tween the polymer chains,[14] the expected bonding as well as chemical properties of a fluorinated $(SN)_x$ would have been quite different.

Acknowledgment. This work was supported by a NATO Grant through the Deutsche Akademische Austauschdienst to M.W. R.W. and a collaborative NATO Grant (198.80) to R.J.L. and H. W. Roesky.

Registry No. S_4N_4 homopolymer, 58813-83-5.

---

(14) (a) G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene, and J. J. Mayerle, *J. Chem. Soc., Chem. Commun.*, 407 (1977); (b) Z. Iqbal, R. H. Baughman, J. K. Kleppinger, and A. G. MacDiarmid, *Solid State Commun.*, **25**, 409 (1978).

Host Recognition in Parasitic Angiosperms: Use of Correlation Spectroscopy To Identify Long-Range Coupling in an Haustorial Inducer

John C. Steffens, James L. Roark, David G. Lynn,* and James L. Riopel

Departments of Chemistry and Biology
University of Virginia, Charlottesville, Virginia 22901

Received October 25, 1982

Simple proximity relationships and relative stereochemistries of substituents in natural and synthetic organic molecules are routinely deduced from ^1H NMR coupling constants. The verification of distant intramolecular relationships frequently requires the measurement of nuclear Overhauser enhancements,[1,2] T_1 relaxation times,[2] or lanthanide-induced chemical shift changes.[3] A recent report by Bax et al.[4] showed that small couplings could be observed by proton correlation spectroscopy (COSY). The intriguing possibility of routinely identifying through-bond proximities over five and six atoms has motivated our exploration of correlation spectroscopy.[5] We now describe the structure assignment of a xenognostic triterpene isolated from a host of the parasitic angiosperm *Agalinis purpurea*, by the identification of long-range couplings.

Host recognition by the parasitic plant *Agalinis purpurea* (Scrophulariaceae) is mediated through the differentiation of a specialized attachment organ termed an haustorium.[6] The differentiation of the haustorium in *Agalinis* is dependent on specific molecular signals produced in the host root, exuded, and thereby recognized by the parasite. Although we have identified structurally specific molecules that induce haustorial differentiation,[7-9] these compounds were not derived from a natural host. For that reason, the fractionation of 400 g of 3-month-old vermiculite-grown *Lespedeza sericea* (Leguminosae) roots has been directed by haustorial-inducing activity in axenic cultures of *A. purpurea.*[7] Droplet countercurrent chromatography (7:13:8 $CHCl_3/CH_3OH/H_2O$) and repeated flash chromatography (SiO_2) of the 50% aqueous MeOH extract[10] yielded 2 mg of a crystalline (MeOH, mp 260-261 °C) solid, **1**. EI MS (70 eV) gave a

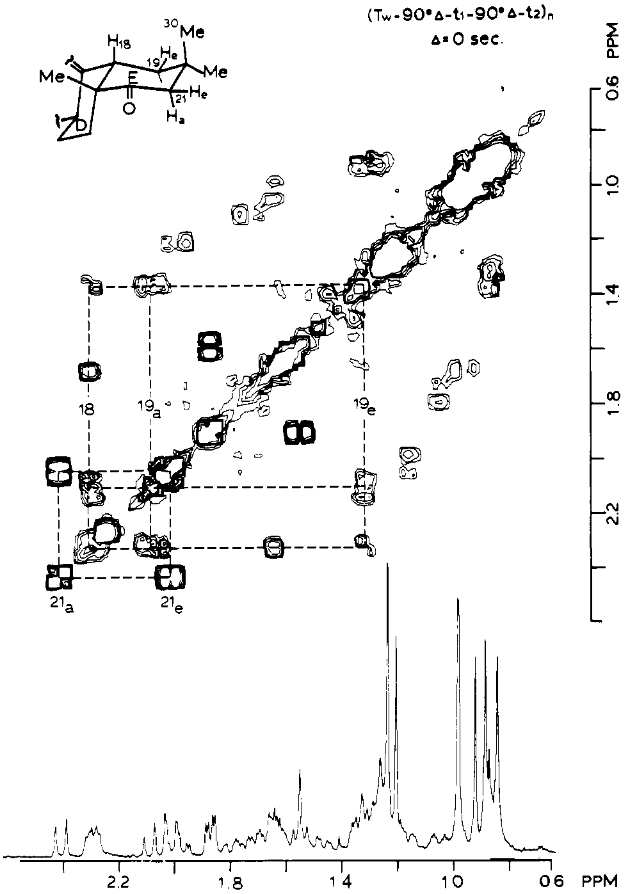
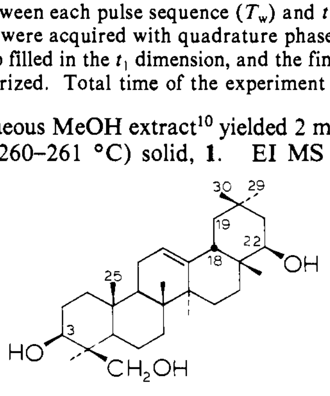


