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THE STEREOCHEMISTRY OF CHROMOMYCINONE AND A NOTE ON THE BENZOATE RULE

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Abstract—It has been shown that chromomycinone can be represented by the absolute configurational structure 1. Molecular rotation differences between the acetate and benzoate of secondary alcohols can be employed for deriving the absolute configuration.

CHROMOMYCINONE (1),[1] $C_{21}H_{24}O_9$, is the common aglycone of closely related antibiotics, chromomycin A_2, A_3 and A_4, the structures of which have recently been elucidated by the present authors.[2] The stereochemistry of this chromophore will be discussed in this paper.

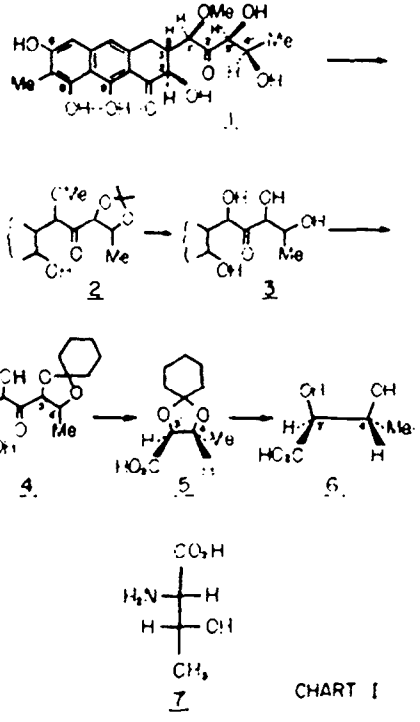


CHART I

[1] M. Miyamoto. K. Morita, Y. Kawamatsu, S. Noguchi, R. Marumoto, K. Tanaka, S. Tatsuoka, K. Nakanishi, Y. Nakadaira and N. S. Bhacca, *Tetrahedron Letters* 2355 (1964).
[2] M. Miyamoto, Y. Kawamatsu, K. Kawashima, M. Shinohara and K. Nakanishi, *Tetrahedron Letters* 545 (1966); see also *Tetrahedron* 22, 2785 (1966).

Absolute configurations at C-3′ *and* C-4′

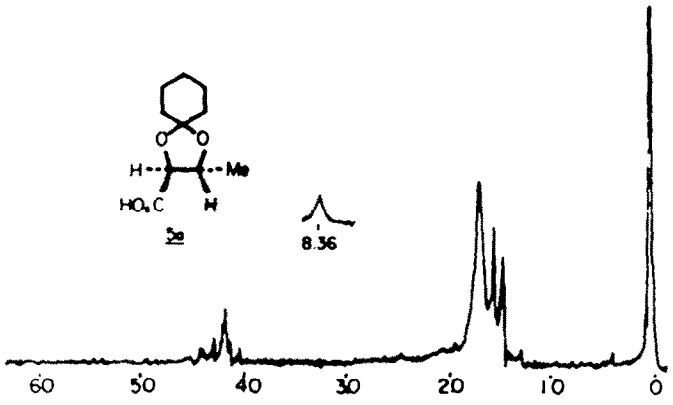
Chromomycinone was first converted to the isopropylidene derivative **2** in order to increase the solubility of the sample in dichloromethane. The derivative **2** was then reacted with boron trichloride[3] in dichloromethane when the ether and ketal linkages were cleaved to afford demethylchromomycinone (**3**). Demethylchromomycinone (**3**) was then converted to the cyclohexylidene ketal **4**, which without purification was oxidized with periodic acid in aqueous tetrahydrofuran to afford an oily acid **5**. The synthesis of cyclohexylidene ketals of DL-*threo*-α,β-dihydroxybutyric acid (**5a**) and its DL-*erythro*-isomer (**5b**) has recently been recorded and it has also been suggested that the two isomers are readily differentiated by the IR absorptions in the region of 900–950 cm^{-1}.[4] The two acids were synthesized according to the literature by oxidation of crotonic acid with osmium tetroxide–silver chlorate (leading to *threo* acid)[5] and tungstic oxide–hydrogen peroxide (leading to *erythro* acid),[6] respectively, followed by reaction with cyclohexanone. An IR spectroscopic comparison suggested that the cyclohexylidene derivative obtained from the natural product belonged to the *threo*-series, but this was much more clearly indicated by the NMR spectra (Fig. 1). Hydrolysis of the ketal **5** with aqueous acetic acid yielded an oily acid **6**, the IR spectrum (liq. film) of which was identical with that of synthetic DL-*threo*-α,β-dihydroxybutyric acid but not with the DL-*erythro*-isomer. Although the acid **6** could not be crystallized, its specific rotation $[\alpha]_D$ of −13° was in good agreement with the reported value of −15·0° for D-*threo*-α,β-dihydroxybutyric acid, which has an established absolute configuration because of its correlation with D_G-(−)-threonine (L_S-(−)-threonine) (**7**).[7] The acid **6** was thus established to have the absolute configuration shown, and therefore the configurations at C_3' and C_4' in chromomycinone are S and R, respectively.

