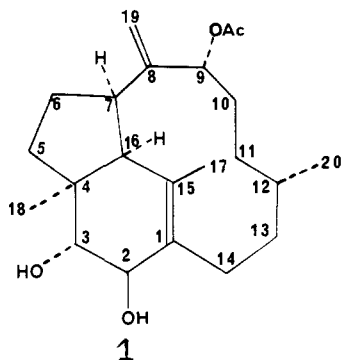


Figure 1. A computer generated perspective drawing of trinervi-2 β ,3 α ,9 α -triol 9-*O*-acetate (**1**). Hydrogens are not shown for clarity, and the absolute configuration is deduced from spectral measurements.

standard unweighted crystallographic residual to 0.039 for the observed data. Tables of fractional coordinates, bond distances, bond angles, and observed and calculated structure factors can be found in the supplemental material.

The conformations of the two crystallographically independent molecules are approximately the same and the two molecules are related by a noncrystallographic twofold axis. Figure 1 is a computer generated drawing of the final x-ray model for one of the unique trinervi-2 β ,3 α ,9 α -triol 9-*O*-acetate molecules. As can be seen, the tricyclic array of **1** has a dome like shape. The bridgehead hydrogens at C(7) and C(16) and



the methyl substituents at C(4), C(8), C(12), and C(15) protrude from the convex surface. The five-membered ring exists in an envelope conformation with C(5) being 0.61 Å below the least-squares plane of the other four atoms. The conformation of the large ring may be affected by the intermolecular hydrogen bonding. Hydrogen bonds occur between O(21) and O(22') (2.89 Å), O(21) and O(25') (2.81 Å), O(22) and O(22') (2.94 Å), and O(25) and O(21') (2.99 Å). There is also a suggestion of disorder at C(11) in one of the independent molecules. In general bond distances and bond angles agree well with expected values and no abnormally short intermolecular contacts occur. Structure **1** also represents the absolute configuration which is based on CD measurements employing Pr(dpm)₃.¹²

In the succeeding communication we describe the isolation and structures of other congeners found in these soldier secretions.¹²

Acknowledgments. The studies have been supported by a grant from United Nations Development Project to ICIPE, NIH AI 10187 to Columbia University. We wish to thank Professors K. Nakanishi and J. Meinwald for helpful discussions.

Supplementary Material Available: Fractional coordinates (Table I), important bond distances (Table II), important bond angles (Table III), and observed and calculated structure factors (Table IV) (16 pages). Ordering information is given on any current masthead page.

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- (13) NIH Postdoctoral Fellow (1976-1977), Fellowship AI 05076.
- (14) Camille and Henry Dreyfus Award (1972-1977).

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Nasute Termite Soldier Frontal Gland Secretions. 2. Structures of Trinervitene Congeners from *Trinervitermes* Soldiers

Sir:

In the preceding communication we presented the structure of trinervi-2 β ,3 α ,9 α -triol 9-*O*-acetate (TG-2), **1**, as elucidated by x-ray crystallography.¹ In the following we describe the isolation and spectral studies of TG-2 and the structures of five other congeners found in the defense secretions of these termites.

Crushed heads of major soldiers (1000-2000 individuals) or minor soldiers (2000-10 000 individuals) of *Trinervitermes graciosus* (Sjostedt) (TG) and *T. bettonianus* (Sjostedt) (TB) were extracted with 3:1 *n*-hexane:ether. The extracts were chromatographed on Florisil and the diterpenes were eluted with mixtures of ethyl acetate and benzene.

Trinervi-2 β ,3 α ,9 α -triol 9-*O*-Acetate (TG-2), **1**: The compound is relatively unstable, as were most of the trinervitenes, but could be stored without decomposition under Ar at 0° in the dark. Pertinent physical data of TG-2 are as follows: high resolution MS, 362 (M⁺) C₂₂H₃₄O₄, 320 (M - 42, ketene), 256 (M - CH₃COOH - H₂O - CO, base); uv (MeOH) end absorption; ir (CCl₄) 3500 (OH), 1735 (OAc), 1665 (=CH₂), 1670 cm⁻¹ (C=C). The nature of the 22 carbon atoms was determined by the techniques of PND, CWD, PRFT, and combined PRFT/CWD⁴ employing a JEOL micro ¹³C NMR probe, PS-100 instrument (Figure 1). The ¹H NMR spectra

