carbon suboxide and $PMePh_2$ do not react (1:1 stoichiometry) in the absence of the metal (^1H and ^{31}P NMR; IR). Attempts to intercept the ketenylidene by using phosphine traps have not been successful. Triphenylphosphoranylideneketene (O=C=C=PPh_3) is a stable molecule[11] and is known to form a moderately stable complex in $(CO)_5W\{\eta^1$-C(CO)$PPh_3\}$.[12] **2**, however, is the first example of a complex containing an η^2, 4-e donor ligand of this type and is closely related to known group 6 complexes containing η^2-ketenyl ligands, M{C,C′:η^2-C(O)CR} (vide infra).[13]

The infrared spectrum of **2** exhibits two strong carbonyl absorptions that arise from the newly formed carbon monoxide ligand (ν(CO) = 1910 cm^{-1}) and the η^2-ketenyl ylide (ν(C=O) = 1673 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum of **2** contains two resonances of relative intensity 2:1, with the larger having ^{183}W satellites and the smaller having none. Two distinct types of phosphorus moieties are also observed in the ^1H NMR spectrum: the methyl resonances for the $PMePh_2$ units appear as a doublet (δ 1.94, J_{PH} = 14.2 Hz) and a virtual triplet (δ 2.03, J_{PH} = 4.0 Hz) in a relative ratio of 1:2, characteristic of a phosphonium species (cf., J_{PH} = 14.5 Hz for [$PMe_2Ph_2^+$]) and a pair of *trans*-phosphine ligands, respectively.[9]

Diffraction quality crystals of unsolvated **2** were obtained by slow diffusion of ether into a saturated CH_2Cl_2 solution.[14] An ORTEP view of the structure of **2** with the atom numbering scheme is shown in Figure 1, along with salient intramolecular metrical parameters. The most striking feature of the structure is the novel η^2-diphenylmethylphosphoranylideneketene ligand. This [η^2-C(O)C$PMePh_2$] fragment bears a close structural resemblance (in all relevant bond distances and angles) to η^2-ketenyl ligands in related tungsten(II) complexes (cf. (Et_2NCS_2)(diphos)(CO)W{C,C′:η^2-C(O)C-CH_2Ph}[13a] and Cp(CO)(PMe_3)W{C,C′:η^2-C(O)C-tol}[13d,e]). In comparison with Ph_3P=C=C=O,[11] the expected structural variations are observed on coordination of the phosphoranylideneketene in an η^2-fashion: (a) the P–C (1.648 (7) Å versus 1.753 (8) Å for **2**, Δ = 0.1 Å) and the C–C (1.210 (10) Å versus 1.368 (12) Å for **2**, Δ = 0.16 Å) bonds lengthen significantly on coordination and (b) the CCO angle deviates noticeably form linearity (175.6 (8)° versus 147.2 (8)° in **2**). The geometry of **2** is approximately octahedral if the η^2-C(O)C$PMePh_2$ ligand is considered as occupying one site in the coordination sphere. The new η^2-C(O)C$PMePh_2$ moiety is essentially planar. The largest deviation from the least-squares plane defined by W, Cl(1), Cl(2), C(1), C(2), C(3), O(1), O(2), and P(3) (i.e., all atoms of **2** except for P(1), P(2), and the Me and Ph groups) is 0.15 Å for Cl(2).

Like $(CO)_5W\{\eta^1$-C(CO)$PPh_3\}$,[12] at temperatures above 35 °C the phosphoranylideneketene moiety of **2** decomposes. As shown in Scheme I, the product of thermal decomposition of **2** in chloroform is the 16-e tungsten derivative $WCl_2(CO)(PMePh_2)_3$ (**3**) and carbon monoxide (determined by a Toepler measurement).[15] A spectroscopically (IR) detected dicarbonyl intermediate (probably $WCl_2(CO)_2(PMePh_2)_3$) is apparently involved in the transformation of **2** → **3**. We are currently attempting to ascertain the fate of the extruded "C atom" in this reaction.[16]

Acknowledgment. Financial support from the National Science Foundation (Grant CHE-8520329) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (17718-AC3) is appreciated by G. L. H. The NMR facilities were supported in part through the University of Chicago Cancer Center Grant (NIH-CA-14599).

