

The Rotatory Dispersion Studies II.
The Rotatory Dispersion and Configuration
of Derivatives of Tartaric Acids

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RD 研究 第 II 報

酒石酸誘導体の旋光分散と立体構造

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酒石酸 (tartaric acid) は重要なオキシ酸の 1 種で, とくに果実などに広く存在する右旋性の酒石酸 (*d*-tartaric acid) は光学活性で旋光分散 (RD) 法による構造研究が可能であり, 多くの報文が見られる。著者の一人は以前ジエチル酒石酸のアルキリデン及びベンジリデン誘導体の RD を調べ, 5 員環を有する酒石酸誘導体の conformation を調べた (K. Satsumabayashi *et al.*, *Bull. Chem. Soc. Japan*, **41**, 1008 (1968))。その結果, ベンジリデン誘導体の場合には, benzoate band の $\pi \rightarrow \pi^*$ transition が旋光分散曲線をみると, 符号の相反する 2 つのコットン効果に分裂して現われ, これらの誘導体は単一 5 員環構造を有して比較的 rigid な分子であるから RD 法による経験則が適用可能となり chirality が決定された。しかし, これまで, 鎖状で flexible な構造をもつ酒石酸について conformation に関して決め手となる情報はなく, flexible な系における優位 conformation を見出すことは困難である。

本報では, RD, CD (円二色性), UV (紫外吸収), および NMR (核磁気共鳴) スペクトルにより flexible system をとる酒石酸誘導体 (diacetyl *d*-tartaric acid) について溶液中における優位 conformation を調べた。

更に詳細な情報を得るために 2 つの異なった酒石酸の環状誘導体 (dimethyl ethylenedene *d*-tartrate と diacetyl *d*-tartaric anhydride) の conformation を調べ比較検討した。

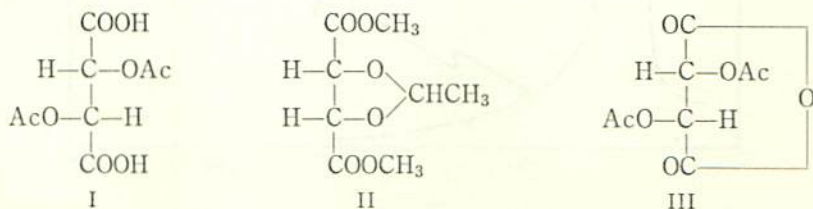
その結果, diacetyl *d*-tartaric acid (化合物 I) は 208 nm にカルボニル基による弱い $n \rightarrow \pi^*$ transition を示すが, その CD 曲線をみると 272 nm に小さな正のコットン効果と 222 nm に大きな負のコットン効果を示し, 2 つに分裂する。これはカルボニル基に, 弱い相互作用が存在することを示し, 従って化合物 I には 3 つの staggered

conformation, A ($-\text{COOH}$ 同志が trans のもの), B ($-\text{OCOCH}_3$ 同志が trans のもの) および C ($-\text{H}$ 同志が trans のもの) が考えられることになる。次いで2種の違った化合物II ($-\text{COOMe}$ 同志が trans) とIII ($-\text{OAc}$ 同志が interaction を有する) について調べたところ, 化合物IのRD, CD曲線はIIIのそれと同様なパターンを示すが, 分裂した正のコットン効果は大きさが $\frac{1}{3}$ 以下となって interaction の弱いことを示している。

以上のことより化合物Iのコンホメーションは溶液中においては conformer A と B の両方が存在するものと推論された。

The Rotatory Dispersion Studies II¹⁾The Rotatory Dispersion and Configuration
of Derivatives of Tartaric Acids

In the past many studies²⁾ were made on the conformation of tartaric acid, but conclusive information has not yet been obtained. One³⁾ of the authors examined the rotatory dispersion (RD) of the alkylidene and benzylinene derivatives of diethyl *d*-tartrate. As a result, the conformations of tartaric acid derivatives with five-membered acetal ring were made clear. However, it is not so easy to find a preferable conformation in the flexible system as in the compounds of comparatively rigid conformation with such an intramolecular ring. In this paper the preferable conformation in the solution of diacetyl *d*-tartaric acid (Compound I) with flexible conformation has been studied by means of RD and circular dichroism (CD). Furthermore, the RD and CD curves and NMR spectra of two different ring derivatives of tartaric acid, namely, dimethyl ethylidene *d*-tartrate (Compound II) and diacetyl *d*-tartaric anhydride (Compound III) have been studied for the purpose of comparison.

