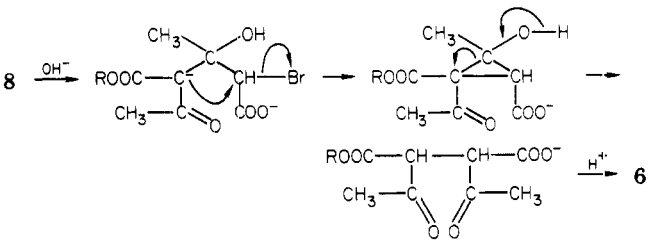
Scheme II



At first, the above synthesis of **6** from **1a** was quite puzzling, since the two methyl groups in the product are separated by four carbon atoms, while the methyl groups in the starting material from which they most certainly originate are separated by only three carbon atoms. However, as shown in Scheme I, there is a mechanism which explains the synthesis of both **5** and **6** from **1a**. It is based on the initial base-catalyzed opening of **1a** into the tautomeric glutaconic acid derivatives **7** and **8**. Further attack by one hydroxide ion onto the ketone carbonyl of **7** will induce the loss of the acetyl group, and displacement of the bromine and saponification will complete the synthesis of **5**.

Base-catalyzed retroaldol cleavage of **8** will lead to the enolate ion of ethyl acetoacetate and to potassium 2-bromoacetoacetate. The alkylation of the latter by the former, followed by an acid-catalyzed cyclization and decarboxylation explains the formation of **6**. It has not been determined whether the decarboxylation precedes the alkylation or even whether the whole process occurs intramolecularly after the addition of the hydroxide ion onto **8**, as shown in Scheme II.

The synthesis of the furoic acid **6** from **1a** appears to be quite sensitive to the base concentration, and a survey where it was varied from 0.01 M to 40% showed that our initial reaction conditions were fortuitously optimal.

Experimental Section

Molten ethyl bromoisodehydroacetate (94 g) was added at once to a boiling solution of 155 g of KOH pellets in 770 mL of water. After the vigorous reaction had subsided, the solution was cooled, acidified, and extracted with EtOAc. The extract was dried and concentrated, and the residue was esterified with ethanol in the presence of H_2SO_4. After workup, the organic products were distilled at 0.03 torr, yielding a fraction (9.25 g) boiling at 30–90 °C and 17 g of Feist's ester, bp 90–100 °C. The forerun was redistilled at 70 °C (1.9 torr). Its acid-catalyzed hydrolysis led to decomposition, but its saponification yielded crystalline 2,5-dimethyl-3-furoic acid, mp 135.9–136.4 °C (this increased to 138.9–139.1 °C after several recrystallizations from aqueous ethanol). The yield from **1a** was about 3%.

For comparison, the sodium salt from 30.4 g of ethyl acetoacetate was treated with 21.3 g of bromoacetone.[5] After distillation, the fraction boiling at 110 °C (2 torr) was treated with cold concentrated H_2SO_4. After workup and saponification of the product, 5.05 g of **6**, mp 136.8–138 °C, was obtained, which was identical with the above product (mp, mmp, and IR).

Acknowledgment. J.K. is grateful to Professor M. G. Ettlinger for his interest in this work, which was initially carried out in his laboratory, and for suggesting the mechanism expressed in Scheme II. Partial support from the National Institutes of Health (GM 24144) is gratefully acknowledged.

Registry No. **1a**, 18152-79-9; **2**, 499-02-5; **4**, 15058-72-7; **6**, 636-44-2; ethyl acetoacetate, 141-97-9; bromoacetone, 598-31-2.