Figure 1. Contour plot of the 360-MHz homonuclear spin correlation map of 3 (2 mg, $CDCl_3$, high-field expansion) with no delay inserted in the pulse sequence shown at the top of the figure. Assignments of cross peaks indicating coupled spins in the E-ring are shown with the dotted lines. The corresponding region of the one-dimensional ^1H NMR spectra is provided on the abscissa. The 2-D correlation map is composed of 128 × 512 data point spectra, each composed of 16 transients. A 4-s delay was allowed between each pulse sequence (T_w) and t_1 was incremented by 554 s. Data were acquired with quadrature phase detection in both dimensions, zero filled in the t_1 dimension, and the final 256 × 256 data set was symmetrized. Total time of the experiment was 2.31 h.



1

molecular ion at m/z 458.3757, $C_{30}H_{50}O_3$ (calcd 458.3760),[11] and the major fragment ions at m/z 234 and 224 suggested a retro-Diels-Alder fragmentation of an olean-12-ene triterpene bearing two oxygen atoms on the A-B ring fragment.[12] Seven quaternary methyl singlets in ^1H NMR (360 MHz, acetone-d_6) and a single olefinic proton (δ 5.5 (t, J = 2.5 Hz)) supported the oleanene assignment. Three hydroxyl substituents were identified with deuterium-exchange negative ion CI MS (EtOD, N_2O)[13] by the

---

(1) Bachers, G. E.; Schaefer, T. *Chem. Rev.* **1971**, *71*, 617-626.

(2) Noggle, J. H.; Schirmer, R. E. "The Overhauser Effect: Chemical Applications"; Academic Press: New York, 1971.

(3) Reuben, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1973**, *9*, 1-70.

(4) Bax, A.; Freeman, R.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 164-168. Bax, A.; Freeman, R. *Ibid.* **1981**, *44*, 542-561.

(5) Lynn, D. G.; Phillips, N. J.; Hutton, W. C.; Shabanowitz, J.; Fennell, D. I.; Cole, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 7319-7322.

(6) Riopel, J. L.; Musselman, L. H. *Am. J. Bot.* **1979**, *66*, 570-575.

(7) Lynn, D. G.; Steffens, J. C.; Kamat, V. S.; Graden, D. W.; Shabanowitz, J.; Riopel, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1868-1870.

(8) Steffens, J. C.; Lynn, D. G.; Kamat, V. S.; Riopel, J. L. *Ann. Bot.* **1982**, *50*, 1-7.

(9) Kamat, V. S.; Graden, D. W.; Lynn, D. G.; Steffens, J. C.; Riopel, J. L. *Tetrahedron Lett.* **1982**, *23*, 1541-1544.

(10) The inducing factor is present in root exudate but is available in larger quantities in the extract.

(11) High resolution EI MS was obtained through Harvey Laboratories, Inc., on a VG-770, and CI MS was obtained on a Finnigan 3200.

(12) Budzikiewicz, H.; Wilson, J. M.; Djerassi, C. *J. Am. Chem. Soc.* **1963**, *85*, 3688-3699.

(13) Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 6953-6963.

