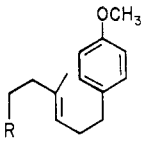
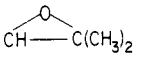
synthesis which, paralleling in important respects the likely biolgenesis, features direct formation of the A–B ring system in a key intermediate (**2**) having the exact functionality and relative stereochemistry characteristic of the A ring in the natural product.

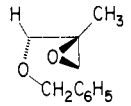
Treatment of phenylgeranyl thioether[6] anion with *p*-methoxybenzyl chloride (THF, −78 °C) provided (86%) the expected alkylation product, which was reduced (Li/NH_3, −78 °C; 47%) to diene **3**. Selective oxidation[7] to the terminal bromohydrin (1.1

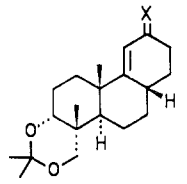


3 R = $CH{=}C(CH_3)_2$

4 R = 

5 R = $CH(OH)C(CH_3){=}CH_2$

6 R = 

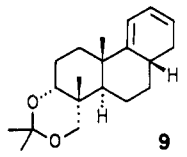


7 X = O

8 X = $NNHC_6H_2(i\text{-}Pr)_3$

equiv of NBS in $THF–H_2O$, 0 °C) followed by exposure to K_2CO_3 in MeOH afforded the 2,3-oxide **4** (33%). Elimination induced by $LiN(Et)_2$ (refluxing Et_2O, 57%) led to allyl alcohol **5**, which on $VO(acac)_2$-catalyzed oxidation with *t*-BuO_2H[8] in benzene[9] was converted (80%) to a single racemate, the erythro glycidol, readily O-alkylated with benzyl iodide (NaH, THF, 90%)[9] to the glycidyl benzyl ether **6**.

In an adaptation of the normal enzymic cyclization process,[10] intermediate **6** was transformed ($FeCl_3$, toluene)[9] to the hydrophenanthrene **2** (OAc, mp 102–103 °C).[11] Simultaneous de-O-benzylation and Birch-type reduction (Li, EtOH–THF, −78 °C) was followed by hydrolysis (0.5 M HCl–EtOH)[9] of the intermediary enol ether and ketalization of the released diol moiety (acetone; TsOH, 100%),[9] yielding (55%) the cyclohexenone **7** (mp 186–188 °C). After formation of the trisylhydrazone (**8**) (70%) (trisylhydrazine, TsOH, THF)[9] a Bamford–Stevens-type reaction (*n*-BuLi, TMEDA, hexane, −78 °C)[12] produced the cyclohexadiene (**9**) needed for elaboration of a fourth carbocyclic ring (82%).



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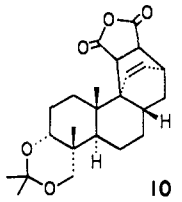

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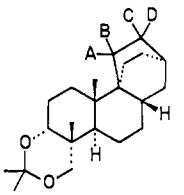
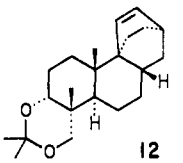
Rigidly stereocontrolled by the bulk of the two α-substituents at C-3 and C-4, the reaction of diene **9** with maleic anhydride (benzene, 80 °C, 86%) gave rise to adduct **10**. Catalytic reduction of the corresponding diacid (Pt black, H_2O–EtOH, 90%)[9] to **11** followed by $Pb(OAc)_4$-induced decarboxylation (O_2-saturated pyridine, 28%)[13] produced olefin **12** (mp 113–115 °C). All at-



11 A = D = H; B = C = CO_2H

13 A = B = C = H; D = α OH

14 A = B = C = H; D = αOSO_2CH_3



12

tempts to functionalize appropriately the bicyclooctene unit failed, except for epoxidation (*m*-$ClC_6H_4CO_3H$, CH_2Cl_2, $NaHCO_3$, 100%)[9] followed by Na metal reduction in refluxing benzene,[14] which yielded (20%) only the alcoholic regio- and stereoisomer (**13**) needed for effecting the biomimetic skeletal isomerization to the aphidicolane ring system.