Marine Natural Products: Dihydroxydeodactol Monoacetate, a Halogenated Sesquiterpene Ether from the Sea Hare *Aplysia dactylomela*[1]

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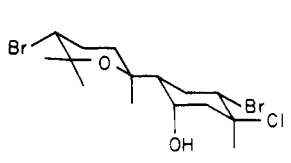
Received September 18, 1979

In an earlier report[2] we described the structure elucidation by X-ray analysis of the mildly cytotoxic sesquiterpenoid deodactol (**1**) isolated from the opisthobranch mollusc *Aplysia dactylomela*. The ether **1** is closely related to caespitol[3a] (**2**) and isocaespitol[3b] (**3**) which were isolated from the alga *Laurencia caespitosa*. A number of other algal metabolites have also been isolated[4] from *A. dactylomela* which, like other sea hares, thrives on algae and concentrates many algal metabolites, some of which are presumably used for chemical defense.[5] In this note we report that further investigation of the extracts of *A. dactylomela* from Bimini, Bahamas, has led to the discovery of a more oxygenated form of **1**, namely dihydroxydeodactol monoacetate, **4**.



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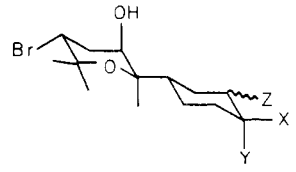

2, X = Cl; Y = CH_3; Z = Br (e)
3, X = CH_3; Y = Br; Z = Cl (a)

The new sesquiterpenoid was isolated from alcohol extracts of sea hare digestive glands by solvent partitioning followed by Sephadex LH-20 and silica gel chromatography as described for 14-bromoobtus-1-ene-3,11-diol.[4a] Dihydroxydeodactol monoacetate (**4**), mp 168–169 °C, $[\alpha]_D$ +40.5° ($CHCl_3$), was assigned the molecular formula $C_{17}H_{27}O_5Br_2Cl$ on the basis of mass spectral data: low resolution, *m/e* 504, 506, 508, 510 (M^+); high resolution, see Experimental Section. The infrared spectrum contained hydroxyl absorption at 3440 cm^{-1} and a single, sharp carbonyl absorption at 1730 cm^{-1} attributable to an acetate group. The ^1H NMR spectrum confirmed the presence of a single acetate group (δ 2.14, 3 H, s) and also contraindicated any carbon–carbon unsaturation, since there were no olefinic proton signals. Hence, it was concluded that **4** was probably bicyclic.

The ^1H NMR spectrum of **4** resembled that of deodactol (**1**) and immediately suggested a close similarity between the two compounds. Four quaternary methyl signals were

(1) This research was supported by National Cancer Institute Grant CA 17256.

(2) K. H. Hollenbeak, F. J. Schmitz, M. B. Hossain, and D. van der Helm, *Tetrahedron*, **35**, 541 (1979).

(3) (a) A. G. Gonzalez, J. Darias, J. D. Martin, and C. Perez, *Tetrahedron Lett.*, 1249 (1974); A. G. Gonzalez, J. Darias, and J. D. Martin, *ibid.*, 2381 (1973); (b) A. G. Gonzalez, J. Darias, J. D. Martin, C. Perez, J. J. Sims, G. H. Y. Lin, and R. M. Wing, *Tetrahedron*, **31**, 2449 (1975).

(4) (a) F. J. Schmitz, K. H. Hollenbeak, D. C. Carter, M. B. Hossain, and D. van der Helm, *J. Org. Chem.*, **44**, 2445 (1979); (b) F. J. Schmitz, F. J. McDonald, and D. J. Vanderah, *J. Org. Chem.*, **43**, 4220 (1978); (c) F. J. Schmitz, K. H. Hollenbeak, and D. J. Vanderah, *Tetrahedron*, **34**, 2719 (1978); (d) D. J. Vanderah and F. J. Schmitz, *J. Org. Chem.*, **41**, 3480 (1976); (e) F. J. McDonald, D. C. Campbell, D. J. Vanderah, F. J. Schmitz, D. M. Washecheck, J. E. Burks, and D. van der Helm, *J. Org. Chem.*, **40**, 665 (1975).

(5) Cf. P. J. Scheuer, *Is. J. Chem.*, 16, 52 (1977), and references cited therein.

