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Studies of Aliphatic Hydroxycarboxylic Acids as Antioxidant. V. Complexes of Copper(II) with *erythro*- and *threo*-2-Methyltartaric, and *meso*- and *threo*-2,3-Dimethyltartaric Acids

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The dissociation constants of *erythro*- and *threo*-2-methyltartaric and *meso*- and *threo*-2,3-dimethyltartaric acids were determined by the potentiometric titration method at the ionic strength of $\mu=0.1$ and at 22°C. The values of the dissociation constants were $pK_1=3.54$ and $pK_2=5.03$ for *erythro*-2-methyltartaric acid, and $pK_1=3.28$ and $pK_2=4.70$ for the *threo*-form. For *meso*-2,3-dimethyltartaric acid, the corresponding values were 3.52 and 4.98, while the *threo*-form had values of 3.04 and 5.30. The complex formation of copper(II) with these acids has been investigated using Job's method of continuous variations at the ionic strength of $\mu=0.2$ and at 22°C. Copper(II) and *erythro*-2-methyltartaric acid react in a 1 : 1 ratio at pH 2.40 and in a 3 : 2 ratio at pH 5.00. On the other hand, the *threo*-form does not combine with copper(II) at pH 2.40, though it does react at pH 5.00 in a 1 : 1 ratio. As for *meso*-2,3-dimethyltartaric acid, the complex formation in a 3 : 2 ratio was observed at pH 5.00. However, the *threo*-form and copper(II) react in a 1 : 2 ratio at pH 5.00. The equilibrium constants (apparent stability constants) were calculated by the method of Turner and Anderson. The values of the equilibrium constant were $\log K=9.71$ (pH 5.00) and $\log K=2.02$ (pH 2.40) for *erythro*-2-methyltartaric acid, $\log K=3.78$ (pH 5.00) for the *threo*-form, $\log K=9.70$ (pH 5.00) for *meso*-2,3-dimethyltartaric acid, and $\log K=5.19$ (pH 5.00) for the *threo*- form. On the basis of these data, the structures of these complexes are discussed.

It is a well-known fact that small quantities of heavy metals have a deteriorating effect on the stability of oils. Especially, copper and iron have long been known to be detrimental to the stability of vegetable oils. Chelating agents, citric or tartaric acids, was added in order to decrease the influence of these metals. In order to study the influence of metal traces on the behaviour and the efficiency of these hydroxycarboxylic acids against the autoxidation of oils, we carried out experiments with a pure substrate, diethyl linoleate, and with soybean oil. These results have been published previously.[1] In a continuation of our study of hydroxycarboxylic acids as antioxidants, the present paper will report the determination of the dissociation constants on methyl derivatives of tartaric acid and of the equilibrium constants with copper(II). It seemed worthwhile to study the stability constants of these methyl derivatives with copper(II), since the composition of the complexes and the stability constants of these chelate compounds might be related to the stabilizing effect on the vegetable oils as antioxidants. Although a great deal of work has been done in the preparation of chelate compounds, for example, copper(II) or iron(III) tartrate and citrate, and upon their structures and formation constants,[2-5] no attempt has yet been made to determine the dissociation constants of methyl derivatives of tartaric acid and the stability constants with copper(II).

In this paper, *erythro*- and *threo*-2-methyltartaric acids were synthesized by the oxidation of diethylcitraconate and diethylmesaconate respectively with permanganate. *Meso*- and *threo*-2,3-dimethyltartaric acids were prepared according to the procedure of Izumi *et al.*[6] The dissociation constants of these acids was determined by means of the potentiometric titration method. In order to calculate the equilibrium constants (apparent stability constants), we used the Turner and Anderson dilution method.[7] The composition of the complexes was studied Job's method of continuous variation.[8,9]

