Optical Activity and Chemical Structure in Tartaric Acid. X.* Influence of Substituent and Solvent Effect.

By Yojiro TSUZUKI.

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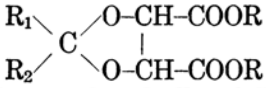
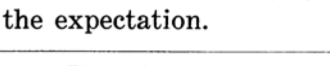
In a previous paper⁽¹⁾ it was shown that in a number of bridged derivatives of tartaric acid,  $\begin{array}{ccl} R_1 & & O-CH-COOR \\ & C & \quad\vert \\ R_2 & & O-CH-COOR \end{array}$ the laevo-rotation of the compound falls off with increasing bulk of R_1 and R_2. And it was discussed that this effect should be expected from the deduction of the molecular theory of optical activity⁽²⁾ and the author's view⁽³⁾ that hydroxyl oxygen of tartaric acid contributes the positive partial rotation.

It was also pointed out that among these bridged derivatives, obtained by condensing carbonyl compounds with alkyl *d*-tartrates, aldehyde condensation products have always a larger molecular rotation than those from ketone of the same molecular weight.

The compounds furnished for discussion were, however, mostly ketone derivatives, and those of aldehyde were only from form aldehyde and acetaldehydes.

In the present investigation, the author has prepared some new derivatives from ethyl *d*-tartrate and higher homologues of acetaldehyde, whose constitution is:  $\begin{array}{ccl} R & & O-CH-COOC_2H_5 \\ & C & \quad\vert \\ H & & O-CH-COOC_2H_5 \end{array}$ and determined their rotatory power and observed the solvent effect on it. The results are all in good agreement with the expectation.

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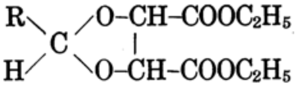
* Part IX, *Scient. Pap. Inst. Phys. Chem. Res.*, Tokyo **36** (1939), 31.

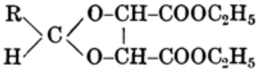
(1) Y. Tsuzuki, *Scient. Pap. Inst. Phys. Chem. Res.*, Tokyo **35** (1939), 466.

(2) R. de Mallemann, *Trans. Farad. Soc.*, **26** (1930), 281; F. S. Boys, *Proc. Roy. Soc.*, (London), A. **144** (1934), 655.

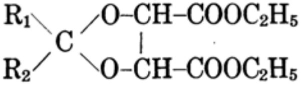
(3) Y. Tsuzuki, *Scient. Pap. Inst. Phys. Chem. Res.*, Tokyo **35** (1939), 425.

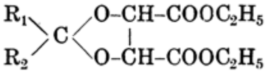
Influence of the Radical R on the Rotation. In Table 1 are given the values of the molecular rotation in the homogeneous state of the bridged derivatives of ethyl *d*-tartrate. We see clearly a definite relation between the rotation and the bulk of R, which can be expressed as parachor, a quantity equivalent to the molecular volume, that is, the laevo-rotation decreases progressively in magnitude, as the bulk of the left-hand side of the molecule increases. This fact is in complete harmony with the conclusion expressed in the previous paper.

Table 1. Molecular rotation of  $\begin{matrix}R\\H\end{matrix}\!>C<\!\begin{matrix}O-CH-COOC_2H_5\\|\\O-CH-COOC_2H_5\end{matrix}$ and parachor of R.

Compound  $\begin{matrix}R\\H\end{matrix}\!>C<\!\begin{matrix}O-CH-COOC_2H_5\\|\\O-CH-COOC_2H_5\end{matrix}$	$[M]_D^{20}$ (no solvent)	$[M]_D^{20}$ (in cyclohexane)	Parachor of R
R = H	-171.1	-160.3 (4)	17.1
R = CH_3	-173.3	-159.9	56.1
R = n-C_3H_7	-144.8	-133.5	134.1
R = i-C_3H_7	-134.9	-126.0	134.1
R = C_6H_{13}	-126.2	-115.6	251.1

It should be noted that in Table 1 we see the effect of isopropyl radical is stronger than *n*-propyl radical. This is possibly due to the vicinal effect of isopropyl group.(5) Since this radical furnishes the dextro-rotatory contribution, as already shown by the present author,(3)

Table 2. Molecular rotation of isomers of  $\begin{matrix}R_1\\R_2\end{matrix}\!>C<\!\begin{matrix}O-CH-COOC_2H_5\\|\\O-CH-COOC_2H_5\end{matrix}$.