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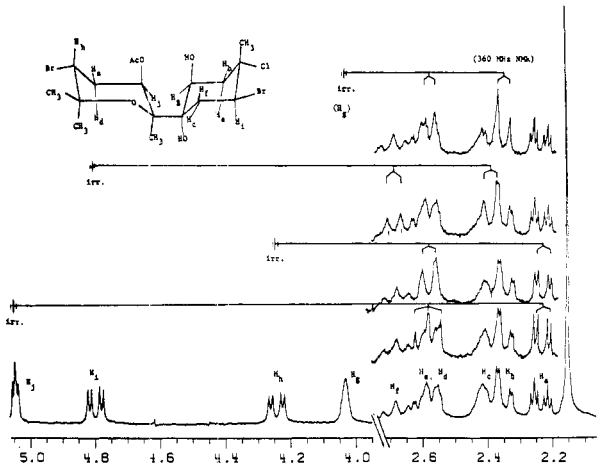


Figure 1. Partial 360-MHz ^1H NMR spectrum of **4** in $CDCl_3$ with selected decoupling.

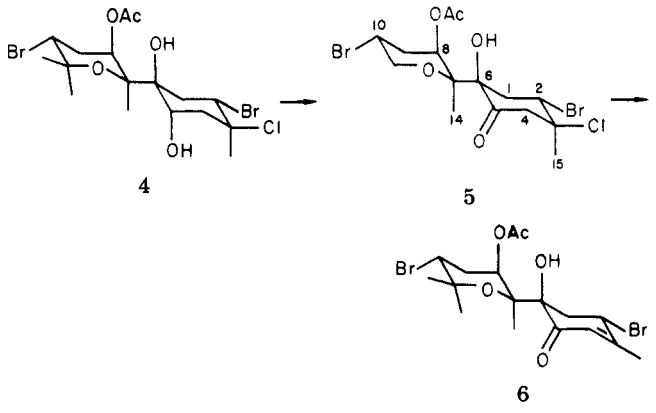
observed for dihydroxydeodactol monoacetate, δ 1.42, 1.44, 1.47 and 1.87, indicating three methyl groups on quaternary carbons deshielded by an ether oxygen and one methyl group deshielded by a halogen plus a 1,3-diaxial interaction with a hydroxyl group just as in deodactol (1). Two one-proton double-doublet signals occurred at δ 4.24 and 4.78, J = 14, 4 Hz for each, corresponding to deshielded axial protons in six-membered rings, suggesting the presence of two >CCHBrCH$_2$– units by further analogy to deodactol (1). Also evident was a one-proton triplet (J = 4 Hz) at δ 5.04 corresponding to an equatorial proton deshielded by an acetoxy group as for >CCH(OAc)CH$_2$–, and a broad one-proton signal ($W_{1/2}$ = 5 Hz) at δ 4.03 attributable to an equatorial, hydroxyl-deshielded methine hydrogen.

The juxtaposition of the above structural units was established by decoupling experiments (360 MHz) which fully elucidated three isolated spin systems in **4**. In the first spin system the acetoxy methine proton H_j (δ 5.04) and one of the bromine deshielded methine protons, H_h (δ 4.24), were found to each be coupled to the same two methylene protons, H_a and H_d (δ 2.24 and 2.58) (see Figure 1), confirming the partial structure >CCHBrCH$_2$CH(OAc)C<. The limited multiplicity of protons H_h and H_j require fully substituted carbons at the termini of this unit. The typical axial–equatorial couplings observed for all these protons implies a six-membered ring, and by analogy with deodactol the substituted tetrahydropyran ring of **4** was proposed.

Confirmatory evidence for this ether ring was derived from the low-resolution mass spectrum which showed prominent fragment ions at m/e 263 and 265 that correspond to the tetrahydropyran ring of **4** and all its substituents. The high-resolution mass spectrum showed high-intensity ions for this fragment minus acetic acid at 203.0080 and 205.0062 ($C_8H_{12}O^{79}Br$ and $C_8H_{12}O^{81}Br$; calcd 203.0071 and 205.0051).