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Experimental

All the melting points are uncorrected. The infrared spectra were determined in Nujol mull using a Shimadzu IR-27 spectrometer in the 2—15 μ region. The potentiometric titrations were made with a Metrohm Herisau Potentiograph, E 336. Optical density measurements from 600 to 800 mμ were made on a Hitachi 139 spectrophotometer. The pH of the reaction mixture was measured by means of a Yanagimoto Model 42-A pH-meter. During potentiometric titrations and spectro photometric measurements, constant ionic strenghts of 0.1 and 0.2 respectively were maintained by adding the requisite amount of a sodium perchlorate solution. Buffer solutions were prepared by adding the proper amount of 0.1 N acetic acid to a 0.1 N solution of sodium acetate. Standard copper(II) perchlorate (commercial reagent) in demetalized water and copper(II) was estimated spectrophotometrically (JIS-H-1101—1961). A sodium perchlorate solution was prepared in a concentration of 1 M. The dissociation constants of these acids were determined by the potentiometric titration of 10^{-3} M solutions, while the equilibrium constants of the copper(II) complexes were obtained spectrophotometrically.

Preparation of Ligands. The Preparation of erythro-*2-Methyltartaric Acid* (erythro-*MTA*): A solution of diethylcitraconate (40 g) dissolved in 200 m*l* of ethanol was oxidized with 2% aqueous potassium permanganate for 5 hr from −20 to −5°C. The reaction solution was then allowed to stand at room temperature overnight. The precipitated inorganic salt was removed by filtration; the filtrate was concentrated *in vacuo* to a syrup, which was then extracted with ether. After the evaporation of the solvent *in vacuo*, the residue was refluxed for 8 hr with 3 N hydrochloric acid. The hydrolysate was then evaporated to dryness *in vacuo*. The residue was dissolved in ethylacetate and was crystallized by the addition of a small amount of petroleum ether. Recrystallization from ethylacetate gave *erythro*-MTA. Mp 144—145°C. IR: 2.92, 2.99 μ. Paper chromatography R_f: 0.37 (*n*-BuOH-HCO$_2$H-H$_2$O, 4 : 1 : 2)

The Preparation of threo-*2-Methyltartaric Acid* (threo-*MTA*): The *threo*-form was similarly prepared by the oxidation of diethylmesaconate and by subsequent hydrolysis. Recrystallization from ethylacetate gave *threo*-MTA. Mp 159—160°C. IR: 2.89, 2.91 μ. R_f: 0.44.

The Preparation of meso- (meso-*DMT*) *and* threo-*2,3-Dimethyl tartaric Acids* (threo-*DMT*): *meso*-DMT and *threo*-DMT were prepared according to the method described by Izumi *et al.*; that is, these acids were prepared from diacetyl and hydrogen cyanide, and their barium salts were separated by solubility difference in water. *meso*-DMT: mp 179—180°C. *threo*-DMT: mp 187°C.

The Determination of the Dissociation Constants of These Acids. The dissociation constants were determined as follows: about a 100-mg portion of acid was dissolved in 25 m*l* of water. A mixture of the acid solution (5 m*l*) and 1 M sodium perchlorate (5 m*l*) was diluted to 50 m*l* with demetalized water (ionic strength 0.1) and then titrated at 22°C with a 0.1 N sodium hydroxide solution, using a Metrohm Herisau Potentiograph, E 336. The dissociation constants were calculated by the procedure of Speakman;[10] that is, the dissociation constants of a dibasic acid, H$_2$A, may be difined by the equations:

$$K_1 = a_{H^+}[HA^-]y_1/[H_2A]y_0,\quad K_2 = a_{H^+}[A^{2-}]y_2/[HA^-]y_1$$

where a_{H^+} signifies the activity of hydrogen ions and where y_0, y_1, and y_2 are the activity coefficients of the H$_2$A, HA$^-$, and A^{2-} species respectively. In a solution with a total acid concentration of *a* (molar):

$$a = [H_2A] + [HA^-] + [A^{2-}]$$

and when a strong monoacid base, which may be taken as completely dissociated, has been added to give a molar concentration of *b*, electrical neutrality requires that:

$$b + [H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$$

If we define *L*, *M*, and *N* by these equations:

$$L = b + [H^+] - [OH^-]$$

$$M = a - b - [H^+] + [OH^-]$$

$$N = 2a - b - [H^+] + [OH^-]$$

it can be shown that:

