A New Bromo Diterpene, *epi*-Aplysin-20, and *ent*-Isoconcinndiol from the Marine Mollusc *Aplysia kurodai*

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(Received March 19,1992)

Synopsis. A New brominated labdane-type diterpene, *epi*-aplysin-20, and *ent*-isoconcinndiol have been isolated from the marine mollusc *Aplysia kurodai*: the structure of *epi*-aplysin-20 has been established on the basis of the spectroscopic data and chemical transformation.

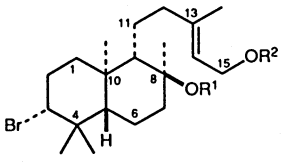
A variety of halogenated terpenoids[1-4] and other unique metabolites[5,6] have been isolated from the marine mollusc *Aplysia kurodai*. In the course of our continuous search for novel compounds of the mollusc,[4,6] we have isolated a new labdane-type bromo diterpene, *epi*-aplysin-20 (**1**), which is the diastereomer at C-8 of aplysin-20 (**2**)[2] together with the enantiomer (**3**) of isoconcinndiol.[1] In this paper we report the isolation of **1** and **3** and structural elucidation of **1**.

The mollusc *A. kurodai* collected in Mie Prefecture, Japan, was extracted with MeOH. The MeOH extract was subjected to solvent partitioning (EtOAc–H_2O) followed by repeated column chromatography of the EtOAc portion on silica gel and C_{18} silica gel to afford two bromo diterpenes. One of these compounds, **3**, was obtained as colorless plates, mp 171—172 °C, $[\alpha]_D^{26}$ −4.7° (*c* 0.42, $CHCl_3$), and the spectroscopic data (^{1}H NMR, IR, and MS) and melting point were identical to those of the known compound, isoconcinndiol, isolated from the marine red alga *Laurencia snyderae* var. *guadalupensis* by Howard and Fenical.[1] The proposed structure[1] of isoconcinndiol was corrected by chemical synthesis[7] and the absolute stereostructure was recently determined[8] by the X-ray analysis of (+)-isoconcinndiol, which was isolated from the marine mollusc *Aplysia dactylomela* and reported to have the same spectral properties as those of the original compound isolated by Howard and Fenical. Since isoconcinndiol which we isolated is levorotatory, our compound is the enantiomer of (+)-isoconcinndiol,[8] that is, *ent*-isoconcinndiol and is represented as the formula **3**.

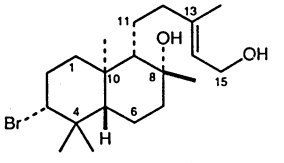
The other bromo diterpene **1** was obtained as colorless needles, mp 150—152 °C, $[\alpha]_D^{13}$ −0.69° (*c* 0.72, MeOH). The high-resolution EIMS indicated that **1** had the same composition $C_{20}H_{35}BrO_2$ as that of aplysin-20 (**2**) and the ^{1}H NMR spectrum was similar to that of **2**. However, the melting point, the IR spectrum, and the optical rotation of **1** were different from those (mp 146—147 °C, $[\alpha]_D^{15}$ −78.1°)[2] of **2** suggesting that **1** was a diastereomer of **2**. The assignment of the signals due to carbons bearing hydrogens in **1** was made by the ^{1}H–^{13}C COSY (J=140 Hz). Four singlets at δ_H=0.84, 0.91, 1.06, and 1.13 were assigned to 10-Me, two 4-Me, and 8-Me, respectively, on the basis of the following cross peaks observed in the 2D COLOC experiment (J=10 Hz):[9] δ_C=69.1 (d, C-3)/δ_H=0.91 and 1.06, δ_C=39.7 (s, C-4)/δ_H=0.91 and 1.06, δ_C=73.6 (s, C-8)/δ_H=1.13, and δ_C=39.2 (s, C-10)/δ_H=0.84. The signal at δ_H=0.91 was assigned to the axial 4-Me due to the observation of an 8.1% NOE enhancement on irradiation of the 10-Me protons (δ=0.84). In the ^{1}H NMR spectra of **1** and **2**, the notable difference is the chemical shift of 10-Me; The signal due to 10-Me is observed at δ=1.00 in **2**, whereas at δ=0.84 in **1**. Since this difference appeared to result from the absence of the anisotropic effect due to the C-8 axial hydroxyl group in **1**, **1** was deduced to be the diastereomer at C-8 of **2**. This is supported by the NOE experiment performed on **1**: An 8.8% signal enhancement of 8-Me (δ=1.13) was observed on irradiation of the 10-Me signal (δ=0.84).

