an atropic[19] molecule. We are currently investigating the detailed chemistry, including a X-ray crystallography, of this simple monocyclic thiepin.

Acknowledgments. The authors thank Dr. Kazuhiro Nakasuji for his effort in the early stage of this work, and Mr. Hideo Naoki (Institute of Food Chemistry) for exact mass measurements. Financial support in part by a Grant-in-Aid for Scientific Research (No. 343007) from the Ministry of Education, Japan is gratefully acknowledged.

Supplementary Material Available: The spectroscopic data for **7–12** (2 pages). Ordering information is given on any current masthead page.

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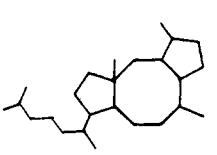
A Total Synthesis of Gascardic Acid

Sir:

In 1960, Brochere and Polonsky reported the isolation and characterization of a new C_{25} terpene acid called gascardic acid from *Gascardia madagascariensis.*[1] Preliminary data suggested that this substance represented a new structural class of the rare C_{25} sesterterpenes. Among the known sesterterpenes, the ophiobolane class (**1**) has over the years proven to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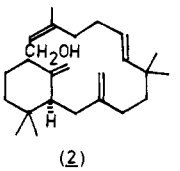
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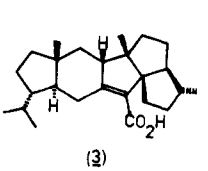
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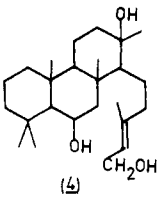
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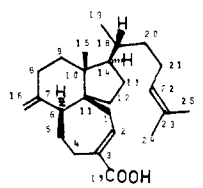
be the most numerous,[2,3] although other structural classes have been uncovered more recently, ranging from monocyclic and acylic polyenes such as diumycyminol (**2**)[4] to the unique polycyclic systems of retijeranic acid (**3**) and cheilanthatriol (**4**).[5,6]

A substantial effort to elucidate the structure, stereochemistry, and biosynthetic origin of gascardic acid was undertaken by Arigoni and Scartazzini.[7] These extensive chemical and spectroscopic studies resulted in the assignment of the carbocyclic skeleton of gascardic acid, as well as the partial elucidation of the relative stereochemistry. Intramolecular cyclization of gascardic acid under the influence of strong acid, as well as other evidence, tentatively suggested the stereostructure **5**.[7] This unique assemblage of three different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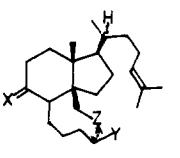
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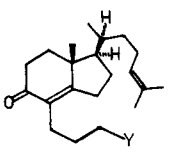
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sized carbocyclic rings spiro-fused about a common carbon (C-11) remains the only example of this structural class yet uncovered in nature. The studies of Arigoni and Scartazzini seemingly failed to unambiguously establish only the relative configuration of C-14 and C-18. The relative stereochemistry of these centers was assigned on the basis of a plausible biogenetic scheme.[7] With the intention of verifying the proposed structure, we have undertaken the total synthesis of gascardic acid described herein.[8]

The spirocyclic system was expected to be derivable from a bicyclic precursor such as **6** by cyclization. Structure **6**, in turn, could be plausibly constructed from hydrindenone **7** by the stereospecific introduction of a suitable functionalized two-carbon appendage into the angular position. This operation, owing to the hindered nature of this site, was considered to be the pivotal transformation in the sequence. We, therefore, set out to devise a route for the efficient preparation of a system such as **7** controlling particularly the relative stereochemistry of the angular methyl and side chain. Since the configuration at C-18 was not firmly established when this work was begun, it was decided to prepare both possible epimers by leaving this center uncontrolled initially.

