correspond to a turnover number of only 5 day^{-1}. Illumination of this solution, maintained at 75 °C, with sunlight causes the solution to become yellow and leads to an abrupt increase in the rate of hydrogen production corresponding to a turnover number of 83 day^{-1}. The hydrogen production by the photolyzed solution is catalytic with respect to $W(CO)_6$, since the production of 18 mL of H_2 constitutes approximately 16 turnovers of catalyst on the basis of $W(CO)_6$ initially present in the solution. The rate of production of CO_2 is found to equal that for H_2 within experimental error for this system in accordance with eq 4-6.[7] Likewise the loss of CO over the duration of the experiment is exactly accounted for by sampling losses, thus indicating that reaction 1 does not proceed to a measurable extent under these conditions. The rate of production of H_2 following illumination is found to be substantially the same (76 day^{-1} measured over four turnovers) when this same experiment is repeated under a N_2 atmosphere.

No measurable hydrogen production is observed with either nonilluminated or photolyzed solutions of $W(CO)_6$ when sodium formate is absent or is replaced by potassium hydroxide. As noted earlier, the reaction of OH^- with CO to produce formate (eq 1) is very slow at 75 °C. Thus the negative results obtained with potassium hydroxide serve to eliminate from consideration any catalytic sequence involving direct base attack on $W(CO)_6$ under the conditions of these experiments. Such a mechanism has been invoked for the water gas shift reaction catalyzed by $Fe(CO)_5$.[8,10]

The data shown on the rising portion of Figure 1 were taken under conditions of approximately constant illumination. However, the solutions once photolyzed have characteristics of a true thermal catalyst retaining catalytic activity over periods of several hours in the dark. Eventually the solutions lose activity for reasons not clearly understood at present.

The electronic spectrum of the yellow solution resulting from photolysis reveals a broad band system having a band maximum at 408 nm which closely resembles the low-energy ligand field bands (^1A-^1E) typically found with $M(CO)_5L$ (L = ligand) complexes.[5] The IR spectra of the catalyst solutions in the CO-stretching region show two bands at 1970 and 1910 cm^{-1} and a weak band at 1850 cm^{-1}. These bands can be assigned to $W(CO)_6$ (ν 1975 cm^{-1} in a 1-butanol-water mixture[4]) and the $HCO_2W(CO)_5^-$ anion; literature values of $\nu(CO)$[11] for Ppn $W(CO)_5HCO_2$ are 1900 (s), 1837 (m), 2060 cm^{-1} (w) in CH_2Cl_2. This suggests that the photochemical conversion of $W(CO)_6$ to $W(CO)_5$ is not complete under the conditions of these experiments.

A series of control experiments were performed by using solutions of $W(CO)_6$ in tetrahydrofuran (THF). Each of these experiments consisted of determining the rate of H_2 production after combining separately prepared solutions of (a) $W(CO)_6$ (0.120 mmol) in 50 mL of THF and (b) sodium formate (40 mmol) dissolved in 150 mL of a 33:67 water-2-ethoxyethanol (v/v) solvent mixture. These experiments were performed in a closed system under argon. The first of these experiments was carried out entirely in the dark. Here the THF solution of $W(CO)_6$, maintained at room temperature, was added to a hot (T = 62 °C) solution of sodium formate in the ethoxyethanol-water mixture. The rate of H_2 production from this final mixture was very low (0.17 day^{-1}). In the second experiment, the $W(CO)_6$-THF solution was photolyzed by sunlight at room temperature prior to mixing. The two solutions were combined as before and maintained in the dark at T = 62 °C. The hydrogen production rate from the final mixture was found to be 13 day^{-1} corresponding to a 77-fold enhancement in rate. The third experiment differed from the second only in that the solutions were mixed and maintained in sunlight. The H_2 production following mixing (14 day^{-1}) was substantially the same as that found in the second experiment of this series. In each case no H_2 was produced prior to mixing, although small amounts of CO were detected immediately following illumination of the $W(CO)_6$-THF solutions. On the basis of the preliminary experiments reported here, it can be concluded that (a) the hydrogen and carbon dioxide produced in these reactions result from the decomposition of formate ion; (b) $W(CO)_6$ is a precursor to the catalytically active $W(CO)_5$ which enters a catalytic cycle originally proposed for the water gas shift reaction (eq 3-6) at eq 3; and (c) as shown by others,[12,13] the photolytic decomposition of a catalyst precursor can provide a very effective means for promoting activity of certain catalytic systems.

