Over the pH 6.9–11.6 range, final ^{13}C NMR spectra showed closely spaced pairs of peaks, representing C-1 resonances of the C-2 deuterio and C-2 protio aldonates, without significant differences in their ratios. Therefore, deprotonation potentially resulting in epimerization did not increase noticeably above pH 10.1.

Although two possible controlling factors have been ruled out, the cause of the pH dependence of the mannonate-to-gluconate ratio remains unknown. Presumably, cyanohydrin formation occurs via attack of cyanide on D-*aldehydo*-arabinose. Conformational equilibria influenced by pH might determine which face of the aldehydo group is preferentially attacked. We have not studied this possibility.

Experimental Section

^{13}C NMR spectra were obtained with a Varian CFT-20 NMR spectrometer system equipped with an 8-mm variable-temperature probe. A 3 vol % [1-^{13}C]acetic acid in water–deuterium oxide (1:1) solution in a coaxial tube was used to obtain lock and provide a reference peak. At 27 °C the $H_3C^{13}CO_2H$ peak was observed at 177.5 ppm when referenced to dioxane (5 vol % in 0.4 M pH 10.1 bicarbonate buffer) as 67.4 ppm. Two sets of parameters were used commonly: spectral width, 500/1603 Hz (ca. 160–185/ca. 105–185 ppm); pulse width, α = 64/39°; number of transients, 250/800 (34/34 min). The free induction decays consisted of 8192 data points. All spectra were proton decoupled. Mannonate-to-gluconate ratios were determined from peak heights, which were shown to be proportional to peak areas. Any errors in the ratios due to differences in T_1 for mannonate and gluconate were ruled out by comparing peak height ratios to those in a small-pulse-width, long-pulse-delay experiment.

^{15}N NMR spectra were obtained with a Varian XL-100 spectrometer (10.2 MHz) equipped with a 12-mm variable-temperature probe and interfaced to a Nova 1210 computer. Lock was obtained with deuterium oxide in a coaxial tube. The carrier frequency was referenced to a 4.2 M [^{15}N]ammonium sulfate solution in deuterium oxide as −18 ppm. Parameters used included spectral width, 5000 (−67 to 423 ppm) or 6666 Hz (−116 to 537 ppm); pulse width, α = 36°; pulse interval, 1.000 s; number of transients, 6700–55 500 (1.9–15.4 h). The free induction decays consisted of 8192 data points. All spectra were proton decoupled.

D-(−)-Arabinose obtained from Eastman Organic Chemicals was recrystallized from ethanol–water with Norit treatment prior to use. D-[1-^{13}C]Glucono-1,5-lactone,[12] D-[1-^{13}C]mannono-1,4-lactone,[12] D-[1-^{13}C]gluconamide,[13] D-[1-^{13}C]mannonamide,[13] D-[1-^{13}C]gluconononitrile,[14] sodium [^{13}C]cyanide,[15] sodium [^{13}C,^{15}N]cyanide,[16] and potassium [^{15}N]cyanide[17] were prepared by published procedures. All other chemicals were commercial products, which were used as received. Buffers used were phthalate (pH 5.1), phosphate (pH 6.9 and 11.6), Tris (pH 8.1), *p*-hydroxybenzoate (pH 9.3), and bicarbonate (pH 10.1). Reaction solutions (1.5–2.5 mL) were 0.40 M in buffer and 0.08 M in both D-arabinose and labeled sodium cyanide unless otherwise stated. Reactant concentrations were doubled for the ^{15}N NMR studies. Isotopic enrichment in cyanide was 91 mol % ^{13}C and/or 99 mol % ^{15}N. Reactions were maintained at 5, 10, 15, or 25 °C to give suitable reaction rates. Spectral data accumulations were carried out consecutively immediately following the start of each reaction, and intermittently as the reactions slowed.

Acknowledgments. We thank Guido H. Daub for many helpful discussions and William E. Wageman, Thomas E. Walker, and Robert E. London for assistance with the ^{15}N NMR experiments. This work was performed under the auspices of the U.S. Department of Energy.