In order to confirm the structure of *epi*-aplysin-20 (**1**), chemical transformation of **1** to *ent*-isoconcinndiol (**3**) was carried out. Thus, two hydroxyl groups of **1** were first protected [Ac_2O, 4-(dimetylamino)pyridine (DMAP), pyridine] to afford 8-*O*-acetoacetyl-15-*O*-acetyl derivative **4**.[10] After deprotection of the acetyl group (K_2CO_3, MeOH), the resulting allyl alcohol **5** was converted into (13*R*,14*R*)-epoxy alcohol **6** by Sharpless epoxidation [Ti(OPr^i)$_4$, (−)-diethyl tartrate, *t*-BuOOH],[11] which was then transformed into epoxy iodide **8** via tosylate **7** [1. *p*-toluenesulfonyl chloride (TsCl), pyridine; 2. NaI, acetone]. On reduction of the epoxy iodide moiety (Zn, NH_4Cl) followed by deprotection of the acetoacetyl group (KOH, MeOH), **8** afforded the compound which was identical with *ent*-isoconcinndiol (**3**) in all respects including the sign of the specific rotation, establishing the absolute stereostructure of *epi*-aplysin-20 (**1**).

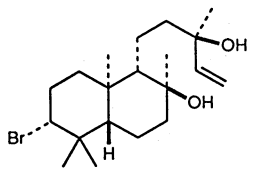
It should be noted that aplysin-20 (**2**) was not detected in *A. kurodai* which we examined, while **2** was isolated[2] from the same animal by Yamamura and Hirata. This difference could be due to the difference of the locations where the molluscs were collected.



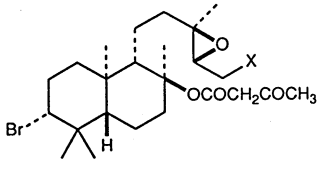
1 $R^1 = R^2 = H$ (*epi*-aplysin-20)
4 $R^1 = COCH_2COCH_3$, $R^2 = COCH_3$
5 $R^1 = COCH_2COCH_3$, $R^2 = H$



2 (aplysin-20)



3 (*ent*-isoconcinndiol)



6 X = OH
7 X = OTs
8 X = I

Experimental

Melting points were uncorrected. Optical rotations were measured on a JASCO DIP-181 polarimeter. IR spectra were recorded on a JASCO IR-810 spectrophotometer by using $CHCl_3$ as solvent. NMR spectra were recorded on a JEOL JNM-C675 (270 MHz for ^1H NMR and 67.8 MHz for ^{13}C NMR) in $CDCl_3$ solution using TMS (δ_H=0.00) and $CDCl_3$ (δ_C=79.0) as internal standards, respectively. Mass spectra (EIMS) were obtained with a JEOL JMS LG-2000 spectrometer at 70 eV. Fuji-Davison silica gel BW-820 MH was used for column chromatography. Organic solutions obtained on extractive workup were washed with saturated brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure.