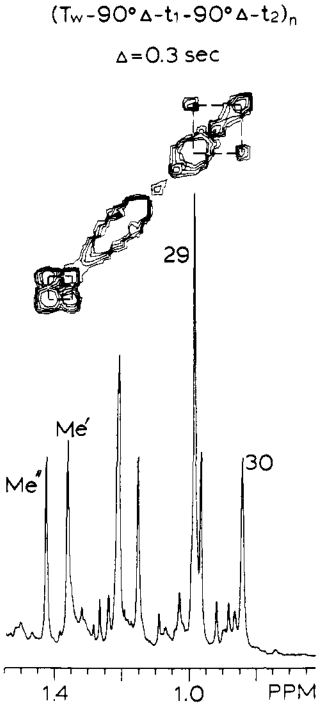


Figure 2. COSY spectra of the methyl region of **2** (2 mg, $CDCl_3$) with a delay, Δ, equal to 0.3 s inserted in the pulse sequence as shown at the top of the figure. Cross peaks arising from four-bond coupling between *gem*-dimethyl groups of the acetonide (Me′, Me″) and the E-ring (29, 30-CH_3) are indicated by the dashed line. The 2-D map is composed of 128 × 512 data point spectra, each composed of 12 transients. A 4-s delay was allowed between each pulse sequence, and t_1 was incremented by 560 s. Data were acquired with quadrature phase detection in both dimensions, zero filled in the t_1 dimension, and the final 256 × 256 data set was symmetrized.

appearance of a molecular ion at m/z 459 ($(M - 1)^-$ with two exchanges). The 3β- and 24-hydroxyl functionalities were suggested by ^1H NMR (δ 3.45 (H-3, dd, J = 5.4, 11 Hz 4.2 (H-24, J = 11 Hz), 3.5 (H′-24, bd, J = 11 Hz)).[14] Disruption of the intramolecular hydrogen bonding with Me_2SO-d_6 and by acetylation, taken together with a 2.9% NOE of the C-25 methyl upon irradiation of H′-24,[15] confirmed this assignment. Although ^1H NMR established the axial orientation of the third hydroxyl group (δ 3.42 (t, J = 4.5 Hz)), extensive mass spectral, NOE, and NMR shift reagent studies did not unambiguously distinguish between oxidation at the 22, 21, or 16 axial positions.

Protection of the A-ring diol as an acetonide (2,2′-dimethoxypropane, acetone, pTsOH) and treatment with PDC (PDC, pyridinium trifluoroacetate, room temperature, 4 h) generated the keto acetonide **2**. The downfield-shifted geminally coupled protons of the methylene α to the resulting carbonyl in **2**, as well as in the deprotected (MeOH, catalytic TsOH) keto diol, **3**, were easily assigned by the COSY experiment shown in Figure 1. The allylic proton, H-18 (δ 2.3), is assignable before and after oxidation as are H-19a (δ 2.07) and H-19e (δ 1.35) as a result of the off-diagonal cross peaks to H-18. Insertion of a 0.3-s delay into this COSY sequence, Figure 2, resolves cross peaks between the E-ring *gem*-dimethyls (δ 0.84, 1.0). The internal check provided by the acetonide methyls (δ 1.38, 1.46) verifies that these cross peaks arise from the same ^4J methyl coupling. A 0.2-s delay and a lower contour slice of **3**, Figure 3, resolve cross peaks resulting from a four-bond coupling between H-19a and the higher field singlet of the E-ring methyls (30-CH_3). An analogous coupling also exists between 30-CH_3 and one of the protons adjacent to the carbonyl, establishing its assignment as H-21a Finally, the presence of a four-bond "W-type" coupling between H-19e and the other methylene proton α to the carbonyl, H-21e, establishes the site of oxidation at C-22 and allows for the assignment of 3β,22β,24-trihydroxyolean-12-ene for **1**.