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(13) The procedure employed was that given for DL-galactaramide by: Morgan, J. W. W.; Wolfrom, M. L. *J. Am. Chem. Soc.* **1956**, *78*, 1897–1899.
(14) Prepared from D-[1-^{13}C]glucose by the procedure of Wohl, A.; Wollenberg, O. *Justus Liebigs Ann. Chem.* **1933**, *500*, 281–286. Attempts to prepare D-[1-^{13}C]mannononitrile from D-[1-^{13}C]mannose by this procedure were unsuccessful.
(15) Ott, D. G.; Kerr, V. N.; Sanchez, T. G.; Whaley, T. W. *J. Labelled Compd. Radiopharm.*, in press.
(16) Whaley, T. W.; Ott, D. G. *J. Labelled Compd.* **1975**, *11*, 307–312.
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Intramolecular Diels–Alder Route to Angularly Substituted Perhydrophenanthrenes. Synthesis of (±)-Fichtelite

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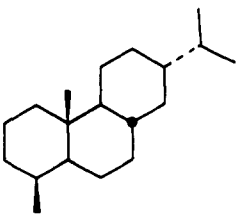
Abstract: A central issue in the synthesis of the steroids and a variety of other complex carbocyclic natural products is stereocontrolled construction of the angularly substituted *trans,anti,trans*-perhydrophenanthrene nucleus. We report a new approach to this problem, the key to which is induction of relative chirality in the course of the intramolecular Diels–Alder reaction. Thus, triene **3** on heating is transformed into the crystalline tricyclic ketone **2**. Ketone **2** is carried on in five steps to (±)-fichtelite (**1**).

Fichtelite, a crystalline hydrocarbon, was first isolated by Bromeis in 1841 from pine trunk remains found in a peat bed in the Fictelgebirge region of Bavaria.[1] The relationship of fichtelite to the resin acids was suspected early on.[2] The presence of an angular methyl group, and hence gross structure **1**, was demonstrated by Ruzicka in 1935.[3] This was supported by a careful molecular-weight determination.[4] This early work was capped by a courageous synthesis by Bogert and Sterling of a mixture of hydrocarbons having the gross structure **1**. Modern analytical techniques would probably have confirmed the presence of authentic fichtelite in that mixture.



1

(1) Bromeis, C. *Justus Liebigs Ann. Chem.* **1841**, *37*, 304.
(2) For a summary of this work, see: Simonsen, J. S.; Barton, D. H. R. "The Terpenes", Vol. III; Cambridge University Press: New York, 1952; p 337.
(3) Ruzicka, L; Waldmann, E. *Helv. Chim. Acta* **1935**, *18*, 611.
(4) Crowfoot, D. *J. Chem. Soc.* **1938**, 1241.
(5) (a) Sterling, E. C.; Bogert, M. T. *Science* **1938**, *87*, 196. (b) *J. Org. Chem.* **1939**, *4*, 20.

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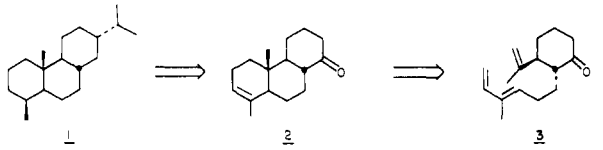
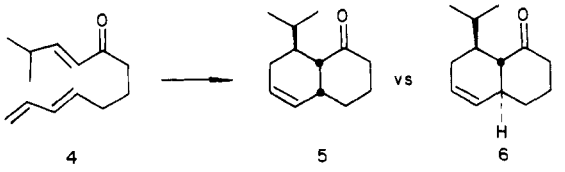
Work continued on the stereochemistry of **1**. Finally, in 1964, Burgstahler and Marx[6] in the course of a synthesis of **1** from abietic acid were able to establish the total stereostructure. This set the stage for the only reported total synthesis, by Johnson and co-workers[7] in 1966.