The second spin system involves the hydroxyl-deshielded proton H_g (δ 4.04). Irradiation of this signal affected only two other resonances: the distinct double doublet for H_b at δ 2.35 (J = 3, 14 Hz) was collapsed to a doublet (J = 14 Hz), and the shape of the overlapping proton signals for H_d and H_e at δ 2.57 was altered (see Figure 1). Since the H_b signal is clearly only a double doublet, accounted for by diequatorial coupling between H_b and H_g and geminal coupling (J = 14 Hz) between H_b and H_e, the methylene group –CH_bH_e– must be joined on one side to a fully substituted center, leading to the partial structure >CCHOHCH$_2$C<.

Scheme I



The final spin system involves the remaining –CHBr– absorption, H_i (δ 4.78). Irradiation of this signal collapsed a triplet at δ 2.68 (H_f, J = 14 Hz) to a doublet (J = 14 Hz) and sharpened the signal for H_c at δ 2.43. Since the H_f signal is a triplet that is fully accounted for by vicinal diaxial coupling between H_f and H_i and geminal coupling between H_f and H_c, the methylene group –CH_cH_f– must be flanked on one side by a fully substituted center, giving rise to the partial structure >CCH$_2$CH(Br)C<.

The sum of all carbon atoms which were identified thus far exceeds by two that allowed by the molecular formula; hence the two quaternary carbons in each of the last two partial structures must be common atoms in the overall structure. Joining these two partial structures by the common atoms yields a cyclohexane ring. Addition of the chlorine atom and the last of the four methyl groups to one of the quaternary carbons in this ring, and the tertiary OH to the other, leaves one valence to join the cyclohexane and tetrahydropyran rings to give **4** as a final structure.[6] High-resolution mass spectral data supports the proposed substituted cyclohexane ring, since fragment ions corresponding to $C_7H_{11}O_2ClBr$ were observed (see Experimental Section).

Confirmatory evidence for structure **4** was obtained by the conversions outlined in Scheme I. Oxidation of **4** gave the ketone **5** whose infrared spectrum showed hydroxyl (3475 cm^{-1}) and two carbonyl absorptions (1740, 1725 cm^{-1}). The 1725-cm^{-1} absorption is in agreement with expectations for an α-hydroxy ketone in a six-membered ring. In the ^1H NMR spectrum the signals corresponding to the protons deshielded by the acetoxy group and the two bromines are shifted only slightly from their positions in **4** and retain the same multiplicity. The signal for the proton corresponding to H_f is shifted to δ 2.94 and is clearly visible as a double doublet, J = 12, 15 Hz, thus more rigorously establishing that it is coupled only to two protons, H_i and H_c.

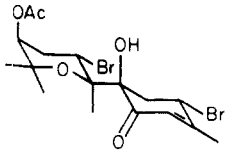
Treatment of **5** with diazabicyclononene in benzene smoothly effected dehydrochlorination and gave the α,β-unsaturated ketone **6** (IR 3450, 1750, 1685 cm^{-1}) whose ^1H NMR spectrum showed the presence of one vinyl methyl group, δ 2.09, and one olefinic proton, δ 6.11 (br s). The loss of chlorine was established by mass spectrometry, M^+ 466, 468, 470 (1:2:1 ratio), and the retention of the tertiary

(6) The structural fragments deduced from spectral analysis alone were processed in the CONGEN computer program for deducing structures [R. E. Carhart, D. H. Smith, H. Brown, and C. Djerassi, *J. Amer. Chem. Soc.*, **97**, 5755 (1975); see also C. J. Cheer, D. H. Smith, C. Djerassi, B. Tursch, J. C. Braekman, and D. Daloze, *Tetrahedron*, **32**, 1807 (1976)]. Eight structures (stereoisomers not considered) were generated by the program including **4** and **7**. The nature of the degradation products obtained (**5** and **6**) eliminated all of these except **4** and **7**. Use of the CONGEN program was made possible through NIH support of biotechnology facilities at Stanford University under Grant No. RR 00612.

hydroxyl group was confirmed by the infrared data. This definitive evidence for location of the chlorine atom confirms the assignment of the bromines to secondary carbon positions.

