oratories, Ann Arbor, Mich.) on two separate samples gave the following observed *vs.* calculated percentages: Na, 10.90 *vs.* 11.05; C, 51.18 *vs.* 51.13; N, 6.64 *vs.* 6.70; H, 8.53 *vs.* 8.62.

(2) The volume and pressure of hydrogen produced by reaction with water[16] yielded 0.94 and 0.95 ± 0.03 mol of H_2 per mole of compound for two samples.

(3) A sample which had been decomposed with water was titrated with HCl. It required 3.98 ± 0.05 equiv per mole. After neutralization of the NaOH produced, the titration curve was identical with that obtained by titration of $NaC^+ \cdot Cl^-$ in water.

(4) When the samples were dissolved in liquid ND_3 the proton nmr spectrum of the resulting deep blue solution was the same as that of a cryptate salt in this solvent except for a paramagnetic shift induced by the presence of the solvated electron. Decomposed samples when dissolved in $CDCl_3$ always gave only the cryptate proton nmr spectrum.

In spite of the shiny metallic appearance, the conductivity of extruded rods and of packed powders was so low that low-current methods were required. The powdered sample was compressed between two aluminum plates in an inert atmosphere box. Teflon spacers were used to prevent contamination by air and moisture. During measurement of the current with a Keithly electrometer, the samples were contained within a variable temperature Faraday cage. Ohm's law was obeyed, the current did not change with time, and reversal of the polarity reversed the current immediately. These results are consistent with electronic conduction. The reversible variation of the resistance with temperature, together with rough estimates of the contact area and thickness yield a specific resistance (ρ) which changes from $\sim 5 \times 10^{13}$ ohm cm at $0°$ to 7×10^9 ohm cm at $60°$. The magnitude of the resistance, its change with temperature and the electronic nature of the conductivity are all characteristics of a semiconductor. However, a graph of log ρ *vs.* $1/T$ shows systematic curvature with a smaller slope at high temperatures. Esr studies of the washed powder show only a barely detectable signal at the highest gain.

Because **1** forms stable complexes with the alkali *cations*, we presumed that Na^+ was trapped in the "crypt" and that the counterion was Na^-. Another possibility was that the "outside" sodium consisted of Na^+ and a partially delocalized electron pair.

Single-crystal X-ray diffraction studies show that the space group is $R32$ with three molecules per unit cell (hexagonal axes). Refinement of the structure ($R = 0.085$) gives the following information.

(1) One of the sodium species is trapped in the "crypt" with interatomic distances which are very close to those reported for the sodium cryptate iodide structure.[17] This strongly indicates that the sodium cation is the trapped species.

(2) The other sodium species is outside of the "crypt" at a large distance from other atoms. For example, the amine nitrogen is at 5.55 Å and the closest oxygen is at 5.76 Å. The logical conclusion is that the outside sodium is negatively charged.

Since both the metal and the complexing agent can be

varied, it is likely that other compounds of this type can be prepared.