Relative configurations at C-2, C-3 *and* C-1′

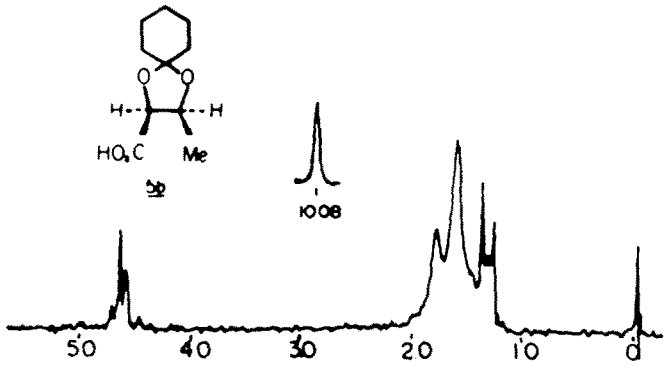
The relative configurations at C-2, C-3 and C-1′ can be deduced on the basis of NMR coupling constants. Namely, in the various acetates of chromomycinone bearing an acetoxyl group at C-2, the NMR signals due to C_2–H invariably appear around 6 ppm as a doublet with J_{23} *ca.* 10 c/s; e.g., in the C-2,6,3′,4′-tetraacetate it is found at 5·67 ppm with a splitting of 11·5 c/s (Chart 2). These large coupling constants show that C_2–H and C_3–H must be trans and diaxial with a dihedral angle of close to 180°;[8] i.e., the two substituents are trans and diequatorial.

The relative configurations of C_3–H and C_1'–H were then deduced as follows. When chromomycinone was treated with 8% potassium carbonate at room temperature, an isomerization involving the C_2' and C_3' oxygen functions took place to give the cyclic hemiketal **11**, isochromomycinone,[9] m.p. 227° (dec.), which could be

[3] S. Allen, T. G. Bonner, E. J. Bourne and N. M. Saville, *Chem. & Ind.* 630 (1958); T. G. Bonner, E. J. Bourne and S. McNally, *J. Chem. Soc.* 2929 (1960).
[4] M. P. Berry and M. C. Whiting, *J. Chem. Soc.* 862 (1964).
[5] B. Braun, *J. Amer. Chem. Soc.* **51**, 228 (1929).
[6] M. Mugdan and D. P. Young, *J. Chem. Soc.* 2988 (1949).
[7] J. D. Crum, *Adv. Carbohydrate Chem.* **13**, 169 (1958); C. E. Meyer and W. C. Rose, *J. Biol. Chem.* **115**, 721 (1936).
[8] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959); *J. Amer. Chem. Soc.* **85**, 2870 (1963).
[9] M. Miyamoto, K. Morita, Y. Kawamatsu, S. Noguchi, R. Marumoto, M. Sasai, A. Nohara, Y. Nakadaira, Y. Y. Lin and K. Nakanishi, *Tetrahedron* **22**, 2761 (1966).

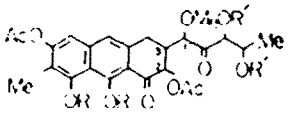


(a) Synthetic DL-*threo*-acid **5a** and natural D-*threo*-acid **5**.



(b) Synthetic DL-*erythro*-acid **5b**.

FIG. 1. NMR spectra of cyclohexylidene ketals of α,β-dihydroxybutyric acids in $CDCl_3$, ppm from TMS.