The mass spectra of ketones **5** and **6**, just like that of **4**, show peaks at m/e 263 and 265 corresponding to the proposed substituted tetrahydropyran ring and thus support the proposed structures.

The above data do not rule out the possible alternate structure **7** which differs from **4** in the relative positions of the acetoxy and bromine groups on the tetrahydropyran ring. Evidence favoring structure **4** was obtained from europium-induced shifts. Specifically, the acetoxy methine proton at C-8 in **6** was shifted downfield in the presence of $Eu(fod)_3$ by 4.5 ppm whereas the C-10 hydrogen was shifted only 1.34 ppm downfield. The opposite order in $\Delta\delta$ would be expected for the analogous ketone derived from **7** with the assumption that the strongest complexation occurs at the hydroxyl group. The overall $\Delta\delta$ shifts seems most compatible with the conformation depicted for **4**. Proton assignments in the shifted spectra are based on multiplicities and decoupling experiments.



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The relative stereochemistry of **4** is based on ^1H NMR data, chemical evidence, and conformational analysis. The orientation of the bromine, acetoxy, and secondary hydroxyl groups was clearly evident from the coupling constants observed for the protons on the carbons bearing these groups as discussed above. An axial disposition for the methyl group deshielded by chlorine at C-3 was indicated by the abnormally low-field position of that signal, 1.87 ppm, since in this orientation there would be additional deshielding from the nearby axial hydroxyl group. A trans-diaxial relationship between the secondary and tertiary hydroxyl groups at C-5,6 was suggested by the failure of **4** to form a boronate ester when heated with phenylboronic acid.[7]

The only remaining stereochemical assignment to be made is that for the methyl group at C-7. An axial orientation as in **4** is proposed based on analogy with deodactol and the following conformation argument. Inversion at C-7 would place the bulky substituted cyclohexane ring in an axial orientation, introducing a severe 1,3-diaxial interaction between this ring and one of the geminal dimethyl groups. The tetrahydropyran ring would then be expected to undergo chair–chair interconversion which would change H_j and H_h from equatorial,axial to axial,-equatorial. This is clearly ruled out by NMR data. Thus, the most probable configuration for C-7 is that shown in **4**.

(7) J. M. Sugihara and C. M. Bowman, *J. Amer. Chem. Soc.*, **80**, 2443 (1958); see also L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, 1967, p 833.

(8) Melting points are uncorrected. Infrared spectra were taken on a Beckman Acculab 3 spectrometer. NMR spectra were taken on Varian T-60, XL-100, and Bruker HXS-360-MHz instruments in the solvents specified; signals are reported in parts per million (ppm or δ) downfield from internal tetramethylsilane. Mass spectra were taken on Hitachi RMU-7 and CEC (Du Pont, Monrovia, CA) 110 mass spectrometers. A Perkin-Elmer 141 polarimeter was used for obtaining optical rotations. Chromatographic adsorbents used were Mallinckrodt SilicAR CC-7 and Brinkmann TLC mesh silica.

Table I. Induced Shifts of ^1H NMR Signals for 6

proton	$CDCl_3$ (no shift reagent)	CCl_4, $Eu(fod)_3$[a]
4	6.11 (br s)	7.10
2 a[b]	4.98 (dd, 5, 10)	5.54 (dd, 5, 11)
1 a		2.82 (dd, 11, 15)
1 e[c]	3.08 (dd, 5, 14)	3.76 (dd, 5, 15)
8	4.95 (t, 2)	9.40 (t, 2.5)
9 a	~2.48 (dt, 3, 13)	3.28 (dt, 2, 14)
9 e	2-2.5 (m)	4.16 (dt, 4, 15)
10 a	4.08 (dd, 5, 12)	5.32 (dd, 4, 12)
15	2.08 (s)	2.46 (s)
14	1.57 (s)	2.33 (s)
12,13	1.28 (s)	1.85 (s)
	1.48 (s)	1.88 (s)
OAc	2.0 (s)	4.97 (s)
OH	4.10 (s)	

[a] The $Eu(fod)_3$/6 molar ratio was ~1:4. [b] a, axial. [c] e, equatorial.