The central issue in the synthesis of fichtelite, as in the synthesis of the steroids and a variety of other complex carbocyclic natural products, is the stereocontrolled construction of the angularly substituted *trans,anti,trans*-perhydrophenanthrene nucleus. There are currently two ways to approach this problem: biomimetic polyolefin cyclization, as developed by Johnson and co-workers,[8] and repetitive annulation coupled with stereocontrolled reduction and alkylation.[9] We report a third approach, the key to which is the induction of relative chirality in the course of the intramolecular Diels–Alder reaction.[10]



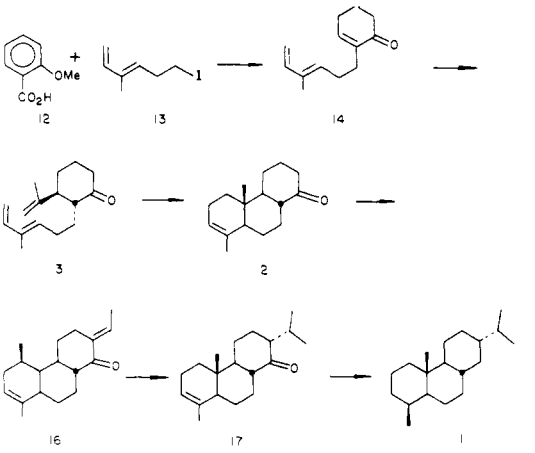
Intramolecular Diels–Alder Reaction. There are three fundamental problems that must be solved to successfully employ an intramolecular Diels–Alder reaction in a natural-products synthesis. The first is the construction of the requisite triene. Substituents on the newly formed cyclohexene ring will retain the same relative configuration they had on the starting olefin (e.g., **4** → **5**). The second difficulty is understanding the factors that

govern exo vs. endo addition of the dienophile to the diene.

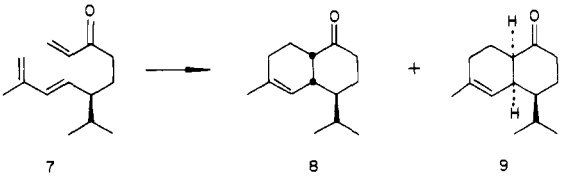


Although there is some tendency toward endo addition, there are apparently many complex factors that influence this outcome. This area is under active investigation in several laboratories.[11,12]

Scheme I

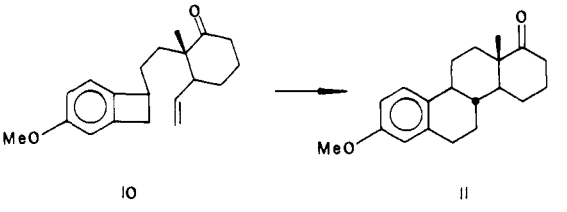


Finally, there is the question of what influence one or more asymmetric centers in the bridge between the diene and the dienophile might have on the relative chirality of ring fusion. This



is the area in which we have been most interested. We have felt that through conformational analysis of the transition states leading to cyclization it should be possible to predict the stereochemical outcome of such cyclizations. We have shown this to be possible in one instance:[13] **8** is favored over **9** by a ratio of 9:1. We detail here the extension of this technique to the more complex triene **3**.

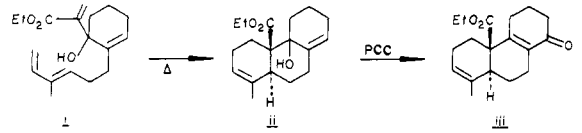
It should be noted that such an approach is not without precedent. In addition to the elegant work of Oppolzer in the heterocyclic series,[10] Kametani[14] has shown that **10** cleanly cyclizes to **11**.



Synthesis of Triene 3. This approach was rendered most attractive by the ready availability of **3** (Scheme I). Thus, alkylation of the dianion of *o*-anisic acid **12**[15] with iodo diene **13**, prepared by the method of Julia,[16] gives enone **14**. Conjugate addition of lithium diisopropenylcuprate then completes the synthesis of **3**.