Supplementary Material Available: Tables of atomic coordinates, bond angles and distances, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); table of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(14) Crystallographic data for **2**: $C_{42}H_{39}Cl_2O_2P_3W$, monoclinic, $P2_1/n$, a = 11.400 (4) Å, b = 16.029 (4) Å, c = 21.569 (9) Å, β = 97.13 (3)°, V = 3910 (2) Å^3, Z = 4, D(calcd) = 1.463 g·cm^{-3}, μ = 43.1 cm^{-1}. Of 6588 reflections collected (Nicolet R3m diffractometer, 23 °C, Mo Kα, 2θ(max) = 50°), 6152 were independent (R_{int} = 1.74%), and 4333 were considered observed. An empirical correction for absorption was applied to the data. The structure was solved by heavy-atom methods. The six phenyl rings were constrained to rigid, planar hexagons (d_{C-C} = 1.395 Å), and hydrogen atoms were treated as idealized, updated isotropic contributions. With all non-hydrogen atoms anisotropic, $R(F)$ = 4.1%, $R(wF)$ = 5.2%, GOF = 1.190, Δ/σ = 0.037, $\Delta(\rho)$max = 1.84 e·Å^{-3} (1.02 Å from W), and N_o/N_v = 11.4. All computations used SHELXTL(5.1) software, Nicolet Corp., Madison, WI.

(15) A 0.51-g (0.6 mmol) sample of **2** was dissolved in $CHCl_3$ (25 mL) and maintained at 35 °C for 48 h. The volume of solution was reduced to 5 mL, and Et_2O was added to give a pink precipitate. Recrystallization from cold CH_2Cl_2 gave red-purple crystals of **3** (0.21 g, 51% yield). For **3**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, 3 H, J_{PH} = 13.2 Hz), 2.20 (t, 6 H, J_{PH} = 3.6 Hz), 6.9–7.6 (m, 30 H); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, H_3PO_4 ref) δ 10.7 (d with W satellites, 2 P, J_{PP} = 4, J_{PW} = 285 Hz), −2.4 (t with W satellites, 1 P, J_{PP} = 4, J_{PW} = 194 Hz); $^{13}C\{^1H\}$ NMR (100.6-MHz, CD_2Cl_2) δ 12.3 (d, J_{PC} = 61 Hz), 14.7 (t, J_{PC} = 14 Hz), 124–140 (m), 219 (br m); IR (Fluorolube mull) ν_{CO} = 1903 cm^{-1}. Anal. Calcd for $C_{40}H_{39}Cl_2OP_3W$: C, 54.38; H, 4.45. Found: C, 53.89; H, 4.17. A referee suggested **3** might actually be $WCl(CO)(CCl)PMePh_2)_3$; owing to its relative insolubility, our ^{13}C NMR data is not of sufficient quality to rigorously exclude this possibility, but the analytical data suggest otherwise.

(16) $(CO)_5W\{\eta^1$-C(CO)$PPh_3\}$ decomposes in the presence of cyclohexene to give $(CO)_5W(PPh_3)$ and 7,7′-spirobinorcarane (i.e., formal addition of "C" across the C–C double bonds of two cyclohexene molecules).[12]

Dercitin, a New Biologically Active Acridine Alkaloid from a Deep Water Marine Sponge, *Dercitus* sp.

