

Figure 2. Proposed structure for $(\text{RSi})_2\text{W}_{11}\text{SiO}_{40}^{4-}$

anions of the composition $(\text{RSi})_2\text{W}_{11}\text{SiO}_{40}^{4-}$.⁷ One WO_4^{4-} unit has been replaced by an $(\text{RSi})_2\text{O}^{4+}$ group. The infrared spectra of these products are somewhat perturbed from that of $\text{W}_{12}\text{SiO}_{40}^{4-}$ in the 1100–700- cm^{-1} region. The most striking variation is the appearance of a strong band at $\sim 1040\text{ cm}^{-1}$, which can be assigned to the Si–O–Si group,⁸ in the spectra of the derivatives. A structure is postulated (Figure 2) for these anions in which one tungsten-centered octahedral array of six oxygen atoms in $\text{W}_{12}\text{SiO}_{40}^{4-}$ is replaced by a similar array which is not metal centered. The oxygen atom located at the normally unshared vertex of this array is bridging the two tetrahedrally coordinated silicon atoms, giving rise to the 1040- cm^{-1} band. ^1H NMR suggests that the two R groups in these $(\text{RSi})_2\text{W}_{11}\text{SiO}_{40}^{4-}$ anions are equivalent, which is consistent with the proposed structure.

Class III. The reaction of CpTiCl_3 with preformed $\text{W}_{11}\text{SiO}_{39}^{8-}$ or with $\text{W}_{12}\text{PO}_{40}^{3-}$ at pH 7 or with $\text{Mo}_{12}\text{SiO}_{40}^{4-}$ at pH 5 gives $\text{CpTiW}_{11}\text{SiO}_{39}^{5-}$, $\text{CpTiW}_{11}\text{PO}_{39}^{4-}$, or $\text{CpTiMo}_{11}\text{SiO}_{39}^{5-}$, respectively.^{9,10} The ^1H NMR spectrum of the tungstates includes one sharp resonance for the cyclopentadienyl ring; two sharp unequal resonances were observed for $\text{CpTiMo}_{11}\text{SiO}_{39}^{5-}$. These varied in intensity from one recrystallization fraction to another and fractions were obtained which had only one such resonance. The analyses were correct for salts of $\text{CpTiMo}_{11}\text{SiO}_{39}^{5-}$ regardless of the ratio of these peaks, implying they were due to isomers and not to compositionally different species. The ^{31}P spectrum of $\text{CpTiW}_{11}\text{PO}_{39}^{4-}$ revealed two singlets in a 40:60 ratio, again suggesting the presence of two isomers despite the singlet observed in the proton nmr spectrum. The infrared spectra of $\text{CpTiW}_{11}\text{SiO}_{39}^{5-}$, $\text{CpTiW}_{11}\text{PO}_{39}^{4-}$, and $\text{CpTiMo}_{11}\text{SiO}_{39}^{5-}$ are exceedingly similar to those of the parent Keggin anions in the 700–1100- cm^{-1} region. The one exception is that the phosphate stretching band at 1080 cm^{-1} , which is a singlet in $\text{W}_{12}\text{PO}_{40}^{3-}$ is split into two bands in $\text{CpTiW}_{11}\text{PO}_{40}^{4-}$. This splitting is not observed in the spectra of the $\text{RSnW}_{11}\text{PO}_{39}^{4-}$ or $(\text{RSn})_2\text{W}_{10}\text{PO}_{38}^{5-}$ derivatives.

It is proposed that the titanium in these anions is formally eight coordinate, as in Cp_2TiCl_2 ; three coordination sites are formally occupied by the π -bonded cyclopentadienyl ring while the remaining five coordination sites are bonded to the W_{11} or Mo_{11} Keggin fragment. Several possible explanations for the apparent "isomers" are being investigated. It is not believed that isomerization of the M_{11} portion of the Keggin fragment has occurred.

