Kasetsart University, it was pressed with the flat of the hand on a wire net. The fermentation was then allowed to proceed to completion. After fermentation, the wines were settled for 4 weeks, and then racked, filtered through membrane filters (0.45 μm), and stored in 1.8−*l* glass bottles at 15℃ until just before analysis.

For the analysis of each wine, two bottles were used; the values given are the averages of the two bottles. There were no significant differences in each analytical value between the two bottles. All analysis was conducted in Yamanashi University in March to June,1992.

General and phenolic analyses The general composition was analyzed according to the methods described in "Methods for Analysis of Musts and Wines" (29).

The total phenol content was determined according to the method of Slinkard and Singleton (30). The flavonoid and nonflavonoid phenols were determined by the method of Kramling and Singleton (31). (*Trans*)-Caftaric acid, coutaric acid, (+)−catechin, and(−)−epicatechin were determined by the methods described in our previous papers (32,33).

Acetaldehyde was analyzed by gas chromatography (34).

Individual cations in ash (30) were determined by atomic absorption spectrophotometry with a Hitachi atomic absorption spectrophotometer (type 170−30).

Optical density measurement at wine pH Color hue and color density were analyzed according to the method of Sudraud (24). Red wine was filtered through a 0.45–μm membrane filter and diluted 20–fold with water whose pH had been adjusted to the same value as that of the wine. The absorbances at 520 nm (*wine color*:WC) and 420 nm were determined at wine pH using 10–mm light path cells. The ratio of the absorbances at 420 to 520 nm and the sum of the absorbances show *color hue* (CH) and *color density* (CD), respectively.

Spectral analysis of red wines was carried out according to the methods of Somers and Evans(25,26). Anthocyanins are immediately decolorized by excess SO_2 (final concentration of about 2,000mg/*l*) at wine pH. 20% sodium metabisulphite prepared freshly daily (150 μl) was added to 1.25 ml of a 20–fold diluted wine and the absorbance at 520 nm was measured after about 1 min. The residual color after such treatment of the red wine is the SO_2–resistant *polymeric pigment color at wine pH* (PPC). The difference between this PPC and the original absorbance at 520 nm of wine at wine pH(WC) is the *anthocyanin color* (AC) (AC=WC–PPC).

Optical density measurement at pH<1.0 A wine sample was diluted 20-fold with 1N HCl and the absorbance was measured after 4h (*wine color at pH<1.0*:WCA). According to the results of Somers, *polymeric pigment color at pH<1.0* (PCA) was calculated by multiplying the PPC by 5/3(35).

Anthocyanin color in acid (ACA) is obtained from ACA=WCA–5PPC/3. *Non-colored anthocyanins* (NA) are calculated from NA=ACA–AC.

Total anthocyanins, ionized anthocyanins, and degree of ionization Total anthocyanins (mg/*l*, TA) were determined from the estimate of ACA. The *degree of ionization of anthocyanins* (α;%) is the percentage ratio of AC to ACA. *Ionized anthocyanins* (mg/*l*) is $\alpha \times$ TA/100.

Chemical age index As red wine ages, polymeric pigments increase and anthocyanins decrease. Based on the increase in polymeric pigments with increasing age, the "*chemical age index*" (PPC/WCA), proposed by Somers and Evans (26), was calculated.

For investigation of the correlations among parameters concerning color, pigments, etc. in the red wines made from various grape varieties in different years, correlation figures were drawn between various pairs of variables.

RESULTS AND DISCUSSION

Contents of alcohol, acetaldehyde, cations and SO_2, and pH The extent to which phenolic compounds including anthocyanins are extracted into juice and wine, the composition of the phenolic compounds, and the color of

