# Absolute Configuration of Dimethyltartaric Acid

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In connection with our studies on the asymmetric synthesis *via* cyclic oxyphosphorane, it was necessary to establish the absolute configuration of (—)-2,3-dimethyltartaric acid, and we have tentatively assigned (*S* : *S*)-configuration[1] to this acid by comparison of the Cotton effect in 200–300 nm region with chiral citramalic acid used as reference.

We have obtained contradictory chiroptical data to the previous deduction and wish, at this time, to make a correction of the configurational assignment.

The dibenzoate chirality rule has recently been developed by Nakanishi[2] for determining the chiralities between hydroxyl groups and has proved to be a useful means of establishing absolute configurations as well as conformations of glycols, triols, sugars and other naturally derived products containing aromatic chromophores. The exciton chirality method originally developed for cyclic compounds has also been applied for acyclic compounds. Thus, a brief comment was made by Satsumabayashi[3] on the chiroptical properties of dibenzoyltartaric acid in association with its possible conformations. The extension of Nakanishi's work to our acid seemed a promising means of absolute assignment of configuration, but the extrapolations as such are fraught with danger because of the conformational mobility of acyclic compounds. The contribution of possible conformations can be circumvented by converting the acyclic dicarboxylic acid into cyclic acid anhydride. The first Cotton effects located at 228 nm for 2,3-dimethyltartaric acid[1] and also at 229 nm for tartaric acid[4] to be employed as reference standard suggested a probable interference with the dibenzoate Cotton effects, so that derivation of these acid anhydrides into *p*-methoxybenzoates was preferred in order to avoid overlap of $\pi$-$\pi^*$ transitions.

The treatment of (+)-(*R* : *R*)-tartaric and (+)-2,3-dimethyltartaric acids with excess anisoyl chloride yielded the respective anhydrides, (+)-(*R* : *R*)-*O,O*-dianisoyltartaric anhydride (I) and (—)-*O,O*-dianisoyl-2,3-dimethyltartaric anhydride (II). The anhydride I showed a UV-absorption at 257 nm ($\epsilon$, 39,000) due to *p*-methoxybenzoate chromophore and exhibited two ORD Cotton effects of opposite signs separated by Davydov splitting, centered at 284 and 260 nm. The CD curve also consisted of two Cotton effects at 265 and 240 nm as shown in Fig. 1.

Of the two stable conformations I-a and I-b conceivable for the (*R* : *R*)-anhydride I, the latter I-b does not contribute to the Cotton effect because these chromophores are oriented in one plane with each other. The other conformer I-a in equilibrium with I-b should exhibit a positive chirality in view of the exciton chirality rule and this was found to be the case as observed in the CD.

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I-a          I-b
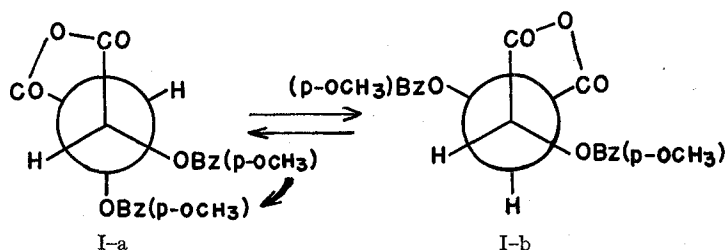
Analogous chiroptical behavior was observed with the (−)-anhydride II, which showed a UV-absorption at 262 nm ($\epsilon$, 32,000) and two ORD Cotton effects at 284 and 255 nm due to di-$p$-methoxybenzoate chromophores. The signs of the two Cotton effects found for II, opposite to I of the well-defined ($R$ : $R$)-configuration, unambiguously showed the opposite configuration of II, that is, the (−)-anhydride II can be assigned the ($S$ : $S$)-configuration. This implies that the parent (+)-2,3-dimethyltartaric acid has the ($S$ : $S$)-configuration in contrast to the previous deduction. Furthermore, the observed negative sign of the CD Cotton effect due to the di-$p$-methoxybenzoate chromophore is consistent with the *a priori* prediction based on the exciton chirality rule with the sole contributing conformer II-a of ($S$ : $S$)-enantiomer in equilibrium with
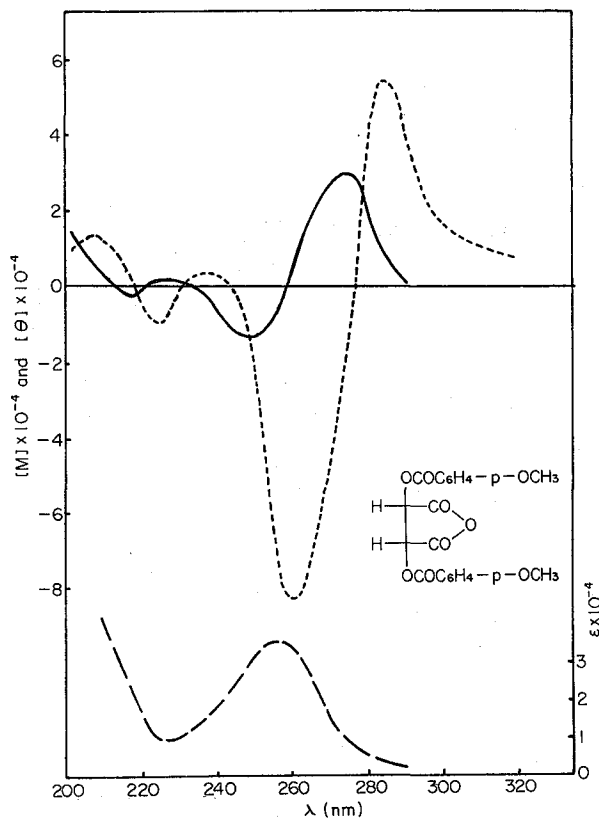