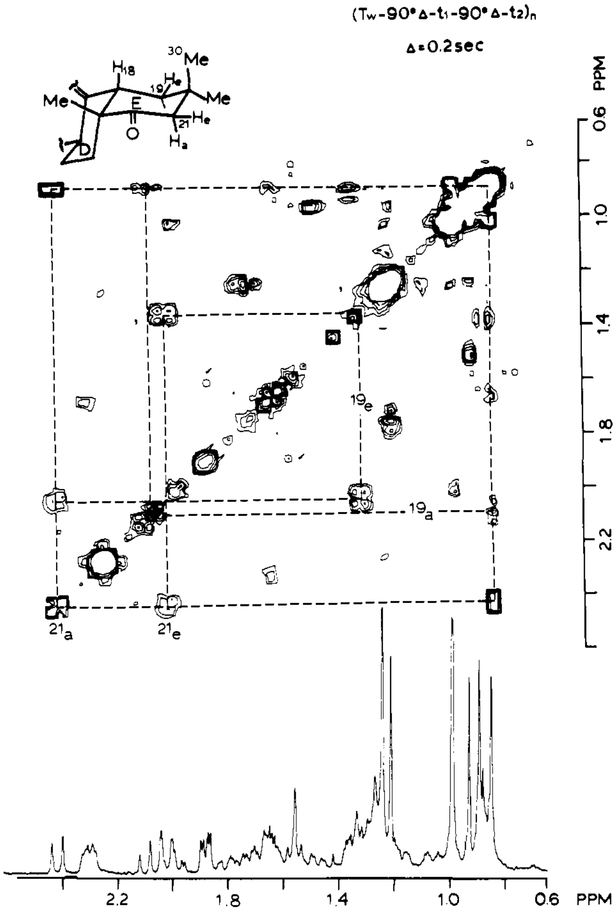


Figure 3. A 0.2-s delayed COSY spectrum of the aliphatic region of **3** (2 mg, $CDCl_3$). Long-range "W-type" coupling of 19 and 21 axial protons to 30-CH_3 and coupling across the gem dimethyls from 19eq to 21eq establish the position of oxidation at C-22. The spectrum was obtained under conditions similar to those in Figure 1, except that 32 transients were acquired for each of 128 × 512 data point spectra.

Methyl chemical shifts in triterpenes are known to be sensitive to substituent effects, and these systematic changes have been tabulated and used in the structural determination of triterpenoids.[16] The correlation of methyl chemical shifts with known members of the same triterpene class is, however, subject to unexpected anomalies. The difference in methyl chemical shifts of the keto acetonide **2** and the diol **3** is a good example of these unexpected chemical shift changes.[17] The ability to assign these methyls through the definitive, nonempirical establishment of long-range couplings provides an important advance in triterpene structure assignment.

The difficulty of making assignments in pentacyclic triterpenoids is further demonstrated by the soyasapogenols. The structure of soyasapogenols A, B, and E were established several years ago[18] and were not questioned until the X-ray crystallographic work

---

(14) Isuda, Y.; Sano, T.; Isobe, K.; Miyauchi, M. *Chem. Pharm. Bull.* **1974**, *22*, 2396–2401.

(15) Preirradiation (selective 180°) of 24-H′ was followed after a delay (0.7 s) by a 90° observed pulse. This spectrum (550–1000 transients) was acquired simultaneously with a spectrum in which one selective pulse was 3 ppm upfield of Me_4Si, and the two spectra were computer subtracted to observe the enhancements. Solomon, I. S. *Phys. Rev.* **1955**, *99*, 559–565. Hall, L. D.; Saunders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1980**, *368*–370.

(16) Itô, S. In "Natural Products Chemistry"; Nakanishi, K., Goto, T., Itô, S., Natori, S., Nozoe, S., Eds.; Kodansha Lts.: Tokyo, 1974, pp 365–366.

(17) For both molecules 30-CH_3 is at δ 0.85, but 29-CH_3 appears at δ 1.02 in the keto acetonide and at δ 0.98 in the diol.

(18) Smith, H. M.; Smith, J. M.; Spring, F. S. *Tetrahedron* **1958**, *4*, 111–131. Wilner, D.; Gestetner, D.; Lavie, D.; Birk, Y.; Bondi, A. *J. Chem. Soc.* **1964**, 5885–5888.

of Chiang and Chang.[19] During the preparation of this paper, X-ray crystallographic and chemical studies revised the structures of soyasapogenols B and E to **1** and **3**, respectively.[20] This paper demonstrates that delayed correlation spectroscopy permits this assignment in a few simple experiments. Variation in the delay time, coupled with a relatively short acquisition time (100–200 ms), simplifies the 2-D maps by enhancing cross peaks of desired J magnitude and allows proton assignments in highly congested regions of the spectrum.