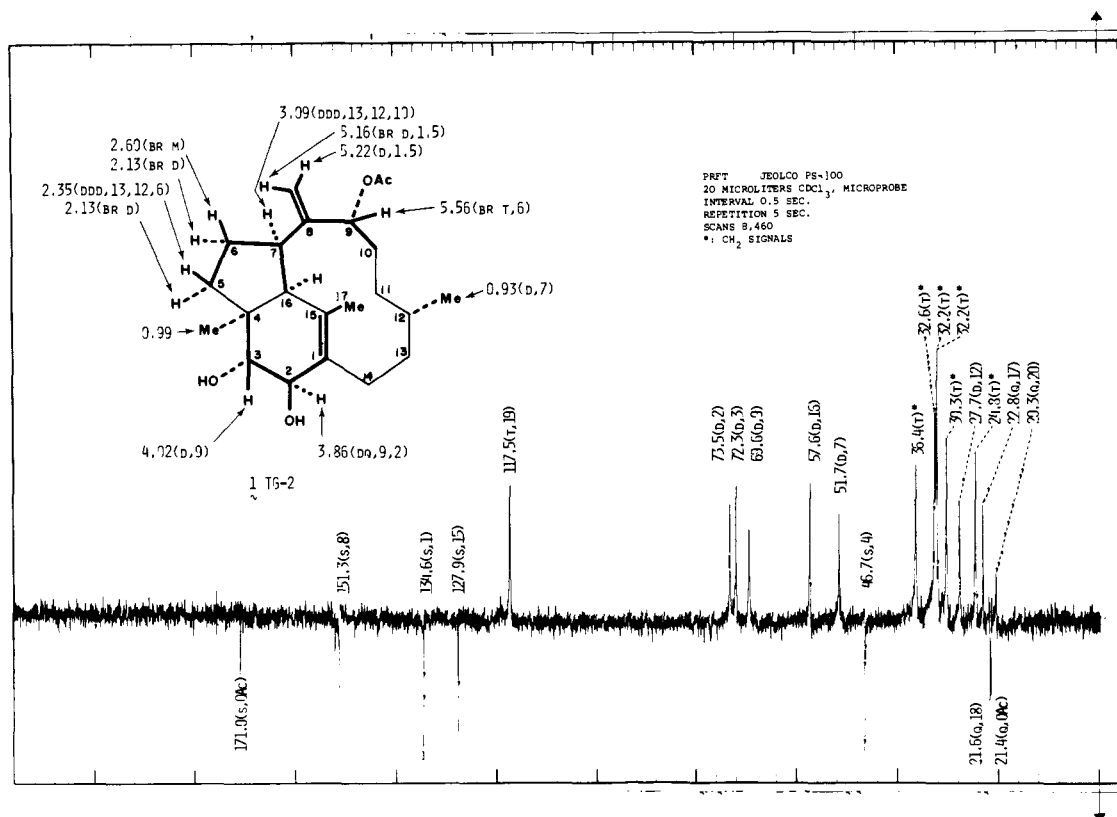


Figure 1. ^1H NMR data (inset) and ^{13}C NMR spectrum of TG-2, **1**. ^{13}C NMR was measured by the PRFT method, $(180^\circ - \tau - 90^\circ - T)_n$, where τ is 0.5 s and T is 5 s. The sample (6 mg) in 20 μl of CDCl_3 was measured by a JEOL ^{13}C NMR microprobe, 8460 scans. The six methylene signals are asterisked.

as measured by Varian 100-MHz and Bruker 360-MHz instruments clarified the proton systems shown by bold lines in structure **1**, Figure 1. Although the presence of three additional methylene groups was evident from the ^{13}C NMR it was not possible to link them to the mentioned proton system due to the overlap of the ^1H NMR peaks.^{5,6} Moreover, the marked instability prevented derivatizations, e.g., reaction with *p*-bromobenzoyl chloride in pyridine yielded the 2-monobenzoate which was more unstable than the parent compound. However, periodate cleavage yielded the 2,3-seco-dialdehyde, CI/MS (methane) 361 (MH^+), 389 ($\text{M} + 29$), uv (MeOH) 250 nm (ϵ 3430). The entire structure of the unique diterpene only became apparent by x-ray crystallographic studies.¹ The x-ray results showed the 7-H to be in the deshielding cone of the exocyclic methylene and this accounted for the anomalously low chemical shift (3.09 ppm).