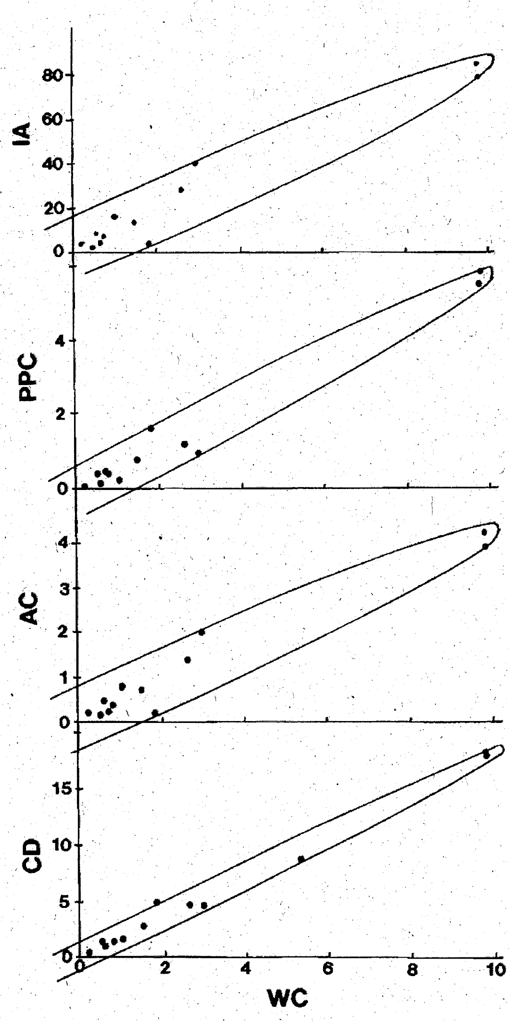

FIG.1. Relation between wine color (WC) and color density (CD), anthocyanin color (AC) polymeric pigment color (PPC), and ionized anthocyanins.

TABLE 1. Contents of alcohol, acetaldehyde, SO_2 and cations, and pH of the red wines made from Thai grapes.

Variety	Year/ month made	Alchohol (vol.%)	pH	CH_3CHO	Total SO_2 (mg/l)	Free SO_2
Muscat Hamburg	'86/12	11.2	3.64	355	74	2
	90/2	10.9	3.77	509	301	8
	90/3[a]	11.8	3.55	19	28	6
PP	87/1	10.6	3.52	1245	104	3
	88/1	10.3	3.54	962	106	4
Troia	88/2	11.2	3.45	1562	81	1
Exotic	88/2	9.2	3.80	309	176	4
	90/3[a]	12.7	3.55	3	34	10
Cardinal	87/8	10.1	3.44	217	36	1
	90/2	10.9	3.63	812	79	0
	90/3[a]	10.4	3.72	26	20	3
Black Queen	90/2	10.9	3.65	1081	27	0
	90/3[a]	13.6	3.97	207	28	1
Ruby Seedless	89/4	12.0	3.94	83	15	1
Beauty Seedless	89/5	11.2	3.91	39	171	3
Kyoho	88/5	11.1	3.42	150	52	1
	89/5	10.9	3.41	1028	68	2
Pinot noir	89/8	11.3	3.77	162	25	1
Pinot munier	89/8	10.0	3.74	162	82	2
Average		11.07	3.65	470	79	3

[a] These 4 wines were made in Yamanashi University; the other 15 wines were made in Kasetsart University.

red wines were influenced by the contents of the alcohol and acetaldehyde produced during fermentation and the SO_2 added before and after fermentation, the species and level of metal ions (such as Fe, Mg, etc.) present, and the pH, as well as the grape variety, growing region and season, the degree of maturity, and the conditions for juice preparation and wine processing. Therefore, alcohol, acetaldehyde, cations and SO_2 were analyzed.

As shown in Table 1, the alcohol content in the 19 Thai red wines ranged from 9.2 to 12.7%. The pH was between 3.41 and 3.97 with an average of 3.65. The acetaldehyde content varied between 3 and 1,562mg/l (average, 470 mg/l), and was generally much higher in the wines made in Thailand than the wines in Japan, perhaps because of higher fermentation temperature and aeration. The total SO_2 content was between 15 and 301mg/l with an average of 79mg/l, whereas the free SO_2 content was very low.

There are interaction equilibria between potassium bitartrate and "complexing factors" such as sulfates, proteins, gums, polyphenols, etc. For example, potassium and tartaric acid (tartrate) are often bound with pigments to form complexes in red wines (36) and with sulfate to form K_2SO_4 and KSO_4^- in white and red wines (37). Table 2 shows the cation contents of the Thai wines. The ranges of potassium and sodium ions were between 463 and 1,293mg/l

TABLE 2. Contents of ash and cations of red wines made from Thai grapes.