$$Ly_2[H^+]^2/Ny_0 = My_2[H^+]K_1/Ny_1 + K_1K_2 \qquad (1)$$

where $\log y_1 = -0.5\sqrt{I}$ and $\log y_2 = -2.0\sqrt{I}$, $y_0 = 1$. (I signifies the ionic strength). Therefore, in the case of an ionic strength of 0.1, Eq. (1) may be written as:

$$0.233L[H^+]^2/N = 0.233M[H^+]K_1/0.695N + K_1K_2 \qquad (2)$$

When *L*, *M*, and *N* can be evaluated from the experimental data, the plot of the $(0.233L[H^+]^2/N)$ term against the $(0.233M[H^+]/0.695N)$ term should give a straight line, the slope of which equals K_1, while the intercept on the *Y* axis should equal K_1K_2.

The Determination of the Equilibrium Constants of the Copper(II) Complexes. The equilibrium constants (apparent stability constants) of copper(II) with these acids were determined as follows: calculated volumes of copper(II) perchlorate (1.536×10^{-2} mol/*l*) and acid solutions (1.536×10^{-2} mol/*l*) were mixed, and then we added the proper amount of sodium perchlorate (1 mol/*l*) to maintain a constant ionic strength $\mu=0.2$; the whole was diluted to the proper volume (*e.g.*, 25 m*l*, 10 m*l*) by adding a buffer solution and allowed to stand 1 hr at 22°C. The optical density was then measured. The absorption cell was not thermostated, but all the solutions were brought to a constant temperature before measurements were made. Preliminary experiments showed that the copper(II)-acid solutions reached equilibrium within 1 hr and showed no measurable variation thereafter for a period of less than 24 hr. In order to calculate the equilibrium constants, we used the Turner and Anderson dilution method; *i.e.*, complex formation proceeds by this pathway:

$$nM + mA \rightleftarrows M_nA_m \qquad (3)$$

in which *M* is a metallic ion, and *A*, an organic molecule or an anion. If *a* and *b* are the initial concentrations of *M* and *A* respectively and if *x* is the equilibrium concentration of the chelate complex, then the equilibrium constant:

$$K = x/(a-nx)^n(b-mx)^m \qquad (4)$$

To determine the value of *x*, Job's method of continuous variations is employed, with different initial concentrations of the reactants. *n* and *m* can be determined from the experimental data by means of Job's method. If two concentrations (a_1+b_1) and (a_2+b_2) of the reactants have the same optical density, then the equilibrium constant:

$$K = x/(a_1-nx)^n(b_1-mx)^m = x/(a_2-nx)^n(b_2-mx)^m \qquad (5)$$

This equation can be solved for *x*. Thus, knowing the value of *x*, at a known concentration of reactants *K* can be calculated.

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TABLE 1. TITRATION OF *erythro*-MTA(1.881×10^{-2} M; 10 m*l*, $NaClO_4$ 1 M; 5 m*l*. total vol.=50 m*l*) WITH 0.1081 M NaOH AT 22°C ($\mu=0.1$).

NaOH (m*l*)	pH	$[H^+]$ ($\times10^{-4}$)	Ly_2 ($\times10^{-3}$)	My_2 ($\times10^{-3}$)	Ny_1 ($\times10^{-3}$)	Ny_0 ($\times10^{-3}$)	$Ly_2[H^+]^2/Ny_0$ ($\times10^{-8}$)	$My_2[H^+]/Ny_1$ ($\times10^{-5}$)
0.6	3.29	5.13	0.4180	0.4480	3.919	5.640	1.95	5.86
0.8	3.40	3.99	0.4895	0.3730	3.685	5.303	1.46	4.04
1.0	3.51	3.09	0.5657	0.2936	3.438	4.948	1.09	2.63
1.2	3.65	2.24	0.6424	0.2134	3.189	4.589	0.702	1.49
1.4	3.79	1.62	0.7237	0.1288	2.927	4.212	0.451	0.71
1.6	3.93	1.18	0.8083	0.0410	2.655	3.821	0.297	0.18