Fig. 1. Chiroptical properties of 0,0-dianisoyltartaric anhydride. ——, CD; ------, ORD; − − −, UV (in acetonitrile)
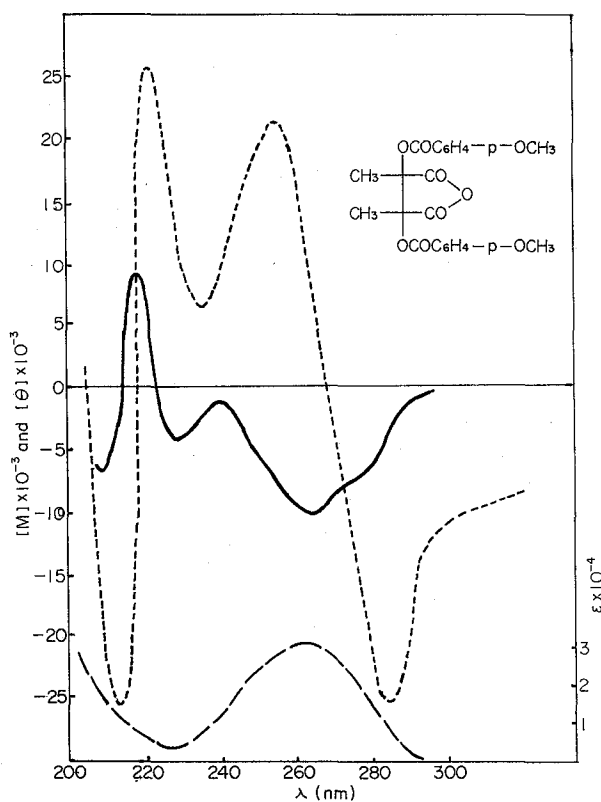
Fig. 2. Chiroptical properties of 0,0-dianisoyl-2,3-dimethyltartaric anhydride.
———, CD; ------, ORD; ----, UV (in acetonitrile)

non-contributing II-b, which enhances the validity of the experimental assignment.

The reason of such a disagreement between assignments by these chiroptical means is obscure and is currently being prosecuted, and the decisive conclusion will be described elsewhere.



II-a          II-b
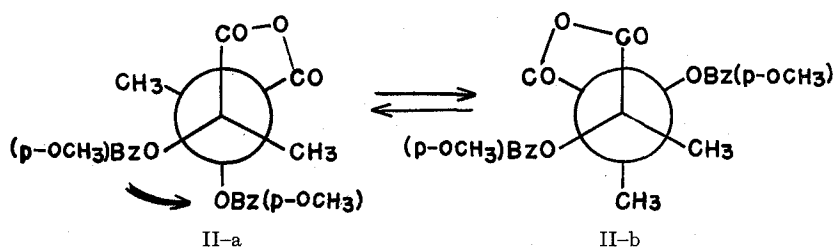
**EXPERIMENTAL**

(+)-(R:R)-O,O-**Dianisoyltartaric Anhydride** (I)