8 R=H, R'=Ac : δ5.67, J 11.5

9 R=Ac, R'=Ac : δ5.57, J 9.5

10 R=Ac, R'=C(Me)(Me) δ5.58, J 12.0

CHART 2. Chemical shifts and coupling constants of C_5–H. The three acetates are described in Ref. 9.

converted into the isopropylidene triacetate **12**. The NMR spectrum of the latter derivative **12** (Fig. 2) established that the hydrogens attached to C-2, C-3, C-1′ and C-2′ should all be axial in view of the large J constant, i.e., 3·58 ppm (triplet, J 9·1 c/s, 1′-H), 4·49 ppm (quartet, J 6·7 c/s, 4′-H), 4·53 ppm (doublet, J 12·1 c/s, 2-H), and 5·04 ppm (doublet, J 9·1 c/s, 2′-H), and this in turn established the relative configurations of C-3 and C-1′ in chromomycinone (**1**). Obviously the configuration at C-1′ is not inverted during alkaline rearrangement of chromomycinone to its isomer **11** because isopropylidenechromomycinone (**2**) was recovered unchanged upon similar alkali treatment.

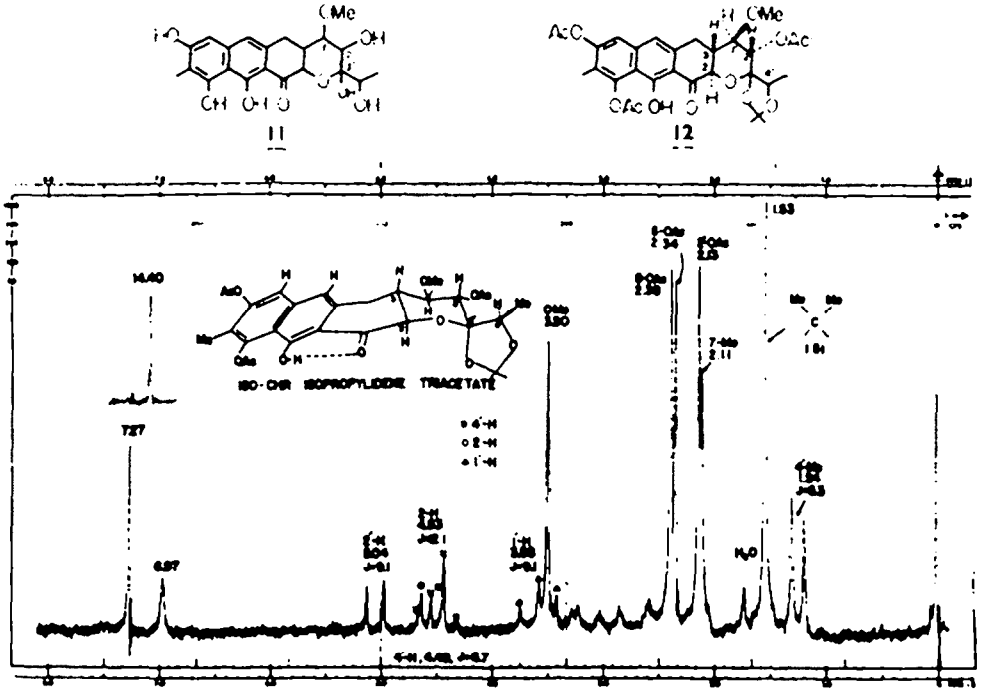
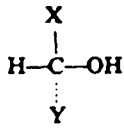


FIG. 2. NMR spectrum of iso-CHR isopropylidene triacetate (**12**) in $CDCl_3$.

Absolute configuration at C-2

The absolute configuration at C-2, and hence of the three optical centers at C-2, C-3 and C-1′, was finally deduced by application of a slightly modified "Benzoate Rule". Brewster[10] has rationalized and extended Freudenberg's so-called "Phthalate Rule"[11] and Mills' rule[12] in terms of conformational dissymmetry,[13,14] and has suggested a more general "Benzoate Rule".[10] Namely, in the carbinol having the absolute configuration **13**, if X and Y represent, respectively, groups with the smaller and larger steric requirements (but similar polarizability), or groups with the larger and smaller polarizability (but similar steric requirements), then the rotation difference $\Delta[M]_D$ between the benzoate and the carbinol ($[M]_D$ of benzoate minus $[M]_D$ of