Results and Discussion

The Dissociation Constants of Ligands. erythro-*2-Methyltartaric Acid*: Table 1 represents the titration of *erythro*-MTA (1.881×10^{-2} mol/*l*, 10 m*l*) with 0.1081 N sodium hydroxide. The plot of the ($Ly_2[H^+]^2/Ny_0$) term against ($My_2[H^+]/Ny_1$) is shown in Fig. 1; the points lie very close to the straight line, from which pK_1 and pK_2 were calculated to be 3.54 and 5.03 respectively at $\mu=0.1$.

threo-*2-Methyltartaric Acid*: The dissociation constants, pK_1 and pK_2, were similarly calculated to be 3.28 and 4.70 respectively. For *meso-2,3-dimethyltartaric acid*, the corresponding values were 3.52 and 4.98 (Fig. 2), on the other hand, for the *threo*-form the corresponding values were 3.04 and 5.30 (Fig. 2).

The Equilibrium Constants of Copper(II) Complexes. Complex with erythro-*MTA, at pH* 2.40: Calculated volumes of copper(II) perchlorate (3.840×10^{-2} M) and this acid (3.840×10^{-2} M) solution were mixed; then a sodium perchlorate solution (1 M, 5 m*l*) was added, and the whole was diluted to 25 m*l* by adding a buffer solution and was allowed to stand 1 hr at 22°C. The optical density was then measured at 760 mμ. The results are shown in Fig. 3A, where the difference in optical density (ΔOD) of the complex and copper(II) perchlorate is plotted against the concentration of the reactants. Maxima are obtained at a mole fraction (copper) value of 0.5 with this acid and indicate a 1 : 1 combination. In order to calculate the eqilibrium constant, therefore, Eq. (4) should become:

$$K = x/(a-x)(b-x) \tag{6}$$

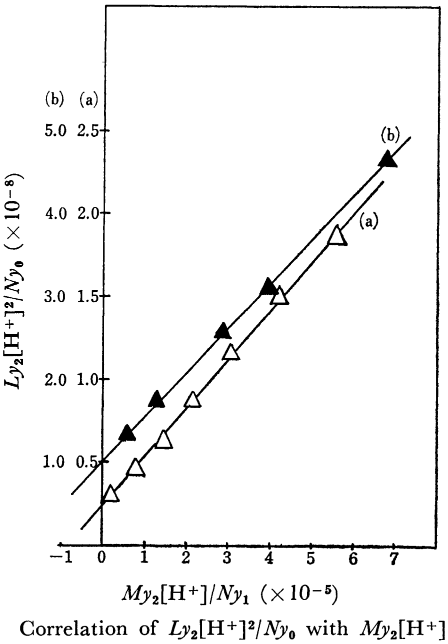


Fig. 1. Correlation of $Ly_2[H^+]^2/Ny_0$ with $My_2[H^+]/Ny_1$.
(a) *erythro*-MTA 1.881×10^{-2} mol/*l*, 10 m*l*
(b) *threo*-MTA 3.178×10^{-2} mol/*l*, 10 m*l*

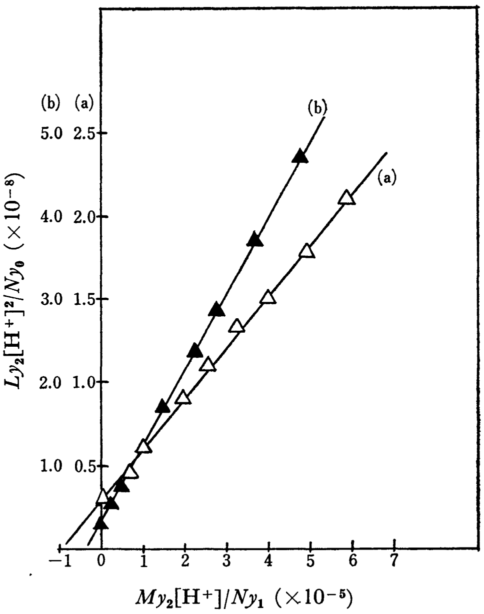


Fig. 2. Correlation of $Ly_2[H^+]^2/Ny_0$ with $My_2[H^+]/Ny_1$.
(a) *meso*-DMT 1.850×10^{-2} mol/*l*, 10 m*l*
(b) *threo*-DMT 2.002×10^{-2} mol/*l*, 10 m*l*