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From our search for compounds from marine organisms with potential pharmacological utility, a violet pigment that exhibits antitumor, antiviral, and immunomodulatory properties in vitro[1] and antitumor properties in vivo was discovered. From spectroscopic analysis, including long-range ^1H–^{13}C correlation and natural abundance ^{13}C–^{13}C NMR experiments, the structure elucidation of this fused pentacyclic aromatic alkaloid, which we have designated dercitin (**1**), was achieved. This alkaloid represents a unique variation on fused-ring alkaloids previously found in marine organisms.[2]

Shipboard extraction (3:1 MeOH-toluene) and screening of fresh sponge material, collected by manned submersible at 160 m near Goulding Cay, Bahamas, showed significant in vitro ac-

(1) Dercitin **1** had in vitro antitumor activity against P388 (IC_{50} 0.05 μg/ml) and human tumor cells (HCT-8, A-549, T47D, 1.0 μg/ml) and in vivo activity against P388 (T/C 170%, 5 mg/kg). Compound **1** had immunosuppressive activity in a murine derived, two-way mixed lymphocyte reaction assay (0% MLR, 0.01 μg/mL) and showed activity against Herpes simplex type 1 (10, ++ at 5 μg/well) and A-59 murine coronavirus (0, +++ at 1 μg/well) viral models (cytotoxicity: 16 = no viable cells, 8 = partial viability, 0 = no toxicity; antiviral activity: +++ = complete inhibition, + = partial inhibition, +/− = marginal inhibition, − = no protection).

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tivity against P388 murine leukemia cells. Subsequent bioassay guided fractionation of the MeOH extract of the frozen sponge lead to the isolation of **1** as the active principle (0.01%) as well as 1,1-dimethyl-5,6-dihydroxyindolinium chloride,[3] which is inactive in our assays. Optimized extraction of the sponge with a mixture of NH_4OH (5%) and CH_2Cl_2 followed by purification with CCCC gave **1** in improved yield (0.69% of wet wt) as a deep violet powder (mp 168 °C).

All attempts to crystallize dercitin **1** and a number of its derivatives were unsuccessful. Because of their hygroscopic natures, satisfactory elemental analyses could not be obtained. HREIMS gave the formula $C_{21}H_{20}N_4S$ (*m/z* 360.1398, Δ 1.1 mmu) for dercitin **1**. Only one major fragment at *m/z* 302 (100%) was observed, indicating a fairly stable structure. Both UV absorption pattern and ^1H NMR chemical shifts were found to be dependent on the pH of the medium, while the latter was shown to be concentration dependent as well. The chemical shift values[4] recorded on a 0.45-mol solution in TFA-*d* is used throughout the discussion as this was the solvent of choice for the 2D INADEQUATE experiment.

Proton decoupling and COSY experiments indicated the presence of three proton spin systems: the four protons on C-4 to C-7 [δ 8.51 (1 H, d, *J* = 8.3 Hz, H-4), 7.74 (1 H, dd, *J* = 8.3, 6.6 Hz, H-5), 8.10 (1 H, dd, *J* = 8.3, 6.6 Hz, H-6), and 7.97 (1 H, d, *J* = 8.3 Hz, H-7)] appeared to be on contiguous carbons on an aromatic ring, while the olefinic protons H-2 and H-3 [δ 8.7 (1 H, d, *J* = 7 Hz, H-2) and 8.17 (1 H, d, *J* = 7 Hz, H-3)] and the methylene protons on C-14 and C-15 [δ 4.14 (2 H, t, *J* = 5.7 Hz, H-14) and 3.95 (2 H, t, *J* = 5.7 Hz, H-15)] formed separate vicinal pairs. The remaining protons appeared as singlets at δ 3.56 (17-CH_3 and 18-CH_3), 5.21 (13-CH_3), and 9.5 (H-11). Due to the large number of quaternary carbons and heteroatoms present in the skeleton of this compound, ^{13}C–^{13}C and long-range ^1H–^{13}C NMR coupling information was paramount in the structure elucidation of **1**. The partial structure **1a** was established from the following: the ready loss of a C_3H_8N fragment in the mass spectrum[5] together with the presence of ^1H NMR signals for two vicinal methylene and six methyl protons confirmed the presence of an *N,N*-dimethyl ethyl moiety in the molecule. From HETCOSY[6] and COLOC[7] NMR experiments, the methylene protons on C-15 showed three-bond coupling to the *N*-methyl carbons (C-17 and C-18) and C-9, while the protons on C-14 showed three-bond coupling to C-8a and C-9a. The proton resonating at δ 9.5 (H-11), which appeared to be on a carbon situated between two heteroatoms from its ^{13}C chemical shift (151.68 ppm) and one-bond C–H coupling (J_{C-H} = 218 Hz),[8] showed long-range coupling to C-9a and C-12a. The *N*-methyl enamine moiety in the partial structure **1b** was evident from the presence of an NOE effect between the 13-CH_3 protons and H-2 and three-bond coupling between the methyl protons and C-2, which must be attached to a heteroatom (δ 149.26, J_{CH} = 187 Hz for C-2/H-2). The C-2 proton also showed three-bond coupling to C-13 and C-3a, while the C-4 proton also showed three-bond coupling to C-3a. A strong NOE between H-3 and H-4 provided additional evidence for the spatial proximity of these two protons.

