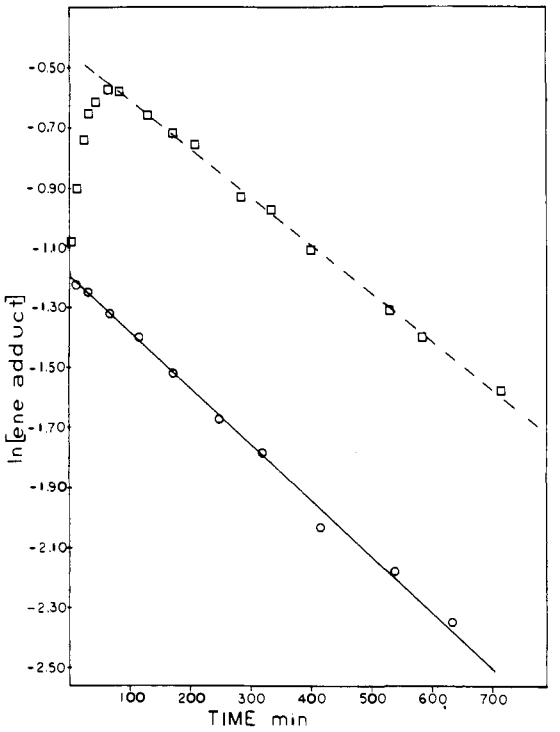

Figure 2. Plots of time vs. concentration of **1** in CD_3CN: (□) reaction starting with TCNE and 1,4-CHD; (○) reaction starting with preformed **1**; (- - -) least-squares line for points after 80 min; (—) least-squares line for all points with preformed **3**.

late stage of the direct TCNE reaction (Figure 2).

As to the further mechanistic details of the formation and decomposition of **1**, it should be noted that there is a modest color change upon mixing the TCNE and 1,4-CHD (to a light orange) presumably from a charge-transfer complex being formed. The tenfold increase in the rate constant for formation of **1** on going from THF to CD_3CN might be considered support for a rather more polar transition state than usual in the ene reaction,[13] though, if the charge-transfer complex is a true intermediate formed with a small but strongly solvent-dependent equilibrium constant, the same kinetic effect would result. The merely fourfold increase in the decomposition rate of **1** would seem small if the reaction proceeds through dissociation to cyclohexadienyl cation, but a preliminary run in a 65:35 acetone-water mixture showed a further large rate increase (more than another tenfold.)

Other 1,4-cyclohexadienes are being examined to see if the ene mechanism is a general one for TCNE-mediated aromatization. Also to be investigated is whether this mechanism extends to any of the quinone-mediated reactions. It has been noted that dichlorodicyanobenzoquinone is comparable with TCNE is its dienophilicity[4a] so that comparable activity as an enophile would be expected.[13,14] Furthermore, all of the experimental evidence cited in support of other mechanisms, such as the preference for axial hydrogen removal[4a-c] and isotope and steric effects,[4c-e] is also quite consistent with a concerted ene mechanism.[15] It should be noted that, in virtually all of the studies of these quinone and TCNE dehydrogenations, rates have been measured by following the decline in UV absorbance of the oxidant. Since that method precluded detection of nonabsorbing intermediates and since disappearance of the oxidant can no longer be assumed to occur as the rate-determining step of the reaction, earlier mechanistic conclusions should probably be reexamined.

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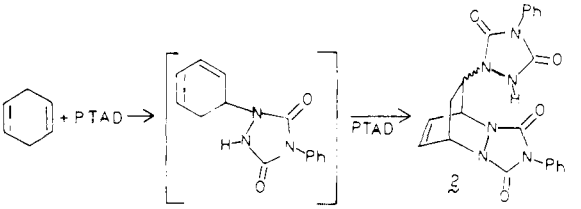
(3) T. Nishiguchi, A. Ohki, H. Sakakibara, and F. Fukuzumi, *J. Org. Chem.*, **43**, 2803 (1978).
(4) (a) L. M. Jackman, *Adv. Org. Chem.*, **2**, 239 (1960); (b) E. A. Braude, L. M. Jackman, R. P. Linstead, and J. S. Shannon, *J. Chem. Soc.*, 3116 (1960); E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *ibid.*, 3123, 3133 (1960); (c) S. H. Burstein and H. J. Ringold, *J. Am. Chem. Soc.*, **86**, 4952 (1964), and references therein; (d) P. Müller and J. Roček, *ibid.*, **94**, 2716 (1972); (e) P. Müller, *Helv. Chim. Acta*, **56**, 1243 (1973); (f) Z. M. Hashish and I. M. Hoodless, *Can. J. Chem.*, **54**, 2261 (1976).
(5) A similar sequence was reported recently for the slow SO_2-mediated aromatization of 1,4-cyclohexadiene.[6]
(6) D. Masilamani and M. M. Rogic, *Tetrahedron Lett.*, 3785 (**1978**).
(7) Least-squares coefficients $r^2 = \geq 0.98$ for both solvents.
(8) Least-squares coefficients $r^2 = 0.98$ in THF and >0.99 in CD_3CN.
(9) This ene adduct could not be isolated because it in turn reacted rapidly with more PTAD to yield the 2:1 adduct of structure **2**.[10]