To determine the value of x, Job's method is again employed, but with a different initial concentration of the reactants. That is, an appropriate amount of copper(II) perchlorate (3.840×10^{-2} M) and this acid (3.840×10^{-2} M) solution were mixed; then we added the sodium perchlorate solution (1 M, 2 m*l*), and the whole was diluted to 10 m*l* by adding a buffer solution. The optical density was measured at the same wave length (760 mμ). The results are shown in Fig. 3B. From this curve and the data of Fig. 3A, a series of pairs of solutions can be selected with equal optical densities (and thus essentially equal concentrations of the complex), but with different concentrations of reactants. Therefore, Eq. (5) becomes:

$$K = x/(a_1-x)(b_1-x) = x/(a_2-x)(b_2-x) \tag{7}$$

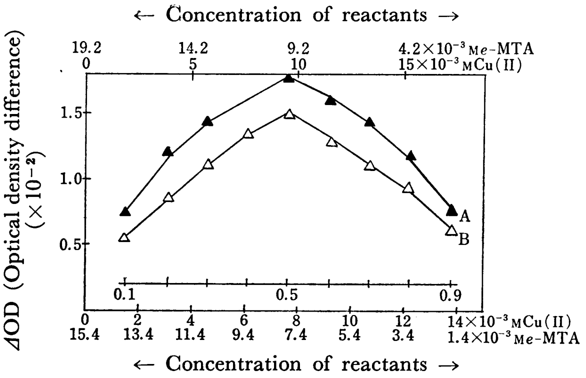


Fig. 3. Variation of ΔOD with varying concentration of Cu(II) and *erythro*-MTA, at pH 2.40, 760 mμ. Upper scale for curve A and lower scale for curve B. (ionic strength $\mu=0.2$)

This equation could be solved for x as follows:

$$x = (a_1b_1 - a_2b_2)/\{(a_1+b_1)-(a_2+b_2)\} \qquad (8)$$

In this case, a line at an optical density difference of 0.011 was drawn parallel to the concentration axis which intersects the curves, A and B. A point corresponding to the intersection at curve A gives a_1 and b_1 on the concentration axis, while the point on curve B gives a_2 and b_2 (on the right side of the peak). Similarly, other pairs, a_1 and b_1, and a_2 and b_2, can be selected on the left side of the peak, and x and also the log K value may be calculated for the complex. The results are shown in Table 3.

At pH 5.00: Copper(II) perchlorate (1.464×10^{-2} M) and this acid (1.464×10^{-2} M) solution were mixed similarly, and the optical density was measured. Maxima are obtained at a mole fraction value of 0.6, indicating that copper(II) and this acid react in a 3 : 2 ratio. Therefore, Eq. (4) becomes:

$$K = x/(a-3x)^3(b-2x)^2,$$

Then,

$$x = (a_1{}^3b_1{}^2 - a_2{}^3b_2{}^2)/\{(9a_1{}^2b_1{}^2+4a_1{}^3b_1)-(9a_2{}^2b_2{}^2+4a_2{}^3b_2)\}$$

The results are shown in Figs. 4A and 4B and in Table 3.

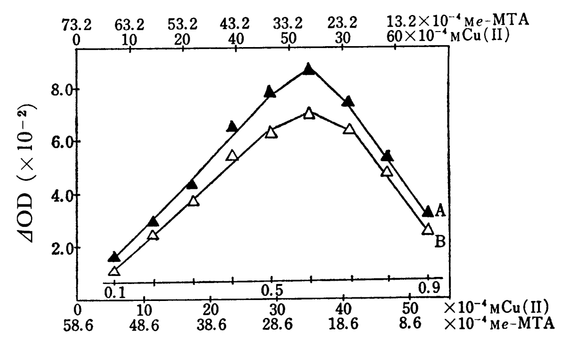


Fig. 4. Variation of ΔOD with varying concentration of Cu(II) and *erythro*-MTA, at pH 5.00, 650 mμ. Upper scale for curve A and lower scale for curve B.