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Structure of a Sesquiterpene, Cuauhtemone, and Its Derivative. Application of Partially Relaxed Fourier Transform ^{13}C Nuclear Magnetic Resonance
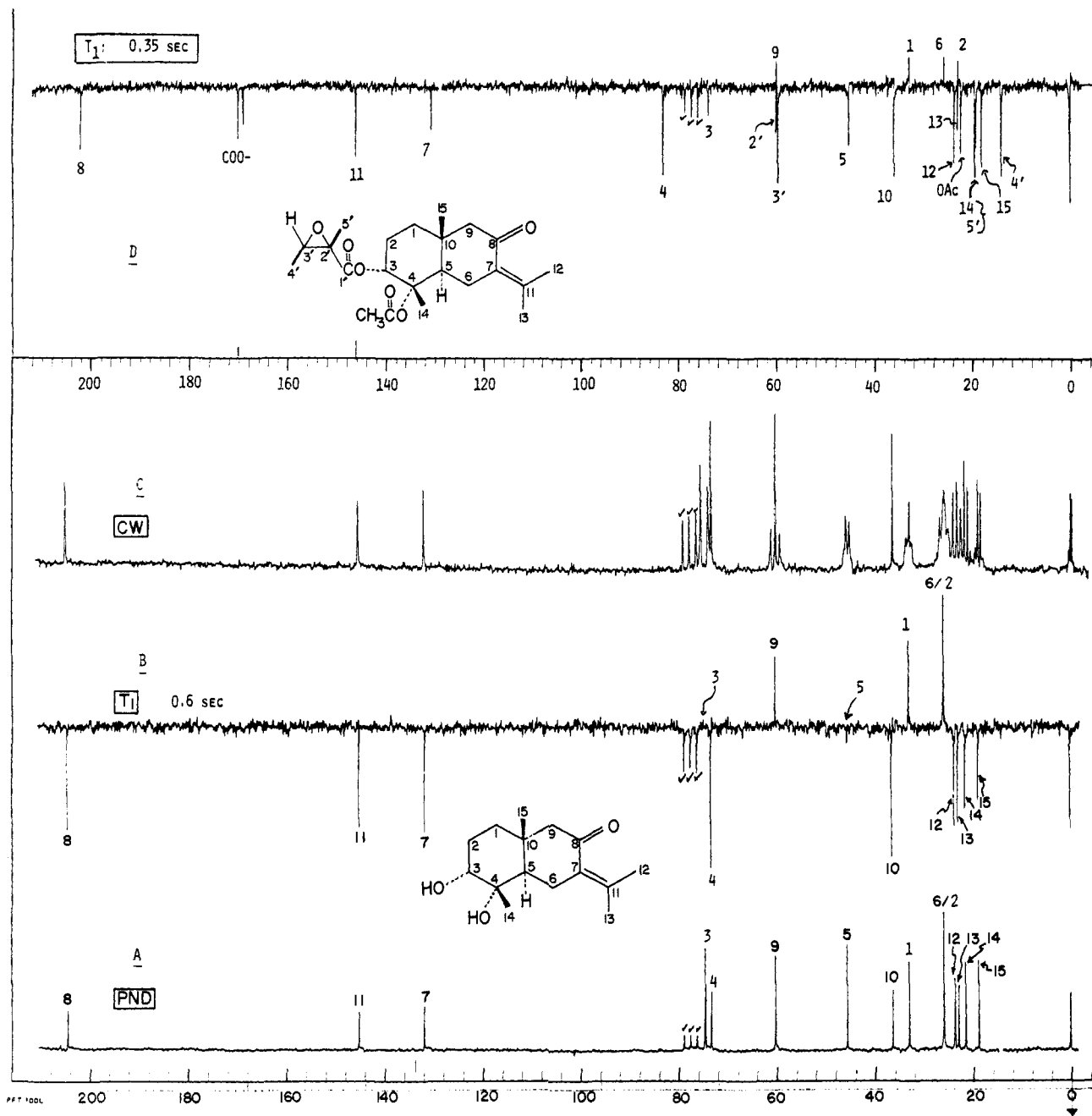
Sir:

The following studies were carried out mainly for the purpose of exploring the usage of partially relaxed Fourier transform (PRFT) ^{13}C nmr techniques to structure determination. Cuauhtemone **1**, a plant growth inhibitor,[1] was obtained in 0.039% yield from the nonsaponifiable matter of the aereal part of *Pluchea odorata* (*Compositae*, the Mexican medicinal shrub "Cuauhtematl"), by silica gel chromatography: mp 140°; [α]D 59.2°; $C_{15}H_{24}O_3$; mass spectrum M^+ 252.1704 (base peak; calcd, 252.1725); uv (MeOH) 254 nm (ϵ 7700); CD (MeOH) 252 nm ($\Delta\epsilon$ -2.76), 322 ($\Delta\epsilon$ +1.25); ir (dilute solution in $CHCl_3$) 3640 (free OH), 3560 (intramolecularly bonded OH), 1675, and 1585 cm^{-1}. The diester **2** was obtained in a 0.012% yield by isopropyl ether extraction of the petroleum ether soluble material of the plant: mp 150°; [α]D +145°; $C_{22}H_{32}O_6$ (correct elemental analysis and osmometric molecular weight); mass spectrum (no M^+ observed) base peak 216.1493 (calcd for $C_{15}H_{20}O$, 216.1514); uv (MeOH) 255 nm (ϵ 7550); CD (MeOH) 248 nm ($\Delta\epsilon$ -1.70), 318 ($\Delta\epsilon$ +0.54); ir ($CHCl_3$) 1740 and 1650 cm^{-1}. Hydrolysis of **2** with sodium carbonate–methanol gave **1**. The uv and ir data suggested the presence of an s-cis tetrasubstituted enone moiety.
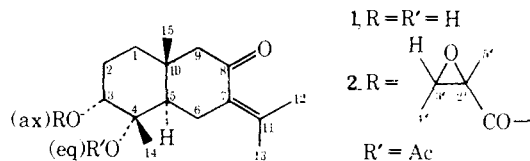
In spite of the relatively small number of protons, the pmr spectrum measured under various conditions was unique in that it only afforded very limited information, due to intensive coupling, overlap of signals, coincidence of magnetically nonequivalent protons (see **3**), and broadening upon addition of shift reagents. Accordingly the techniques of PFRT ^{13}C nmr[2] were employed maximally (Figure 1).