Extraction and Separation. *A. kurodai* (21 kg, wet wt) was collected at Azuri-hama of the Shima Peninsula in Mie Prefecture, Japan, in May 1985 and extracted with MeOH (40 l). The methanolic extract was concentrated to ca. 2 l in vacuo and then extracted with EtOAc (4×2 l). After concentration under reduced pressure, the EtOAc extract (54 g) was subjected to column chromatography over silica gel (700 g) with C_6H_6–EtOAc (4:1), EtOAc, and MeOH, successively. The fraction (8.83 g) eluted with EtOAc was chromatographed on silica gel (180 g) with hexane–acetone (3:1 then 2:1) and MeOH, successively. The fraction (5.1 g) eluted with hexane–acetone (3:1) was chromatographed on silica gel (100 g) with hexane–acetone (5:1 then 4:1) and EtOAc, successively, to afford fractions A—E in order of increasing polarity. The fraction B (991 mg) eluted with hexane–acetone (5:1) was separated by chromatography on silica gel (30 g) with hexane–EtOAc (3:1, 2.5:1, then 2:1), and subsequently by medium pressure liquid chromatography [Micro Bead silica gel B(30—70)μ (65 g), Fuji-Davison Chemical Ltd.; flow rate 10 ml min^{-1}; hexane–EtOAc–acetone (47.5:47.5:5 to 43:43:14), gradient elution] to afford a crude oil containing *ent*-isoconcinndiol (**3**) (80 mg). The crude oil was chromatographed on silica gel (5.5 g) with $CHCl_3$–acetone (95:5) and then recrystallized from hexane–$CHCl_3$ to furnish 7.0 mg of pure **3**: Colorless plates; mp 171—172 °C (hexane–$CHCl_3$); $[\alpha]_D^{26}$ −4.7° (*c* 0.42, $CHCl_3$).[12] IR, MS, and ^1H NMR spectra were identical to those reported in the literature.[1] Found: C, 62.14; H, 9.16%. Calcd for $C_{20}H_{35}BrO_2$: C, 62.01; H, 9.11%.

On the other hand, the fraction D (795 mg) eluted with hexane–acetone (5:1 and 4:1) described above was separated twice by medium pressure liquid chromatography [1. Micro Bead silica gel B(30—70)μ (65 g), Fuji-Davison Chemical Ltd.; flow rate 10 ml min^{-1}; hexane–EtOAc (3:1 to 1:3), gradient elution; 2. Develosil ODS 30/60 (60 g), Nomura Chemical Ltd.; flow rate 10 ml min^{-1}, MeOH–H_2O (85:15)] to afford 61.7 mg of *epi*-aplysin-20 (**1**): Colorless needles; mp 150—152 °C (MeOH); $[\alpha]_D^{13}$ −0.69° (*c* 0.72, MeOH); IR 3600, 3430 (br), 1665, 1155, 1080, 1000, 980, 960, and 910 cm^{-1}; MS *m/z* (rel intensity) 370 [$(M+2)^+$; 8], 368 (M^+; 8), 355 (37), 353 (39), 337 (15), 335 (15), 272 (29), 271 (28), 270 (33), 296 (23), and 191 (100); ^1H NMR δ=0.84 (3H, s, 10-Me), 0.91 (3H, s, 4-Me_{ax}), 1.05 (2H, m, H-5 and 9), 1.06 (3H, s, 4-Me_{eq}), 1.13 (3H, s, 8-Me), 1.15 (1H, ddd, *J*=13.0, 13.0, and 5.0 Hz, H-1a), 1.33 (1H, m, H-11a), 1.37 (2H, m, H-6a and 7a), 1.53 (1H, m, H-11b), 1.66 (1H, m, H-1b), 1.67 (3H, d, *J*=1.3 Hz, 13-Me), 1.71 (1H, m, H-6b), 1.87 (1H, m, H-7b), 2.07 (2H, m, H-12), 2.09 (1H, m, H-2a), 2.19 (1H, dddd, *J*=12.5, 12.5, 12.5, and 3.5 Hz, H-2b), 3.99 (1H, dd, *J*=12.5 and 4.8 Hz, H-3), 4.10 (1H, dd, *J*=12.2 and 6.9 Hz, H-15a), 4.15 (1H, dd, *J*=12.2 and 6.9 Hz, H-15b), and 5.41 (1H, ddq, *J*=6.9, 6.9, and 1.3 Hz, H-14); ^{13}C NMR δ=15.4 (q, 10-Me), 16.4 (q, 13-Me), 18.1 (q, 4-Me_{ax}), 22.0 (t, C-6), 23.5 (t, C-11), 23.9 (q, 8-Me), 30.6 (q, 4-Me_{eq}), 30.7 (t, C-2), 39.2 (s, C-10), 39.7 (s, C-4), 41.0 (t, C-1), 42.7 (t, C-12), 44.4 (t, C-7), 56.4 (t, C-5), 59.3 (t, C-15), 60.8 (d, C-9), 69.1 (d, C-3), 73.6 (s, C-8), 123.4 (d, C-14), and 140.6 (s, C-13). Found: C, 62.09: H, 9.07%. Calcd for $C_{20}H_{35}BrO_2$: C, 62.01; H, 9.11%.