Variety	Year/ month made	K	Na	Ca	Mg	Fe	Zn	Cu	Total	Ca+Mg +Fe+ Zn+Cu	Ash	K/ Na
		(mg/l)										
Muscat Hamburg	'86/12	891	210	10	34	13	3	t	1161	60	2230	4.2
	90/2	1021	349	6	32	1	3	t	1412	42	2100	2.9
	90/3[a]	955	198	7	31	12	3	1	1207	54	3600	4.8
PP	87/1	931	315	11	70	10	4	1	1342	96	3290	3.0
	88/1	1021	171	13	70	4	4	1	1284	92	3200	6.0
Troia	88/2	830	316	18	39	12	3	3	1221	75	2300	2.6
Exotic	88/2	690	189	17	39	19	3	6	963	84	1790	3.7
	90/3[a]	765	99	6	25	7	3	t	905	41	2720	7.7
Cardinal	87/8	617	256	5	34	11	3	t	926	53	2540	2.4
	90/2	530	142	9	34	4	3	t	722	50	2140	3.7
	90/3[a]	995	205	4	39	15	3	1	1262	62	3420	4.9
Black Queen	90/2	495	99	6	32	2	3	5	642	48	1840	5.0
	90/3[a]	1293	144	4	34	10	3	1	1489	52	3300	9.0
Ruby Seedless	89/4	746	282	7	34	6	3	3	1081	53	3320	2.6
Beauty Seedless	89/5	830	140	11	34	5	3	3	1026	56	3780	5.9
Kyoho	88/5	463	92	12	29	2	3	t	601	46	2200	5.0
	89/5	505	132	15	31	1	3	t	687	50	2380	3.8
Pinot noir	89/8	746	267	10	27	23	3	t	1076	63	3440	2.8
Pinot munier	89/8	880	370	9	31	11	3	1	1305	55	3540	2.4
Average		800	209	9	37	9	3	1	1069	62	2796	4.3

[a] These 4 wines were made in Yamanashi University; the other 15 wines were made in Kasetsart University.

with an average value of 800mg/l, and between 92 and 370mg/l with an average of 209mg/l, respectively. The ranges of the potassium values are close to those reported for the table wines of several other countries, while the sodium ranges are about twice those values(38–41). The overall range for calcium was 4–18mg/l; the average value being 9 mg/l, which is lower than that reported for California red table wines. The range for magnesium in this study was 29–70mg/l with an average value of 37mg/l; these values are lower than those reported for California wines. For iron, a range of 1–19 mg/l, with an average value of 9mg/l, was found in this study; these values are at the same level as those reported for California red wines. The most notable differences in cations between the red table wines in this study and California wines are in the sodium content and the K/Na ratios. The ratios for the wines in this study were between 2.4 and 9.0 with an average value of 4.3, while those for California wines range from 3.6 to 109.9 (40), and from 1 to 328 with an average of 28 (38). Although the final metal content of wine is affected by many variables, including soil minerals, fertilization rates and type, soil type, climatic conditions, grape variety, harvesting practices and processing conditions, the higher amount of sodium and higher ratio of K/Na in this study seemed to be due to the grapes being grown under frequent irrigation with water of high

TABLE 3. Composition of phenolic compounds of red wines made from Thai grapes.