New methodology developed in our laboratories several

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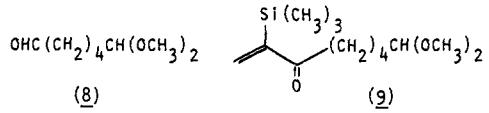
years ago appeared particularly applicable to the preparation of systems such as **7.** Conjugate addition–annelation utilizing α-silylated vinyl ketones was demonstrated to afford side-chain and angular groups cis disposed.[9] Treatment of 6,6-dimethoxyhexanal (**8**)[10] with 1-trimethylsilylvinylmagnesium



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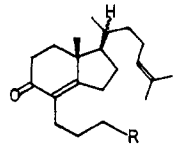
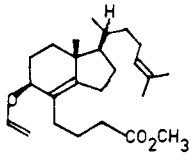


(10) R = $CH(OCH_3)_2$
(11) R = CO_2CH_3

bromide in THF, followed by oxidation (CrO_3·pyHCl CH_2Cl_2, $NaHSO_4$), afforded α-trimethylsilylvinyl ketone (**9,** bp 95–97 °C (0.5 mm)) in 65% yield.[11,12] Assembly of the key bicyclic intermediate **10** was then accomplished in a one-pot procedure. 2-Methyl-2-cyclopenten-1-one[13] (1.07 equiv) was added to the mixed diorgano cuprate reagent derived from copper *n*-pentyne[14] and 6-methyl-5-penten-2-yllithium[15] in ether (1.0 equiv) at −78 °C and warmed to −20 °C over 2 h.[16] To the resulting intermediate at −20 °C vinyl ketone **9** (1.0 equiv) was added dropwise over 30 min and the mixture was held at −20 °C for 2 h. Workup and cyclization of the crude adduct with methanolic base provided, after chromatographic purification (Florisil), hydrindenone **10** (oil; NMR δ 5.06 (br t, 1), 4.33 (t, 1), 3.28 (s, 6), 1.67 (br s, 3), 1.61 (br s, 3), 1.09 (s, 3)) in 80–85% overall yield. Examination of **10** by LC and ^{13}C NMR indicated that it consisted of an ~1:1 mixture of epimers at the side-chain center but was homogeneous otherwise.[12,17]

As was expected, construction of the C-11 quaternary center proved to be rather difficult. Either intramolecular or intermolecular conjugate addition of a variety of nucleophiles and organometallic reagents was investigated without success, owing apparently to the extremely congested steric environment around C-11. However, intramolecular rearrangement processes were expected to have sufficient driving force to permit the desired functionalization. In order to prepare the acetal side chain for eventual cyclization, hydrindenone **10** was first transformed by hydrolysis (HCl, H_2O, THF), oxidation (1.2 equiv of CrO_3–acetone at 0 °C) and esterification (CH_2N_2–ether) to methyl ester **11** (oil; NMR δ 5.05 (br t, 1), 3.63 (s, 3), 1.69 (br s, 3), 1.61 (br s, 3), 1.06 (s, 3)) in 65% overall yield. Reduction of hydindenone ester **11** with $NaBH_4$ in ethanol (1.1 equiv at 0 °C), followed by vinyl ether exchange (10 equiv of $CH_2{=}CHOC_2H_5$, $Hg(OAc)_2$), afforded the vinyl ether **12** (oil; NMR δ 6.33 (q, 1), 5.09 (br t, 1), 4.10 (m, 3,



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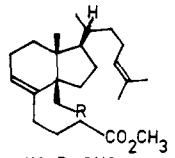
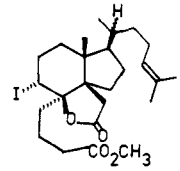


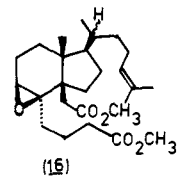
(13) R = CHO
(14) R = CO_2H



(15)

C*H*-OR and vinyl H), 1.71 (br s, 3), 1.63 (br s, 3), 0.99 (s, 3)) in 72% overall yield. The stereochemistry of reduction was crucial since the relative stereochemistry will be transferred by rearrangement to C-11. As anticipated, the equatorial alcohol was the only observed product.[18]