In related work, reaction of $\text{C}_6\text{H}_5\text{SnCl}_3$ with $\text{W}_{17}\text{P}_2\text{O}_{61}^{10-11}$ and with $\text{W}_{16}\text{P}_2\text{O}_{59}^{12-12}$ has given $\text{C}_6\text{H}_5\text{SnW}_{17}\text{P}_2\text{O}_{61}^{7-}$ and $(\text{C}_6\text{H}_5\text{Sn})_2\text{W}_{16}\text{P}_2\text{O}_{60}^{8-}$, respectively. Studies on the chemistry described here and on related heteropolyanion derivatives are continuing and will be reported shortly.¹³

References and Notes

- M. T. Pope et al., *J. Less-Common Met.*, **54**, 129 (1977), and references therein.
- M. Filowitz and W. G. Klemperer, *J. Chem. Soc., Chem. Commun.*, 233 (1976).
- C. M. Tourne, G. F. Tourne, S. A. Malik, and T. J. R. Weakley, *J. Inorg. Nucl. Chem.*, **32**, 3875 (1970).
- Typical analyses: Calcd (found) for $[(\text{CH}_3)_4\text{N}]_5\text{C}_6\text{H}_5\text{SnW}_{11}\text{SiO}_{39}\cdot 6\text{H}_2\text{O}$: C, 9.32 (9.86); H, 2.32 (2.27); N, 2.09 (2.17); Si, 0.84 (0.79); Sn, 3.54 (3.51); W, 60.39 (60.77); H_2O , 3.23 (2.99); neut equiv, 670 (658), by titration after H^+ ion exchange; $\text{CH}_3\text{:C}_6\text{H}_5$ proton ratio, 12:1 (12:1). Calcd (found) for $[(\text{CH}_3)_4\text{N}]_4\text{K}(\text{CH}_3\text{Sn})_2\text{W}_{10}\text{PO}_{38}\cdot \text{H}_2\text{O}$: C, 6.98 (7.14); H, 1.82 (1.84); N, 1.81 (2.17); K, 1.26 (1.36); Sn, 7.66 (7.22); W, 59.33 (58.96); H_2O , 0.58 (0.50), $\text{CH}_3\text{:CH}_3\text{Sn}$ proton ratio, 8:1 (8.3:1). Calcd (found) for $[(\text{CH}_3)_3\text{NH}]_5\text{HO}(\text{O})\text{CH}_2\text{CH}_2\text{SnW}_{11}\text{SiO}_{39}\cdot 3\text{H}_2\text{O}$: C, 6.71 (6.67); H, 1.91 (1.80); N, 2.17 (2.12); O, 21.86 (22.30); Si, 0.87 (0.94); Sn, 3.69 (3.62); W, 62.79 (62.77); H_2O , 1.68 (1.66).
- Acknowledgement is given to F. Davidson for determining the ^{31}P spectra.
- (a) L. C. W. Baker and J. S. Figgis, *J. Am. Chem. Soc.*, **92**, 3794 (1970); (b) M. T. Pope, *Inorg. Chem.*, **15**, 2008 (1976).
- Typical analyses: Calcd (found) for $[(\text{CH}_3)_3\text{NH}]_4(\text{C}_6\text{H}_5\text{Si})_2\text{W}_{11}\text{SiO}_{40}\cdot 3\text{H}_2\text{O}$: C, 9.02 (9.29); H, 1.77 (1.74); N, 1.75 (1.82); Si, 2.64 (2.64); W, 63.29 (63.17); H_2O , 1.69 (1.77); $\text{CH}_3\text{:C}_6\text{H}_5$ proton ratio, 3.6:1 (4.2:1). Calcd (found) for $[(\text{CH}_3)_3\text{NH}]_4\text{K}(\text{C}_6\text{H}_5\text{Si})_2\text{W}_{11}\text{SiO}_{40}$: C, 6.31 (6.05); H, 1.65 (1.64); N, 1.84 (1.75); O, 21.02 (21.38); Si, 2.77 (2.47); W, 66.41 (66.55); $\text{CH}_3\text{:C}_6\text{H}_5$ proton ratio, 3.6:1 (3.7:1).
- L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, N.Y., 1954, pp 278–280.
- Since this manuscript was first submitted, Professor W. G. Klemperer has published a nonaqueous preparation of $\text{CpTiW}_{11}\text{PO}_{39}^{4-}$ [R. K. C. Ho and W. G. Klemperer, *J. Am. Chem. Soc.*, **100**, 6772 (1978)].
- Typical analyses: Calcd (found) for $[(\text{CH}_3)_3\text{NH}]_5\text{CpTiW}_{11}\text{SiO}_{39}\cdot \text{H}_2\text{O}$: C, 7.73 (7.78); H, 1.85 (1.81); N, 2.25 (2.26); Ti, 1.54 (1.39); Si, 0.90 (0.88); W, 65.11 (65.15); H_2O , 0.58 (0.53); $\text{CH}_3\text{:Cp}$ proton ratio 9:1 (9.7:1). Calcd (found) for $[(\text{CH}_3)_3\text{NH}]_4\text{K}(\text{CpTiMo}_{11}\text{SiO}_{39}\cdot \text{H}_2\text{O})$: C, 9.64 (10.03); H, 2.24 (2.25); N, 2.64 (2.62); K, 1.85 (1.83); Ti, 2.26 (1.83); H_2O , 0.85 (1.31); $\text{CH}_3\text{:Cp}$ proton ratio, 7.2:1 (8:1).
- S. A. Malik and T. J. R. Weakley, *J. Chem. Soc. A*, 2647 (1968), and references therein.
- R. Contant and J. P. Ciabrini, *J. Chem. Res. M*, 2601 (1977).
- Professor M. T. Pope has independently prepared several anions belonging to Class I, including $\text{CH}_3\text{SnW}_{11}\text{SiO}_{39}^{5-}$ (M. T. Pope, private communication; F. Zonneville and M. T. Pope, to be published).
- T. J. R. Weakley, *Struct. Bonding (Berlin)*, **18**, 137–143 (1974).