Variety	Year/month made	Total phenol (mg/*l*, GAE)[a]	Flavonoid (mg/*l*, GAE)[a]	Non-Flavonoid (mg/*l*, GAE)[a]	Caftaric acid (mg/*l*)	Coutaric acid (mg/*l*)	Catechin (mg/*l*)	Epicatechin (mg/*l*)
Wine								
Muscat Hamburg	'86/12	665	960	705	26	10	6	1
	90/2	2140	1845	295	120	27	28	39
	90/3[b]	1156	1001	155	6	6	trace	44
PP	87/1	2485	730	1775	7	56	7	54
	88/1	2424	813	1611	12	35	16	trace
Troia	88/2	1473	1128	345	11	8	60	37
Exotic	88/2	848	506	342	6	2	26	10
	90/3[b]	479	332	147	6	5	97	7
Cardinal	87/8	885	630	255	12	10	41	45
	90/2	1672	1514	158	4	trace	11	73
	90/3[b]	836	618	218	12	3	16	24
Black Queen	90/2	1066	741	325	67	5	26	12
	90/3[b]	585	418	167	4	trace	27	29
Ruby Seedless	89/4	1645	1055	590	25	9	15	40
Beauty Seedless	89/5	1009	506	503	29	22	4	57
Kyoho	88/5	1360	1105	255	89	32	15	56
	89/5	1427	1149	278	129	4	28	25
Pinot noir	89/8	4950	4745	225	100	38	539[c]	380[c]
Pinot munier	89/8	4640	4385	255	120	42	548[c]	350[c]
Average		1723	1273	453	41	16	25	33
Juice								
Muscat Hamburg	90/3	897	686	211	147	2	0	0
Exotic	90/3	511	323	188	46	1	0	0
Black Queen	90/3	694	393	301	98	3	0	0
Cardinal	90/3	663	329	334	115	3	0	0
Average		691	433	259	102	2	0	0

[a] Gallic acid equivalent.

[b] These 4 wines were made in Yamanashi University; the other 15 wines were made in Kasetsart University.

[c] Omitted when averaged.

sodium content in the Bangkok area. Calcium, magnesium, iron, copper and zinc were detected as major cations other than alkaline cations such as potassium and sodium. The percentage of the 5 cations was between 3.0 and 8.7% of the total. The effects of acetaldehyde, alcohol, SO_2, and metal ions on the color and pigments of the red wines will be discussed later.

General phenolic composition Total phenol, flavonoid, and non-flavonoid phenol of the Thai red wines were, respectively, between 479 and 4,950mg/l with an average of 1,723mg/l; between 418 and 4,385mg/l with an average of 1,273mg/l; and between 155 and 1,775mg/l with an average of 453mg/l. The total phenol, flavonoid, and non-flavonoid phenol contents were lower in the 4 red wines made in Yamanashi University than in the 11 wines produced in Kasetsart University in each of the same four varieties. The higher phenol contents of the wines made in Kasetsart University may be partly due to the different methods used for crushing and pressing the grapes in the two Universities. In making the wines in Kasetsart University, a wire net was used, resulting in the production of musts rich in suspended fine solids. This crushing and pressing method might cause more bruising and injury to grape tissues such as seeds and skins, and fermentation of such a must might then give wines rich in total phenols. There is, however, another reason for the higher phenol content. The Thai grapes seemed to have softer skins than those of grapes harvested in the good quality wine grape-growing areas of the world, and although data cannot be shown, flavonoids would thus be extracted easily and abundantly from the skins into the juice when the grapes were pressed. Wines made from only pulp or free-run juice should have a small amount of flavonoid phenols, but the red wines made here from the Thai grapes had a high flavonoid content. Flavonoids are poor in free-run juice, but rich in press juice, in which a large amount of flavonoids from seeds and skins are extracted. Therefore, it is apparent that the high total phenol and flavonoid contents of the wines in this study were due to extraction from skins and seeds.

Hydroxycinnamates and catechin phenols Caftaric and coutaric acids, catechin, and epicatechin, which are easily oxidized enzymatically and non-enzymatically followed by browning, were determined (Table 3). The caftaric acid content was between 4 and 129 mg/l (average 41mg/l), while the couaric acid content ranged from a trace to 56mg/l (average 16mg/l). The ratios of the coutaric acid to caftaric acid in PP variety were 8.00 in the wine made in February 1990 and 2.92 in March 1992, but those in the other varieties were less than 1. The caftaric acid content in the juices from four varieties, Muscat Hamburg, Exotic, Black Queen, and Cardinal was between 4 and 12mg/l, whereas that in the corresponding red wines was between 46 and 147mg/l. The two hydroxycinnamates comprised 25.0 to 70.6% of non-flavonoid phenol with an average of 41.1% in the 4 juices (Table 3), and 2.4 to 7.7% with an average of 6.1% in the corresponding wines. From this finding, it was evident that the hydroxycinnamates comprised a large part of non-flavonoid phenol in the juices, but most of them were destroyed during vinification.