(10) White powder: mp 250–251 °C; NMR (CD_3CN) δ 7.5 (m, 11 H), 6.6 (m, 2 H), 5.1 (m, 3 H), 2.6 (m, 1 H), 2.0 (m, 1 H); IR (pellet) 3450, 3100, 1690, 1400 cm^{-1}; Anal. ($C_{22}H_{18}N_6O_4$) C, H, N.
(11) In a separate experiment it was found that tetracyanoethane alone with PTAD in acetonitrile yielded TCNE and 4-phenylurazole.
(12) **1**: white powder: mp 87.5–88 °C with almost immediate resolidification and second mp 170 °C with blackening; IR (pellet) 3040, 2900, 2230, 1630, 1405 cm^{-1}. Absent are significant peaks for TCNE (e.g., 1355 and 800 cm^{-1}) and for tetracyanoethane (e.g., 1190 and 900 cm^{-1}).
(13) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).
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(15) L. M. Stephenson and D. L. Mattern, *J. Org. Chem.*, **41**, 3614 (1976), and references therein.

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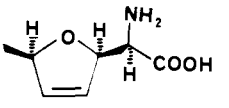
Total Synthesis and Revised Structural Assignment of (+)-Furanomycin

Sir:

The antibiotic (+)-furanomycin was isolated by Katagiri and co-workers from a culture filtrate of *Streptomyces threomyceticus*. The structure of (+)-furanomycin was determined by spectroscopic and degradative techniques to be (+)-$\alpha(R)$-amino(2,5-dihydro-5(R)-methyl)furan-2(R)-acetic acid (**1**) but the configurations at the asymmetric centers have



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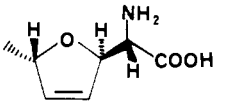

2a

not been confirmed either by X-ray studies or by a stereospecific synthesis.[1] The deceptively simple structure of **1** stands in contrast to the difficulties attached to its synthesis. A long and laborious route to **1**, involving 16 steps and an overall yield of <0.02% was reported in 1975.[2] As a result of our continuing studies on the synthesis of natural products by chirality transfer from carbohydrates, we sought to prepare furanomycin and its configurational isomers. In this communication we describe the asymmetric synthesis of 5(S),2(R),$\alpha(S)$-furanomycin (**2a**) and its isomer (**2b**) with the opposite configuration at the amino acid functionality.[3] Unexpectedly, 5(S),2(R),$\alpha(S)$-furanomycin was found to be identical with the natural (+)-furanomycin in every respect (360-MHz NMR, IR, optical rotation, melting point, mixture melting point, TLC, etc.).[4]

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Therefore, we suggest that the structure of naturally occurring furanomycin be revised as (+)-α(*S*)-amino(*trans*-2,5-dihydro-5(*S*)-methyl)furan-2(*R*)-acetic acid.