W. H. Knott

Contribution No. 2613

Central Research and Development Department
E. I. du Pont de Nemours and Company
Experimental Station, Wilmington, Delaware 19898
Received September 27, 1978

Enhancement of Nuclear Magnetic Resonance Signals by Polarization Transfer

Sir:

We report here a new method for enhancing the intensity of NMR signals from nuclei of low magnetogyric ratio. The method is independent of relaxation mechanisms, unlike the nuclear Overhauser effect,¹ and hence is likely to be particularly useful for nuclei such as ^{15}N and ^{29}Si which have negative magnetogyric ratios. The enhancement arises from the transfer of nuclear spin polarization from the S spins (usually protons) with large Boltzmann population differences, to the nuclear species under investigation, the I spins. It provides an alternative to rotating frame cross-polarization experiments,^{2,3} which have recently been used on liquid-phase systems.⁴

The pulse sequence for the proposed experiment can be written

$$90^\circ_S(X) - \tau - 180^\circ_S(X), \\ 180^\circ_I - \tau - 90^\circ_S(Y), 90^\circ_I - \text{acquisition}$$

where the transmitter pulses applied to the S spins can be phase shifted so that the B_1 field is directed along either the X or Y axes of the appropriate rotating reference frame. This pulse sequence is closely related to one used in heteronuclear two-dimensional Fourier transform spectroscopy⁵⁻⁸ but relies on the excitation of spin echoes and employs a fixed delay τ , equal to $1/(4J_{IS})$ s. For a simple system of two spins I and S , the components of S magnetization $M(\alpha)$ and $M(\beta)$ corresponding to the two I spin states can be represented by the vectors α and β (Figure 1). The first two pulses excite a spin echo for the S