The oleanene triterpene **1** is structurally very different from the previously isolated xenognostic flavonoids active in the *Agalinis* system.[8] It is perhaps relevant to the broad host range of this parasite that both **1** (soyasapogenol B) and **3** (soyaspogenol E) appear to be widely distributed in the Leguminosae. Interestingly, although both molecules are present in *Lespedeza sericea* root exudate, **3** does not appear to induce haustorial differentiation in *Agalinis.*

Acknowledgment. We thank W. C. Hutton and Jeffrey Shabanowitz for valuable suggestions during the course of the work and Dr. Mike Thompson for much of the initial biological study. Support from USDA Competitive Research Grant 5901-0410-9-0257, USDA Cooperative Research Agreement 58-7B30-0-196, Research Corp., and Frausch Foundation as well as partial support for the NTC 360 from NSF is gratefully acknowledged.

---

(19) Chiang, T. C.; Chang, H. M. *Planta Med.* **1982**, *46*, 52–55.

(20) Kitagawa, I.; Yoshikawa, M.; Wang, H. K.; Saito, M.; Tosirisuk, V.; Fujiwara, T.; Tomita, K. *Chem. Pharm. Bull.* **1982**, *30*, 2294–2297.

Evidence for a Silylenium Ion in Solution

Joseph B. Lambert*[1] and William J. Schulz, Jr.

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received November 17, 1982

One of the key organic intermediates that heretofore has not been observed in solution is trivalent, positively charged silicon, the silylenium ion (R_3Si^+, the silicon analogue of the carbenium ion).[2,3] Evidence has been presented for such species in the gas phase,[4,5] but numerous efforts in solution have met with failure.[6,7] Undoubtedly a major contributor to these negative results is the poor ability of silicon to undergo p_π–p_π bonding. Whereas carbenium ions are readily stabilized by 2p–2p resonance, the silylenium ion is more weakly stabilized through 2p–3p overlap over longer bonds with lone pairs or π electrons on carbon, nitrogen, or oxygen.[5] Furthermore, the very large single-bond energies of silicon with oxygen, nitrogen, and most halogens render unavailable many common leaving groups.

Our current strategy is to provide stabilization to the silylenium ion through the use of highly polarizable substituents. Our choice of sulfur (alkylthio) as the substituent on silicon was guided not only by its high polarizability but also by the low electronegativity of sulfur and by the possibility that 3p–3p overlap would be more effective than 2p–3p overlap. After these experiments were well underway, Apeloig[8] and Godleski[8,9] showed by ab initio calculations that HS provides net stabilization to the $XSiH_2^+$ ion (X = HS). The leaving group problem had already been solved by J. Y. Corey, who suggested that silylenium ions could be generated by abstraction of hydride by trityl salts.[10] Maximization of stabilization through polarization and 3p–3p overlap thus suggested that $(RS)_3SiX$ would be an ideal precursor for a silylenium ion, and the Corey procedure required that X must be H. Further polarization could be obtained from the use of a reasonably large alkyl group for R such as isopropyl. Fortunately, tris(alkylthio)silicon hydrides are readily available from the reaction of trichlorosilane with alkanethiols.[11] Consequently, we prepared tris(2-propylthio)silane in this fashion and subjected it to the Corey conditions (eq 1).

$$(i\text{-PrS})_3SiH + Ph_3C^+ClO_4^- \rightarrow Ph_3CH + (i\text{-PrS})_3Si^+ClO_4^- \qquad (1)$$

Our previous results showed that a wide variety of silanes undergo the Corey reaction to give nonconducting, presumably covalent perchlorates, e.g., Ph_3SiH gives $Ph_3SiOClO_3$.[6] In contrast, a 1/1 mixture of tris(2-propylthio)silane (4.61×10^{-4} mol) and trityl perchlorate, prepared in dilute methylene chloride solution at room temperature, gave a solution with a specific conductance of 110.8 μmho cm^{-1}. This value is comparable to that of a fully ionic species such as trityl perchlorate (5.03×10^{-4} mol), which was 102.0 μmho cm^{-1}. An analogous solution of triphenylsilane (6.86×10^{-4} mol) and trityl perchlorate had a specific conductance of only 2.2 μmho cm^{-1}.