[10] J. H. Brewster, *Tetrahedron* **13**, 106 (1961).
[11] K. Freudenberg, *Stereochemie* p. 696. Deuticke, Leipzig (1933).
[12] J. A. Mills, *J. Chem. Soc.* 4976 (1952).
[13] D. H. Whiffen, *Chem. & Ind.* 964 (1956).
[14] J. H. Brewster, *J. Amer. Chem. Soc.* **81**, 5475, 5483, 5493 (1959); *Tetrahedron Letters* No. 20, 23 (1959).



carbinol) will be positive. Although the benzoate rule[15] has already been applied to deduce the absolute configuration of several natural products[16–18] it cannot be applied to chromomycinone itself since the effect of the C_1-carbonyl on the rotation shift resulting from esterification at C-2 cannot be estimated.

Accordingly, 1-deoxochromomycinone (**14**)[1,9] (Chart 3), the catalytic hydrogenation product of chromomycinone, was employed, but again the rotation shift accompanying benzoylation at C-2 cannot be utilized because of its hemiketal structure.[1,9] However, a literature survey (see below) showed that absolute configurations of secondary hydroxyls can also be derived from rotation differences between the benzoates and acetates instead of benzoates and the original alcohol. Thus, as indicated in Chart 3, three pairs of acetates and benzoates were prepared starting from 1-deoxochromomycinone (**14**), and the following $\Delta[M]_D$ values were found: +292° for pair **15**; +395° for pair **16**; and +260° for pair **17**. The acetyl and

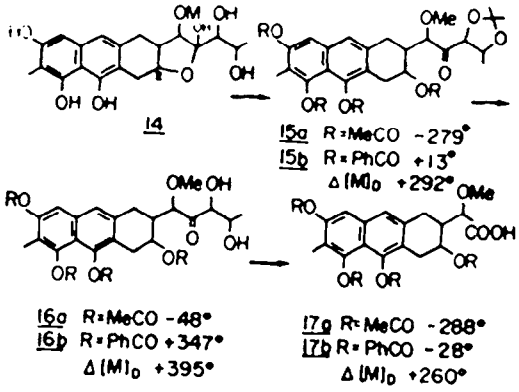


CHART 3. Numerals denote $[M]_D$ values in $CHCl_3$, *c*:1·0, 23–24°; $\Delta[M]_D$ (benzoate–acetate) values are also given.

benzoyl groups on the naphthalene nucleus are far removed from the optical center at C-2, and would not interfere with the application of the benzoate rule at this center. Therefore, the molecular rotation differences noted in the three pairs of derivatives **15** to **17**, which were found to be consistently positive and large, can be attributed to the differences at C-2. The positive values lead to an R configuration for C-2, and consequently S and R configurations for C-3 and C-1′, respectively.

The validity of the benzoate rule as applied to molecular rotational differences between benzoates and acetates was tested on some steroids and triterpenoids of

[15] A further generalized treatment of the Benzoate Rule will be published shortly: Mo. Ohashi and K. Nakanishi.

[16] Illudin S (Lampterol): K. Nakanishi, M. Ohashi, M. Tada and Y. Yamada, *Tetrahedron* **21**, 1231 (1965).

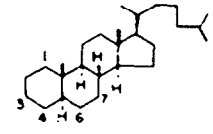
[17] Grayanotoxins: H. Kakisawa, T. Kozima, M. Yanai and K. Nakanishi, *Tetrahedron* **21**, 3091 (1965).

[18] Caucalol: S. Sasaki, Y. Itagaki, H. Moriyama, K. Nakanishi, E. Watanabe and T. Aoyama, *Tetrahedron Letters*, No. 6, 623 (1966).