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(7) Gas-phase concentrations of CO_2 and H_2 produced in equimolar quantities in solution will not necessarily be equal due to differences in the liquid-phase solubilities of these two gases. With methanol-water mixtures, the gas-phase concentration of CO_2 is less than that for H_2 due to the relatively high solubility of CO_2 in the liquid phase.[4,8] Laine, Rinker, and Ford report that the gas-phase concentrations of CO_2 and H_2 are equal for a similar reaction carried out over mixtures of 2-ethoxyethanol and water suggesting that the solubility of CO_2 is relatively low in this latter solvent system.

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Isolation and Characterization of the First Host Recognition Substance for Parasitic Angiosperms

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Parasitic angiosperms develop a specialized organ for host attachment termed the haustorium. This organ becomes both a morphological and a physiological bridge between the host and parasite. We (Riopel and Musselman)[1,2] and others[3] have shown that parasitic angiosperms cultured in the absence of host roots develop few or no haustoria. Initiation is achieved rapidly with exposure of *Agalinis purpurea* (Scrophulariaceae) to host root exudate or gum tragacanth, a commercially available exudate of *Astragalus spp.* (Leguminosae). Haustorial formation is central to the parasitic attack and is common to virtually all parasitic angiosperms.[4] Using haustorial initiation as a bioassay, we wish to describe the rapid, small-scale isolation and characterization of the first host recognition substance.

In order to understand the nature of the compounds responsible for host recognition, we have concentrated our efforts on gum tragacanth. Soxhlet extraction of the gum (250 g) serially with hexane (1.5 L) and ether (1.5 L), each for 24 h, resulted in an activity-rich ether fraction which was concentrated to yield 600 mg of crude material. Partition between CCl_4 and 50% aqueous

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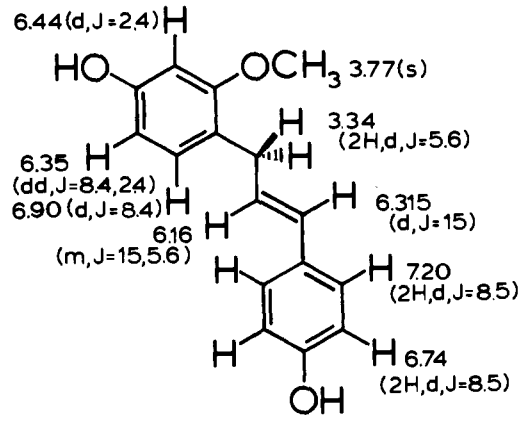

Figure 1. ^{1}H NMR (100 MHz) assignments of the xenognosin (400 μg) in 0.25 mL of acetone-d_6.

MeOH and application of the aqueous layer (300 mg) to droplet countercurrent chromatography (DCC), C_6H_6–MeOH–$CHCl_3$-H_2O (2:3:2:1, upper phase mobile), resulted in two distinct bands of biological activity, the more polar showing a significantly greater haustorial stimulation response. The more polar fraction was chromatographed on Sephadex LH-20, 2 × 34 cm, MeOH, giving a 2 mg sample which was purified by reverse-phase high-pressure liquid chromatography using a Waters Radial Pac B column (45% aqueous MeOH). The entire purification can be done in less than 1 week and the rapid, small-scale purification was shown to be essential for obtaining maximum yields of 200 μg.