Fig. 1. Structures of three Compounds (Ac=COCH₃).

Results and Discussion

In fig. 2 are given the RD, CD, and UV curves of diacetyl *d*-tarttaric acid. The absorption band at 218 nm of the UV curve is due to the weak $n \rightarrow \pi^*$

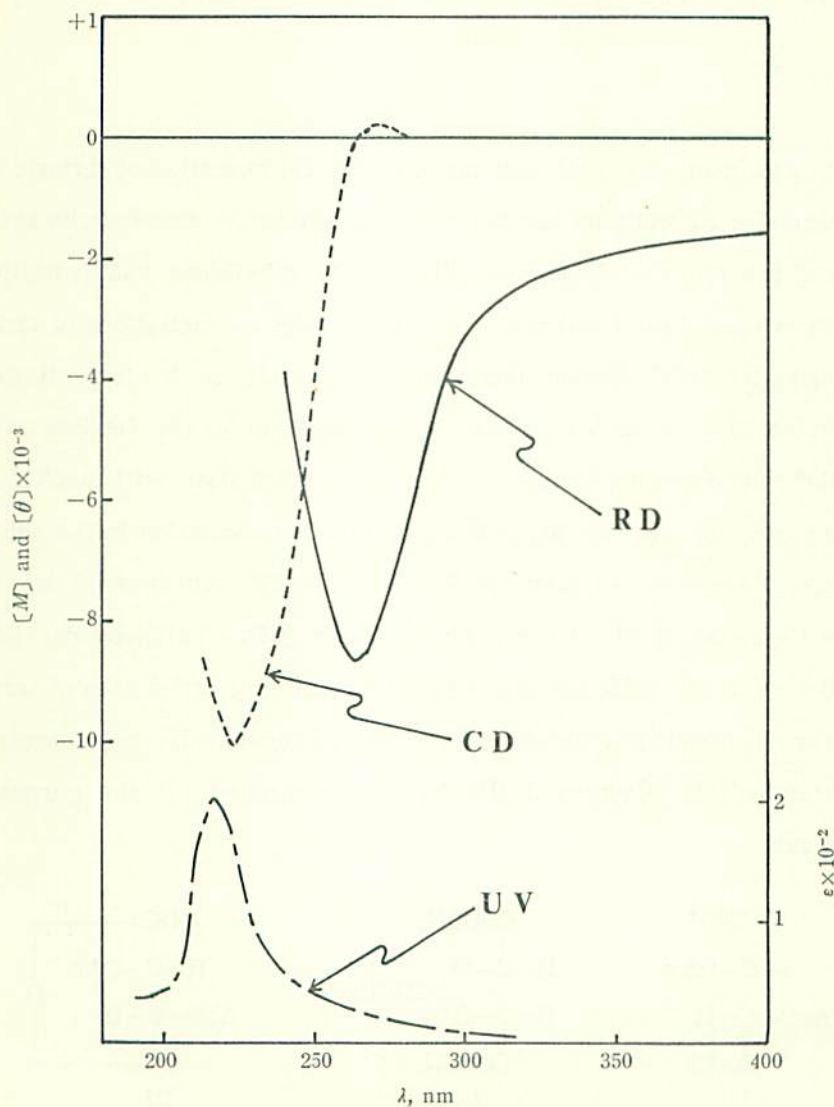


Fig. 2. RD, CD and UV of Compound 1.

transition of the carboxyl group. While the RD curve shows a negative Cotton effect with a negative first extreme at 230 nm, the CD curve shows a very small positive peak at 272 nm and a large negative peak at 216 nm. This slight positive Cotton effect is due to the splitting of $n \rightarrow \pi^*$ transition of the carboxyl group and shows the presence of interaction, though very little, within the carboxyl group. Compound I may take any one of the following three staggered conformations, all of which can bring about carbonyl interaction (Fig. 3).