Nuclear magnetic resonance spectra of the ionic species in CD_2Cl_2 (about 0.8 M) were extremely clean. The ^{13}C spectrum showed only a single pair of isopropyl resonances (δ 27.1 and 37.5) in addition to those of triphenylmethane. The ^1H spectrum showed one isopropyl doublet (δ 1.35), one isopropyl septet (δ 3.37), the triphenylmethane methinyl singlet (δ 5.38), and the aromatic resonances. When less than 1 equiv of trityl perchlorate was added, only resonances from the starting material and the single product were observed. Thus, in a titration-type experiment, the loss of the SiH resonance (δ 5.70) and the simultaneous gain of the triphenylmethane methinyl resonance could be followed, as could the loss (δ 1.28, 3.17) and gain (δ 1.35, 3.37) of the appropriate isopropyl methyl resonances. The magnetic resonance experiments showed that (1) only one species is formed, (2) the species has only one type of isopropyl group (or is exchanging rapidly) and no other alkyl group, and (3) the species is formed by removal of the hydride on silicon, because of loss of SiH and gain of triphenylmethane CH.

The ionic species could be further characterized spectroscopically. The electronic spectrum had a single, intense λ_{max} at 352 nm, quite distinct from the values for trityl perchlorate at 410 and 435 nm. The infrared spectrum contained bands characteristic of ionic perchlorates, at 1100 (s) and 620 (m) cm^{-1}, although these are mixed with various other bands. Trityl perchlorate itself has bands at 1095 (vs) and 625 (m) cm^{-1}. The extremely weak ^{29}Si resonance was at 18 ppm to high frequency (low field) of Me_4Si, compared with 1 ppm for the starting material, $(i\text{-PrS})_3SiH$. The lack of nearby protons makes for very slow ^{29}Si relaxation, and the silylenium peak may be unobservable. The observed peak may be from polymer that develops during the 16 h utilized for spectral acquisition. An EPR spectrum (3×10^{-2} M sample) showed no signal. A lower limit to the concentration of radical cations was set at 10^{-9} M. The molecular weight was measured to be 376 ± 22 (theory 353) for two particles in sulfolane.[12]

---

(1) This work was supported by the National Science Foundation (Grant CHE80-25601).

(2) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1–28. Bøe, B. *Ibid.* **1976**, *107*, 139–217.

(3) West, R.; Barton, T. J. *J. Chem. Educ.* **1980**, *57*, 334–340.

(4) Weber, W. P.; Felix, R. A.; Willard, A. K. *Tetrahedron Lett.* **1970**, 907–910. Kudryavtsev, R. V.; Lyakhovetskii, Y. I.; Parnes, Z. N.; Kursanov, D. N. *J. Org. Chem. USSR* (*Engl. Transl.*) **1974**, *10*, 919–923.

(5) Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 4329–4332.

(6) Lambert, J. B.; Sun, H.-n. *J. Am. Chem. Soc.* **1976**, *98*, 5611–5615.

(7) Barton, T. J.; Hovland, A. K.; Tully, C. R. *J. Am. Chem. Soc.* **1976**, *98*, 5695–5696. Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485–1487.

(8) Apeloig, Y.; Godleski, S. A.; Heacock, D. J.; McKelvey, J. M. *Tetrahedron Lett.* **1981**, *22*, 3297–3300.

(9) Further calculations on phosphino-substituted silylenium ions have appeared. Godleski, S. A.; Heacock, D. J.; McKelvey, J. M. *Tetrahedron Lett.* **1982**, *23*, 4453–4456.

(10) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237–3238.

(11) Wolinski, L.; Tieckelmann, H.; Post, H. W. *J. Org. Chem.* **1951**, *16*, 395–398.

0002-7863/83/1505-1671$01.50/0