Tartaric acid ($[\alpha]_D^{20}+12.0°$ ($c$, 10.0 water)) and anisoyl chloride of three mole equivalent were heated at 150–160°C for 2 hr. After cooling, the reaction mixture was washed with small amounts of ether and benzene was added. Sparingly soluble anisic acid was

filtered off and benzene was removed. After several repetitions of this treatment, pure anhydride I was obtained by recrystallization from benzene-$n$-hexane, mp 135–6°C, $[\alpha]_D^{20}$ +182° ($c$, 1.6, acetone). Ir(KBr); $\nu_{C=O}$ 1810, 1725, 1705 cm$^{-1}$. UV(CH$_3$CN); $\lambda_{max}$ 257 nm ($\varepsilon$, 39,000). Nmr(CD$_3$COCD$_3$); $\delta$ 3.90 (6H, singlet, OCH$_3$), $\delta$ 6.55 (2H, singlet, methine proton), $\delta$ 7.10 and 8.00 (8H, doublet doublet, aromatic proton). Anal. Found: C, 60.17; H, 4.07%; Calcd for C$_{20}$H$_{16}$O$_9$: C, 60.00; H, 4.03%. Yield 5.0%.

## (−)-*O,O*-Dianisoyl-*2,3*-Dimethyltartaric Anhydride (II)

In exactly the same procedure as described above, 2,3-dimethyltartaric acid ($[\alpha]_D^{20}$+ 13.6° ($c$, 0.99, water)) was converted to the pure anhydride II, mp 204–5°C (from acetonitrile-ether), $[\alpha]_D^{20}$–136° ($c$, 0.6, acetone). Ir(KBr); $\nu_{C=O}$ 1790, 1705 cm$^{-1}$. UV(CH$_3$CN); $\lambda_{max}$ 262 nm ($\varepsilon$, 32,000). Nmr(CDCl$_3$); $\delta$ 1.75 (6H, singlet, CH$_3$), $\delta$ 3.90 (6H, singlet, OCH$_3$), $\delta$ 6.90 and 8.00 (8H, doublet doublet, aromatic proton). Anal. Found: C, 61.64; H, 4.68%; Calcd for C$_{22}$H$_{20}$O$_9$: C, 61.68; H, 4.71%. Yield 28%.

## Optical Rotatory Dispersion and Circular Dichroism Curves Measurement

The ORD and CD were measured on a Jasco Model J-20 (ORD/CD) using a 1-mm cell at 20°C in acetonitrile solution.

(+)-*O,O*-Dianisoyltartaric anhydride: ORD ($c$, 0.022) [M]×10$^{-4}$; [M]$_{300}$+1.65°, [M]$_{284}$+5.5°, [M]$_{275}$ 0°, [M]$_{260}$—8.34°, [M]$_{243}$ 0°. [M]$_{237}$+0.37°, [M]$_{230}$ 0°, [M]$_{222}$—1.1°, [M]$_{218}$ 0°, [M]$_{210}$+1.3°. CD ($c$, 0.022) [$\theta$]×10$^{-4}$; [$\theta$]$_{292}$ 0, [$\theta$]$_{274}$+3.03, [$\theta$]$_{258}$ 0, [$\theta$]$_{250}$— 1.15, [$\theta$]$_{234}$ 0, [$\theta$]$_{227}$+0.15, [$\theta$]$_{221}$ 0, [$\theta$]$_{218}$—0.18, [$\theta$]$_{214}$ 0, [$\theta$]$_{200}$+1.7.

(−)-*O,O*-Dianisoyl-2,3-dimethyltartaric anhydride: ORD ($c$, 0.032) [M]× 10$^{-4}$; [M]$_{300}$—1.13°, [M]$_{284}$—2.47°, [M]$_{269}$ 0°, [M]$_{255}$+2.1°, [M]$_{235}$+0.67°, [M]$_{222}$+2.5°, [M]$_{219}$ 0°, [M]$_{214}$—2.5°, [M]$_{205}$ 0°. CD ($c$, 0.032) [$\theta$]×10$^{-3}$; [$\theta$]$_{298}$ 0, [$\theta$]$_{265}$—9.6, [$\theta$]$_{240}$—0.8, [$\theta$]$_{227}$—3.5, [$\theta$]$_{223}$ 0, [$\theta$]$_{218}$+9.25, [$\theta$]$_{214}$ 0, [$\theta$]$_{209}$—6.73.

### REFERENCES

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