TABLE 2. TITRATION OF *threo*-MTA(3.178×10^{-2} M; 10 m*l*, $NaClO_4$ 1 M; 5 m*l*. total vol.=50 m*l*) WITH 0.1081 M NaOH AT 22°C ($\mu=0.1$).

NaOH (m*l*)	pH	[H⁺] ($\times10^{-4}$)	Ly_2 ($\times10^{-3}$)	My_2 ($\times10^{-3}$)	Ny_1 ($\times10^{-3}$)	Ny_0 ($\times10^{-3}$)	$Ly_2[H^+]^2/Ny_0$ ($\times10^{-8}$)	$My_2[H^+]/Ny_1$ ($\times10^{-5}$)
1.4	3.16	6.92	0.8472	0.5929	6.065	8.726	4.64	6.76
1.6	3.22	6.03	0.9213	0.5135	5.812	8.362	4.00	5.32
1.8	3.30	5.02	0.9921	0.4373	5.568	8.012	3.12	3.94
2.0	3.37	4.27	1.0681	0.3558	5.308	7.638	2.54	2.86
2.4	3.51	3.09	1.2256	0.1873	4.771	6.865	1.70	1.21
2.6	3.59	2.57	1.3048	0.1027	4.505	6.482	1.33	0.58
2.8	3.67	2.14	1.3854	0.0167	4.232	6.090	1.04	0.08

TABLE 3. EQUILIBRIUM CONSTANTS OF COPPER(II) WITH *erythro*- AND *threo*-MTA

Cu(II) with *e*-MTA at pH 2.40, $\mu=0.2$, 760 mμ.

a_1 ($\times10^{-3}$ M)	b_1 ($\times10^{-3}$ M)	x ($\times10^{-3}$)	log K	a_2 ($\times10^{-3}$ M)	b_2 ($\times10^{-3}$ M)	x ($\times10^{-3}$)	log K
3.31	15.89	1.88	1.97	4.00	11.36	1.88	1.97
11.5	3.86	2.03	2.07	15.81	3.39	2.03	2.03
Mean log K 2.02±0.05, Cu : acid=1:1							
Cu(II) with *e*-MTA at pH 5.00, $\mu=0.2$, 650 mμ.							
2.015	5.305	0.210	9.52	1.850	4.010	0.210	9.95
6.281	1.039	0.207	9.46	4.875	0.985	0.207	9.92
Mean log K 9.71±0.25, Cu : acid=3:2							
Cu(II) with *t*-MTA at pH 5.00, $\mu=0.2$, 690 mμ.							
1.906	5.414	1.82	3.75	1.950	3.910	1.82	3.82
Mean log K 3.78±0.03, Cu : acid=1:1							

Complex with threo-*MTA, at pH* 5.00: Equimolar solutions (1.464×10^{-2} M) were similarly mixed, and the optical density was measured. Maxima are obtained at a mole fraction value of 0.5 with this acid, indicating a 1 : 1 combination. The results are shown in Figs. 5A and 5B and in Table 3.

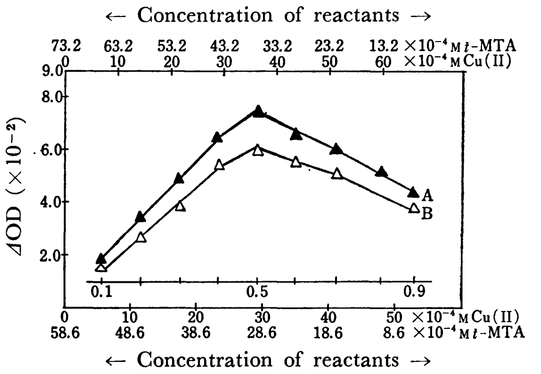


Fig. 5. Variation of ΔOD with varying concentration of Cu(II) and *threo*-MTA, at pH 5.00, 690 mμ. Upper scale for curve A and lower scale for curve B.