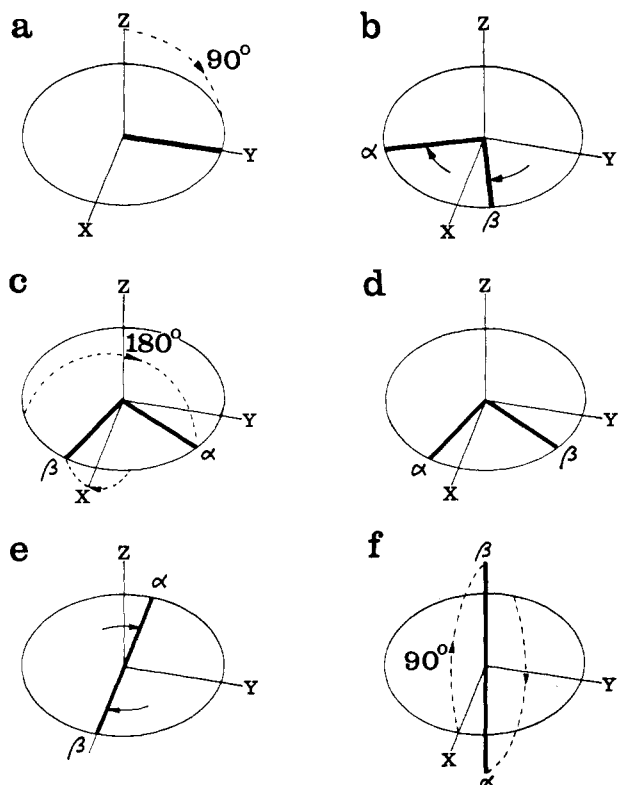


Figure 1. Behavior of the S spin magnetization vectors in a population transfer experiment, viewed in a frame rotating in synchronism with the radiofrequency field. After an initial 90° pulse (a) the two vectors precess for a period τ and accumulate a relative phase angle of 90° (b). A 180° pulse about the X axis flips them into mirror-image positions (c) while a simultaneous 180° pulse on the I spins interchanges the spin-state labels (d). Further precession for a period τ leaves the vectors along the $\pm X$ axes (e) when a 90° pulse about the Y axis aligns them along the $\pm Z$ axes (f). The magnetization represented by the α vector now has inverted spin populations.

nuclei at time 2τ . The 180° pulse applied to the I spins interchanges the spin-state labels α and β (Figure 1d), causing a continued divergence of the α and β vectors throughout the interval 2τ ; this is the phenomenon responsible for the modulation of spin echoes.^{9,10} A knowledge of the approximate value of the coupling constant J_{IS} permits the delay τ to be selected such that the divergence between α and β is just 180° and they are left diametrically opposed along the $\pm X$ axes at time 2τ (Figure 1e). The chemical shift effect is exactly refocused.

The third pulse applied to the S spins has a relative phase shift of 90° , since it must rotate the magnetization vectors by 180° about the Y axis, leaving them aligned along the $\pm Z$ direction (Figure 1f). If relaxation during the short period 2τ is neglected, this corresponds to a population inversion across one S transition but equilibrium populations across the other. Because they share common energy levels, the I transitions now have spin population differences appropriate to S spins, larger by a factor $K = \gamma_S/\gamma_I$. When the I spins are excited by a 90° pulse, one component of the doublet is therefore enhanced by a factor K and the other similarly enhanced but inverted, no overall transfer of magnetization having occurred; if K is negative these positive and negative enhancements are interchanged.

We illustrate this technique using protons as the S spins and carbon-13 as the I spins. Experiments for the enhancement of carbon-13 signals by means of selective proton pulses have been described by several workers;^{11,12} the technique proposed here is effective over a wide band of proton frequencies and requires no knowledge of the proton chemical shifts. When proton-coupled carbon-13 spectra are measured by this method, the

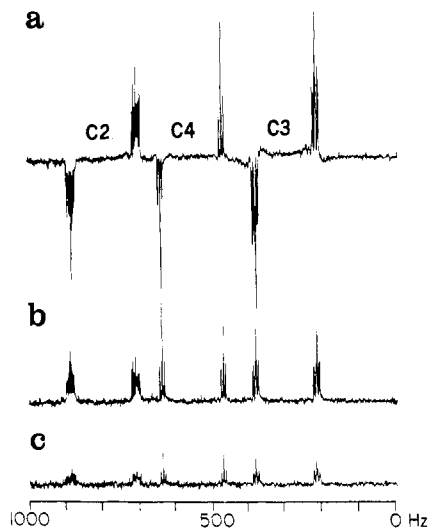


Figure 2. Proton-coupled carbon-13 spectra of pyridine (a) enhanced by polarization transfer, (b) enhanced by the nuclear Overhauser effect, and (c) unenhanced. The three experiments utilized the same total instrument time.

normal binomial intensity ratios for multiplets no longer apply, the ratios obtained being $-1:1$ for doublets, $-1:0:1$ for triplets, and $-1:-1:1:1$ for quartets.^{5,6} As a result, mutual cancellation of signals occurs if proton decoupling is employed immediately after the carbon 90° excitation pulse; however, if a suitable delay is introduced between this pulse and the application of the decoupler field,⁷ this cancellation is prevented, and an enhanced decoupled spectrum is obtained.