On treatment of **1** with $NaBH_4$ a reduction product **2** was formed, but it underwent reoxidation readily on workup. Dercitin

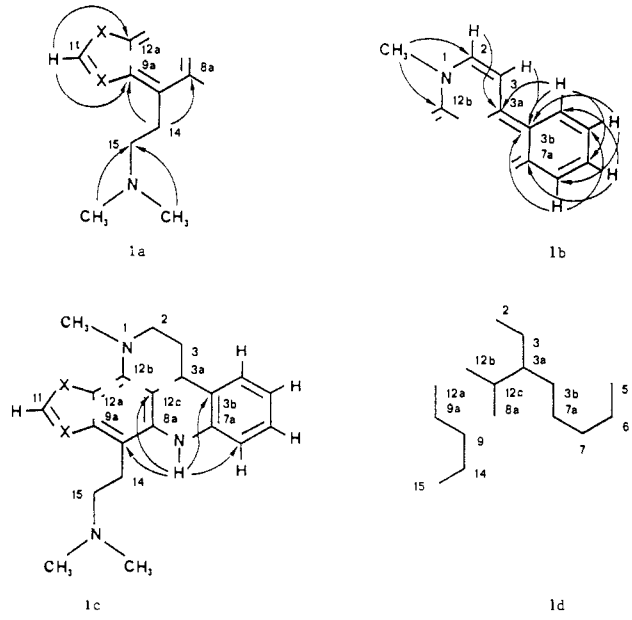
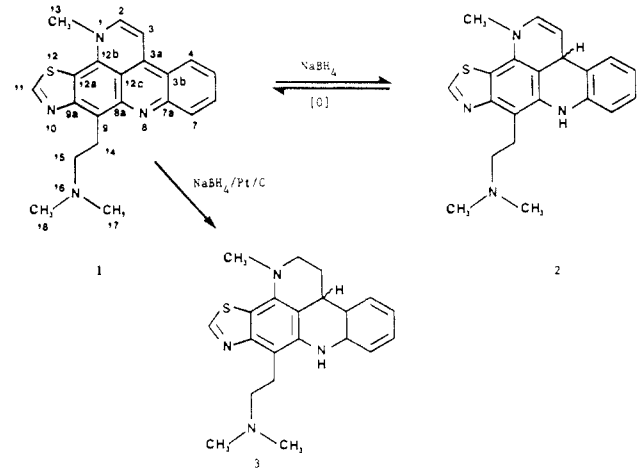


Figure 1.

Scheme I



(**1**) was found to be resistant to hydrogenation with Pt catalyst but underwent complete hydrogenation with Raney Ni catalyst giving complex mixtures. However, a tetrahydro product **3** was isolated by $NaBH_4$ reduction followed by further in situ reduction in modification of the Brown and Brown procedure[9] (Scheme I).

The ^1H spectrum of **3** had an exchangeable downfield one proton singlet at δ 9.68 that showed three-bond coupling to C-3b, C-7, C-9, and C-12c. This allowed for the combination of the two partial structures **1a** and **1b** to give the partial structure **1c** (Figure 1). This also confirmed the presence of an N atom at position 8.