Solvolytic rearrangement of the derived mesylate **14** (refluxing acetone–H_2O, $CaCO_3$) generated the desired bicyclo[3.2.1]octanol **15** (60% overall from **12**), readily oxidized (CrO_3–py, CH_2Cl_2, 90%)[9] to the corresponding (±)-ketone **16** (mp 137–139 °C).[4,5] NMR, IR, and mass spectral as well as GC behavior of our synthetic **16** was indistinguishable from that of corresponding material derived from the natural product. In view of the known conversion of the norketone to the natural product system[4,5] the work described herein constitutes a total synthesis of (±)-aphidicolin.

Acknowledgment. National Science Foundation for financial support (CHE-8002661), Dr. B. Hesp for an aphidicolin sample, NSF (GP28142) for provision of XL-100-FT NMR facility are thanked.

Supplementary Material Available: NMR as well as certain IR and mass spectra, corroborated structures assigned to all intermediates (3 pages). Ordering information is given on any current masthead page.

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^1H NMR Studies of Nitrogen-15-Labeled *Escherichia coli* $tRNA_f^{Met}$. Assignments of Imino Resonances for Uridine-Related Bases by ^1H–^{15}N Heteronuclear Double Resonance Difference Spectroscopy

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We recently reported that the imino protons of uridine and bases derived from uridine biosynthetically in *E. coli* $tRNA_f^{Met1}$ can be identified in a ^1H NMR spectrum by ^1H–^{15}N couplings.[2,3] On the basis of the X-ray structure of the molecule,[4] we expected to

(1) Abbreviations used are tRNA, transfer ribonucleic acid; ppm, parts per million; NOE, nuclear Overhausen effect; ψ, pseudouridine; rT, ribothymidine; s^4U, 4-thiouridine; EDTA, ethylenediaminetetraacetic acid; P, phosphate.

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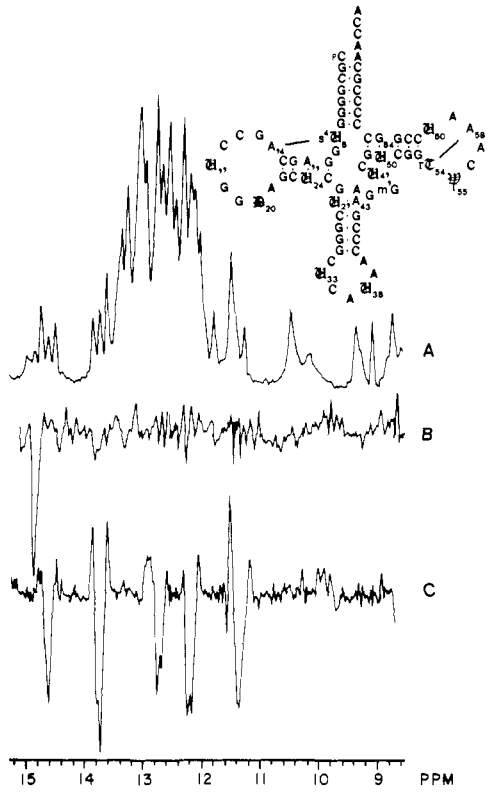

Figure 1. ^1H spectra of *E. coli* $tRNA_f^{Met}$ acquired on a Nicolet 360-MHz NMR spectrometer equipped with probe triply tuned for ^1H, ^2H, and ^{15}N (5-mm insert) by using a Redfield "2-1-X" pulse sequence for a 1 mM sample of tRNA in 10 mM sodium cacodylate, 50 mM sodium chloride, 10 mM magnesium chloride, and 1 mM EDTA, pH 7.0 with 5% deuterium oxide: A, normal spectrum at 30 °C; B, ^1H–^{15}N double resonance difference spectrum at 14 °C with irradiation at 36.487132 MHz; C, ^1H–^{15}N double resonance difference spectrum at 14 °C with irradiation at 36.486450 MHz.