Compound  $\begin{matrix}R_1\\R_2\end{matrix}\!>C<\!\begin{matrix}O-CH-COOC_2H_5\\|\\O-CH-COOC_2H_5\end{matrix}$	$[M]_D^{20}$ (no solvent)	$[M]_D^{20}$ (in cyclohexane)
R_1 = n-C_3H_7 R_2 = H	-144.8	-133.5
R_1 = C_2H_5 R_2 = CH_3	-91.10(6)	-82.25
R_1 = C_6H_{13} R_2 = H	-134.9	-126.0
R_1 = C_3H_7 R_2 = C_3H_7	-59.74(6)	-54.91

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(4) Y. Tsuzuki, this Bulletin, **11** (1936), 363.
(5) P. A. Levene and A. Rothen, *J. Org. Chem.*, **1** (1936), 76.
(6) Y. Tsuzuki, this Bulletin, **14** (1939), 19.

it is conceivable that this vicinal effect depresses the laevo-rotation of the derivatives of tartaric acid.

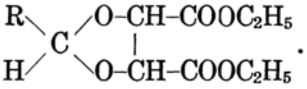
It was already noticed in the previous paper⁽¹⁾ that the compounds, in which R_1 is different from R_2 (Formula in Table 2), have a larger molecular rotation than those isomers in which R_1 and R_2 are equal. This difference is more remarkable when $R_2 = H$, i.e. in the case of aldehyde condensation products the molecular rotation is far greater than that of the isomeric ketone condensation product. This is evident from Table 2.

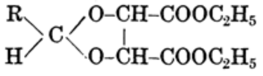
Influence of Solvent. As may be seen in Table 3 to the sequence of solvents arranged in order of their effect on the molecular rotation of the newly synthesized bridged derivatives of ethyl *d*-tartrate is:

Benzene > Alcohol > Cyclohexane.

This series is just the same found in the previous investigation,⁽¹⁾ which was observed about ketone condensation products of the analogous structure. The result can be satisfactorily explained by taking into consideration the refractive index and the associable character of the liquid, as in the case of the previous paper.

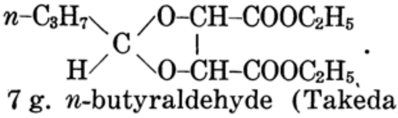
It is to be noticed that the molecular rotation in the homogeneous state is nearly the same as in alcohol. This fact is easily explained by considering that the hydroxyl and carboxyl groups in tartaric acid have partial rotations which are in direction opposite to each other.

Table 3. Molecular rotation of  .

Compound 	$[M]_D^{20}$ in			
	no solvent	benzene	alcohol	cyclohexane
$R = n\text{-}C_3H_7$	−144.8	−157.0	−142.9	−133.5
$R = i\text{-}C_3H_7$	−134.9	−154.3	−134.9	−126.0
$R = C_6H_{13}$	−126.2	−148.3	−123.1	−115.6

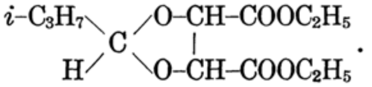
Experimental.

Ethyl n-*butyral*-d-*tartrate* $C_{12}H_{20}O_6$ (260.16)



. To a mixture of 9 g. ethyl *d*-tartrate and 7 g. *n*-butyraldehyde (Takeda, b.p. 67–74°) was added 10 g. phosphorus pentoxide in portions at room temperature during a period of 40 minutes. The liquid coloured brownish red. The reaction product was extracted with ether. The ethereal solution was washed three times with a saturated solution of borax to remove unchanged ethyl *d*-tartrate and was finally dried over anhydrous sodium sulphate. After evaporating off the ether, the product was purified by fractional distillation in vacuo. This process of purification was repeated three times. Colourless liquid. Yield 4.5 g. Boiling point 160° (15 mm), $n^{20}_D = 1.4376$, $d^{20}_4 = 1.0942$, $M_D =$ 62.36 (62.01), $[\alpha]^{20}_D = -55.80°$, $[M]^{20}_D = -144.8°$. $[\alpha]^{20}_D = -54.94°$ (in ethyl alcohol, 4.874%), $[M]^{20}_D = -142.9°$ (in ethyl alcohol). $[\alpha]^{20}_D = -60.37°$ (in benzene, 2.956%), $[M]^{20}_D = -157.0°$ (in benzene). $[\alpha]^{20}_D = -51.32°$ (in cyclohexane, 2.533%), $[M]^{20}_D = -133.5°$ (in cyclohexane).