The average content of total catechin phenols such as catechin and epicatechin in the 9 varieties other than Pinot noir and Pinot munier was 42mg/l. The value was very small compared to the values of flavonoid phenol content. This means that oligomeric or polymeric flavonoids were present in amounts greater than monomeric flavonoids in the wines.

Color and pigments The Thai red wines were poorer in red pigments (Table 4) than red wines made from Gamay grapes in France (27) and Cabernet Sauvignon and Shiraz grapes in Australia (25). The values of WC were between 0.55 and 9.80 with an average of 2.92, while WCA was between 1.37 and 28.15 with an average of 8.93. Although it is difficult to compare these values with the reported values because of different varieties (25,27), the values for WC and WCA of the Thai red wines were lower than those for Australian red wines (25), but similar to those for French

TABLE 4. Color measurements of red wines made from Thai grapes.

Variety	Year/ month made	At Wine pH					at pH<1.0		
		WC[a]	CD[b]	PPC[c]	AC[d]	CH[e]	WCA[f]	ACA[g]	NA[h]
Muscat Hamburg	'86/12	1.83	4.95	1.63	0.20	1.71	19.0	16.79	16.59
	90/2	0.79	1.44	0.39	0.39	0.83	3.21	2.55	2.16
	90/3[i]	0.62	0.99	0.16	0.46	0.61	3.26	3.00	2.54
PP	87/1	9.77	18.47	5.52	4.25	0.89	28.15	18.95	14.70
	88/1	9.80	18.10	5.85	3.95	0.85	22.10	12.90	8.95
Troia	88/2	5.34	8.85	0.65	4.69	0.66	9.60	8.52	13.83
Exotic	88/2	3.91	7.42	3.30	0.61	0.90	4.95	−0.55	−1.16
	90/3[i]	0.57	0.85	0.12	0.45	0.48	3.39	3.19	2.74
Cardinal	87/8	0.55	1.40	0.41	0.14	1.54	2.75	2.07	1.93
	90/2	1.38	2.35	0.82	0.56	0.70	2.10	0.73	0.17
	90/3[i]	0.24	0.36	0.04	0.20	0.50	1.37	1.30	1.10
Black Queen	90/2	4.59	7.65	3.23	1.36	0.67	6.60	1.22	−0.14
	90/3[i]	1.03	1.67	0.22	0.81	0.62	5.98	5.61	4.80
Ruby Seedless	89/4	6.40	11.54	5.82	0.58	0.80	14.30	4.60	4.02
Beauty Seedless	89/5	2.94	4.72	0.94	2.00	0.61	9.93	8.36	6.36
Kyoho	88/5	0.73	1.52	0.49	0.24	1.08	4.70	3.88	3.64
	89/5	0.82	1.64	0.47	0.35	0.99	3.81	3.03	2.68
Pinot noir	89/8	2.61	4.77	1.21	1.40	0.83	13.20	1.19	9.79
Pinot munier	89/8	1.49	2.85	0.79	0.70	0.91	10.80	9.49	8.79
Average		2.92	5.34	1.69	1.23	0.85	8.93	2.86	6.55

[a] Wine color, $WC = A_{520}$
[b] Color density, $CD = A_{520} + A_{420}$
[c] Polymeric pigment color, $PPC = A_{520}(SO_2)$
[d] Anthocyanin color, $AC = WC - PPC$
[e] Color hue, $CH = A_{420}/A_{520}$
[f] Wine color in acid, $WCA = A_{520}(HCl)$
[g] Anthocyanin color in acid, $ACA = WCA - 5PPC/3$
[h] Non-colored anthocyanin, $NA = ACA - AC$
[i] These 4 wines were made in Yamanashi University; the other 15 wines were made in Kasetsart University.

Gamay red wines (25).

Wine color (WC) is an integration of contributions from (monomeric) anthocyanin and polymeric pigment forms. Anthocyanins are immediately decolorized by addition of excess SO_2 to a red wine, while the residual color after such treatment of the wine is due to the polymeric pigment form. At pH <1.0, anthocyanins are entirely in the colored flavylium form, but polymeric pigments are much less affected by lower pH. Because the difference in pH among the 19 Thai wines was not large (Table 1), it did not influence significantly the difference in color among the wines. Also, the concentrations of both total and free SO_2 were not so high as to influence WC.

