d,l-1,2-dichloro-1,2-diphenylethane, respectively. (*E*)-**4**: bp 111–113 °C mp (0.5 mmHg) (lit.[17] bp 97–99 °C (0.25 mmHg)). (*Z*)-**4**: mp 52–53 °C (lit.[17] mp 52–54 °C).

(*E*)- and (*Z*)-Fluorostilbenes (6) were obtained by dehydrofluorination of a mixture of *meso*- and *d,l*-1,2-difluoro-1,2-diphenylethanes with potassium *tert*-butoxide in *tert*-butyl alcohol. The two fluoroolefins were isolated by column chromatography on SiO_2 after elution with petroleum ether and identified by ^{1}H NMR spectroscopy.[16,18]

Kinetic Study. Kinetic experiments were carried out by following the appearance of the reaction products spectrophotometrically at 284–290 nm and by using the procedure described elsewhere.[1] The concentration of the substrate was in the range of 5.0×10^{-5}–9.0×10^{-5}.

Product analyses were performed by following the procedure previously described. The concentration of the base was the same as in the kinetic studies, and that of the substrate was in the range of 5×10^{-3}–6×10^{-3} M. The reaction products were analyzed by GLC on a 1.0 × 0.002 m column packed with 20% LAC 728 on 60–80-mesh Chromosorb W at 150 °C. The olefins **4** and **6** had the same molar response. The molar response of **5** was 1.05 with respect to that of the olefins. The retention times of (*E*)-**4**, (*Z*)-**4**, (*E*)-**6**, (*Z*)-**6**, and **5** were 29, 88, 13, 50, and 42 min, respectively (N_2 carrier gas at 15 mL/min). Under these conditions no thermal isomerization of the olefins was observed. Moreover, the (*E*)-halostilbenes were recovered unchanged following exposure to the reaction conditions.

H–D Exchange Experiments. *tert*-BuOK in *tert*-BuOD (0.5 mL) was added to a known amount of **2** or **3** (the base:substrate molar ratio was 0.5) and the mixture was analyzed by ^{1}H NMR. When the reaction was complete the pattern of the aliphatic protons of the starting material was unchanged, thus showing no appreciable deuterium incorporation in the substrate.

Acknowledgment. Thanks are due to the Italian National Council of Research (CNR) and the Ministero della Pubblica Istruzione for financial support.

Registry No. 1, 15951-99-2; **2**, 39600-82-3; **3**, 14090-31-4; (E)-**4**, 948-98-1; (Z)-**4**, 948-99-2; (E)-**6**, 671-19-2; (Z)-**6**, 671-18-1.

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Structure of Brianthein W, from the Soft Coral *Briareum polyanthes*[1]

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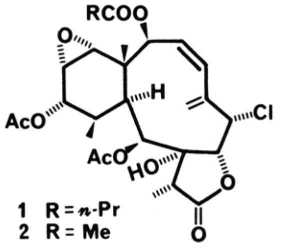
Received March 28, 1984

In the course of purifying briantheins Y and Z (**1** and **2**)[2] by HPLC, we encountered a modest amount of a tan solid. ^{1}H NMR analysis of this material suggested an isoprenoid constituent seemingly quite different from the aforementioned diterpenes. Crystallization from either acetone–isooctane or dichloromethane–hexane gave large rectangular prisms, mp 205–209 °C. Additional quantities of this new compound were obtained from the carbon tetrachloride soluble extracts (in all, about 0.4% of the total organic solubles).