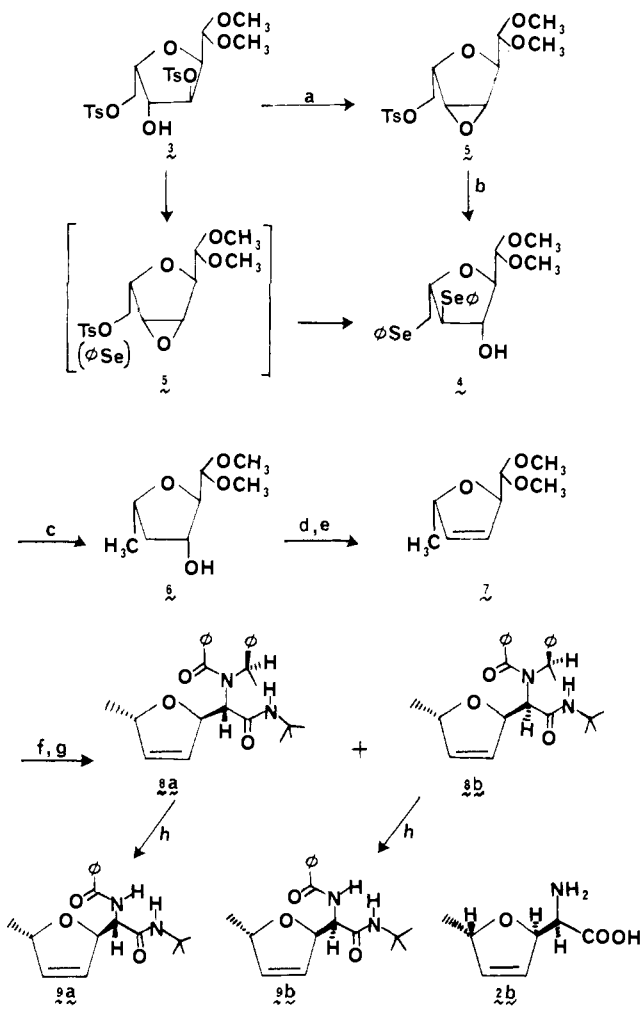
Our synthetic route is particulary attractive and efficient since it controls not only the relative but also the absolute stereochemistry. The overall yield for the synthesis of **2a** is 6% from α-D-glucose. The 2,5-dihydrofuran ring system is first constructed by chirality transfer from α-D-glucose followed by the introduction of the optically active amino acid functionality.

Furanose **3**, obtainable in 64% overall yield from D-glucose,[5] was treated with 2.5 equiv of NaSePh in refluxing DMF to afford the corresponding diselenide **4** in quantitative yield (Scheme 1).[6,7] The formation of diselenide compound **4** is believed to proceed via the intermediacy of epoxide **5**, formed by back-side attack of the hydroxyl group at C-4, followed by nucleophilic attack of NaSePh on the epoxide from the less sterically hindered side of C-4.[8,9] Support for this mechanism was obtained from the reaction of **3** with 1.1 equiv of NaH in THF at ambient temperature which gave epoxide **5** in 93% yield.[6,7] Furthermore, treatment of **5** with 2.5 equiv of NaSePh in refluxing DMF affords diselenide **4**, previously obtained directly from **3**. Reductive removal of the phenylseleno group with W-4 Raney nickel[10] in THF at 25 °C produces **6** in 96% yield.[6,7] Tosylation of **6** followed by base-catalyzed elimination with $NaOCH_3$ in refluxing methanol affords 2,5-dihydrofuran **7** in 72% yield (25% overall yield from D-glucose).[7] The sensitive aldehyde obtained on acid hydrolysis of **7** with *p*-TsOH in THF is treated with *d*-(+)-α-methylbenzylamine, benzoic acid, and *tert*-butylisonitrile[11] to afford a "four-component condensation" (4CC)[12] adduct, separable by column chromatography (Merck silica gel 60, 1:1 ether-petroleum ether, $R_{f(1)} = 0.60$, $R_{f(2)} = 0.28$) into two diastereomers, **8a** and **8b**,[7] in a 1:1 ratio. The overall yield for this facile one-pot hydrolysis and condensation is 63%. The 4CC adduct **8a** ($R_f = 0.60$) was debenzylated with 95% formic acid at 40–50 °C to afford **9a** in 85% yield.[7] Hydrolysis of **9a** with 6 N hydrochloric acid at 100 °C (2 h) proceeds smoothly to give **2a.** The synthetic amino acid was isolated by treatment with a weakly basic ion-exchange resin (Amberlite IR-4B) followed by column chromatography (silica gel, 9:1 *n*-PrOH–H_2O). Recrystallization of the crude product from aqueous acetone afforded **2a** in 50% yield as colorless plates. This compound was identical in all respects with the natural product.