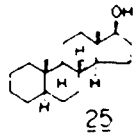
TABLE 1. MOLECULAR ROTATION DIFFERENCES OF SOME STEROIDS AND TRITERPENOIDS

Compd	$[M]_D$			$\Delta[M]_D$			Ref.
	Carbinol	Acetate	Benzoate	Δ_1*	Δ_2*	Prediction	
18	+76	+120	+1	−75	−119	—	10, 19
19	+89	+56	+99	+10	+43	0	
20	+12	+69	−99	−111	−168	—	
21	+113	+84	+281	+168	+197	+	
22	+136	+299	+308	+172	+9	+	
23	+43	−52	−108	−151	−56	—	
24	+202	−263	+429	−227	+692	+	
25	+33	+13	+197	+164	+184	+	19
26	+55	+21	+49	−6	+28	0	
27	+379	+384	+530	+5	+151	+	20
28	+358	+370	+498	+12	+140	+	
29	−77	−9	+144	+68	+251	+	
30	+115	+201	+318	+86	+203	+	
31	+261	+273	−378	+12	+117	+	
32	+258	+306	−392	+48	+134	+	

* $\Delta_1 = \Delta[M]_D$ (benzoate–carbinol), $\Delta_2 = \Delta[M]_D$ (benzoate–acetate).



18 1β-ol
19 3β-ol
20 4α-ol
21 4β-ol
22 6α-ol
23 7α-ol
24 7β-ol



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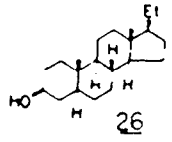

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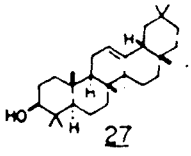

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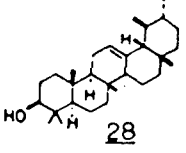

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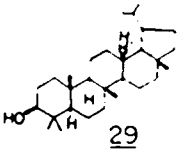

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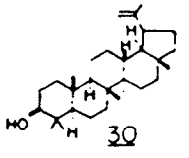

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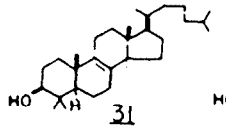

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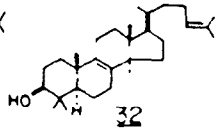

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[19] J. P. Mathieu and A. Petit, *Tables de Constantes et Données Numériques. 6. Constantes Selectionnées. Pouvoir Rotatoire Naturel. I. Stéroïdes.* Masson, Paris (1956).

[20] W. Klyne and W. M. Stokes, *J. Chem. Soc.* 1979 (1954).

known configurations (see Table 1, compounds **18** to **32**). The Δ_1 values are in good agreement with the prediction following from the original benzoate rule;[10,15] the Δ_2 values are also seen to follow prediction, thus verifying that it can also be applied to benzoate and acetate pairs, although in some cases (compounds **22** and **23**) the magnitudes are not sufficiently large to be employed for configuration studies. Interestingly, all Δ_2 values are larger than the Δ_1 values in the triterpenoids **27** to **32** (and in most steroids), so that Δ_2 values may be used to advantage when the inference from the conventional Δ_1 value is not conclusive. To summarize, the Δ_2 value can be used for assigning absolute configurations to carbinols when the magnitude is sufficiently large, which is the case for chromomycinone derivatives.

EXPERIMENTAL

UV and IR spectra were recorded on a Hitachi model EPS-2 and Hitachi model EPI-S2, respectively. NMR spectra were measured with a Varian A-60 instrument for $CDCl_3$ solutions; chemical shifts are given in ppm relative to internal tetramethylsilane: s, singlet; d, doublet; m, multiplet. The silica gel used for column and thin-layer chromatography (TLC) was pre-treated with a 1% AcOEt solution of oxalic acid. A mixture of $CHCl_3$ and AcOEt (1:1 v/v) was used as the solvent for TLC. M.p.'s are uncorrected.

Demethylchromomycinone (**3**)

To a solution of isopropylidenechromomycinone (**2**) (2·90 g) in CH_2Cl_2 (120 ml) chilled in a dry ice–acetone bath, was added BCl_3 (25 g) similarly chilled. The reaction mixture was left standing for 1 hr at room temp and then poured into ice water and extracted with AcOEt. The crude crystalline product (1·10 g), which precipitated during the extraction, was collected by filtration; an additional crop of crystals (0·35 g) was obtained by chromatography of the filtrate on silica gel using AcOEt as solvent. The pure product crystallized from acetone as fine needles, m.p. 216° (dec.). (Found: C, 57·67, 57·86; H, 5·55, 5·56. $C_{36}H_{38}O_9 \cdot \frac{1}{2}H_2O$ requires: C, 57·83; H, 5·58%.) λ_{max}^{EtOH} (log ε) 232 mμ (4·32), 281 (4·54), 325 (3·79), 340 (3·79), 415 (3·95). ν_{max}^{KBr} 3400, 1719, 1635 cm^{-1}.