Conversion of *epi*-Aplysin-20 (1) into 8-*O*-Acetoacetyl-15-*O*-acetyl-*epi*-aplysin-20 (4). A mixture of **1** (10.2 mg), acetic anhydride (0.5 ml), and pyridine (0.5 ml) was stirred at room temperature for 1 h. After addition of DMAP (3.1 mg), the mixture was stirred at room temperature for 23 h. The reaction mixture was concentrated and the residual oil was chromatographed on silica gel (1.5 g) with hexane–EtOAc (8:1) to afford **4** (7.6 mg, 57%) as a colorless oil: $[\alpha]_D^{19}$ +7.8° (*c* 0.74, $CHCl_3$); IR 1730, 1715, 1240, 1120, and 1020 cm^{-1}; MS *m/z* (rel intensity) 412 [$(M+2-CH_3COCH_2CO_2H)^+$; 4], 410 [$(M-CH_3COCH_2CO_2H)^+$; 4], 352 (50), 350 (47), 284 (99), and 282 (100); ^1H NMR δ=0.89, 0.92, 1.07, 1.50, and 1.70 (3H, s each), 1.95—2.30 (4H, m), 2.01 and 2.24 (3H, s each), 2.71 (1H, m), 3.32 (2H, s), 3.98 (1H, dd, *J*=12.1 and 4.7 Hz), 4.58 (2H, d, *J*=6.9 Hz), and 5.32 (1H, br t, *J*=6.9 Hz). Found: *m/z* 410.1808. Calcd for $C_{22}H_{35}{}^{79}BrO_2$: M−$CH_3COCH_2CO_2H$, 410.1820.

Conversion of 4 into Allyl Alcohol 5. A mixture of **4** (8.4 mg), K_2CO_3 (2.3 mg), and MeOH (0.2 ml) was stirred at room temperature for 5 h under nitrogen. The reaction mixture was diluted with water (0.5 ml) and extracted with $CHCl_3$ (4×5 ml). The combined extracts were washed with saturated NH_4Cl solution and concentrated. The crude oil obtained was purified by column chromatography over silica gel with hexane–ether (1:1, 1:3) to furnish **5** (5.3 mg, 70%) as a colorless oil: $[\alpha]_D^{18}$ +14° (*c* 0.50, $CHCl_3$); IR 3600, 3450 (br), 1730, 1710, 1160, and 1120 cm^{-1}; MS *m/z* (rel intensity) 370 [$(M+2-CH_3COCH_2CO_2H)^+$; 12], 368 [$(M-CH_3COCH_2CO_2H)^+$; 14], 355 (58), 353 (64), 352 (15), 350 (17), and 191 (100); ^1H NMR δ=0.89, 0.92, 1.07, 1.50, 1.67, and 2.24 (3H, s each), 1.92—2.30 (4H, m), 2.69 (1H, ddd, *J*=12.4, 3.0, and 3.0 Hz), 3.33 (2H, s), 3.99 (1H, dd, *J*=12.1 and 4.9 Hz), 4.16 (2H, d, *J*=6.9 Hz), and 5.39 (1H, br t, *J*=6.9 Hz). Found: *m/z* 368.1710. Calcd for $C_{20}H_{33}{}^{79}BrO$: M−$CH_3COCH_2CO_2H$, 368.1715.