Cyclization of Triene 3. As outlined above, there are two uncertainties in the cyclization of **3**. The first is whether the cyclization will proceed in the endo sense, to give an A, B trans ring fusion, or in the exo sense, to give the cis fusion. The work

(6) (a) Burgstahler, A. W.; Marx, J. N. *Tetrahedron Lett.* **1964**, 3333. (b) *J. Org. Chem.* **1969**, *34*, 1562.
(7) Johnson, W. S.; Jensen, N. P.; Hooz, J. *J. Am. Chem. Soc.* **1966**, *88*, 3859.
(8) Johnson, W. S. *Acc. Chem. Res.* **1968**, *1*, 1.
(9) Jung, M. E. *Tetrahedron* **1967**, *32*, 3.
(10) For a review of the intramolecular Diels–Alder reaction, see: Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10.
(11) If a dienophile activated by a single carbonyl is employed, the ring fusion is often enforced by the preference for a transition state in which the activating carbonyl is endo[10] to the diene. Thus i smoothly cyclizes (110 °C, 18 h) to ii, which on oxidation gives enone iii. It should be noted that use of an activated dienophile also allows direct access to angularly oxygenated derivatives.

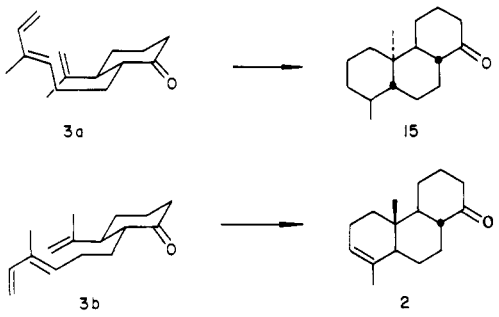


(12) (a) Roush, W. R. *J. Org. Chem.* **1979**, *44*, 4008, and references cited therein. (b) We acknowledge stimulating discussions on this topic with Professors G. Stork (Columbia), S. R. Wilson (Indiana), R. K. Boeckman, Jr. (Wayne State), and W. Roush (MIT).

(13) Taber, D. F; Gunn, B. P. *J. Am. Chem. Soc.* **1979**, *101*, 3992.
(14) Kametani, T.; Nemoto, H.; Ishikawa, H.; Shiroyama, K.; Fukumoto, K. *J. Am. Chem. Soc.* **1976**, *98*, 3378.
(15) (a) Taber, D. F. *J. Org. Chem.* **1976**, *41*, 2649. (b) This procedure has been improved to the point that ordinary alkylating agents give the 2-substituted cyclohexenone in better than 50% yield: Taber, D. F.; Gunn, B. P., submitted for publication in *Org. Synth.*
(16) Prepared by NaI–acetone exchange on the corresponding bromo diene: Julia, M.; Julia, S.; Stalla-Bourdillon, B.; Descoins, C. *Bull. Soc. Chim. Fr.* **1964**, 2533.

of Wilson[17] clearly indicates the preference for the former mode of cyclization for trienes having this substitution pattern, and only sp^3 centers bridging the diene and dienophile.

The other factor to consider is what influence the asymmetric centers in the bridge will have on the relative chirality of ring fusion. Thus, cyclization could proceed through transition state **3a**, to give **15**, having the angular methyl α, or through **3b**, to give **2**, having the angular methyl β. It is apparent that inclusion of



the cyclohexyl centers in the bridge in **3a** forces the incipient B ring into a boat conformation. In **3b** on the other hand, the B ring can adopt an energetically more favorable chair conformation. Thus, it seemed likely that **2** would be favored over **15**. This was the case: cyclization of **3** proceeded smoothly to give the crystalline tricyclic ketone **2** as the preponderant (73%) product.

Synthesis of Fichtelite. The structure and stereochemistry of **2** were confirmed by conversion to fichtelite (**1**) (Scheme I). Thus, the isopropyl group was introduced by the method of Martin[18] and Watt:[19] condensation with acetaldehyde, to give enone **16**, followed by addition of lithium dimethylcuprate. Ketone **17** was then reduced, deoxygenated by the method of Tsuchiya et al.,[20] and hydrogenated to give a mixture of two isomeric hydrocarbons in a ratio of 1:2.[21] The major isomer corresponded (TLC, GC–MS, ^{1}H NMR) to authentic fichtelite.