Cyclohexylidene ketal **4** *of demethylchromomycinone*

A suspension of demethylchromomycine (**3**) (154 mg) and a small amount of *p*-toluenesulfonic acid in cyclohexanone (1 ml) was stirred at room temp for 50 min, during which time the suspended material dissolved gradually. The excess of cyclohexanone was removed by steam distillation. Chromatography of the residue on silica gel using $CHCl_3$–AcOEt (1:1) as solvent yielded an amorphous substance which was shown to be homogeneous by TLC. ν_{max}^{KBr} 3400, 1722, 1634 cm^{-1}. Characterization of the structure **4** was effected with the non-crystalline pentaacetate, which was prepared by standard treatment with acetic anhydride and pyridine. (Found: C, 61·82; H, 6·06. $C_{56}H_{66}O_{14}$ requires: C, 62·06; H, 5·79%.) λ_{max}^{EtOH} (log ε) 260 mμ (4·84), 300 (3·87), 361 (3·45). $\nu_{max}^{CHCl_3}$ 1765 (br.), 1704, 1634, 1190 cm^{-1}. NMR δ 1·6 (13H, m), 2·12, 2·16, 2·26, 2·38, 2·44, 2·50 (each 3H, s, OAc and arom. CH_3), 4·18 (2H), 5·5 (1H), 5·67 (1H), 7·45 (1H, s, arom. H), 7·53 (1H, s, arom. H).

Periodic acid oxidation of the cyclohexylidene ketal **4**

A solution of the ketal **4** (130 mg) in water (1 ml) and tetrahydrofuran (4 ml) was treated with $HIO_4 \cdot 2H_2O$ (130 mg) and left standing overnight at room temp. The resulting dark colored solution was evaporated under red. press. at room temp. A solution of the residue in AcOEt was washed with water and evaporated. The residue was extracted with CCl_4 and absorbed on a column packed with active C. Elution with $CHCl_3$ afforded an oily acid **5** (37 mg). $[\alpha]_D^{29} = -18°$ (c = 1, in $CHCl_3$). IR (liq. film), PPC* and NMR (Fig. 1) were all identical with those of the synthetic cyclohexylidene ketal of DL-*threo*-α,β-dihydroxybutyric acid.

D-threo-α,β-*Dihydroxybutyric acid* (**6**)

A solution of the acid **5** described above in AcOH (2 ml) and water (1 ml) was heated at 70° for 2 hr. The reaction mixture was evaporated to dryness, taken up with AcOEt, and the solution was

* Paper partition chromatography; solvent system, n-butanol saturated with 1·5N NH_4OH.

passed through a column packed with active C. Evaporation of the solvent yielded a colorless oily acid **6**, $[\alpha]_D^{31} = -13°$ ($c = 1{\cdot}5$ in H_2O), lit.[7] $[\alpha]_D^{20} = -15{\cdot}0°$ (solvent not stated). IR (liq. film) and PPC were in good accord with those of synthetic DL-*threo*-α,β-dihydroxybutyric acid.

DL-threo-α,β-*Dihydroxybutyric acid*

DL-*threo*-α,β-Dihydroxybutyric acid was obtained by oxidation of crotonic acid with silver chlorate in the presence of OsO_4 catalyst following the method of Braun,[8] m.p. 73–75°, lit. m.p. 74°. ν_{max}^{KBr} 1730, 1144, 1073, 1010, 950, 898, 850 cm^{-1}. PPC $R_f = 0{\cdot}06$.

DL-erthro-α,β-*Dihydroxybutyric acid*

DL-*erythro*-α,β-Dihydroxybutyric acid was obtained by oxidation of crotonic acid with H_2O_2 in the presence of tungstic oxide catalyst following the method of Mugdan and Young,[9] m.p. 75–80°, lit. m.p. 82–83°. ν_{max}^{KBr} 1725, 1137, 1080, 1009, 938, 912, 841 cm^{-1}. PPC $R_f = 0{\cdot}06$.