(1) Cuauhtemone exhibits growth inhibition against corn and bean seeds; unpublished results by Dr. M. R. Grarciduenar, Monterrey Institute of Technology, Monterrey, Mexico.
(2) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968); R. Freeman and H. D. W. Hill, *ibid.*, **53**, 4103 (1970); A. Allerhand, D. Doddrell, V. Gushko, D. W. Cochran, E. Wenkert, P. J. Lawson, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, **93**, 544 (1971); D. Doddrell and A. Allerhand, *Proc. Nat. Acad. Sci. U. S.*,

(16) R. R. Dewald and J. L. Dye, *J. Phys. Chem.*, **68**, 128 (1964).
(17) D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, **29**, 396 (1973).

Figure 1. (A) Proton noise decoupled (PND) natural abundance ^{13}C Fourier transform nmr spectra of the spectrum of 1 in CDCl₃ at 25.149 MHz. The recycle time was 2 sec and the number of scans was 16,384, ∼100-mg sample. The instrument used was a JEOLCO PS-100. (B) PRFT spectrum of 1 at interval time τ = 0.6 sec, recycle time 10 sec, and 25,524 scans, ∼100-mg sample. (C) Continuous wave (CW) decoupled spectrum of one irradiated at 1.1 ppm upfield from TMS in the ¹H spectrum; the number of scans and recycle time used are the same as for A. (D) PRFT spectrum of 2 at interval time τ = 0.35 sec, recycle time 10 sec, 26,107 scans, ∼100-mg sample. Peaks with check marks denote CDCl₃ signals.

Note that in the T_1 spectrum of 1 at τ 0.6 sec (Figure 1B), only the methylene peaks appear as positive signals while the methine peaks are nulled and the other carbon peaks remain negative. The continuous wave (CW) decoupled spectrum (Figure 1C) accounted for the missing carbon in the PND spectrum (Figure 1A) by showing the coincidence of C-2 and C-6 signals. In the T_1 spectrum of 2 at τ 0.25 sec (Figure 1D), again only the methylene peaks are seen as positive. The congested

68, 1083 (1971); G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *J. Amer. Chem. Soc.*, **95**, 1527 (1973); F. W. Wehrli, *J. Chem. Soc., Chem. Commun.*, 379 (1973); K. Nakanishi, V. P. Gullo, I. Miura, T. Govindachari, and N. Visawanathan, *J. Amer. Chem. Soc.*, **95**, 6473 (1973).

23- and 60-ppm regions in Figure 1D especially show the advantage of the T_1 technique in simplifying assignments. The s-cisoid enone moiety is substantiated by the following cmr data for pulegone³ (cuauhtemone numbering): C-7, 131.7; C-11, 141.5; C-12, 22.0; C-13, 22.9; C-9, 50.7 ppm.

A single frequency decoupling of the two-proton peak at 2.21 ppm (pmr, 9-H) in 1 (see 3) sharpened the cmr 60.2-ppm signal, and this correlated the two signals. The singlet nature of the 2.21-ppm methylene peak re-

(3) J. Jautelat, H. B. Grutzner, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **65**, 288 (1970); L. F. Johnson and W. Janowiski, "Carbon-13 NMR Spectra," Wiley, New York, N. Y., 1972, p 399.

quires this to be adjacent to a quaternary carbon (C-10, and not to C-5) and hence the cisoid enone is linked as shown.

3(pmr data)

4(cmr data)

5(pmr data)

6 (cmr data)
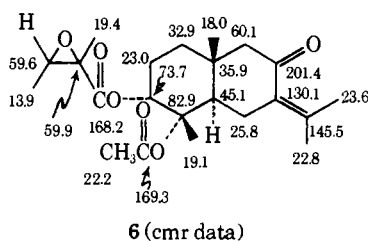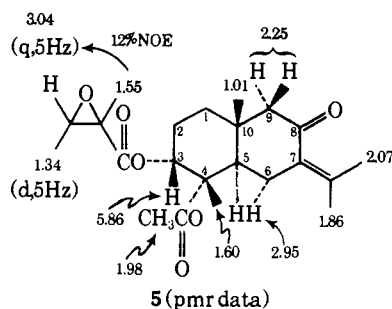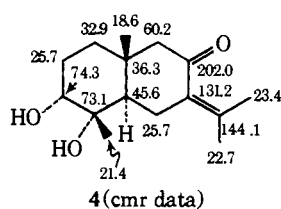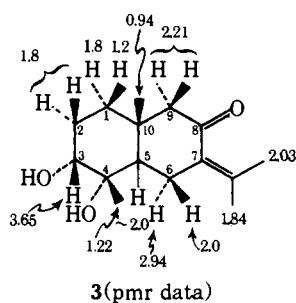
The α-glycol system was proven by consumption of 1 mol of periodate to give the C-3–C-4 cleaved aldehyde ketone with an expected M^+ peak at m/e 250. The α-glycol is cis in view of the ready formation of an acetonide.[4] Moreover, the fact that the 3-H pmr peak of 1 at 3.65 ppm ($W_{1/2}$ = 4 Hz) still retained its narrow half-band width of 4 Hz at 3.94 ppm in the acetonide indicated that the 3-OH and 4-OH are axial and equatorial, respectively, and thus no conformational change had occurred upon acetonide formation; this was corroborated by its CD data, 252 ($\Delta\epsilon$ −2.50) and 318 nm ($\Delta\epsilon$ +1.17), which were similar to those of cuauhtemone itself.