As this data did not permit the unambiguous assignment of a structure for dercitin, natural abundance ^{13}C–^{13}C coupling information was obtained from a 2D INADEQUATE experiment.[10] The observed connectivities (**1d**) enabled the confirmation of the partial structures **1a** and **1b**. The coupling between C-9a and C-12a confirmed the presence of a five-membered heterocycle in the molecule. The combination of the partial structures **1a**, **1b**, and **1d** and the assumption of a bond between the carbons 12a and 12b completed the carbon skeleton of dercitin. The regiochemistry of the thiazole ring was assigned based on the chemical shift comparison of C-9a and C-12a to the respective carbons in thiazole derivatives[11] giving the new structure *N,N*-1-trimethyl-

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(4) ^{13}C (90 MHz, TFA-*d*), δ 151.7 (d C-11), 150.9 (s, C-3a), 149.3 (d, C-2), 148.2 (s, C-9a), 141.1 (s, C-7a), 138.2 (d, C-6), 136.6 (s, C-126), 136.1 (s, C-12a), 135.5 (s, C-8a), 126.5 (d, C-4), 126.5 (d, C-5), 122.0 (s, C-12c), 119.1 (d, C-7), 116.4 (s, C-36), 109.8 (d, C-3), 107.0 (s, C-9), 56.5 (t, C-15), 51.4 (q, C-13), 45.2 (2C, q, C-17, 18), 28.5 (t, C-14).

(5) HREIMS: *m/z* 360.1398 (7%, $C_{21}H_{20}N_4S$, Δ 1.1 mmu), 314.0746 (5, $C_{19}H_{12}N_3S$, Δ 0.6), 302.0731 (100, $C_{18}H_{12}N_3S$, Δ 2.1), 288.0570 (2, $C_{17}H_{10}N_3S$, Δ 1.9).

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1*H*-pyrido[4,3,2-*mn*]thiazolo[5,4-*b*]acridine-9-ethanamine for dercitin (**1**). This is the first report of a pentacylic aromatic alkaloid bearing the thiazole functionality.

Acknowledgment. This is Harbor Branch Oceanographic Institution Contribution No. 648. We thank Dr. S. Pomponi for identification of the sponge, Drs. S. S. Cross, R. Longley, M. Lui, and J. Clement for biological assays, and Dr. Kurt L. Loening, Director of Nomenclature, Chemical Abstracts Service, Columbus, OH, for the IUPAC nomenclature of dercitin.

Supplementary Material Available: Isolation procedure, UV and MS data of **1**, spectral data of **3**, and ^1H and ^{13}C NMR data of dercitin (**1**) (3 pages). Ordering information is available on any current masthead page.

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Synthetic Studies on Arene-Olefin Cycloadditions. 10.[1] A Concise, Stereocontrolled Total Synthesis of (±)-Laurenene

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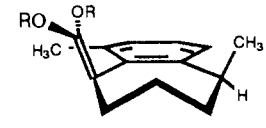
The term fenestrane was introduced in 1972 by Georgian and Saltzman[3] for tetracyclo[3.3.1.0^{3,9}.0^{7,9}]nonane, a hydrocarbon of considerable theoretical interest due to the expected planar geometry of its central carbon atom. The novel synthetic problems posed by this tetracycle and, more generally, by other rosettanes[4] have attracted much attention,[5] which has been further stimulated by the 1979 report of the first naturally occurring member of this novel class, lauren-1-ene (**1**).[6,7] We describe herein a total synthesis of **1**, which represents an unprecedentedly concise and stereocontrolled solution to this problem. This synthesis is based on the most complex example of an arene-olefin meta photocycloaddition reported to date and provides a novel and general strategy for the synthesis of analogous rosettanes.