The purified haustorial initiator was found to be sparingly soluble in organic as well as aqueous solvents and very soluble in MeOH. The UV spectrum (MeOH) showed no evidence for extended conjugation (λ_{max} 260 nm) and the ^{1}H NMR spectrum (100 MHz, acetone-d_6)[5] supported the presence of two separated aromatic chromophores. Double-resonance experiments clarified an A_2B_2 pattern and a separate three-proton aromatic spin system (Figure 1). EI–MS[6] (70 eV, 200 °C) gave an apparent molecular ion at m/z 256, and this assignment was supported by CI–MS (CH_4),[7] m/z 257 (M + 1). Deuterium exchange CI–MS (CH_3OD)[8] provided evidence for two exchangeable protons, m/z 260 (M + D with two exchanges). Microscale acetylation (20 μg, Ac_2O/pyridine, 4 °C) supported the presence of two hydroxyl groups, m/z 341.1407 (M + H + 2 Ac, $C_{20}H_{21}O_5$ (calcd 341.1390) and established a molecular formula of $C_{16}H_{16}O_3$. The third oxygen can be assigned to a methyl ether to account for the three-proton singlet at δ 3.77 in the ^{1}H NMR spectrum.

Double-resonance experiments also identified a high-field two-proton doublet, δ 3.34, coupled to a one-proton multiplet, δ 6.16. Taken together with a one-proton doublet at δ 6.315, a three-carbon olefinic bridge can be assigned to connect the aromatic chromophores. Computer simulations of the spin system[9] have confirmed a 15 Hz coupling between the olefinic protons, establishing the *trans* configuration.[10] The olefin was placed in conjugation with the *para*-substituted aromatic chromophore as a result of PRFT experiments. The short T_1 relaxation times of the low-field doublet, δ 7.20 of the A_2B_2 spin system relative to both the high-field doublet at δ 6.74 and the aromatic doublet (δ 6.90) of the other ring, can be accounted for by relaxation through the adjacent olefinic proton.[11]

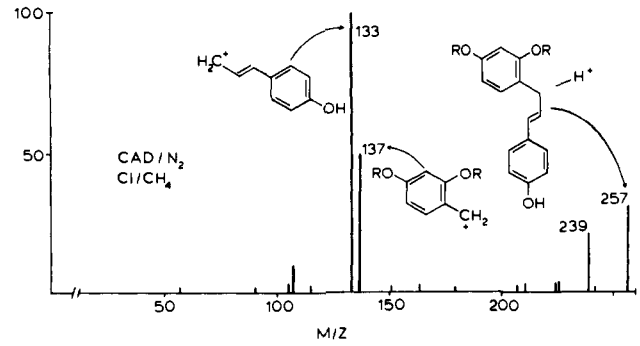

Figure 2. The xenognosin was chemically ionized (CH_4, ca. 150 °C) and the (M + 1) ion quadrupole selected and subjected to collision activated decomposition (N_2) to give the mass spectrum.