see characteristic trio patterns (the ^1H–^{14}N singlet from residual unlabeled tRNA flanked by the ^1H–^{15}N doublet) for imino protons in s^4U8-A14, A11-U24, U27-A43, U50-G64, and rT54-A58 pairs. Five trios were indeed detected in the ^1H spectrum at 11.38, 12.20, 13.75, 14.65, and 14.90 ppm, respectively. One, however, was judged to belong to ψ55 or U60 on the basis of its high-field chemical shift (11.38 ppm).[3] Of the remaining trios, we assigned the signal at 12.20 ppm to U50 in the U50-G64 wobble base pair by NOE difference spectroscopy.[3] The pattern at 14.90 ppm is consistent with earlier assignments to s^4U8-A14 based on chemical modification.[5,6] We could not assign the trios at 13.75 and 14.65 ppm, nor did we detect a sixth trio now expected for resonances from the five crystallographic base pairs and the high-field pattern at 11.38 ppm. In this communication we describe ^1H–^{15}N heteronuclear double resonance difference experiments that permit us to expose the hidden sixth resonance and to assign ^1H chemical shifts by ^1H–^{15}N chemical shift correlation.

Without decoupling, the imino hydrogens at labeled nitrogen appear as approximately 1:1:1 trios (60–65% incorporation of ^{15}N) as shown in Figure 1a.[2] Irradiation at the nitrogen resonance frequencies collapses the ^1H–^{15}N doublets onto the ^1H–^{14}N singlets, and subtraction of the decoupled from the coupled spectrum results in new three-line patterns consisting of strong negative peaks at the ^1H resonance positions flanked by less intense positive peaks from the ^1H–^{15}N doublets. All other ^1H signals disappear. Six distinct negative peaks are found in the ^1H double resonance difference spectra (Figure 1A,C). ^1H and ^{15}N spectra were

Table I. ^1H and ^{15}N Chemical Shifts for *E. coli* $tRNA_f^{Met}$

assignment	^1H,[a] ppm	^{15}N frequency,[b] MHz	^{15}N,[c] ppm
s^4U8-A14	14.90	36.487 132 ± 10	177.8
A11-U24	14.65	36.486 445 ± 10	159.0
rT54-A58	13.75	36.486 317 ± 10	155.6
U27-A43	12.66[d]	36.486 412 ± 10	158.0[d]
U50-G64	12.20	36.486 280 ± 10	154.5
ψ55-P58	11.38	36.486 300 ± 10	155.0

[a] Relative to dimethylsilapentanesulfonate, ±0.01 ppm. [b] Measured at incremental frequencies. Values represent best "collapse" of the ^1H–^{15}N doublet. [c] Downfield from ammonia at 25 °C; Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley: New York, 1979; pp 28–31. [d] Measured at 14 °C.

correlated by reducing the power needed to decouple the trio at 14.90 ppm to a minimum and collecting difference spectra as the decoupling frequency was varied in increments through the ^{15}N region.[7]

We recently reported an unambiguous assignment for the ^1H signal at 12.20 ppm (U50-G64) by an NOE difference experiment.[3] This peak correlates with an ^{15}N resonance at 154.5 ppm (see Table I), which we assign to N(3) of U50. The peak at 14.90 ppm attributed to s^4U8-A14 from chemical modification is generally considered to be reliable, although the ranges of chemical shifts reported for imino hydrogens in s^4U-A and U-A pairs do overlap. That assignment is confirmed by correlation of the peak with a nitrogen resonance at 177.8 ppm. This ^{15}N chemical shift is downfield from the others by 20 ppm and is close to the value of 179.1 ppm which we measured at natural abundance for 4-thiouracil in dimethyl sulfoxide.

The trio pattern at 11.38 ppm previously attributed to ψ55-P58 (or perhaps U60)[3] correlates with a ^{15}N resonance at 155.0 ppm. This peak is 0.5 ppm downfield from the ^{15}N resonance in the U50-G64 wobble pair and 4–5 ppm downfield from the expected position for a "free" uridine. A shift of this magnitude is consistent with the value of 3.4 ppm we found for N(3) of tri-*O*-benzoyluridine in the presence of tetrabutylammonium dibutylphosphate in chloroform[8] and supports our previous contention that the resonance at 11.38 is the N(3) imino hydrogen of ψ55.