1 R = *n*-Pr
2 R = Me

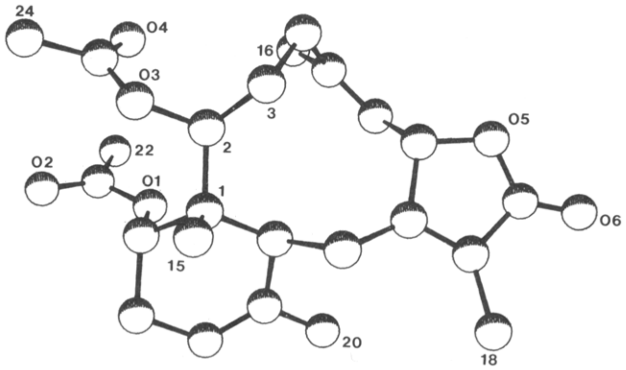
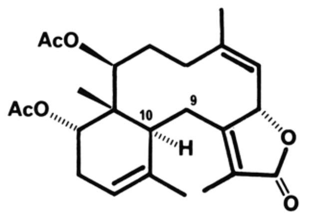


Figure 1. Computer-generated perspective drawing of brianthein W. Hydrogens are omitted for clarity and no absolute configurations is implied.

High-resolution mass spectrometry established the molecular formula of the new entity as $C_{24}H_{32}O_6$, and major fragments at m/z 356 and 296 were in accord with the two acetate groups expected after examination of the ^{1}H NMR spectrum. The infrared spectrum indicated the absence of hydroxyl groups, but a carbonyl stretch at 1750 cm^{-1} and λ_{max} 228 nm (ϵ 7500) indicated an α,β-unsaturated γ-lactone, thereby accounting for the remaining oxygen atoms. The ^{13}C NMR spectrum indicated three olefinic bonds, two trisubstituted and the other fully substituted; therefore, two carbocyclic rings had to be incorporated into the structure.

The ^{1}H NMR spectrum corroborated our initial assessments—two acetates, two olefinic protons, three methines bearing heteroatoms, three vinyl methyls, and a quaternary methyl—but shed no conclusive light on the structure. Almost all the signals were broadened by small couplings and the extensive overlap of signals precluded successful decoupling experiments and assignment of couplings and the associated coupling constants. Decoupling and 2D/*J*-resolved NMR experiments did establish that the protons at δ 2.85, 2.68, and 2.50 were mutually coupled in an AMX array (the protons on C-9 and C-10).

These conclusions and the supposition that we had encountered another compound possessing the briaran skeleton, but one strikingly different from the other briantheins[2] or briarein A,[3] led us to consider structure **3** for this compound, for which we propose the trivial name



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briantheln W.[4] X-ray diffraction analysis conveniently provided a final solution to this structure problem, substantiating our hypothesis and establishing the relative stereochemistry shown in **3** and Figure 1.

Crystals of brianthein W belonged to the orthorhombic crystal class with $a = 8.783$ (2) Å, $b = 9.486$ (2) Å, and $c = 28.231$ (6) Å. The space group was uniquely determined to be $P2_12_12_1$ with one molecule of $C_{24}H_{32}O_6$ forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer with graphite monochromated Cu Kα radiation (1.54178 Å) and a variable speed 1° ω scan. After correction for Lorentz, polarization, and background effects, 1212 (84%) reflections were judged observed ($|F_o| \geq 3\sigma(F_o)$). A phasing model was found by direct methods, and least-squares refinements with anisotropic heavy atoms and isotropic hydrogens have converged to a standard crystallographic residual of 0.0722. A computer-generated perspective drawing of the final X-ray model is given in Figure 1.

It is quite intriguing that the functional array of brianthein W more closely resembles those of the diterpenes found in the sea pen *Scytalium tentaculatum*[5] than it does any previously identified metabolites of either species of *Briareum*. Since the diterpenes of other sea pens, *Ptilosarcus gurneyi*,[6] *Stylatula* sp.,[7] and *Pteroides laboutei*,[8] are much like briarein A and briantheins X, Y, and Z, it is apparent that the secondary metabolism patterns of these organisms are more consonant than their current taxonomic distinction might suggest.