Cyclohexylidene ketals **5a** *and* **5b** *of the* α,β-*dihydroxybutyric acids*

Ketalization was effected by the use of anhydrous $CuSO_4$ following the method of Berry and Whiting,[4] m.p. *threo*-isomer, 50–52°; *erythro*-isomer, 83–85°, lit. m.p. 48·5–52° and 83·5–85°, respectively. $\nu_{max}^{CHCl_3}$ *threo*-isomer 1778, 1730, 940 (sh.), 930, 911 cm^{-1}, *erythro*-isomer 1780, 1732, 944, 920, 908 cm^{-1}. PPC *threo*-isomer $R_f = 0{\cdot}48$, *erythro*-isomer $R_f = 0{\cdot}47$. NMR (Fig. 1) *threo*-isomer δ 1·49 (3H, d, J = 5·3, sec. Me), 1·67 (10H), 4·14 (2H), 8·63 (1H, s, CO_2H); *erythro*-isomer δ 1·33 (3H, d, J = 6·0, sec. Me), 1·61, 1·80 (10H), 4·58 (2H), 10·08 (1H, s, CO_2H).

Alkali treatment of isopropylidenechromomycinone (**2**)

A solution of **2** (400 mg) in 8% K_2CO_3 (10 ml) was left standing at room temp for 4 hr. The mixture was neutralized with oxalic acid, extracted with AcOEt and evaporated. Chromatography of the residue on silica gel using $CHCl_3$–AcOEt (1:1) as solvent yielded unchanged starting material (200 mg). Further purification was effected by crystallization from methanol to afford fine needles, m.p. 118–120° (dec.), having an IR spectrum superimposable on that of authentic **2**.

Tetraacetate **15a**

A suspension of 1-deoxochromomycinone (**14**) (1·7 g) and a small amount of *p*-toluenesulfonic acid in acetone (10 ml) was left standing at room temp for several hours. The clear solution was poured into ice-water and the precipitate collected. The crude isopropylidene derivative was treated with acetic anhydride–pyridine (1:1, 10 ml) at room temp for 4 days. An amorphous acetate **15a** (1·8 g) exhibiting a single spot on TLC was obtained after chromatography on silica gel. $[\alpha]_D^{24} = -45{\cdot}3°$ ($c = 1{\cdot}0$ in $CHCl_3$) (Found: C, 62·34; H, 6·22; OCH_3, 4·73. $C_{33}H_{36}O_{18}$ requires: C, 62·53; H, 6·23; OCH_3, 5·04%.) λ_{max}^{EtOH} (log ε) 234 mμ (5·05), 283 (4·07). $\nu_{max}^{CHCl_3}$ 1760, 1725, 1200 cm^{-1}. NMR δ 1·40 (9H), 2·06 (3H, s), 2·07 (3H, s), 2·30 (3H, s), 2·36 (6H, s), 3·35 (3H, s), 4·18 (2H, m), 4·34 (1H, d, J = 3·0), 5·25 (1H, m), 7·39 (2H, s).

Diol tetraacetate **16a**

The tetraacetate **15a** (0·8 g) was dissolved in 50% AcOH (8 ml) and heated on a water-bath at 70° for 1 hr. Evaporation of the solvent followed by chromatography on silica gel afforded an amorphous product (0·4 g), which gave a single spot on TLC. $[\alpha]_D^{24} = -8{\cdot}4°$ ($c = 1{\cdot}0$ in $CHCl_3$). (Found: C, 60·39; H, 5·92. $C_{29}H_{34}O_{18}$ requires: C, 60·62; H, 5·96%.) λ_{max}^{EtOH} (log ε) 235 mμ (5·07), 284 (3·74). $\nu_{max}^{CHCl_3}$ 3500, 1765, 1723, 1191 cm^{-1}. NMR δ 1·31 (3H, d, J = 6·0), 2·09 (6H, s), 2·35 (3H, s), 2·39 (6H, s), 3·36 (3H, s), 4·2 (3H, m), 5·2 (1H, m), 7·40 (1H, s), 7·45 (1H, s).