The remaining ^1H resonances at 12.66, 13.75, and 14.65 ppm result from the A11-U24, U27-A43, and rT54-A58 pairs. The ^1H signals at 12.66 and 14.65 ppm correlate with ^{15}N resonances at 158.0 and 159.0 ppm, respectively, while the peak at 13.75 ppm correlates with a nitrogen at 155.6 ppm. Markowski et al.[9] have shown that N(3) in uridine 5′-phosphate is approximately 3 ppm downfield from N(3) in the corresponding thymidine derivative, and additional shifts due to hydrogen bonding should be comparable for both bases. Thus, the signal at 13.75 ppm is assigned to the rT54-A58 pair.[10] By the process of elimination the two remaining peaks belong to secondary A-U pairs. The resonance at 12.66 ppm is temperature sensitive and disappears as the sample is warmed from 14 to 25 °C. We assign this peak to the U27-A43 pair at the end of the anticodon stem. Fraying, with concomitant exchange of imino hydrogens with water, is a commonly observed phenomenon for base pairs at the ends of helical strands.[11] While 12.66 ppm is a surprisingly high-field value for an A-U secondary pair,[12] X-ray structure of *E. coli* $tRNA_f^{Met}$ does suggest that A44 stacks directly over U27-A43. It follows that the peak at 14.65 belongs to A11-U24 in the dihydrouridine stem.

^1H–^{15}N heteronuclear double resonance difference spectroscopy and correlation of ^1H and ^{15}N chemical shifts has permitted us

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to complete the assignments for the six pyrimidine imino hydrogens in *E. coli* $tRNA_f^{Met}$ seen between 11 and 15 ppm.[13] The power of the method is further illustrated by the discovery of the temperature-sensitive resonance for U27-A43. At the lower temperatures needed to observe the peak, all of the ^1H signals are significantly broader, and it would have been difficult to detect the appearance of the new signal at 14 °C without the difference experiment. The U27-A43 resonance accounts for one of the "missing" peaks in the 35 °C spectrum.[2]

Acknowledgment. We thank Professor Redfield for informing us about his NOE experiments and the National Science Foundation for support of this research by Grants PCM 79-16861 (to C.D.P.) and CHE 78-18581 (to the regional NMR facility at Colorado State University).

Registry No. Uridine, 58-96-8; 4-thiouridine, 13957-31-8; ribothymidine, 1463-10-1; pseudouridine, 1445-07-4; adenosine, 58-61-7; guanosine, 118-00-3.

(13) The technique should be generally useful for detection of ^1H resonances and for chemical shift correlation in biopolymers labeled with NMR-active isotopes.

Circular Polarization of Luminescence as a Probe for Intramolecular $^1n\pi^*$ Energy Transfer in *meso*-Diketones

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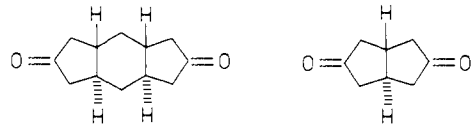
When a racemic mixture is excited with circularly polarized light, the degree of circular polarization in the luminescence (CPL) provides information on the rate of racemization in the excited state.[1,2] It appears, however, that the CPL technique can also be used to study intramolecular excitation energy transfer.

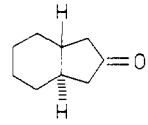
We here report measurements on aliphatic diketones that contain two remote carbonyl chromophores of opposite chirality and thus are, in the ground state, meso structures (*RS*). In the $^1n\pi^*$ state they may occur in two enantiomeric forms, *R*S* and *RS**, provided the excitation energy remains localized at a carbonyl group. If the excited state is formed by irradiation with circularly polarized light, the concentrations of *R*S* and *RS** are unequal, and the fluorescence will to some extent be circularly polarized. In complete analogy to the case of racemates,[2,3] the observed circular anisotropy equals $G_L = {}^1/_2 g_a g_e$, where the index L denotes the (left) handedness of the excitation light and g_a (g_e) the dissymmetry factor in absorption (emission) of the *R* and *S* carbonyl moieties. Irradiation with *R* light has the opposite effect: $G_R = -G_L$. So in the absence of energy transfer, the differential circular anisotropy $G_L - G_R$ equals $g_a g_e$. When during the fluorescence lifetime τ_F energy transfer (rate k_{ET}) occurs, a lower anisotropy will be observed, viz.