In a similar series of reactions, the amino acid derivative **8b** was converted into 5(*S*),2(*R*),α(*R*)-furanomycin (**2b**).[6,7] The configurations of the amino acid functionalities were assigned on the basis of the chemical shifts of the *tert*-butyl groups in compounds **8a** and **8b** according to Ugi.[13] We are planning to obtain an X-ray diffraction analysis on either **8a** or **9a** to confirm the absolute configuration of the amino acid functionality. Investigations using different synthetic approaches to furanomycin and its stereoisomers are currently in progress.[14,15] All configurational isomers of furanomycin prepared in our studies will be tested for their biological activity.

Acknowledgments. We thank Dr. Ken Katagiri for a generous sample of natural (+)-furanomycin. The financial support of the Research Corporation is gratefully acknowledged.

Scheme I[a]



[a] (a) NaH–THF, 25 °C; (b) NaSePh–DMF, reflux; (c) Raney Ni W-4–THF, 25 °C; (d) TsCl–C_5H_5N, 0 °C; (e) $NaOCH_3$–CH_3OH, reflux; (f) TsOH–THF, reflux; (g) *d*-(+)-α-methylbenzylamine, PhCOOH, *t*-BuNC–CH_3OH, 25 °C; (h) HCOOH, 40–50 °C.

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(2) T. Masamune and M. Ono, *Chem. Lett.*, 626 (1975).
(3) Some of our results were presented at the EUCHEM Conference on "Uses of Carbohydrates as Starting Materials for Chiral Organic Synthesis", Belle-Ile-en-Mer, France, June 3–6, 1979.
(4) Naturally occurring (+)-furanomycin: mp 220–223 °C dec; $R_f = 0.41$ (7:3 *n*-PrOH–H_2O); $[\alpha]^{27}_D$ +136.1 ± 2° (*c* 1, H_2O), $[\alpha]^{25}_D$ +164 ± 2° (*c* 1, 1 N HCl); IR (KBr) 3050, 2800, 2500, 2000, 1780, 1620, 1550, 1380, 1345 1300, 1240, 1090, 1055, 1020, 990, 680 cm^{-1}; ^1H NMR (D_2O, 360 MHz) δ 1.26 (d, 3 H, Me), 3.86 (d, 1 H, α-H), 5.12 (t, 1 H, 5-H), 5.45 (br m, 1 H, 2-H), 5.86 (d, 1 H, =CH), 6.19 (d, 1 H, =CH). **2a**: mp 222.5–224.5 °C dec; R_f = 0.41 (7:3 *n*-PrOH–H_2O); $[\alpha]^{25}_D$ +140 ± 2° (*c* 1, H_2O), $[\alpha]^{25}_D$ +160 ± 2° (*c*, 1, 1 N HCl); IR (KBr) and ^1H NMR (D_2O, 360 MHz) spectra identical with the corresponding spectra of the naturally occurring product. The 360-MHz ^1H NMR spectra were recorded at the Middle Atlantic Regional NMR Facility (NIH No. PR 542) at the University of Pennsylvania directed by Dr. G. McDonald. The optical rotations were measured on a Perkin-Elmer polarimeter, Model 241, at the Chemistry Department of Drexel University.
(5) T. Ogawa, M. Matsui, H. Ohrui, H. Kuzuhara, and S. Emoto, *Agr. Biol. Chem.*, **36**, No. 8, 1448–1451 (1972).
(6) This compound has been fully characterized by spectroscopic means and elemental composition established by elemental analysis and/or high resolution mass spectroscopy.
(7) **4**: IR (neat) 3350, 1575 cm^{-1}; 220-MHz ^1H NMR δ 2.73 (br s, 1 H), 3.02 (dd, 1 H), 3.33 (s, 3 H), 3.37 (s, 3 H), 3.35–3.60 (m, 2 H), 3.88 (dd, 1 H), 4.09–4.20 (m, 2 H), 4.26 (d, 1 H), 7.10–7.25 (m, 10 H). **5**: IR (neat) 1590 cm^{-1}; 220-MHz ^1H NMR δ 2.46 (s, 3 H), 3.44 (s, 3 H), 3.47 (s, 3 H), 3.80 (q, 2 H), 4.05–4.11 (m, 3 H), 4.20–4.30 (m, 2 H), 7.35 (d, 2 H), 7.80 (d, 2 H). **6**: IR (neat) 3400 cm^{-1}; 220-MHz ^1H NMR δ 1.31 (d, 3 H), 1.55–1.90 (m, 1 H), 2.25–2.40 (m, 1 H), 2.65–2.86 (br s, 1 H), 3.43 (s, 3 H), 3.45 (s, 3 H), 4.06–4.25 (m, 2 H). **7**: IR (neat) 1580 cm^{-1}; 60-MHz ^1H NMR δ 1.22 (d, 3 H), 3.38 (s, 3 H), 3.40 (s, 3 H), 4.10 (d, 1 H), 4.58–5.15 (m, 2 H), 5.68–5.92 (m, 2 H). **8a**: IR (neat) 3200, 3000, 1725, 1675, 1650, 1620, 1540 cm^{-1}; 60-MHz ^1H NMR δ 1.06 (d, 3 H), 1.37 (s, 9 H), 1.58 (d, 3 H), 3.28–3.50 (m, 1 H), 4.85–5.38 (m, 2 H), 5.50–5.95 (m, 3 H), 7.08–8.10 (m, 11 H); ^{13}C NMR δ 173.7, 170.0, 138.9, 137.4, 133.0, 130.0, 129.5, 128.1, 127.6, 127.2, 126.0, 82.3, 81.0, 68.1, 58.9, 51.0, 28.6, 21.3, 17.9. **8b**: IR (neat) 3300, 2995, 1690, 1650, 1530, 1510 cm^{-1}; 60-MHz ^1H NMR δ 1.10 (s, 9 H), 1.24 (d, 3 H), 1.51 (d, 3 H), 3.63 (d, 1 H), 4.86–5.31 (m, 2 H), 5.73–6.12 (m, 2 H), 6.22 (br s, 1 H), 7.20 (s, 5 H), 7.32–7.58 (m, 6 H); ^{13}C NMR δ 172.1, 167.3, 139.0, 137.3, 132.6, 130.0, 129.5, 128.7, 128.0, 126.1, 85.3, 81.9, 63.5, 57.7, 50.6, 28.6, 21.6, 18.3. **9a**: mp 116–117 °C; IR (KBr) 3150, 2980, 1770, 1600, 1500 cm^{-1}; 60-MHz ^1H NMR δ 1.25 (d, 3 H), 1.30 (s, 9 H), 4.75 (q, 1 H), 4.88–5.28 (m, 1 H), 5.28–5.52 (m, 1 H), 5.72–6.0 (m, 2 H), 6.25