Conclusion

Induction of relative chirality in the course of the intramolecular Diels–Alder reaction, as outlined here and in our preceding communication,[13] promises to be a powerful technique for the stereocontrolled construction of carbocyclic natural products. In particular, the method adumbrated here for the elaboration of angularly substituted *trans,anti,trans*-perhydrophenanthrene derivatives is both shorter and more flexible than the conventional annulative approach. Finally, we note that the readily available ketone **2** is suitably functionalized for elaboration to the potent antineoplastic agent tripdiolide.[22]

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are corrected. ^{1}H NMR spectra were determined on a JEOLCO MH-100 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference tetramethylsilane. Couplings (J) are in hertz (Hz). The infrared spectra (IR) were recorded on a Perkin-Elmer 257 spectrometer as solutions in CCl_4 and are reported in reciprocal centimeters (cm^{-1}). Mass spectra (MS) were determined at 70 eV on an LKB 9000 gas chromatograph–mass spectrometer interfaced with a PDP-12 computer system and are reported as mass per unit charge (m/z), with intensities as a percentage of the peak of greatest ion current having $m/z \geq 100$. Organic chemicals were purchased from Aldrich Chemical Co. Organometallics were purchased from Alfa Inorganics and titrated prior to use. Solvent mixtures (e.g., 5% ethyl acetate–hexane) are volume/volume. R_f values indicated refer to thin layer chromatography on microscope slides coated with EM silica gel 60 PF254. Column chromatography was carried out using the short-column technique,[23] running the columns under air pressure (5–20 psig). We have found EM 7747 silica gel to be very effective in this application. Analytical samples were prepared by short-column chromatography followed by bulb-to-bulb distillation. Analyses were performed by Galbraith Laboraties, Inc., Knoxville, Tenn.

Iodo Diene 13. To a solution of 27.7 g (158 mmol) of 1-bromo-4-methylhexa-3,5-diene, prepared by the method of Julia,[16] in 50 mL of acetone in a 250-mL Erlenmeyer flask were added 30 g (200 mmol) of sodium iodide and 200 mg of copper–bronze powder. The resulting suspension was stirred magnetically for 2 h, then diluted with aqueous sodium thiosulfate solution and extracted with petroleum ether. The combined petroleum ether extracts were dried over potassium carbonate, concentrated in vacuo, and distilled from copper–bronze powder through a short-path apparatus to give 31.7 g (90%) of colorless oil, bp 80 °C (5.0 mm). NMR showed two isomers[24] in a ratio of about 70:30. Major: 1.80, s, 3 H; 2.74, q, J = 8 Hz, 2 H; 3.17, t, J = 8 Hz, 2 H; 4.96–5.5, m, 3 H; 6.4, dd, J = 10, 16 Hz, 1 H. Minor: inter alia, 1.84, s, 3 H; 6.72, dd, J = 10, 16 Hz, 1 H. This material was best stored in the freezer over copper wire.

Enone 14. The reductive alkylation was carried out by a modification of our published[15] procedure. Thus, a three-neck 250-mL round-bottom flask was charged with 6.08 g (40 mmol) of *o*-methoxybenzoic acid and 40 mL of THF. A dry ice–acetone condensor was attached, the flask immersed in a dry ice–acetone bath, and ammonia (100 mL) distilled in. The resulting thick, white suspension was stirred mechanically, and Li dispersion (30% in mineral oil, 2% Na) (2.33 g, 100 mmol) suspended in hexane was added in small portions over 15 min. As soon as the solution attained the deep blue indicative of excess Li, iodo diene **13** (10.5 g, 47 mmol) and 1,2-dibromoethane (1 mL) were added in one portion. The ammonia was evaporated under a stream of nitrogen. The residual material was diluted with water, washed with hexane, acidified with concentrated hydrochloric acid, and extracted with ethylene chloride.