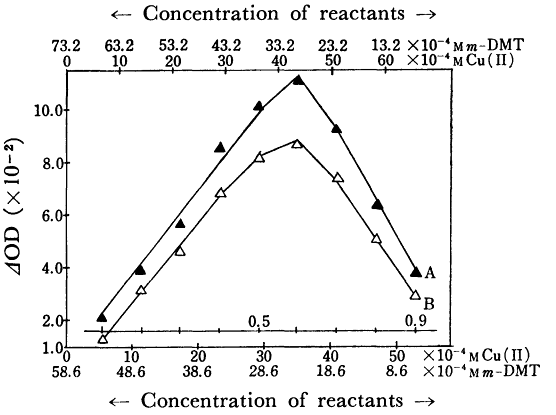


Fig. 6. Variation of ΔOD with varying concentration of Cu(II) and *meso*-DMT, at pH 5.00, 640 mμ. Upper scale for curve A and lower scale for curve B.

Complex with meso-*DMT, at pH* 5.00: Equimolar solutions (1.464×10^{-2} M) were similarly mixed, and the optical density was measured. The results are shown in Figs. 6A and 6B and in Table 4.

Complex with threo-*DMT, at pH* 5.00: The results are shown in Figs. 7A and 7B and in Table 4.

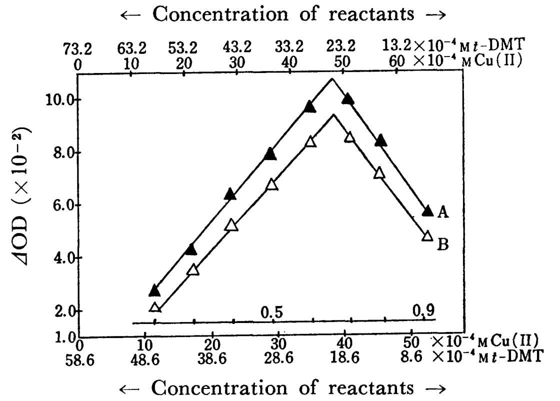


Fig. 7. Variation of ΔOD with varying concentration of Cu(II) and *threo*-DMT, at pH 5.00, 660 mμ. Upper scale for curve A and lower scale for curve B.

It would be reasonable to assume that these hydroxycarboxylic acids function as quadridentate chelating agents, and that both carboxyl and adjacent hydroxyl groups are involved in bond formation, and a tentative structure could be presumed for them (Fig. 8). The most stable conformations in *threo*-MTA and *erythro*-MTA would, respectively, be 1 and 2, where the two carboxyl groups are in anti positions (Fig. 9). Five- and six-membered rings are by far the most common among metal chelates. In *threo*-MTA, if the complex formation with copper(II) occurred at the carboxyl and hydroxyl groups in the vicinal position, as is shown in Fig. 9, the combination ratio would be the same as in the *erythro*-MTA-copper(II). Hence, the chelate formation in this manner does not explain the observed difference in the combination ratio between *threo* and *erythro* forms. Accordingly, it seemed to

Table 4. Equilibrium constants of copper(II) with *meso*- and *threo*-DMT

Cu(II) with *m*-DMT at pH 5.00, $\mu=0.2$, 640 mμ.

a_1 ($\times10^{-4}$ M)	b_1 ($\times10^{-4}$ M)	x ($\times10^{-4}$)	log K	a_2 ($\times10^{-4}$ M)	b_2 ($\times10^{-4}$ M)	x ($\times10^{-4}$)	log K
19.37	53.83	2.01	9.54	18.37	35.23	2.01	10.08
73.20	10.70	2.15	9.25	47.37	6.23	2.15	9.93

Mean log K 9.67±0.41, Cu : acid=3:2

Cu(II) with *t*-DMT at pH 5.00, $\mu=0.2$, 660 mμ.