Conversion of 5 into Epoxy Alcohol 6. To a solution of $Ti(OPr^i)_4$ (25 mg) and (−)-diethyl tartrate (18.5 mg) in dry CH_2Cl_2 (0.9 ml) were added a solution of **5** (7.0 mg) in dry CH_2Cl_2 (0.4 ml) and a solution of *t*-BuOOH in toluene (0.33 mol dm^{-3}, 0.54 ml), successively, at −50 °C under nitrogen, and the mixture was stirred at −50 °C for 2 h. After addition of water (0.5 ml), the reaction mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×2 ml). The organic layers were combined, washed with aqueous $Na_2S_2O_3$ solution (0.1 mol dm^{-3}), and concentrated. The resulting crude oil was chromatographed on silica gel (1.5 g) with hexane–Et_2O (1:1 then 1:10) to give a mixture of **6** and the isomer (5.5 mg, selectivity, 4:1). The mixture was subjected to reversed-phase HPLC [Develosil ODS 10 (20×250 mm), 65% CH_3CN, 8.0 ml min^{-1}, detection at 274 nm] to afford pure **6** (2.9 mg, 40%) as a colorless oil: $[\alpha]_D^{18}$ +28° (*c* 0.24, $CHCl_3$); IR 3670, 3600, 3480 (br), 1735, 1710, 1160, 1125, 1080, and 1020 cm^{-1}; MS *m/z* (rel intensity) 386 [$(M+2-CH_3COCH_2CO_2H)^+$; 4], 384 [$(M-CH_3COCH_2CO_2H)^+$; 4], 368 (16), 366 (16), 352 (35), 350 (32), and 191 (100); ^1H NMR δ=0.90, 0.92, 1.07, 1.29, and 1.50 (3H, s each), 2.03—2.27 (2H, m), 2.25 (3H, s), 2.68 (1H, m), 2.93 (1H, dd, *J*=6.3 and 4.9 Hz), 3.32 (2H, s), 3.71 (1H, dd, *J*=12.1 and 6.3 Hz), 3.82 (1H, dd, *J*=12.1 and 4.9 Hz), and 3.97 (1H, dd, *J*=12.0 and 4.8 Hz). Found: *m/z* 384.1624. Calcd for $C_{20}H_{33}{}^{79}BrO_2$: M−$CH_3COCH_2CO_2H$, 384.1664.

Conversion of 6 into Tosylate 7. To a solution of **6** (2.9 mg) in dry pyridine (0.2 ml) was added TsCl (10.8 mg) in portions over 9 h with stirring at 0 °C. The excess reagent