(br s, 1 H), 7.20–8.00 (m, 6 H); ^{13}C NMR δ 170.0, 167.1, 134.1, 133.6, 131.7, 128.6, 127.2, 125.8, 85.4, 83.3, 56.3, 51.0, 28.8, 21.8. **9b**: mp 127–129 °C; IR (KBr) 3200, 3000, 1730, 1620, 1590 cm^{-1}; 60-MHz ^1H NMR δ 1.22 (d, 3 H), 1.35 (s, 9 H), 4.74–5.35 (m, 3 H), 5.82–6.08 (m, 2 H), 6.82 (br s, 1 H), 7.79 (br s, 1 H), 7.84–7.97 (m, 5 H); ^{13}C NMR δ 168.6, 167.3, 134.4, 133.8, 131.6, 128.4, 127.3, 126.7, 86.7, 82.8, 56.9, 51.5, 28.8, 21.8. **2b**: mp 224.5–225.5 °C; R_f = 0.43 (7:3 *n*-PrOH–H_2O); $[\alpha]^{25}_D$ +251 ± 2° (*c* 1.2, 1 N HCl); IR (KBr) 3250, 2840, 1660, 1500, 1300 cm^{-1}; ^1H NMR (D_2O, 360 MHz) δ 1.28 (d, 3 H, Me), 4.02 (d, 1 H, α-H), 5.14 (t, 1 H, 5-H), 5.44 (br s, 1 H, 2-H), 5.69 (d, 1 H, =CH), 6.19 (d, 1 H, =CH).

(8) The intermediacy of an epoxide under similar reaction conditions has been reported in the reaction of **3** with NaOAc in refluxing DMF: T. Ogawa, M. Matsui, H. Ohrui, H. Kuzuhara, and S. Emoto, *Agr. Biol. Chem.*, **36**, No. 9, 1655–1657 (1972).