Proton-coupled carbon-13 spectra of pyridine (Figure 2) were recorded on a Varian CFT-20 spectrometer which had minor hardware modifications to improve the timing stability and to allow a computer-controlled 90° phase shift of the 80-MHz proton transmitter. The delay τ was set equal to 1.5 ms, which is $\sim 1/(4J_{CH})$ for the direct CH couplings in pyridine. Long-range couplings can be used in these experiments, although they require long τ delays; the experiment is however best suited to the enhancement of signals from nuclei directly bonded to protons. Since the range of one-bond couplings is usually relatively small, a value of τ can be selected which gives a good enhancement for all proton-bearing sites in a molecule.

Figure 2 compares the enhanced proton-coupled pyridine spectrum (a) with that obtained in an experiment of the same duration employing gated decoupling¹³ to establish the nuclear Overhauser effect (b), and with the conventional unenhanced spectrum (c). In spectrum a, contributions from the unenhanced carbon-13 signals have been suppressed by a phase alternation method, since otherwise they introduce a slight asymmetry between the positive and negative signals. The improvement in sensitivity in spectrum a compared with spectrum c is a factor of ~ 5 or 6. It arises from two distinct sources. The spin population effect enhances the signals by a factor $K \approx 4$, while the rate at which the entire sequence can be repeated is governed by the relatively short proton spin-lattice relaxation times. In contrast, the maximum possible nuclear Overhauser enhancement is $1 + 1/2K$, and the rate at which this experiment can be repeated is determined by cross-relaxation rates which are appreciably slower than proton relaxation rates.¹⁴

For these reasons the polarization transfer experiment can show a significant improvement over the nuclear Overhauser enhancement method, even in those cases where the dipolar relaxation mechanism dominates all others and the full Overhauser effect is obtained. The improvement is greater for nuclei of low magnetogyric ratio, and is most dramatic for

nuclei such as ^{15}N and ^{29}Si where the Overhauser enhanced the signal is inverted and where an incomplete Overhauser effect can result in signal cancellation. One solution to this problem has been to suppress the nuclear Overhauser effect in ^{15}N spectra; under such conditions the polarization transfer experiment would provide an enhancement factor K of ~ 10 , in addition to the benefits of faster spin-lattice relaxation.

The proposed polarization transfer experiment bears a superficial resemblance to another technique for sensitivity enhancement which also employs spin echoes and restores the focussed magnetization to the Z axis.¹⁵ This is the "driven equilibrium Fourier transform method" (DEFT). We have consequently adopted the code name INEPT (insensitive nuclei enhanced by polarization transfer).

Acknowledgments. This work was made possible by an equipment grant from the Science Research Council and a Research Studentship to G.A.M. Dr. Moniz kindly provided a copy of his manuscript⁴ prior to publication.

References and Notes

- (1) Solomon, I. *Phys. Rev.* **1955**, *99*, 559.
- (2) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042.
- (3) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
- (4) Bertrand, R. D.; Moniz, W. B.; Garroway, A. N.; Chingas, G. C. *J. Am. Chem. Soc.* **1978**, *100*, 5227.
- (5) Ernst, R. R. Eighteenth Experimental NMR Conference, Asilomar, Calif., 1977; Sixth International Symposium on Magnetic Resonance, Banff, Canada, 1977.
- (6) Maudsley, A. A.; Ernst, R. R. *Chem. Phys. Lett.* **1977**, *50*, 368.
- (7) Maudsley, A. A.; Müller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 463.
- (8) Bodenhausen, G.; Freeman, R. *J. Magn. Reson.* **1977**, *28*, 471.
- (9) Hahn, E. L.; Maxwell, D. E. *Phys. Rev.* **1952**, *88*, 1070.
- (10) Freeman, R.; Hill, H. D. W. *J. Chem. Phys.* **1971**, *54*, 301.
- (11) Pachler, K. G. R.; Wessels, P. L. *J. Magn. Reson.* **1973**, *12*, 337; **1977**, *28*, 53.
- (12) Sørensen, S.; Hansen, R. S.; Jakobsen, H. J. *J. Magn. Reson.* **1974**, *14*, 243. Jakobsen, H. J.; Linde, S. A.; Sørensen, S. *ibid.* **1974**, *15*, 385.
- (13) Freeman, R.; Hill, H. D. W. *J. Magn. Reson.* **1971**, *5*, 278.
- (14) The proton spin-lattice relaxation can be accelerated by the addition of relaxation reagents such as chromium acetylacetonate.
- (15) Becker, E. D.; Ferretti, J. A.; Farrar, T. C. *J. Am. Chem. Soc.* **1969**, *91*, 7784.