Experimental Section[8]

Isolation of Dihydroxydeodactol Monoacetate (4). The fractions prepared earlier[4a] from extracts of digestive glands of a batch of sea hares, *A. dactylomela*, from Bimini, Bahamas, were utilized. The 13th fraction of the Sephadex LH-20 chromatography of fraction G[4a] was chromatographed over TLC mesh silica gel with chloroform to give 61 mg of **4**: mp 168–169 °C after recrystallization from hexane-benzene; $[\alpha]_D$ +40.5° ($CHCl_3$); IR (KBr) 3440, 1730, and 1270 cm^{-1}; 360-MHz ^1H NMR ($CDCl_3$) δ 1.58 (br s, 2 H, -OH); see text and Figure 1 for remainder; mass spectrum (70 eV), m/e (relative intensity) 510 (0.34), 508 (1.2), 506 (1.7), 504 (0.85), 490 (0.88), 488 (1.2), 486 (0.6), 471 (0.85), 469 (1.3), 467 (0.71), 265 (29), 263 (30), 233 (6), 221 (6), 206 (11), 205 (9), 204 (12), 203 (8), 186 (28), 141 (11), 125 (17), 124 (14), 123 (27), 109 (32), 81 (22), 43 (100); high-resolution mass spectrum, obsd. m/e (composition, interpretation, calcd millimass) 477.9654 ($C_{15}H_{23}O_3{}^{35}Cl^{81}Br_2$ or $C_{15}H_{23}O_3{}^{37}Cl^{79}Br^{81}Br$, M^+ - AcOH, 447.9662, 447.9653), 445.9678 ($C_{15}H_{23}O_3{}^{35}Cl^{79}Br^{81}Br$ or $C_{15}H_{23}O_3{}^{37}Cl^{79}Br_2$, M^+ - AcOH, 445.9682, 445.9673), 443.9713 ($C_{15}H_{23}O_3{}^{35}Cl^{79}Br$, M^+ - AcOH, 443.9702), 425.0733 ($C_{17}H_{27}O_5{}^{35}Cl^{79}Br$, M^+ - HBr, 425.0730; all three halogen isotope peaks are observed), 265.0301 ($C_{10}H_{16}O_3{}^{81}Br_2$, ring B, 265.0262), 240.9617 ($C_7H_{11}O_2{}^{35}Cl^{79}Br$, ring A, 240.9631, other expected halogen isotope peaks are observed), 205.0062, 203.0080 ($C_8H_{12}O^{81}Br$, $C_8H_{12}O^{79}Br$, ring B - AcOH, 205.0051, 203.0071), 188.9724, 186.9739 ($C_7H_8O^{81}Br$, $C_7H_8O^{79}Br$, ring A - H_2O + HCl, 188.9738, 186.9758), 183.1008 ($C_{10}H_{15}O_3$, ring B - HBr, 183.1021), 163.0323, 161.0365 ($C_7H_{10}O_2{}^{37}Cl$, $C_7H_{10}O_2{}^{35}Cl$, ring A - HBr, 163.0315, 163.0369), 125.0606 ($C_7H_9O_2$, ring A - HBr + HCl, 125.0603), 123.0836 ($C_8H_{11}O$, ring B - AcOH + HBr, 123.0810).