(9) N. R. Williams, *Adv. Carbohydr. Chem.*, **25**, 155 (1970).

(10) Prepared according to L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, 1967, p 729.

(11) *tert*-Butylisonitrile was prepared by a modification of the procedure of Ugi et al. ("Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 300). Diphenyl ether was used instead of petroleum ether.

(12) (a) I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **14**, 61 (1975); (b) H. R. Divanfard, Z. Lysenko, P. C. Wang, and M. M. Joullié, *Synth. Commun.*, 269 (1978).

(13) D. Marquarding, P. Hoffmann, H. Heitzer, and I. Ugi, *J. Am. Chem. Soc.*, **92**, 1969 (1970).

(14) During these investigations, we have prepared the 5(*R*),2(*R*),α(*R*) isomer which was presumed to be identical with natural furanomycin. The physical properties of this isomer are different from those of the natural product: mp 204–205 °C dec; R_f = 0.41 (7:3 *n*-PrOH–H_2O), $[\alpha]^{25}_D$ +47.4 ± 2° (*c* 1, 1 N HCl); IR (KBr) 3270, 3000, 2890, 2600, 1620, 1520, 1490, 1405, 1370, 1345, 1330, 1312, 1110, 1087, 1060, 1007, 980 cm^{-1}; ^1HNMR (D_2O, 360 MHz) δ 1.31 (d, 3 H, Me), 4.01 (d, 1 H, α-H), 5.03 (m, 1 H, 5-H), 5.32 (br m, 1 H, 2-H), 5.71 (d, 1 H, =CH), 6.13 (d, 1 H, =CH). Full details pertaining to the cis series will be reported in a forthcoming publication.

(15) A recent communication from Professor Morris J. Robins at the University of Alberta informed us that he had also synthesized the 5(*R*),2(*R*),α(*R*) isomer from ribose and that this compound did not have the same physical properties as natural furanomycin.

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A Total Synthesis of *dl*-Pentalenolactone†

Sir:

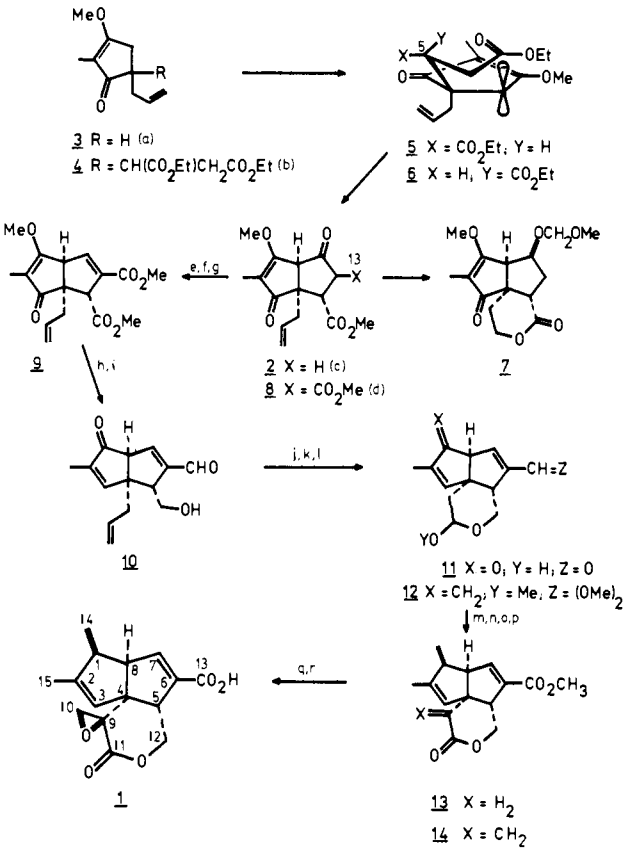
In 1970 an UpJohn group described the isolation and characterization of an acidic lipophilic antibiotic, pentalenolactone (**1**)—a substance which possesses a highly compacted tricyclic structure and which exhibits cytotoxic activity.[1] These interesting properties elicited considerable chemical activity culminating in an intriguing total synthesis of **1** by Danishefsky and co-workers.[2] Herein, we describe a quite different synthetic route to **1** which commences with a brief formulation of the pentalene system **2**, followed by an interlude of functional group reorganization, and concluding with the introduction of carbons 14 and 10.[3]