Gareth A. Morris, Ray Freeman*

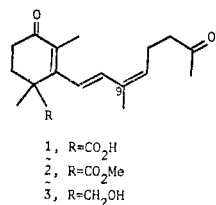
Physical Chemistry Laboratory, Oxford University
Oxford, England

Received October 10, 1978

Stereospecific Synthesis of (\pm)-Trisporol B, a Prohormone of *Blakeslea Trispora*, and a Facile Synthesis of (\pm)-Trisporic Acids

Sir:

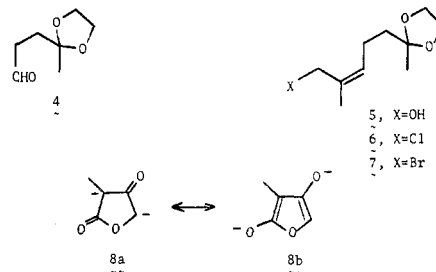
Sexual differentiation in Mucoraceous fungi is mediated by a system of C_{18} apocarotenoid hormones based on the trisporic acids (e.g., **1**) and congeners such as (9*Z*)-methyl trisporate **B** (**2**).¹ Extensive studies with plus and minus mating types of



B. trispora has led to the identification of certain prohormones² which are characteristic of the mating strain and are converted to a trisporic acid by the sexual partner. Trisporol B (**3**) is produced in very small amounts by minus cultures of this organism and has proven to be the most biologically active of the mating prohormones so far isolated.³ The chemical synthesis

of **3** and related members of the trisporic acid group is likely to be a key element in elucidating the reproductive process in fungi of the Mucorales, and we have therefore sought a practical, synthetic solution to the stereochemical and functional group problems posed by these regulatory substances.⁴

The requirement for 9*Z* stereochemistry in **3**, coupled with the desirability of fashioning the corresponding olefinic link in the trisporic acid and esters in a geometrically defined manner, dictated an approach strategically different from that adopted in previous syntheses of methyl trisporates.⁵ First, a unit functionally equivalent to the C(8)–C(14) segment of **3** was prepared from ketal aldehyde **4**, readily obtainable from ethyl levulinate.^{5a} Thus, **4** was treated with ethylideneetri-



phenylphosphorane (THF, -78°C , 5 min), and the derived oxido ylide (*n*-BuLi, THF, 0°C) was allowed to react with paraformaldehyde (1 h at 0°C and then 8 h at room temperature) to give the *Z* alcohol **5**: 69%; NMR δ 5.28 (1 H, t, $J = 7$ Hz), 4.10 (2 H, s), 3.92 (4 H, s), 2.66 (1 H, s, disappears in D_2O), 1.78 (3 H, s), 1.30 (3 H, s).⁶ This alcohol was converted via its tosylate (MeLi, Et_2O -HMPA (3:1) and then $\text{C}_7\text{H}_7\text{SO}_2\text{Cl}$ - Et_2O , 0°C) to chloride **6** (82%; NMR δ 5.38 (1 H, t, $J = 7$ Hz), 4.01 (2 H, s)) with LiCl (15 h, room temperature)⁷ and then to bromide **7** (85%; NMR δ 5.41 (1 H, t, $J = 7$ Hz), 3.93 (2 H, s)) with NaBr (DMF, 3 h, room temperature).

The dianion **8a** of α -methyltetronic acid (**8**)⁸ was generated using sodium hydride (1 equiv, THF-HMPA (1:1)), followed by butyllithium (1 equiv in hexane). A consideration of the resonance forms of this species, which logically include the furanoid structure **8b** as a major contributor, suggested that alkylation should occur with high selectivity at the γ position.⁹ In fact, treatment of **8** with **7** (THF, -60°C and then 24 h at room temperature) afforded the γ -substituted tetronic acid **9** (NMR δ 8.8 (1 H, br), 5.23 (1 H, t, $J = 7$ Hz), 4.67 (1 H, m),