Previous studies from these[1] and other laboratories[8] have established a set of selection rules which allows for the prediction of mode, regio, facial, and stereoselectivities for photoinduced cyclizations of 5-arylpent-1-enes. For the application of this methodology to lauren-1-ene, however, two previously unexplored but significant issues arise. First, in contrast to previous studies, the tether between the alkene and arene subunits in this application (**3**→**2**; Scheme I) would be subjected to an untested rotational restriction (about C-8,C-9), potentially disfavoring the conformation required for cycloaddition.[1] Moreover, for all three modes of meta cycloaddition (i.e., alkene addition to C-5, C-8, to C-4, C-1, or to C-8, C-2), the alkene substituents would be forced into a potentially adverse steric interaction with a non-arene ring. Models suggested that of these three possibilities, alkene addition to C-5,C-8 (**3**→**2**) would encounter the least steric hindrance, but it was not clear whether even this approach trajectory would have sufficient clearance and whether this steric problem would be exacerbated by rotational restrictions and the conflicting directing effects of the donor groups at C-1, C-4, and C-8. Second, the success of this plan would require that the photoaddition proceed with the formation of three contiguous quaternary centers (**2**: C-4,C-8,C-9), a sterically demanding process which could be superseded by energy transfer.[9]

The substrate required to test these points was prepared as illustrated in Scheme II.[10] Thus, Diels-Alder reaction of cyclohepta-1,3-diene and toluyne[11] allowed for the 5C + 2C construction of the target seven-membered ring, providing direct access to arene **4** (65% yield; 84% based on recovered starting material). Alternatively, this tricycle was also obtained, albeit in six steps (37% overall yield), by using a similar cycloaddition strategy involving an initial Diels-Alder reaction of benzoquinone and cyclohepta-1,3-diene.[12] Subsequent elaboration of arene **4** required that carbons C-17 and C-16, present in the alkene subunit, be differentiated and modified such that the former could be employed to assist the introduction of the homoprenyl chain at C-9, while the latter could be parlayed into the requisite C-16 methyl group. This differentiation was achieved efficiently through ozonolysis of **4**, which proceeded with in situ aldolization to afford only one set of aldol isomers **5**. The regiospecificity and facility of this aldol reaction are attributable to the peri-methyl group (C-20), which sterically inhibits enolization at C-9 and enforces C-15,C-17 propinquity. Exploitation of this result—involving selective formation and Grob fragmentation of keto tosylate **8** and hydrogenation of the fragmentation product **9**—allowed for the elaboration of **14**, possessing the requisite differentiated appendages at C-9 and C-15. Unfortunately, all attempts to use ester **14** or ester derivatives (CO_2H, CN, CHO, etc.) for introduction of the homoprenyl chain at C-9 were unsuccessful. The once-beneficial peri-methyl presumably served at this point to cant the enolate out of the arene plane (by 68° as calculated by Macromodel) and thereby block electrophilic attack on the only accessible enolate face.



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The problem with alkylative introduction of the C-9 homoprenyl chain was finally solved through the use of lactone **10**, in which the previously troublesome C-20, C-17 nonbonded interaction is

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(10) All new compounds furnished appropriate spectroscopic data and combustion analyses or exact mass. Partial spectroscopic data for key intermediates is as follows: **4**, PMR 7.02 (m, 2 H), 6.94 (m, 1 H), 3.72 (m, 1 H), 3.41 (m, 1 H), 2.32 (s, 3 H), 1.60 (m, 3 H), 1.50 (m, 2 H), 1.30 (m, 1 H). **3**, 7.18 (t, 1 H, J = 7.5), 7.10 (d, 1 H, J = 7.5), 6.87 (d, 1 H, J = 7.5), 5.14 (d, 1 H, J = 5.5), 5.05 (tm, 1 H, J = 7), 5.02 (d, 1 H, J = 15), 4.78 (d, 1 H, J = 15), 3.19 (m, 1 H, J = 7.5), 2.43 (d, 1 H, J = 5.5), 2.06 (m, 2 H), 1.89 (dd, 1 H, J = 8.15), 1.65 (s, 3 H), 1.59 (s, 3 H), 1.34 (d, 3 H, J = 7). **2**, 5.35 (br t, 1 H, J = 2), 4.69 (d, 1 H, J = 5), 4.04 (d, 1 H, J = 11), 3.82 (d, 1 H, J = 11) 2.76 (d, 1 H, J = 5), 2.34 (dd, 1 H, J = 7, 13), 1.29 (d, 1 H, J = 7.5), 1.14 (d, 3 H, J = 7), 1.05 (s, 3 H), 1.02 (s, 3 H).

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