Oxalic acid (5 g) and water (5 mL) were added to the combined ethylene chloride extracts, and the resulting mixture was refluxed under N_2 for 45 min. After cooling, the mixture was diluted with aqeuous $NaHCO_3$ and extracted with methylene chloride. The combined extracts were dried over potassium carbonate and concentrated in vacuo to give an oil that showed two spots on TLC (10% EtOAc/hexane), R_f 0.40, 0.42.

This material was chromatographed on 50 g of silica gel with 3% EtOAc–petroleum ether; 20-mL fractions were collected. Fractions 11–13 contained the faster spot. Concentration of these fractions yielded 1.002 g of colorless oil. By NMR this was largely the β,δ isomer of the enone. Fractions 14–29 contained the slower spot. Concentration of these fractions yielded 2.22 g of **14** as a colorless oil. NMR ($CDCl_3$): δ 1.64, m, 2 H; 1.66, s, 3 H; 2.0, m, 2 H; 2.22, m, 6 H; 4.8–5.8, m, 3 H; 6.36, dd, J = 12, 17 Hz, 1 H; 6.69, bs, 1 H. IR (CCl_4) cm^{-1}: 1670, 1605, 895. MS m/z (%): 190 (88), 175 (33), 161 (39), 134 (72), 122 (83), 109 (100). Anal. ($C_{13}H_{18}O$) C, H.

To 414 mg of the faster running material in 10 mL of methanol was added 50 mg of sodium methoxide. After 1 min this mixture was diluted with aqueous HCl and extracted with CH_2Cl_2. The combined extracts were dried over K_2CO_3, concentrated in vacuo, and chromatographed as above to yield 149 mg of **14**. Thus, the total yield of **14** was 2.58 g (34%).

Triene 3. A flame-dried 500-mL round-bottom flask charged with 2-bromopropene (3.63 g, 30 mmol) and THF (150 mL) was stirred magnetically under N_2 in a dry ice–acetone bath. *tert*-Butyllithium (31.6 mL of a 1.9 M solution, 60 mmol) was added dropwise by syringe. The flask was transferred to a −40 °C bath (dry ice–aqueous $CaCl_2$). $CuI{\cdot}Me_2S$[26] (3.78 g, 15 mmol) in dimethyl sulfide (10 mL) was added dropwise. The initially yellow solution became deep orange as the complex was added. Enone **14** (1.47 g, 7.7 mmol) in 15 mL of THF was added dropwise over 20 min. Stirring was continued for an additional 5 min. The reaction mixture was quenched with an aqueous mixture of NH_4Cl and NH_4OH and extracted with petroleum ether. The combined organic extracts were dried over K_2CO_3, concentrated in vacuo, and chromatographed on 50 g of silica gel using 2.5% EtOAc–petroleum ether to give 1.51 g (84%) of **16** as a colorless oil, R_f (10% EtOAc–hexane) 0.45. NMR ($CDCl_3$): δ 1.24–2.8, m, 12 H; 1.80, s, 6 H;

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(24) In subsequent procedures, spectra are reported for the major isomer only. Only this isomer undergoes cyclization.
(25) Birch, A. J.; Slobbe, J. A. *Aust. J. Chem.* **1977**, *30*, 1045.
(26) House, H. O.; Chu, C. Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.

4.88-5.84, m, 5 H; 6.68, dd, J = 11, 18 Hz, 1 H. IR (CCl_4) cm^{-1}: 1705, 1640, 1600, 890. MS m/z (%): 232 (8), 150 (10), 137 (72), 122 (100). Anal. ($C_{16}H_{24}O$) C, H.