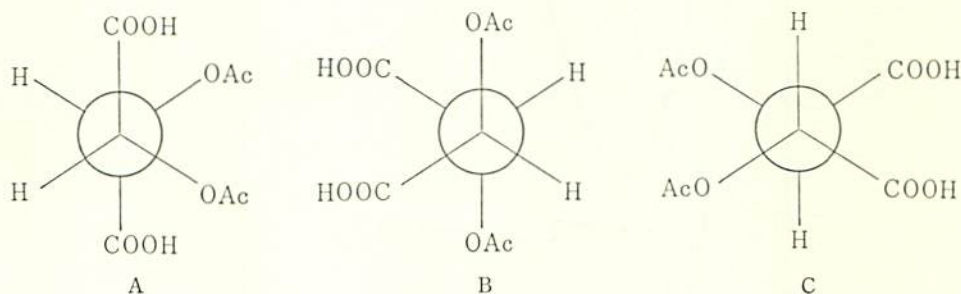


Fig. 3. Three Conformations of Compound I.

In order to obtain information about the above conformations the compounds II and III were studied.

The RD, CD and UV curves of dimethyl ethylidene *d*-tartrate are shown in Fig. 4. As is clear from the RD curve, Compound II exhibits a negative Cotton effect with a negative peak at 218 nm. As may be seen from UV_{max} , this is due to the $n \rightarrow \pi^*$ transition of the carboxylate group.

On the other hand, as two hydrogen atoms attached to two asymmetric carbons give spin-spin coupling in the case of Compound II, the conformation of the acetal ring can be examined by measurement of NMR spectra. When the dihedral angle of $H_A-C-C-H_B$ was calculated by applying Shimizu's equation⁴⁾, $J_{AB} = C + A|\cos \theta|$, to the results of NMR measurement, it was 54° . This approximates to the angle 60° which is formed when the two carboxyl

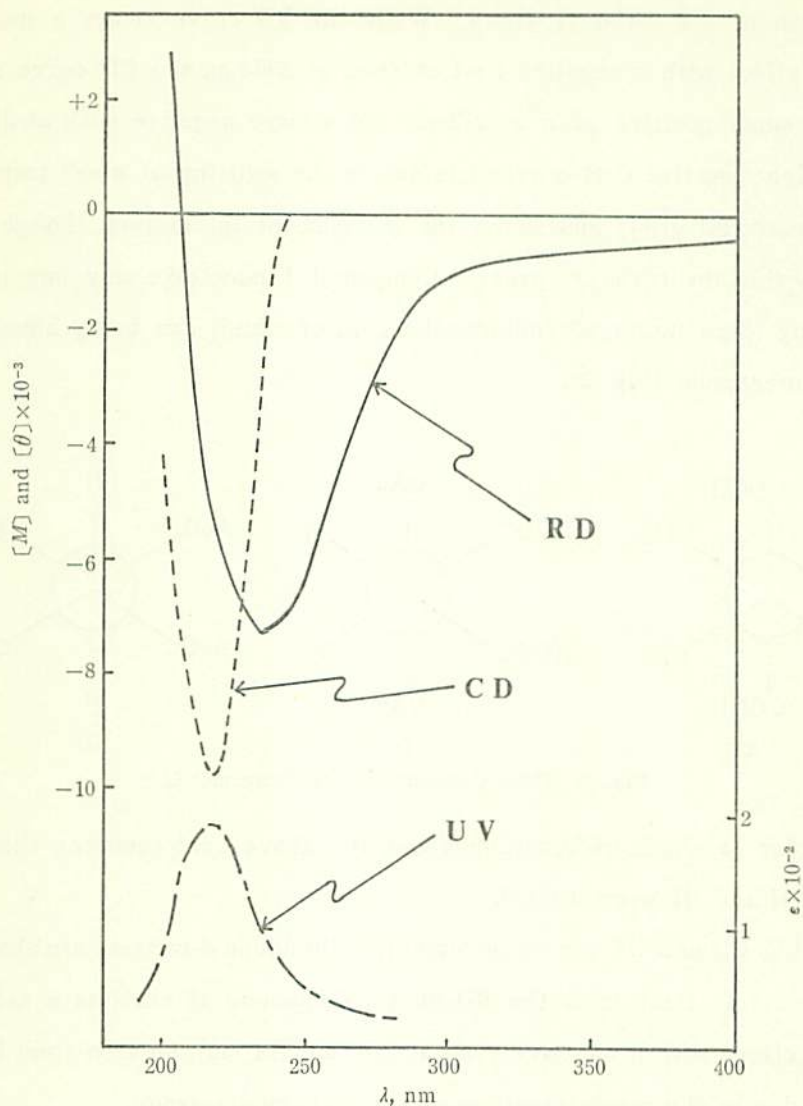


Fig. 4. RD, CD and UV of Compound II.