The vinylogous ester 3-methoxy-2-methylcyclopentenone[4] was kinetically deprotonated at −78 °C with lithium diisopropylamide (LDA), and the enolate thus formed was alkylated with allyl bromide to give **3** [90%, bp 70–75 °C (4×10^{-6} Torr)] (Scheme I).[5] Compound **3** was further appended by deprotonation with LDA and subsequent reaction with diethyl maleate. The resulting adduct, **4** (mp 88–89 °C), was determined by ^1H NMR to be a 1:1 mixture of epimers about C_5. Hence, enolate generation stemming from the vinylogous ester residue of this substance would yield two anions, **5** and **6**, with differing configurations about C_5. Molecular models suggested that **5** would undergo cyclization into the pentalene **2**—a material possessing the desired cis relationship between the allyl group and the carboxylate residue at C_5. A significant inhibition to cyclization was indicated for **6** stemming from a serious interaction between the five-membered-ring vinylogous ester enolate and the C_5 carboxylate residue. Therefore, we anticipated that only compound **2** would result from cyclization of **4** and were gratified to find that treatment of the latter with a mixture of sodium hydride, dimethyl carbonate, and DME at 0–22 °C for 1 h did indeed yield **2** [bp 145–155 °C (4×10^{-6} Torr), mp 72–73.5 °C, 75% yield from **3**].[6] The ^1H NMR spectrum of **2** indicated it to be a single compound, and its relative stereochemistry was readily confirmed by high yield conversion into the cis lactone **7**.[7]

The C_{13} carboxyl residue present in the natural product was next introduced by deprotonation of **2** at −78 °C with potassium hexamethyldisilazane (thermodynamic mode) followed by carbonation (CO_2) of the cyclopentanone derived enolate.[8] Acidification of this reaction mixture at −15 °C with 3% HCl, rapid extraction with methylene chloride, and esterification with diazomethane at −78 °C gave the diester **8**. Methanolic sodium borohydride reduction of **8**, mesylation of the resulting β-hydroxy ester, and elimination of the elements of methanesulfonic acid (collidine, 180 °C) afforded the acrylate ester **9** (mp 103.5–105 °C, 65% yield from **2**).

A sequence of reactions leading to a tricyclic substance amenable to introduction of the C_{14} methyl group was now

Scheme I[a]



[a] (a) LDA, THF (1 M), allyl bromide (1.1 equiv), −78 °C; (b) LDA, THF (1 M), diethyl fumarate, −78 °C; (c) NaH (5 equiv), $OC(OMe)_2$ (1 M), 0 °C, 30, min, DME (0.25 M), 22 °C, 1 h; (d) KHMDS (1 equiv), THF (0.5 M), −78 °C, CO_2, −78–0 °C, 3% HCl, −15 °C, CH_2N_2, CH_2Cl_2, −78 °C; (e) $NaBH_4$, MeOH (0.25 M), −20 °C; (f) $MeSO_2Cl$ (2 equiv), Et_3N (3 equiv), THF (0.2 M), 22 °C, 8; (g) collidine (1 M), 180 °C, 2 h; (h) diisobutylaluminum hydride (6 equiv), toluene (0.3 M), 0 °C, 6 N HCl; (i) MnO_2 (15 equiv), benzene (0.2 M), 22 °C, 4 h; (j) O_3, CH_2Cl_2 (0.25 M), pyridine (1.1 equiv), −78 °C, Me_2S; (k) MeOH (0.2 M), $CH(OMe)_3$ (5.0 equiv), HCl (0.2 equiv), 0 °C, 45 min; (l) Ph_3PCH_2Br (3 equiv), *n*-BuLi (3 equiv), THF (1 M), 0–40 °C; (m) $(Ph_3P)_3RhCl$ (0.1 equiv), benzene (0.1 M), H_2 (300 psi), 22 °C; (n) 10% H_2SO_4, acetone, H_2O, 40 °C, 12 h; (o) Jones, 22 °C, 3 h; (p) CH_2N_2, Et_2O, CH_2Cl_2, (q) MMC (20 equiv), 180 °C, 2 h, CH_2Cl_2, 3% HCl, −20 °C; (r) 30% CH_2O, Et_2NH, 40 °C.

† Dedicated to the memory of R. B. Woodward.

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