Oxidation of 4. Jones reagent (0.1 mL) was added dropwise to a solution of **4** (35.4 mg) in acetone (5 mL) at room temperature until a permanent yellow color was observed. After the addition of water, the ketone was extracted with ether, washed with water, and recrystallized from hexane to give **5** as white crystals in quantitative yield: mp 154.5–155 °C; IR (KBr) 3475, 1740, 1725, and 1250 cm^{-1}; 100-MHz NMR($CDCl_3$) δ 1.47, 1.48, 1.53 (s, 3 H ea, C-12,13,14), 1.83 (s, 3 H, C-15), 2.00 (s, 3 H, -OAc), 2.10–2.70 (m, 3 H), 2.94 (dd, 1 H, J = 12, 14 Hz, C-1 H_{ax}), 3.20 (d, 1 H, J = 13 Hz, C-4 H_{ax}), 3.73 (d, 1 H, J = 13 Hz, C-4 H_{eq}), 3.83 (s, 1 H, -OH), 4.12 (dd, 1 H, J = 4, 12 Hz, C-10 H), 4.36 (dd, 1 H, J = 4, 12 Hz, C-2 H), 5.02 (dd, 1 H, J = 3, 4 Hz, C-8 H); mass spectrum (70 eV), m/e (relative intensity) 427 (1.3), 425 (5), 423 (4) [M^+ - Br], 398 (0.7), 396 (2), 394 (2), 329 (0.5), 327 (1), 325 (0.5), 287 (0.9), 285 (2), 283 (2), 265 (13), 263 (13), 223 (4), 221 (4), 205 (6), 203 (5), 186 (11), 141 (8), 125 (12), 123 (16), 69 (16), 43 (100).

Dehydrochlorination of 5. A solution of **5** (13.4 mg) and diazabicyclononene (3.4 mg) in benzene was refluxed under nitrogen for 15 min. The cooled mixture was poured on ice, washed with 1 N sulfuric acid, and extracted with hexane to yield **6** as a clear oil: IR (KBr) 3450, 1750, 1685, and 1245 cm^{-1}; 100-MHz NMR ($CDCl_3$), see Table I; mass spectrum (heating elements off),

m/e (relative intensity) 470 (0.6), 468 (1), 466 (0.6), 265 (88), 263 (85), 223 (22), 221 (21), 206 (22), 205 (32), 204 (22), 203 (32), 141 (21), 125 (58), 124 (32), 123 (69), 109 (32), 95 (30), 43 (100).

Acknowledgment. High-resolution mass spectra were provided by the mass spectrometry facility at Massachusetts Institute of Technology, supported by a grant (Principal Investigator Professor K. Biemann) from the Biotechnology Research Branch, Division of Research Resources. The 360-MHz NMR data were obtained from the Stanford Magnetic Resonance Laboratory supported by NSF Grant GR 23633 and NIH Grant RR 00711. We acknowledge with thanks grants from NSF (GP 38410) and the Phillips Petroleum Company, Bartlesville, Ok, which aided in the purchase of NMR spectrometers.

Registry No. 4, 72926-49-9; 5, 72926-50-2; 6, 72926-51-3.

Circular Dichroism of Prostaglandin Benzoates. Assignment of Configuration at C-15

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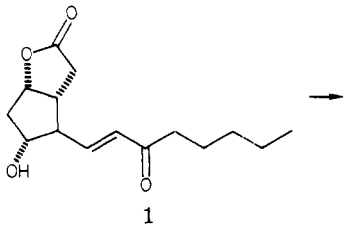
Received September 10, 1979

The synthesis of prostaglandin analogues frequently proceeds through intermediates such as **1** and **2** with the



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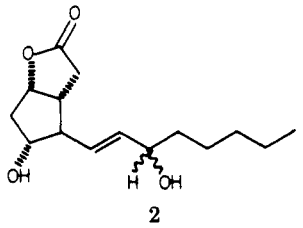

2

result that a mixture of epimers at C-15 (prostaglandin numbering) is produced.[1] This mixture is either separated and each epimer carried on to the final prostaglandin analogue or is carried on as the mixture and the epimers separated at the stage of the final analogue. The assignment of configuration at C-15 has often been made on the basis of the relative thin-layer chromatographic (TLC) mobilities of the epimers. The slightly more polar nature of the 15*S* epimer at the intermediate stage of **2** or in the final products has been consistent with the expectation that the 15*S* epimer of the final analogue will have greater biological activity than the 15*R* epimer.