was decomposed by the addition of ice-water (1 ml) and the mixture was extracted with Et_2O (5×2 ml). The combined extracts were concentrated to afford an oil, which was purified by column chromatography over silica gel (1 g) with C_6H_6–Et_2O (10 : 1) to give **7** (3.3 mg, 86%) as a colorless oil: $[\alpha]_D^{17}$ +31° (*c* 0.26, $CHCl_3$); IR 1730, 1710, 1600, 1175, 970 cm^{-1}; MS *m/z* (rel intensity) 368 [$(M+2-CH_3COCH_2CO_2H-C_7H_7SO_3H)^+$; 31] and 366 [$(M-CH_3COCH_2CO_2H-C_7H_7SO_3H)^+$; 34], 343 (32), 341 (30), 325 (36), 323 (41), 271 (100), and 270 (77); ^1H NMR δ=0.88, 0.91, 1.06, 1.22, and 1.49 (3H, s each), 2.02—2.23 (2H, m), 2.23 and 2.46 (3H, s each), 2.69 (1H, m), 3.00 (1H, t, *J*=5.6 Hz), 3.30 (2H, s), 3.96 (1H, dd, *J*=12.2 and 4.9 Hz), 4.07 (1H, dd, *J*=11.1 and 5.6 Hz), 4.16 (1H, dd, *J*=11.1 and 5.6 Hz), 7.36 (2H, d, *J*=8.3 Hz), and 7.81 (2H, d, *J*=8.3 Hz). Found: *m/z* 366.1552. Calcd for $C_{20}H_{31}{}^{79}BrO$: $M-CH_3COCH_2CO_2H-C_7H_7SO_3H$, 366.1558.

Conversion of 7 into Iodide 8. A mixture of **7** (2.6 mg), $CaCO_3$ (4.6 mg), NaI (4.7 mg), and dry acetone (0.3 ml) was stirred in the dark at room temperature for 16 h under nitrogen and then at 40 °C for 1.8 h. After addition of 4% aqueous $NaHCO_3$ solution (0.5 ml), the mixture was extracted with Et_2O (5×2 ml) and the combined extracts were concentrated. The residue was chromatographed on silica gel with hexane–Et_2O (3 : 1) to give **8** (2.2 mg, 90%) as a colorless oil: $[\alpha]_D^{16}$ +9.2° (*c* 0.20, $CHCl_3$); IR 1730, 1710, and 1115 cm^{-1}; MS *m/z* (rel intensity) 496 [$(M+2-CH_3COCH_2CO_2H)^+$; 5], 494 [$(M-CH_3COCH_2CO_2H)^+$; 4], 369 (18), 367 (19), 343 (11), 341 (11), and 97 (100); ^1H NMR δ=0.90, 0.92, 1.07, 1.28, and 1.51 (3H, s each), 2.02—2.23 (2H, m), 2.25 (3H, s), 2.71 (1H, m), 3.04 (2H, m), 3.32 (2H, s), 3.35 (1H, dd, *J*=8.2 and 4.0 Hz), and 3.96 (1H, dd, *J*=12.2 and 4.9 Hz). Found: *m/z* 494.0678. Calcd for $C_{20}H_{32}{}^{79}BrIO$: $M-CH_3COCH_2CO_2H$, 494.0681.

Conversion of 8 into *ent*-Isoconcinndiol (3). A mixture of **8** (1.9 mg), NH_4Cl (4 mg), zinc powder (2.6 mg), and EtOH (0.5 ml) was stirred under reflux for 5 min under nitrogen. The reaction mixture was filtered and the residual solid was washed with EtOH. The filtrate and the washing were combined and concentrated. The residue was suspended in water (0.5 ml) and then extracted with Et_2O (5×2 ml). The combined extracts were concentrated to give a crude oil (2.2 mg), which was dissolved in methanolic KOH solution (1 mol dm^{-3}, 0.5 ml) and the solution was stirred at 60 °C for 25 h. The reaction mixture was diluted with water (1 ml) and extracted with Et_2O (5×2 ml). The combined extracts were concentrated and the resulting crude oil was chromatographed on silica gel (1 g) with $CHCl_3$–acetone (10 : 1 then 5 : 1) to give **3** (0.8 mg, 65%) as colorless plates: mp 168.0—169.0 °C (hexane–$CHCl_3$); $[\alpha]_D^{21}$ −4° (*c* 0.05, $CHCl_3$). IR, MS, and ^1H NMR spectra were identical with those of natural **3**.

We are grateful to Professor Shosuke Yamamura (Faculty of Science and Technology, Keio University) for the authentic sample of aplysin-20 (**2**).

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