a_1 ($\times10^{-4}$ M)	b_1 ($\times10^{-4}$ M)	x ($\times10^{-4}$)	log K	a_2 ($\times10^{-4}$ M)	b_2 ($\times10^{-4}$ M)	x ($\times10^{-4}$)	log K
27.96	45.24	7.33	5.04	26.25	32.35	7.33	5.34
65.00	8.20	6.03	5.19	49.75	8.85	6.03	5.20

Mean log K 5.19±0.15, Cu : acid=2:1

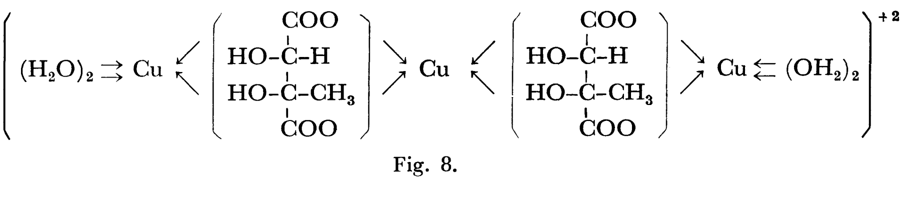
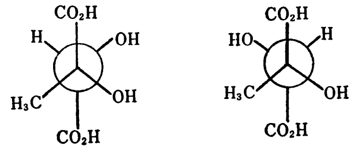


Fig. 8.



1 2

Fig. 9.

be reasonable to assume that the copper(II) complexes have a 5-membered ring and that copper(II) attaches to geminally-situated carboxyl and hydroxyl groups. In *erythro*-MTA, both sets of carboxyl and hydroxyl groups are set in opposite directions, thus forming the complex in a 2 : 3 ratio. The chelate from *threo*-MTA in this ratio is unstable. Among the equilibrium constants of the acid-copper(II) complexes, the *erythro*-form ligands have larger values, $\log K=9.71$ for *erythro*-MTA and $\log K=9.70$ for *meso*-DMT. It is known that the stability constant difference is correlated with the dissociation constant of the ligand.[11] Strictly speaking, the stability constant does not agree with the equilibrium constant, but the equilibrium constant can be regarded as the apparent stability constant.[7,9] A close parallelism between the equilibrium constant and the dissociation constant is observed also in our case. When comparing the pK values of *threo*-form ligands with those of *erythro*-form ligands, the former are found to have lower values of pK. The pK values of the *erythro*-form are similar to each other, while there is a remarkable difference in the *threo*-form ligands. These tendencies also reflect the values of the equilibrium constants of *erythro*-form ligands; that is, the $\log K$ values of *erythro*-form ligand-copper(II) are also similar to each other.

The stabilizing effect of the substituted tartaric acids, *erythro*- and *threo*-MTA, and *meso*- and *threo*-DMT, on the vegetable oil as antioxidants in o/w-type emulsion has been evaluated in our previous work.[1] The influence of the metallic ion and the effect of these acids as antioxidants on the dissolved oxygen in o/w-type emulsion was investigated by employing a polarographic Beckman Oxygen Analyzer, Model 777. Soybean oil with different P.O.V.'s (peroxide values) and water were emulsified into o/w-type emulsions using Tween-40 as the emulsifiser, and the absorption of dissolved oxygen was measured in the presence of the Cu(II) ion. In order to evaluate the effect of these acids, an acid solution (10^{-1} mol/l, 1 ml) was added to the emulsion. Then, the metallic solution (0.5×10^{-1} mol/l, 1 ml) was added to the same emulsion, and the variation in the dissolved oxygen was measured. The results of these measurements revealed that the oxygen absorption increased in the presence of Cu(II) and, that the deteriorating effect was suppressed by the addition of these acids. When comparing the stabilizing effect of *erythro*-form acid with those of *threo*-form ligands, the former is clearly seen to function as a more effective antioxidant. Moreover, in the test for antioxidant activity by means of AOM (Active Oxygen Method) and the Shaal Oven Test, the results similarly revealed that *erythro*-form acid functions as a more effective antioxidant. On the basis of these data, it cab be concluded that the stabilizing effect on the oil as antioxidant can be attributed to the equilibrium constants of these acid-metal complexes. Detailed results will be published later.

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