Ketone 2. Two separate Pyrex tubes were charged with 4 mL each of a solution of 1.44 g of **3** in 8 mL of toluene. Methylene blue (50 mg) was added to each. The tubes were sealed and maintained at 170 °C for 68 h. After cooling, the tubes were opened and the contents combined, concentrated in vacuo, and chromatographed on 50 g of silica gel with 3% EtOAc-petroleum ether to give 654 mg (65% based on E diene in **3**) of **2** as a thick oil, R_f (10% EtOAc-hexane) 0.37. VPC analysis ($^1/_8$ in. × 6 ft 3% OV-17, 190 °C, 120 mL/min) showed six peaks, with retention times of 3.5, 3.9, 4.7, 5.0, 6.1, and 6.8 min. The 6.1-min peak (ketone **2**) accounted for 73% of the total. Three crystallizations of the ketone mixture from petroleum ether (-78 °C, 6, 2, and 2 mL/g of mixture) gave 367 mg (77% recovery) of **2** as a white solid, mp 65-70 °C. This material was pure by VPC. NMR ($CDCl_3$): δ 0.85, s, 3 H; 1.0-2.6, m, 17 H; 1.66, s, 3 H; 5.33, bs, 1 H. IR (CCl_4) cm^{-1}: 1705. MS m/z (%): 232 (100), 217 (33), 203 (47), 122 (86), 121 (86), 106 (96). ^{13}C NMR:[27] 11.78 (q), 21.36 (q), 22.39 (t), 22.88 (d), 24.94 (t), 25.75 (t), 26.40 (t), 34.37 (t), 36.04 (s), 41.68 (t), 47.8 (t), 49.64 (d), 53.81 (d), 120.72 (d), 134.53 (s), 213.68 ppm (s). Anal. ($C_{16}H_{24}O$) C, H.

Enone 16. To a solution of lithium diisopropylamide prepared from 101 mg (1.0 mmol) of diisopropylamine and 300 mL (0.8 mmol) of 2.66 M n-butyllithium in 8 mL of THF in a 25-mL flame-dried round-bottom flask stirred magnetically in a dry ice-acetone bath was added **2** (156 mg, 0.67 mmol) in 2 mL of THF dropwise over 3 min. Stirring was continued for 5 min: then acetaldehyde (0.5 mL, large excess) was added in one portion. Stirring was continued for an additional 5 min. The reaction mixture was then diluted with aqueous HCl and extracted with CH_2Cl_2. The combined extracts were dried over K_2CO_3 and concentrated in vacuo.

The resulting oil was taken up in 10 mL of ethylene chloride, 30 mg of p-toluenesulfonic acid monohydrate added, and the solution refluxed for 10 min. The reaction mixture was diluted with aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined extracts were dried over K_2CO_3 and concentrated in vacuo. The residue was chromatographed on 5 g of silica gel with 2% EtOAc-petroleum ether to give 47 mg of unreacted **2** and 66 mg (59% based on unrecovered **2**) of **16** as oil, R_f (10% EtOAc-hexane) 0.43. NMR ($CDCl_3$): δ 0.78, s, 3 H; 1.0-3.0, m, 15 H; 1.62, s, 3 H; 1.72, d, J = 7 Hz, 3 H; 5.36, bs, 1 H; 6.62, bq, J = 7 Hz, 1 H. IR (CCl_4) cm^{-1}: 1675, 1605. MS m/z (%): 258 (90), 243 (12), 229 (15), 134 (87), 122 (100). Anal. ($C_{18}H_{26}O$) C, H.

Isopropyl Ketone 17. Methyllithium (2.22 mL of 1.80 M in Et_2O, 4.0 mmol) was added to CuI·Me_2S 26 (630 mg, 2.5 mmol) in 5 mL Et_2O in a 25-mL round-bottom flask stirred magnetically under N_2 in an ice-water bath, to give a thick yellow suspension. Enone **16** (60 mg, 0.23 mmol) in 2 mL of Et_2O was added dropwise over 1 min. Stirring was continued for 5 min. The mixture was quenched with aqueous HCl, rendered alkaline with aqueous NH_4OH, diluted with saturated aqueous NaCl, and extracted with Et_2O. The combined extracts were dried over K_2CO_3 and concentrated in vacuo. The residue was chromatographed on 5 g of silica gel with 20% CH_2Cl_2-petroleum ether to give 36 mg (56%) of **17** as an oil, R_f (30% CH_2Cl-hexane) 0.27. NMR ($CdCl_3$): δ 0.82, s, 3 H; 0.92, m, 6 H; 1.0-2.4, m, 17 H; 1.60, s, 3 H; 5.32, bs, 1 H. IR (CCl_4) cm^{-1}: 1700, 1370, 1360. MS m/z (%): 274 (100), 259 (33), 147 (39), 132 (45), 121 (88), 106 (71). Anal. ($C_{19}H_{30}O$) C, H.