The crucial rearrangement was conducted by heating vinyl ether **12** in *s*-collidine at ~160 °C under argon (4 h)[19] producing the required olefinic aldehyde **13** (oil; NMR δ 9.70 (t, 1), 5.62 (m, 1), 5.11 (br t, 1), 3.68 (s, 3), 1.68 (br s, 3), 1.61 (br s, 3), 0.88 (br s, 3)) in 60–65% yield.[20] In order to permit selective refunctionalization of the endocyclic trisubstituted double bond, aldehyde **13** was oxidized (1.2 equiv of CrO_3–acetone at 0 °C, 1.5 h) to acid **14** in 90% yield. Acid **14** was directly converted into the sensitive iodolactone **15** (oily solid; NMR δ 5.06 (br, t, 1), 1.70 (br s, 3), 1.62 (br s, 3), 0.95 (s, 3); IR 1770, 1725 cm^{-1}) in 75% yield by treatment with KI_3 (1 equiv) and aqueous sodium bicarbonate at 25 °C (~1 h). Transposition of the oxygen function to C-7 and creation of the side-chain stereochemistry at C-6 was then accomplished by immediate transformation of iodolactone **15** ($NaOCH_3$, CH_3OH; 25 °C; 2 h) to epoxide **16** (oil; NMR δ 5.08 (br t, 1),



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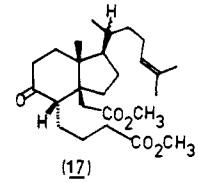

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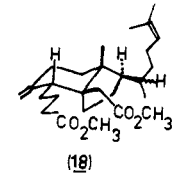
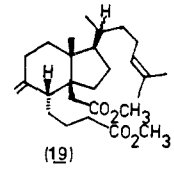


(18)

3.68 (s, 6), 3.08 (d, 1), 1.68 (br s, 3), 1.62 (br s, 3), 0.70 (s, 3)) in 90% yield, followed by rearrangement of epoxide **16** with boron trifluoride etherate (0 °C–room temperature, 0.5 h) affording keto diester **17** (oil; NMR δ 5.12 (br t, 1), 3.69 (s, 3), 1.72 (br s, 3), 1.64 (br s, 3), 0.94 (s, 3); IR 1725, 1700 cm^{-1}) in 65% yield.[21] The stereochemistry of **17** follows from the concerted 1,2 rearrangement of the α proton followed by epimerization.[22] Further confirmation of this assignment was gained by the lack of isomerization of **17** upon exposure to $NaOCH_3$ in CH_3OH. The apparently most favorable conformation of **17** has the C-6 side chain equatorially disposed (cf. **18**) and, therefore, in the most stable configuration.[23] Comparison with natural material then provided the final structural correlation.

Methylenation of **17** was accomplished with some difficulty. Direct Wittig reaction provided only low yields of the desired methylene diester **19,** possibly owing to interaction with the two-carbon ester side chain at C-11.[24] However, methylene diester **19** (oil; NMR δ 5.03 (m, 1), 4.83 (br s, 1), 4.58 (br s,



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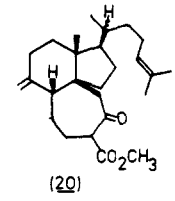

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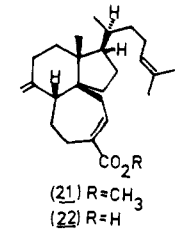


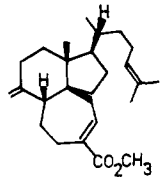
(21) R = CH_3
(22) R = H

1), 3.60 (s, 3), 1.65 (br s, 3), 1.57 (br s, 3), 0.77 (s, 3)) could be prepared in ~70% overall yield by saponification of **17** (Na_2CO_3, aqueous CH_3OH, 65 °C, 20 h), treatment of the diacid with *N*-methylphenylsulfonimidoylmethyllithium (5.0 equiv, THF, −78 °C, 10 h),[25] in situ reduction of the crude adduct with aluminum amalgam (aqueous acetic acid, THF, −78–25 °C), and reesterification (ethereal diazomethane).