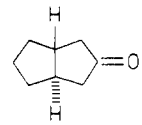
$$(G_L - G_R)_{obsd} = g_a g_e (2k_{ET}\tau_F + 1)^{-1}$$

Provided $g_a g_e$ is known, the observed differential polarization directly measures k_{ET} relative to τ_F.

We have studied the effect of the 1,7-diketone (1*S*,3*R*,7*R*,9*S*)-tricyclo[7.3.0.0^{3,7}]dodecane-5,11-dione (**1**)[4] and







the 1,5-diketone *trans*-bicyclo[3.3.0]octane-3,7-dione (**2**).[5] The absorption spectra of **1** and **2** essentially are equal in shape and twice as intense as the spectra of the relevant monoketones **3** and **4**, respectively.[6] Also the fluorescence spectra of **1** and **2** closely resemble those of **3** and **4**, respectively.[6] Apparently in **1** and **2** the local $^1n\pi^*$ states are only very weakly coupled, justifying a description of absorption and emission in terms of local transitions.[7] Like in **3** and **4**, the carbonyl groups in **1** and **2** are contained in chirally twisted cyclopentane rings. Therefore, one expects that their g_a and g_e values equal those of **3** and **4** to a good approximation. It is known from experiment that the dissymmetry factors of **3**[8,9] and **4**[10,11] are large and virtually equal ($g_a \simeq 0.2$ in the long wavelength part of the n $\rightarrow \pi^*$ absorption band and $g_e \simeq 0.03$ in the short wavelength part of the fluorescence band).

When exciting at 310 nm and collecting the fluorescence at 400 nm, we observed[12] for **1** the large differential polarization $G_L - G_R = (58 \pm 3) \times 10^{-4}$, whereas for **2** it proved to be zero: $G_L - G_R = (0 \pm 1) \times 10^{-4}$. The quantitative correspondence of $G_L - G_R$ of **1** with $g_a g_e$ of **3** (better than 95% as found from the experimental error in $G_L - G_R$) implies that $k_{ET} \lesssim 1 \times 10^7\ s^{-1}$ (calculated with $\tau_F = 2$ ns, the value found[13] for **3**).[14] On the other hand the complete disappearance (>98%) of the differential

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(5) Prepared as follows: 1 g of *trans*-8-acetoxy[4.3.0]nonane-3,4-dione[22] was heated with 3.5 g of KOH and 7 g of H_2O in a Carius tube for 30 min at 125 °C. The reaction mixture was cooled to room temperature, diluted with water, and acidified to pH 1 with 1 N HCl. *trans*-3,7-Dihydroxybicyclo-[3.3.0]octane-3-carboxylic acid was isolated by extraction with ethanol and subsequently refluxed with PbO_2/H_2SO_4. Extraction with CH_2Cl_2 yielded *trans*-7-hydroxybicyclo[3.3.0]octan-3-one (**2a**). Oxidation with pyridinium chlorochromate[23] yielded crude **2**. Purification of **2** proceded by extraction with ether and crystallization from ether. **2a**: ^1H NMR ($CDCl_3$, 100 MHz) δ 4.7 (quartet-like, 1 H), 2.7-2.2 (4 H), 2.2-1.2 (6 H), complex spectrum; ^{13}C NMR ($CDCl_3$, 25 MHz) δ 219.80 (s), 75.02 (d), 47.63 (d), 45.90 (d), 43.62 (t), 43.47 (t), 39.04 (t), 38.74 (t). **2**: ^1H NMR ($CDCl_3$, 100 MHz) δ 2.8-2.25 (4 H), 2.25-1.7 (6 H), complex spectrum; ^{13}C NMR ($CDCl_3$, 25 MHz) δ 215.99 (s), 45.08 (d), 43.26 (t); MS, *m/e* 138 (M^+); UV (nm, ε; CH_3CN) 318 (37.5), 308 (70), 297 (70), 289 sh (56); mp 165.5-166.5 °C.
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