groups of tartaric acid are of the trans-form. Therefore it can be concluded that the five-membered ring is not of the plane structure but of the half-chair conformation as in Fig. 5.

Two conformations of the acetal ring are possible: one in which the COOCH_3 groups are of the trans-form, and the other in which hydrogen

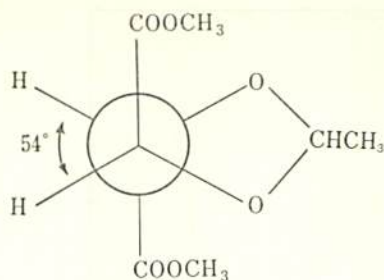


Fig. 5. Conformation of Compound II.

atoms are of the trans-form. The results of the measurement of NMR spectra supported the former (Fig. 5). From this fact it can be deduced that, in the case of Compound I, either, conformer C (which has naturally large repulsion and is considered energetically unsta-

ble) does not contribute (Fig. 3).

The RD, CD and UV curves of diacetyl *d*-tartaric anhydride (Compound III) are given in Fig. 6. Compound III shows a weak absorption due to the $n \rightarrow \pi^*$ transition at 208 nm, and the negative Cotton effect at 215 nm observed in the CD curve is to be assigned to this absorption. If the lactone rule⁵⁾ of the plane five-membered ring is applied to this anhydride ring, regarding it as a sort of lactone, the oxygen atom attached to the asymmetric carbon enters the negative octant, and the sign of Cotton effect is in accordance with this. Furthermore, the CD curve in Fig. 6 shows a positive peak at 243 nm, showing the existence of a positive Cotton effect. It is considered that this is due to the exciton band⁶⁾ which arises from the coupling of two carbonyl groups. Therefore it may be considered that, in the case of Compound I too, the two carbonyl groups are in a site (conformer C) which can give rise to coupling, because a weak positive Cotton effect is observable. But the fact that negative CD_{max} at 216 nm of Compound I is almost equal to that of Compound II, while positive CD_{max} is less than 1/3 of the latter suggests that the probability of the coupling of the carboxyl groups is slight.

In the conformation of Compound I the two conformers A and B are in the relation: $A \rightleftharpoons B$.