The ring system was completed by Dieckmann cyclization of **19.** Treatment of **19** with lithium tetramethylpiperidide (6.0 equiv) in THF at 25 °C for 18 h afforded crude β-keto ester **20** in 60–70% yield. Ester **20** was then converted in ~68% overall yield into *dl*-methyl gascardate (**21**) and *dl*-18-*epi*-methyl gascardate by reduction (1.0 equiv of $NaBH_4$–ethanol, −20–0 °C, 6 h) and mesylation with methanesulfonyl chloride (pyridine–CH_2Cl_2, 0 °C, 22 h), followed by elimination (DBN, benzene, 80 °C, 1.5 h). The mixture of epimers (~1:1) was resolved by LC (Porosil, hexane–0.5% ethyl acetate) providing *dl*-methyl gascardate identical with natural methyl gascardate by TLC, LC, and IR, NMR, and mass spectral compari-

son.[26,27] *dl*-Methyl gascardate was converted into *dl*-gascardic acid (**22**) by saponification (NaOH, CH_3OH, THF, 12 h) completing the total synthesis.[28]

Since the assignment of stereochemistry at C-11 and C-14 has now been confirmed by the foregoing, the only remaining stereochemical question is the relative configuration at C-18.[8] It is interesting to note that the correlation of side-chain stereochemistry at C-20 encountered in the cholesterol–demosterol series[29] cannot be tested in this series. The natural methyl gascardate has the C-19 methyl signal essentially overlapping the C-19 methyl signal in the 18-epi isomer **23**. The expected



(23)

trend in chemical shifts cannot be clearly observed in this series as it was in the previous studies by the Hoffmann–La Roche group.[29]

The configuration at C-6 is somewhat unexpected on the basis of Arigoni's studies; thus the mode of formation of the key acid cyclization product must now be reformulated in light of the structural and synthetic studies.[7,8] Our studies have now fully established the relative stereostructure of gascardic acid as **22**.

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(12) All new compounds have satisfactory spectral data and combustion analysis or exact mass data.
(13) Fischli, A.; Klaus, M.; Mayer, H.; Schoenholzer, P.; Rueegg, R. *Helv. Chim. Acta* **1975,** *58,* 564.
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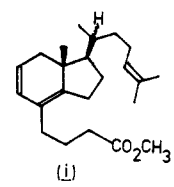
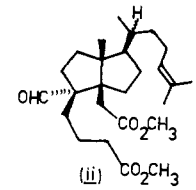
(16) This reagent was not completely homogeneous; however, no problems were encountered with reactivity.
(17) The ^{13}C NMR spectrum of **10** shows doubled resonances only for several of the seven side-chain carbons.
(18) Reduction with L-Selectride provided a mixture of isomers with the axial isomer predominating; cf. also ref 19b.
(19) (a) Burgstahler, A. W.; Nordin, I. C. *J. Am. Chem. Soc.* **1961,** *83,* 198. (b) Dauben, W. G.; Dietsche, T. *J. Org. Chem.* **1972,** *37,* 1212. (c) For a recent use of this rearrangement in a hindered situation, see: McMurry, J. E.; Andrews, A.; Ksander, G. M.; Mosser, J. H.; Johnson, M. A. *J. Am. Chem. Soc.* **1979,** *101,* 1330.
(20) A significant byproduct encountered is the elimination product, diene (i).