Experimental Section

General procedures, instrumentation, and the collection, extraction and initial chromatographic separation work with *Briareum polyanthes* have been described previously.[2b]

Brianthein W. The CCl_4-soluble extracts of *B. polyanthes*, 3.755 g,[2b] were permeated through Sephadex LH-20 with CH_2Cl_2–hexane (4:1). Fraction 5, 1.2009 g, was permeated through Bio-Beads S-X4 with hexane–CH_2Cl_2–EtOAc (4:4:1). Fraction 5, 382 mg, was subjected to HPLC on an Ultrasphere-Cyano column (0.9 × 25 cm); elution with hexane–isopropyl alcohol (5:1) yielded 119 mg of **3**: prisms from acetone–isoctane, mp 205–209 °C; $\lambda_{max}{}^{EtOH}$ 228 nm (ϵ 7500); $\nu_{max}{}^{CHCl_3}$ 1750 (sh), 1735, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 5.46 (1 H, br d, $J = 8$), 5.19 (1 H, br d, $J = 5.5$), 5.13 (1 H, d, $J = 10$), 4.86 (1 H, br s), 4.81 (1 H, br s), 2.85 (1 H, br d, $J = 15$), 2.68 (1 H, m), 2.55 (1 H, m), 2.50 (1 H, dd, $J = 15, 6$), 2.35–2.10 (2 H, overlapping m), 2.10–1.65 (3 H, obscured m), 2.00, 195, 1.85, 0.97 (each 3 H, s), 1.57 (3 H, br s); ^{13}C NMR (C_6D_6) δ 173.47 (s), 170.38 (s), 170.19 (s), 159.48 (s), 143.24 (s), 136.87 (s), 124.75 (s), 123.64 (d), 116.76 (d), 80.36 (d), 74.47 (d), 72.38 (d), 53.43 (t), 41.48 (s), 37.64 (d), 33.70 (t), 29.22 (t), 27.38 (q), 26.36 (t), 21.48 (q), 20.78 (q), 20.66 (q), 14.48 (q) 9.54 (q); MS, m/z (relative intensity) 416.2213 (M$^+$, calcd for $C_{24}H_{32}O_6$ 416.2198, <1), 356 (11), 314 (12), 296 (33), 228 (13), 215 (30), 119 (32), 43 (100).

X-ray Diffraction Studies. All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN78, a system of computer programs for the automatic solution of crystal strcutures from X-ray diffraction data (locally modified to perform all Fourier calculations, including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

Acknowledgment. Work at Montana State University was funded by the Lilly Research Laboratories and a state match to NSF-EPSCOR Grant ISP-8011449. Fieldwork at the Bermuda Biological Station was supported by a grant from the EXXON Foundation. NMR and MS facilities at M.S.U. were developed with funds from the National Science Foundation and the Murdock Foundation. Work at Cornell University was supported by a New York State Sea Grant and NIH CA 24487.

Registry No. 3, 91178-23-3.

Supplementary Material Available: X-ray data for brianthein W, including (a) Table 1 listing fractional coordinates and thermal parameters, (b) Table 2 listing bond distances, and (c) Table 3 listing bond angles (5 pages). Ordering information is given on any current masthead page.

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(4) We have elected to call the briaran diterpenes from *B. polyanthes* "briantheins" to distinguish these compounds and their parent organism taxonomically from *B. asbestinum* and the briareins.

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A New Route to 1,4-Disubstituted Cyclohexa-1,3-diene Derivatives: The Synthesis of a Highly Conjugated Bis(benzothiazoline) Derivative

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Received March 19, 1984

There is currently great interest in the preparation of symmetrical bis(1,3-dithiole) and bis(1,3-thiazoline) derivatives with extended conjugation between the two heterocyclic rings. Some of these are electron donors that form organic metals when complexed with suitable electron acceptors. For example, molecules of types **1**,(1) **2**,(2) **3**,(3) **4**,(4) and **5**(5) have recently been studied. A standard route to these compounds involves condensation of 2 equiv of a 1,2-dithiol or 1,2-amino thiol with 1 equiv of the appropriate dialdehyde or diacid chloride, followed by oxidation to yield the conjugated system. In order to prepare a donor of type **6** we needed the difunctional cyclohexa-1,3-diene derivative **10**.

Cyclohexa-1,3-diene derivatives bearing electron-withdrawing substituents in the 1- and 4-positions are relatively inaccessible and have been reported in only a limited number of cases.(6) They are not available via Birch re-

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