Fichtelite (1). To ketone **17** (29 mg, 0.11 mmol) in 5 mL of hexane in a 25-mL round-bottom flask stirred magnetically under N_2 was added diisobutylaluminum hydride (0.5 mL of 1.0 M, excess). Stirring was continued for 5 min. The reaction mixture was diluted with aqueous HCl and extracted with CH_2Cl_2. The combined extracts were dried over K_2CO_3 and concentrated in vacuo.

To the residue in 5 mL of CH_2Cl_2 in a 25-mL round-bottom flask stirred magnetically under N_2 in a -10 °C bath (dry ice-brine) was added pyridine (300 mL) followed by sulfuryl chloride (80 mL, 1.0 mmol). Stirring was continued for 20 min. Dimethylamine in CH_2Cl_2 (prepared by adding 0.5 mL of 25% aqueous dimethylamine to 2 mL of CH_2Cl_2, followed by repetitive drying with K_2CO_3) was added. The cooling bath was removed and stirring continued for 20 min. The mixture was then diluted with aqueous HCl and extracted with CH_2Cl_2. The combined extracts were dried over K_2CO_3 and concentrated in vacuo.

The residue was transferred with 5 mL of THF to a 100-mL three-neck round-bottom flask. Liquid ammonia (30 mL) was distilled in, the solution stirred magnetically, and sodium metal (washed with hexane) added in small pieces, until a solid blue solution with blue foam was maintained. Methanol was added to discharge the color, and the ammonia was evaporated under a stream of nitrogen. The residue was diluted with water and extracted with petroleum ether. The combined extracts were dried over K_2CO_3 and concentrated in vacuo.

PtO_2 (10 mg) suspended in 1 mL of acetic acid was exposed to an atmosphere of hydrogen for 15 min. The above residue in 1 mL of acetic acid was added and stirring continued for 1 h. The mixture was diluted with water and extracted with petroleum ether. The combined extracts were washed with aqueous $NaHCO_3$, dried over K_2CO_3, and concentrated in vacuo. The residue was filtered through 300 mg of silica gel with petroleum ether. Evaporation of the solvent left 17 mg (61%) of a colorless oil, R_f (petroleum ether) 0.85. This material showed two peaks on VPC ($^1/_8$ in. × 5 ft, 3% OV-1, 180 °C, 35 mL/min, 4.7 and 5.2 min) in a ratio of 1:2. The latter was identical (t_R, MS) with authentic fichtelite. A pure sample isolated by preparative VPC gave a ^1H FT NMR[27] spectrum that was identical with that of authentic fichtelite recorded under the same conditions: 0.80, s, 3 H; 0.83, d, J = Hz, 6 H; 0.89, d, J = 7 Hz, 3 H.

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(27) These spectra were recorded on a JEOLCO FX-90Q spectrometer, in $CDCl_3$ with Me_4Si as internal standard.

The Asbestinins, a Novel Class of Diterpenes from the Gorgonian *Briareum asbestinum*

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Abstract: The gorgonian *Briareum asbestinum* contained two classes of diterpenes, the briareins and the asbestinins. The structure of asbestinin-1 (**3**) was determined from a single-crystal X-ray diffraction study on the corresponding diol **8**. The structures of asbestinins-2, -3, -4, and -5 (**4**-**7**) were determined by analysis of spectral data. The relationships between asbestinins-2, -3, -4, and -5 (**4**-**7**) and asbestinin-1 (**3**) were confirmed by chemical interconversions.

The gorgonian coral *Briareum asbestinum* is a common inhabitant of shallow Caribbean reefs. Previous studies of the metabolites of *B. asbestinum* led to the isolation of a series of chlorinated diterpenes,[1,2] one of which, briarein A (**1**), has been

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(1) Hyde, R. W. Thesis, University of Oklahoma, 1966.

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