(i)



(ii)

(21) The other isolated product from this reaction is the expected C–C bond migration product, aldehyde ii.
(22) (a) Blackett, B. N.; Coxon, J. M.; Hartshron, M. P.; Jackson, B. L. J.; Muir, C. N. *Tetrahedron* **1969,** *25,* 1499. (b) Blackett, B. N.; Coxon, J. M.; Hartshorn, M. P.; Richards, K. E. *Ibid.* **1969,** *25,* 4999. (c) Coxon, J. M.; Hartshorn, M. P.; Rae, W. J. *Ibid.* **1970,** *26,* 1019. (d) In several instances, equilibration of the initially formed ketone occurs; Whitsell, J. K.; Matthews, R. S.; Wang, P. K. S. *Synth. Commun.* **1977,** *7,* 355.
(23) The chair–chair *cis*-hydrindan with the angular acetic ester and C_7 side chains in axial-like environments is favored. The steroidal hydrindan conformation is preferred somewhat surprisingly. We cannot absolutely rule out equilibration during methylenation (**17** → **19**).
(24) For similar difficulties encountered, see: Zurfluh, R.; Dunham, L. L.; Spain, V. L.; Siddal, J. B. *J. Am. Chem. Soc.* **1970,** *92,* 425. Gueldner, R. C.; Thompson, A. C.; Hedin, P. A. *J. Org. Chem.* **1972,** *37,* 1854.
(25) Johnson, C. R.; Shanklin, J. R.; Kirchhoff, R. A. *J. Am. Chem. Soc.* **1973,** *95,* 6462.
(26) The methyl ester was prepared by treatment of natural gascardic acid with ethereal diazomethane; cf. ref 1.
(27) Separation was effected after the terminal stage; however, separation could be effected at any one of a number of previous stages by conventional chromatography.
(28) We thank Professors Duilio Arogoni, Andrew S. Kende, and Jon Clardy for generous samples of natural gascardic acid.
(29) (a) Partridge, J. J.; Faber, S.; Uskokovic, M. R. *Helv. Chim. Acta* **1974,** *57,* 764. (b) Narwid, T.; Cooney, K. E.; Uskokovic, M. R. *Ibid.* **1974,** *57,* 771. (c) Narwid, T.; Blount, J. F.; Iacobelli, J. A.; Uskokovic, M. R. *Ibid.* **1974,** *57,* 781.
(30) Fellow of the Alfred P. Sloan Foundation (1976–1980); recipient of a Cancer Development Award (CA-00273) from the National Cancer Institute of the NIH (1976–1981).

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Intermolecular Energy Exchange of Infrared-Laser Excited $CHClF_2$ or SiF_4 with Br_2 at Excitation Energies of 70–200 kJ/mol[1]

Sir:

Intermolecular energy transfer at the high levels of vibrational excitation characteristic of reacting molecules is fundamental in chemical kinetics.[2] By use of pulsed infrared lasers, mean vibrational excitation energies of 100–200 kJ/mol of absorbing species in well-defined gas volumes are readily attained[3] in 300 ns or less. Consecutive energy transfer to a nonabsorbing species can then be measured if specific indicators of vibrational excitation are available.[4]

We report here preliminary studies of vibrational energy transfer from laser-excited $CHClF_2$ or SiF_4 to Br_2 in binary gas phase, using absorbance at 436 nm as an indicator of Br_2 vibrational excitation. The visible absorption of Br_2 is a well-known function of temperature[5-7] and can serve as a Br_2 vibrational thermometer: its features are reproduced by quantum-mechanical theory which neglects possible effects of translational and rotational excitation.[6-8] Absorbance by $CHClF_2$ and SiF_4 at 436 nm is nil.

Our kinetic results, interpreted in this way, indicate that energy transfer proceeds according to mechanism 1, where *A* denotes the IR absorbing component ($CHClF_2$ or SiF_4) and *B* denotes Br_2. *V* denotes vibrational energy and *W* translation/rotational energy. Direct $V_A - V_B$ transfer appears to be relatively unimportant.

$$V_A \overset{1/\sigma}{\rightleftharpoons} W(\mathrm{T/R,\ gas}) \overset{1/\tau}{\rightleftharpoons} V_B \qquad (1)$$

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