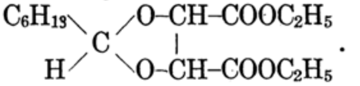
Ethyl isobutyral-d-*tartrate*. $C_{12}H_{20}O_6$ (260.16)



$$\begin{array}{l} i\text{-}C_3H_7\diagdown\ \diagup O\text{-}CH\text{-}COOC_2H_5 \\ \qquad\quad C \qquad\ | \\ \quad H\diagup\ \ \diagdown O\text{-}CH\text{-}COOC_2H_5 \end{array}$$

. To a mixture of 12 g. ethyl *d*-tartrate and 10 g. isobutyraldehyde (Kahlbaum) was added 12 g. phosphorus pentoxide in portions at 70° during a period of 40 minutes, and heating was continued for 40 minutes at 80–90°. Almost colourless liquid. Yield 5 g. Boiling point 160° (20 mm), $n^{20}_D = 1.4375$, $d^{20}_4 = 1.0847$, $M_D = 62.89$ (62.01). $[\alpha]^{20}_D = -54.17°$, $[M]^{20}_D = -141.0°$. $[\alpha]^{20}_D = -51.86°$ (in ethyl alcohol, 4.830%), $[M]^{20}_D = -134.9°$ (in ethyl alcohol). $[\alpha]^{20}_D = -59.29°$ (in benzene, 2.941%), $[M]^{20}_D = -154.3°$ (in benzene). $[\alpha]^{20}_D = -48.43°$ (in cyclohexane, 2.503%), $[M]^{20}_D = -126.0°$ (in cyclohexane).

Ethyl oenanthal-d-*tartrate* $C_{15}H_{26}O_6$ (302.21).



$$\begin{array}{l} C_6H_{13}\diagdown\ \diagup O\text{-}CH\text{-}COOC_2H_5 \\ \qquad\quad C \qquad\ | \\ \quad H\diagup\ \ \diagdown O\text{-}CH\text{-}COOC_2H_5 \end{array}$$

. The condensation of 10 g. ethyl *d*-tartrate with 10 g. oenanthol (Takeda, b.p. 154–6°) by means of 10 g. P_2O_5 at 50–60°, gave 6 g. colourless liquid boiling at 190° (16 mm). $n^{20}_D = 1.4414$, $d^{20}_4 = 1.0451$, $M^{20}_D = 76.42$ (75.87). $[\alpha]^{20}_D = -41.76°$, $[M]^{20}_D = -126.2°$. $[\alpha]^{20}_D = -40.72°$ (in ethyl alcohol, 2.469%), $[M]^{20}_D = -123.1°$ (in ethyl alcohol). $[\alpha]^{20}_D = -49.08°$ (in benzene, 2.217%), $[M]^{20}_D = -148.3°$ (in benzene). $[\alpha]^{20}_D = -38.25°$ (in cyclohexane, 2.504%), $[M]^{20}_D = -115.6°$ (in cyclohexane).

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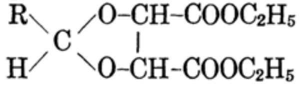
Summary.

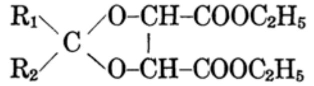
By comparing the molecular rotation of some bridged derivatives of tartaric acid,



$$\begin{array}{l} R\diagdown\ \diagup O\text{-}CH\text{-}COOC_2H_5 \\ \quad C \qquad | \\ H\diagup\ \diagdown O\text{-}CH\text{-}COOC_2H_5 \end{array}$$

obtained by condensing aliphatic aldehydes with ethyl *d*-tartrate, it has been found that the laevo-rotation of the compounds diminishes with increasing bulk (parachor) of R, that is, R affects the positive partial rotation.

It has been shown that the molecular rotation of these compounds is greater than the isomer,



$$\begin{array}{l} R_1\diagdown\ \diagup O\text{-}CH\text{-}COOC_2H_5 \\ \qquad C \qquad | \\ R_2\diagup\ \diagdown O\text{-}CH\text{-}COOC_2H_5 \end{array}$$

obtained by the condensation of ketone with ethyl *d*-tartrate. This phenomenon is to be explained by the idea of vicinal effect of the radicals R_1 and R_2.

It has been shown that the sequence of solvents arranged in order of the effect on the rotation of these compounds is

Benzene $>$ alcohol $>$ cyclohexane.

and that it is related with the refractive index together with the association of the liquid.

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