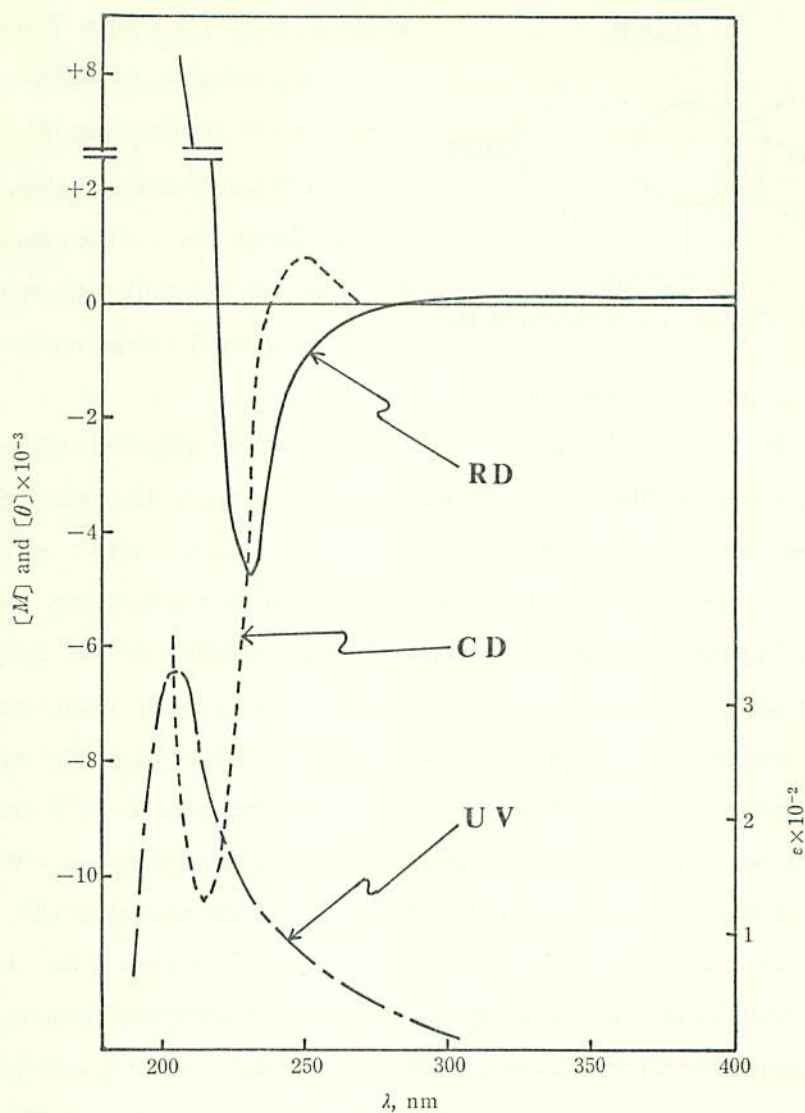


Fig. 6. RD, CD and UV of Compound III.

Experimental

The samples were all prepared according to the method described in the literature⁷⁾. The rotatory dispersion and circular dichroism were measured

in ethanol at about 25°C in the wavelength region from 200 nm to 600 nm with a JASCO optical rotatory dispersion recorder of the ORD/UV-5 type. The ultraviolet absorption was measured in ethanol with self-recording spectrophotometer of Hitachi EPS-3T type. The NMR spectra were measured with a Varian A-60 spectrometer in carbon tetrachloride with tetramethylsilane as an internal reference.

Diacetyl *d*-tartaric acid (Compound I). — Colorless needles; mp 118–119°C. The RD and CD were measured at 25°C (*c* 0.049): $[\alpha]_{600} -39.5^\circ$, $[\alpha]_{589} -40.8^\circ$, $[\alpha]_{232} -3710^\circ$ (trough), $[\alpha]_{220} -1630^\circ$, $[\alpha]_{207} +3550^\circ$, $[\theta]_{280} 0^\circ$, $[\theta]_{272} +90.0^\circ$ (peak), $[\theta]_{222} -10100^\circ$ (trough), $[\theta]_{212} -9450^\circ$. The UV spectrum was measured at 20°C. ϵ_{\max} 208 at 218 nm.

Dimethyl ethylidene *d*-tartrate (Compound II). — Colorless liquid; bp 140°C/17 mmHg. The RD and CD were measured at 25°C (*c* 0.396). $[\alpha]_{600} -75.3^\circ$, $[\alpha]_{589} -77.0^\circ$, $[\alpha]_{400} -195^\circ$, $[\alpha]_{300} -495^\circ$, $[\alpha]_{234} -3560^\circ$ (trough), $[\alpha]_{215} +1360^\circ$, $[\theta]_{253} 0^\circ$, $[\theta]_{218} -9780^\circ$ (trough), $[\theta]_{200} -4220^\circ$. The UV spectrum was measured at 25°C. ϵ_{\max} 190 at 216 nm.

Diacetyl *d*-tartaric anhydride (Compound III). — Colorless needles; mp 135.0–136.0°C. The RD and CD were measured at 25°C (*c* 0.194). $[\alpha]_{400} +10.3^\circ$, $[\alpha]_{303} +25.8^\circ$ (peak), $[\alpha]_{230} -2220^\circ$ (trough), $[\alpha]_{210} -1950^\circ$, $[\theta]_{270} 0^\circ$, $[\theta]_{243} +720^\circ$ (peak), $[\theta]_{215} -10500^\circ$ (trough), $[\theta]_{205} -6680^\circ$. The UV spectrum was measured at 24°C. ϵ_{\max} 330 at 208 nm.

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