Somers and Evans (26) proposed a "chemical age index" for the observation of aging changes in the composition of wine color. The index is given by the ratio PPC/WCA. In their paper, the ratio ranged from 0.02 to 0.2 for 6 young wines, while 4 aged wines had ratios of 0.34 to 0.82. On the basis of the "chemical age index" of the 19 red wines (Table 5), the 4 wines made from Exotic in 1988, Cardinal and Black Queen in February 1990, and Ruby Seedless in 1989, the "chemical ages" of which were more than 0.3, were removed and the other 14 wines were used for statistical analysis.

The increase in absorbance at 520 nm on acidification of the 19 wines varied from 1.4 to 10.7 times (average, 4.3)(Table 4). The degree of ionization (α) varied from 1.2 to 26.7% (Table 5). These values were within the ranges reported by Somers and Evans (25,26) and Jackson et al. (27), except for Muscat Hamburg wine in 1986. Statistical analysis (Fig.1) shows that there was an apparent relation between WC and CD, and also between WC (or CD) and PPC, AC, and IA.

The percentage of absorbance at 520 nm for the contribution of PPC to WC (PPC/WC x 100%) was found to vary from 12 to 89%. Although the percentage tended to increase with an increase in the age of wine of the same grape variety from 1.5 to 5.4 years after production, there was no apparent correlation between wine age and the percentage of absorbance among the 14 wines. This means that the age at which each red wine reaches its peak of quality varies with variety.

At wine pH (pH<4.0), the main equilibrium form is the red-colored flavylium

TABLE 5. Paramenters of color and pigments of the red wines made from Thai grapes.

Variety	Year/ month made	TA[a] (mg/l)	α[b] (%)	IA[c] (mg/l)	Chemical age PPC/WCA
Muscat	'86/12	336	1.2	4.0	0.08
Hamburg	90/2	51	15.3	7.8	0.12
	90/3[d]	60	15.3	9.2	0.05
PP	87/1	379	22.4	84.9	0.20
	88/1	258	30.6	78.9	0.25
Troia	88/2	17	55.0	9.4	0.07
Exotic	88/2	—	—	—	0.67
	90/3[d]	64	14.1	9.0	0.04
Cardinal	87/8	41	6.8	2.8	0.15
	90/2	15	76.7	11.5	0.39
	90/3[d]	26	15.4	4.0	0.03
Black Queen	90/2	24	111.5	26.8	0.49
	90/3[d]	112	12.6	16.1	0.04
Ruby Seedless	89/4	92	12.6	11.6	0.41
Beauty Seedless	89/5	167	23.9	39.9	0.09
Kyoho	88/5	78	6.2	4.8	0.10
	89/5	61	11.6	7.1	0.12
Pinot noir	89/8	224	12.5	28.0	0.09
Pinot munier	89/8	190	7.4	14.1	0.07

[a] Total anthocyanins, $TA=20\times(WCA-5PPC/3)$

[b] Degree of ionization, $\alpha=AC/ACA\times100$

[c] Ionized anthocyanin, $IA=\alpha\times TA/100$

[d] These 4 wines were made in Yamanashi University; the other 15 wines were made in Kasetsart University.

ion (AC) and its colorless pseudobase (NA). Therefore, at wine pHs greater than 3.0, non-colored anthocyanins (NA=ACA−AC) were much greater than AC. Non-colored anthocyanins constituted the greater part of the total anthocyanins (ACA) and there was a significant and positive correlation between ACA and NA.

Although CH, pH, α, IA, SO_2, total phenol, acetaldehyde, ash, and total cations (Table 2) were not interrelated, there were considerable or significant and positive correlations between the sum of cations becoming bivalent ions (Ca+Mg+Fe+Zn+Cu) (Table 2) and WC, CD, PPC, AC, and IA (Fig. 2), and between non-flavonoid phenols (Table 3) and WC, PPC, and CD (Fig.3). The influence of two parameters such as cations and non-flavonoid phenols on the evaluation of wine color and pigment has not previously been reported.