Originally the sec-OH–t-OH glycol was considered to be attached to C-2–C-3. This was due to the nmr observation that the 1.8-ppm pmr peaks (a 2 H doublet with J = 2.5 Hz overlapping a broad 1 H multiplet) collapsed to a singlet upon decoupling of the 3.65-ppm methine proton. At this point, however, preliminary results of an independent direct X-ray analysis of cuauhtemone showed the glycol was most likely to be

(4) (a) Structure fully supported by spectroscopic data. (b) Compound prepared by the method of J. McCloskey and M. McClelland, J. Amer. Chem. Soc., 87, 5090 (1965).

attached to C-3 and C-4.[5] The proton peaks in question, i.e., 1-H and 2-H, in the ester 2 were totally submerged under other signals and thus afforded no information. However, decoupling experiments carried out after addition of Eu(fod)₃ showed the presence of the grouping $^1CH_2$–$^2CH_2$–$^3CH(O)$ and this now leads to planar structure 1.[6]

The cis-glycol hydroxyls and 10-Me are trans since (i) the 10-Me pmr signal remained unchanged at 0.97 ppm in the 3-monoacetate[4a] and (ii) only a negligible shift of the 10-Me signal was seen upon Eu(dpm)₃ addition to the diol 1. In contrast, the Eu reagent caused a large shift in the ∼1.8-ppm 1-H[7] and 2.94-ppm 6-H peaks; these shifts, together with the significantly lower chemical shifts of these protons as compared to their geminal partners (see 3), are accounted for by a trans ring junction and a 1,3 relation between 3α-OH(ax)–1α-H(ax) and between 4α-OH(eq)–6α-H(eq).

Flexibility of the enone group prevented application of the various rules proposed for determining the enone chirality,[8] and hence the following method was employed for determining the absolute configuration. A differential CD curve before and after addition of Pr-(dpm)₃ to a CCl₄ solution of the diol showed a negative peak at 317 nm ($\Delta\Delta\epsilon$ −0.8), corresponding to a negative chirality between the glycol hydroxyl groups,[9] and this leads to the absolute configuration shown in 1.

The ester functions in 2 were shown to be an acetate and a 2,3-epoxy-2-methylbutyrate by pmr. Detection of a 12% NOE on 3′-H upon irradiation of 2′-Me showed the latter ester to be epoxyangelate. As the 3-H signal in 2 is at 5.86 ppm in contrast to the 3-H chemical shift of 4.83 ppm in cuauhtemone 3-monoacetate,[4a] the epoxyangelate is located at C-3, and this leads to structure 2.

(5) We are most indebted to Professor W. H. Watson, Jr., Texas Christian University, for this preliminary information. The X-ray studies have since been completed (relative configuration) and will be published elsewhere by Dr. Watson.

(6) The cuauhtemone pmr signals of $^1CH_2$–$^2CH_2$–^3CH thus constitute a complex proton system which is not amenable to first-order analysis.

(7) The two C-1 methylene protons were found to be in the 1.2- and 1.8-ppm regions since single frequency irradiation around 1.4 ppm, the intermediate position (and a blank region in the pmr), decoupled the 32.9-ppm C-1 cmr signal.

(8) C. Djerassi, R. Records, E. Bunnenberg, K. Mislow, and A. Moscowitz, J. Amer. Chem. Soc., 84, 870 (1962); W. B. Walley, Chem. Ind. (London), 1024 (1962); R. E. Ballard, S. F. Mason, and G. W. Vane, Discuss. Faraday Soc., No. 35, 43 (1963); G. Snatzke, Tetrahedron, 21, 439 (1965); A. W. Burgstahler and R. C. Barkhurst, J. Amer. Chem. Soc., 93, 4058 (1971).

(9) K. Nakanishi and J. Dillon, J. Amer. Chem. Soc., 93, 4058 (1971).

(10) National Institutes of Health Postdoctoral Fellow, 1972–1974.

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The Benzocyclononatetraenyl Anion and 1,2-Benzocyclonona-1,3,5,7-tetraene

Sir:

The cyclononatetraenyl anion (1) occupies a rather unique position among all-cis π-carbomonocycles in