Only in two cases have the configurations at C-15 been determined in an absolute sense. The absolute configuration of the naturally occurring prostaglandins was determined in two steps. First the relative configuration was determined by X-ray crystallography,[2] and then the absolute configuration was determined by correlation of the ozonolysis product L-2-hydroxyheptanoic acid with authentic material of known configuration.[3] The absolute configuration of the 15-methylprostaglandins has been determined by X-ray crystallography.[4]

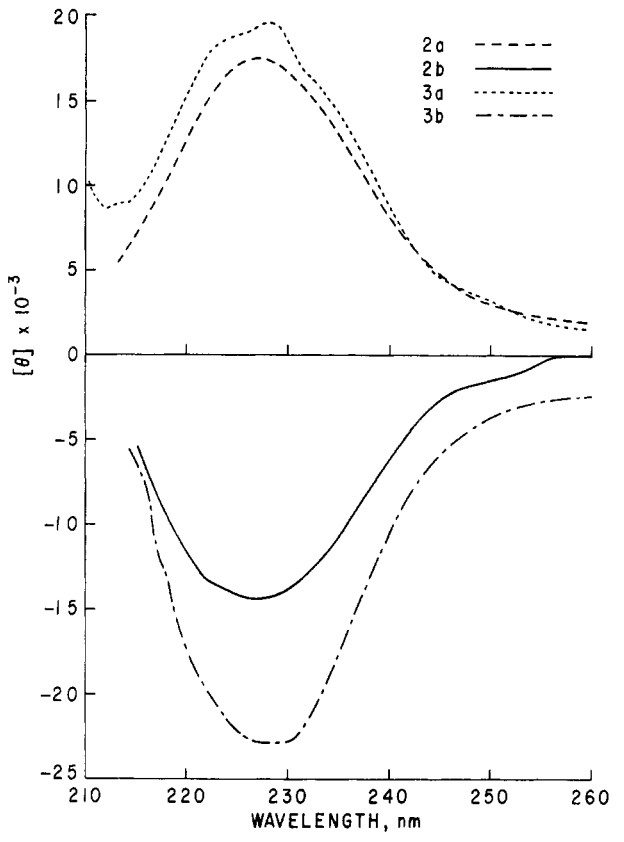

Figure 1. CD curves of 15-monobenzoates **2a**, **2b**, **3a**, and **3b** in MeOH.

In this report, we present circular dichroism (CD) data for the 15-benzoate derivatives of several synthetic intermediate and final prostaglandins. From these data, we have found an empirical correlation between CD spectra and the configuration at C-15 of the benzoate derivatives. That correlation is the subject of this note.

The compounds prepared and their ultraviolet and CD spectral properties are outlined in Table I. The absorption maxima in the ultraviolet spectra are typical of the benzoate chromophore. The intense band at 229 nm is due to a charge-transfer transition and the weaker maxima between 265 and 280 nm to the B_{2u} transition. The intensities of the extinction coefficients are consistent with the number of benzoate groups present in each compound, i.e., $\epsilon_{229} \simeq 13\,000$ per benzoate group.

Listed first in Table I are two epimeric pairs of 15-benzoates, **2a** and **2b** and **3a** and **3b**. All have strong CD bands at about 230 nm, but these bands have opposite signs of rotation depending on the configuration at C-15 (see Figure 1). The two 15(*S*)-benzoates (**2a** and **3a**) have a positive sign of rotation while the two 15(*R*)-benzoates (**2b** and **3b**) have a negative sign of rotation. The CD of

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