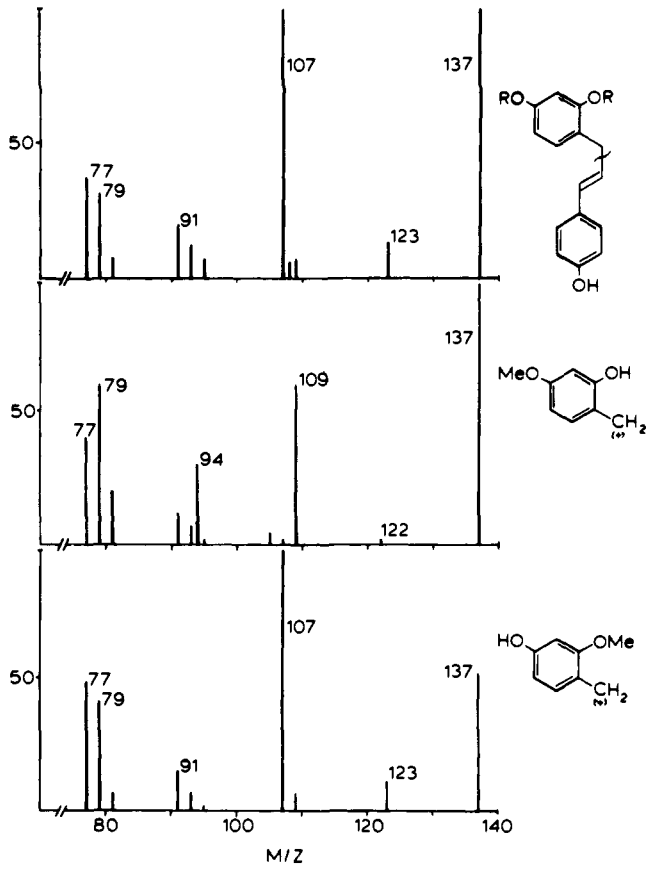

Figure 3. The indicated spectral fragments arising from chemical ionization (CH_4, 150 °C) were quadrupole selected and collided with N_2 to give the collisional activated decomposition (CAD) spectra shown. The top spectrum is the fragment arising from the isolated xenognosin and the bottom two spectra arise from the isomeric benzyl alcohols.

The establishment of the 4-substituted styrene chromophore greatly aided assignment of the CI (CH_4) mass spectral fragment ions. Utilization of a triple quadrapole mass spectrometer provided the same fragment ions in greater relative abundance when the chemically ionized molecular ion, m/z 257, was quadrapole selected and subjected to nitrogen collision activated decomposition (CAD)[12] (Figure 2). These fragments allowed assignment of the methoxy ether to the trisubstituted aromatic ring. Silylation resulted in a bis(trimethylsilyl) derivative, CI (CH_4), m/z 401, which on CAD analysis gave clean fragmentation to m/z 205 and 209, supporting the presence of one hydroxyl function on each of the chromophores.

(5) ^{1}H NMR spectra obtained on a JEOL FX-100 equipped for FT measurements. All values reported as ppm downfield of Me_4Si.

(6) Electron-impact mass spectral data obtained with an Hitachi RMU-6E.

(7) Chemical-ionization high-resolution mass spectral data were obtained with an AEI-MS 902 modified for chemical ionization by Scientific Research Instruments Corp., Baltimore, MD.

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(11) The same distinctive difference has been observed in several 4-substituted model systems. Even 4-methoxystyrene has a T_1 difference of 0.5 s between the doublets of the A_2B_2 quartet.

The high-field (δ 6.74) and low-field (δ 7.20) doublets of the A_2B_2 system in the presence of 20% pyridine-d_5 (in acetone-d_6) were shifted downfield by 3-Hz and 1-Hz, respectively. Under the same conditions, 4-Hz and 3-Hz respective downfield shifts of the aromatic signals at δ 6.35 and 6.44 were observed with no measurable effect on the other protons. These data suggested the free hydroxyl group had two ortho protons and led to the structural assignment seen in Figure 1. Mass spectral confirmation of that assignment was obtained by CAD analysis of the m/z 137 fragment ion (Figure 3, top). The major fragmentation is the loss of formaldehyde ($M^+ - 30$) from the methyl ether. Since this fragmentation must be dependent on regiochemistry, both possible methyl ether isomers were independently synthesized as the benzyl alcohols. Chemical ionization of these benzyl alcohols gives a major $M + 1 - H_2O$ fragment to generate the isomeric benzyl cations which upon CAD give the fragments shown in Figure 3. These data establish the *o*-methoxybenzyl cation as the structure of the m/z 137 fragment of the isolated material.

The new structure **1**, which has oxygen functionality on both rings of the 1,3-diphenylpropene system, can be biogenetically derived from flavanoids. The significance of a flavanoid serving as a host recognition substance for the hemiparasite *Agalinis purpurea* is not entirely clear, but it stands as the first natural host recognition substance for parasitic angiosperms. For that reason we have named it xenognosin or host recognition substance.[13] Studies are under way to determine if this and related substances will function in host recognition for *Striga asiatica* and other root parasites that are of agronomic importance.