Acid tetraacetate **17a**

To a solution of the diol tetraacetate **16a** (257 mg) in tetrahydrofuran (4 ml) and water (1 ml), was added $HIO_4 \cdot 2H_2O$ (240 mg). After being allowed to stand at room temp for 30 min, the reaction mixture was poured into a large excess of water, which caused the product to precipitate. Volatile matter was driven off from the vessel by a stream of N_2 and passed into a 2N HCl solution of 2,4-dinitrophenylhydrazine. After leaving the solution for 1 hr, the crystalline hydrazone (47 mg) was collected and identified as acetaldehyde 2,4-dinitrophenylhydrazone. The precipitate, which remained

after removal of volatile products, was taken up in AcOEt and chromatographed on silica gel to yield a solid (204 mg). Crystallization from benzene yielded colorless fine needles, m.p. 127–130° (dec.). $[\alpha]_D^{24} = -55{\cdot}7°$ ($c = 1{\cdot}0$ in $CHCl_3$). (Found: C, 59·89, 60·01; H, 5·37, 5·85. $C_{66}H_{88}O_{11}$ requires: C, 60·46, H, 5·46%.) λ_{max}^{EtOH} (log ε) 234 mμ (5·08), 283 (3·75). $\nu_{max}^{CHCl_3}$ 3500–2300 (CO_2H), 1763, 1190 cm^{-1}. NMR δ 2·14 (6H, s), 2·38 (3H, s), 2·43 (6H, s), 3·47 (3H, s), 4·2 (1H, m), 5·3 (1H, m), 7·49 (1H, s), 7·56 (1H, s), 8·03, (1H, CO_2H).

Tetrabenzoate **15b**

The crude isopropylidene derivative[9] obtained from **14** (2 g) was treated with benzoyl chloride (3 ml) and pyridine (6 ml) at room temp for 1 day. Chromatography on silica gel afforded a homogeneous (TLC) product (1·6 g). $[\alpha]_D^{24} = +1{\cdot}5°$ ($c = 1{\cdot}0$ in $CHCl_3$). (Found: C, 72·75; H, 5·54. $C_{58}H_{44}O_{13}$ requires C, 72·38; H, 5·37%.) λ_{max}^{EtOH} (log ε) 236 mμ (5·13). $\nu_{max}^{CHCl_3}$ 1734, 1250 cm^{-1}. NMR δ 1·46 (9H), 2·16 (3H, s), 3·34 (3H, s), 4·2 (2H, m), 4·6 (1H), 5·6 (1H, m), 7·0–8·4 (20H, m).

Diol tetrabenzoate **16b**

The tetrabenzoate **15b** (1·2 g) was hydrolysed in the same manner as described for the diol tetraacetate **16a**. Crystallization from EtOH afforded colorless fine needles (1·0 g), m.p. 172° (dec.). $[\alpha]_D^{21} = +42{\cdot}2°$ ($c = 1{\cdot}0$ in $CHCl_3$). (Found: C, 71·46; H, 4·94. $C_{58}H_{42}O_{14}$ requires C, 71·52; H, 5·15%.) λ_{max}^{EtOH} (log ε) 237 mμ (5·14). $\nu_{max}^{CHCl_3}$ 3500, 1740 1255 cm^{-1}. NMR δ 1·32 (3H, d, $J = 6{\cdot}0$), 2·15 (3H, s), 3·34 (3H, s), 4·3 (2H, m), 4·6 (1H), 5·5 (1H, m), 7·0–8·4 (20H, m).

Acid tetrabenzoate **17b**

The diol tetrabenzoate **16b** (447 mg) was oxidized in the same manner as described for the acid tetraacetate **17a**. Acetaldehyde was identified as its 2,4-dinitrophenylhydrazone. Chromatography of the non-volatile portion followed by crystallization from benzene afforded colorless short prisms (368 mg), m.p. 148–149° (dec.). $[\alpha]_D^{25} = -3{\cdot}6°$ ($c = 1{\cdot}0$ in $CHCl_3$). (Found: C, 70·57; H, 4·81. $C_{44}H_{30}O_{11}\cdot H_2O$ requires: C, 70·58; H, 4·89%.) λ_{max}^{EtOH} (log ε) 237 mμ (5·11). $\nu_{max}^{CHCl_3}$ 3500–2300 (CO_2H), 1740, 1260 cm^{-1}. NMR δ 2·15 (3H, s), 3·38 (3H, s), 4·2 (1H, m), 5·5 (1H, m), 6·19 (3H, CO_2H and H_2O), 6·9–8·4 (20H, m).

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