Thus, there were statistically significant linear corre lations among various parameters of color and pigment in the red wines of 9 grape varieties grown in Thailand.

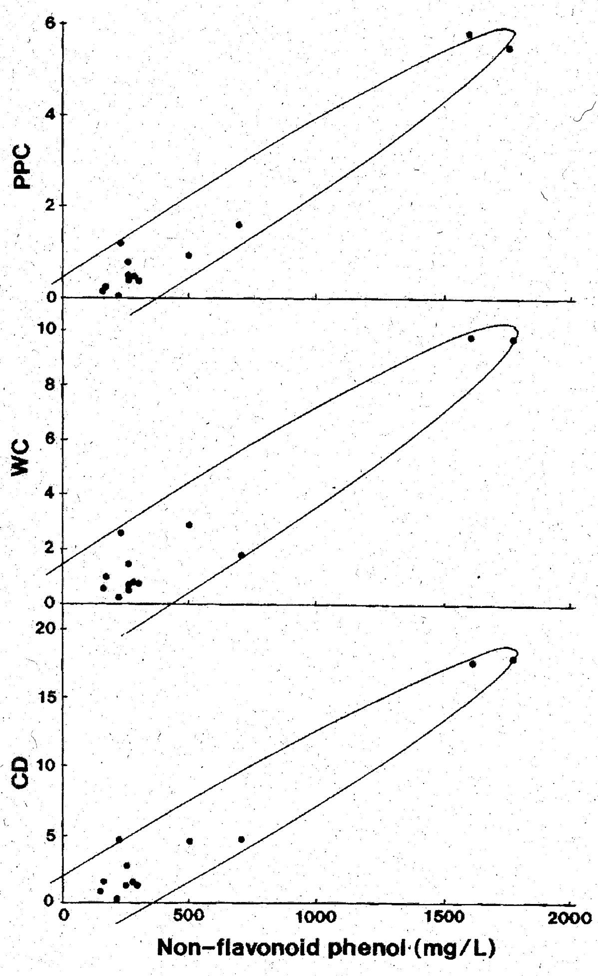

FIG. 2. Relation between metals (Mg+Ca+Fe +Zn+Cu) and wine color (WC), anthocyanin color (AC), polymeric pigmet color (PPC), and ionized anthocyanins (IA).

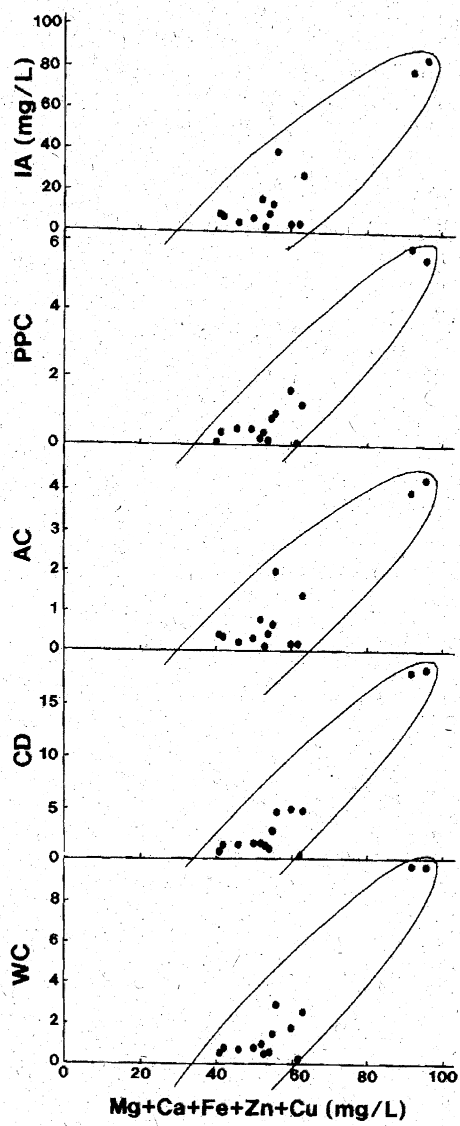

FIG. 3. Relation between non-flavonoid phenol and color density (CD), wine color (WC), and polymeric pigment color (PPC).

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