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Oxygen Chiral Phosphodiesters. 3. Use of ^{17}O NMR Spectroscopy To Demonstrate Configurational Differences in the Diastereomers of Cyclic 2'-Deoxyadenosine 3',5'-[^{17}O,^{18}O]Monophosphate

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This laboratory recently reported the syntheses of both diastereomers of cyclic 2'-deoxyadenosine 3',5'-[^{16}O,^{18}O]monophosphate (cyclic [^{16}O,^{18}O]dAMP) and assigned their absolute configurations at phosphorus by measuring the ^{18}O perturbations on the phosphorus chemical shifts[1] of the ethyl esters formed by reaction of the chiral diesters with diazoethane.[2] The oxygen chiral phosphodiesters were subsequently reacted with pyrophosphate and glycerol in the presence of a bacterial adenylate cyclase and glycerol kinase to yield oxygen chiral samples of 2'-deoxyadenosine 5'-[α-^{16}O,^{18}O]diphosphate ([α-^{16}O,^{18}O]dADP) and glycerol phosphate; the absolute configurations at the α-phosphorus atoms were assigned by measuring the ^{18}O perturbations on the phosphorus chemical shifts of the $Co_3(NH_3)_4$dADP complexes formed from the chiral samples of [α-^{16}O,^{18}O]dADP.[3]

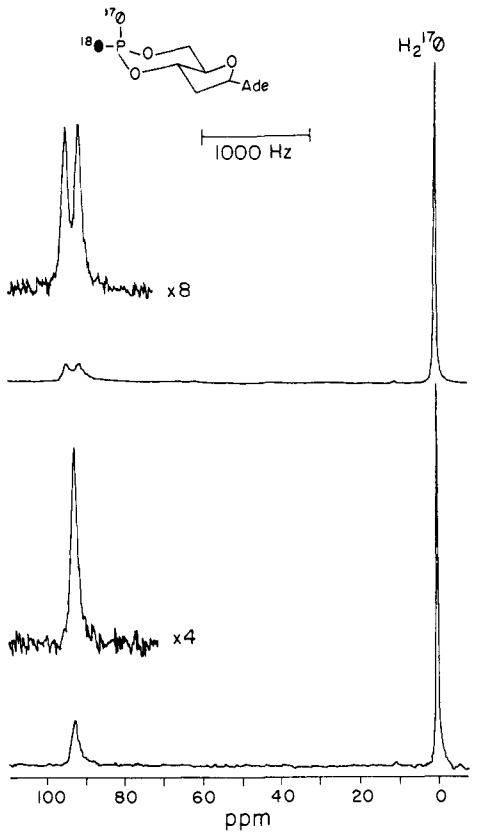

Figure 1. ^{17}O NMR spectra at 36.6 MHz of the R_P diastereomer (axial ^{17}O) of cyclic [^{17}O,^{18}O]dAMP: top, ^{31}P coupled; bottom, ^{31}P decoupled. Sample preparation and spectral acquistion parameters are described in ref 12; a 2-Hz line broadening factor was applied to each free induction decay prior to Fourier transformation.

We are interested in determining the stereochemical course of both enzymatic and nonenzymatic hydrolyses of phosphodiesters; for this reason, we are synthesizing several cyclic and acyclic chiral [^{17}O,^{18}O]phosphodiesters[4] so that the hydrolysis reactions can be most economically and conveniently performed in $H_2{}^{16}O$. In the course of characterizing the diastereomers of cyclic [^{17}O,^{18}O]-dAMP, we discovered that these oxygen chiral phosphodiesters can be distinguished on the basis of their ^{17}O NMR spectra. In particular, the chemical shifts of the diastereomers are sufficiently different that their resonances can be resolved in a ^{31}P decoupled spectrum of a racemic sample. In addition, both the ^{31}P–^{17}O coupling constants and the line widths of the separated diastereomers are significantly different. Thus, ^{17}O NMR spectroscopy is the first spectroscopic technique that has been found to directly detect configurational differences in oxygen chiral phosphate esters.

The diastereomeric ^{17}O-enriched *P*-anilidates of cyclic dAMP were synthesized according to procedures developed in this laboratory for the preparation of unlabeled materials,[5] except that [^{17}O]$POCl_3$[6] was used to prepare the required *o*-(chlorophenyl)-*N*-phenyl[^{17}O]phosphoramidic chloride. The [^{17}O]-*P*-anilidates were reacted separately with a 10-fold excess of 99% enriched $C^{18}O_2$, and the products were purified by chromatography on DEAE-Sephadex A-25.[2] The chiral [^{17}O,^{18}O]phosphodiesters which were obtained[7] were identical with authentic cyclic dAMP

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