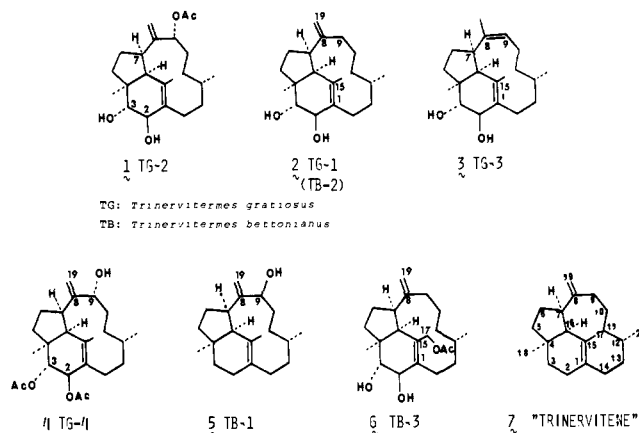
The absolute configuration of TG-2, **1**, was determined by CD measurements carried out in CCl_4 in the presence of $\text{Pr}(\text{dpm})_3$,⁷ $\Delta\epsilon_{313} -14.35$, which indicated that the 2,3-diol group has a negative chirality.

The structures of the remaining congeners followed from comparisons of ^{13}C NMR and ^1H NMR spectra with those of TG-2, and other spectral data.

Trinervi-2 β ,3 α -diol (TG-1), **2**: Raman (solid), 1650 (1,15-ene) and 1631 cm^{-1} (8,19-ene); absence of 9-acetoxyl function (^{13}C NMR, ^1H NMR).

Isotrinervi-2 β ,3 α -diol (TG-3) **3**: Raman (CCl_4), 1651 (1,15-ene) and 1664 cm^{-1} (8,9-ene); ^1H NMR, absence of exocyclic methylene and the low-field 3.09 ppm 7-H signals, and appearance of 8-Me at 1.59 ppm (d, $J = 1.8$ Hz) and 9-H at 5.28 ppm (ddq, $J = 12, 6$ and 1.8 Hz)

Trinervi-2 β ,3 α ,9 α -triol 2,3-*O*-diacetate (TG-4), **4**: ^1H NMR, 5.35 (d, $J = 9.5$ Hz, 2-H), 5.59 (br d, $J = 9.5$ Hz, 3-H), 4.94 ppm (m, 9-H); ^{13}C NMR, 77.66 ppm (C-9); ir (CCl_4), 3470 cm^{-1} (strong br, intermolecular H-bond). The low chemical shift of the 9-H signal (4.94 ppm, deshielding cone



of the 8,19-ene) and intermolecularly H-bonded character of the 9-OH establish the configuration at C-9.

Trinervi-9 β -ol (TB-1), **5**: ^1H NMR, 4.07 ppm (dd, $J = 10, 6$ Hz, 9-H); ir (CCl_4), 3620 cm^{-1} (w, free OH). The high chemical shift of the 9-H ^1H NMR signal (shielding cone of 8,19-ene) and the ir hydroxyl band are in contrast to the data of TG-4. This information indicates that the 9-OH is β -oriented, i.e., inside the 11-membered ring structure, and is sterically prevented from intermolecular H-bonding.

Trinervi-2 β ,3 α ,17-triol 17-*O*-acetate (TB-3) **6**: Raman (CCl_4), 1646 (1,15-ene) and 1639 cm^{-1} (8,19-ene); ^1H NMR absence of olefinic Me and appearance of AB quartet (2 H) centered at 4.75 ppm ($J = 12$ Hz, 17-H).

Except for diacetate TG-4, **4**, which was found only in *T. graciosus* minor soldiers, and TB-3, **6**, which was found only in *T. bettonianus* soldiers, these compounds were universally present among these and other *Trinervitermes* species examined.³ Based on the widespread occurrence of these diterpenes, we propose the name "trinervitene" for the parent diene hy-

drocarbon (7). The close structural resemblance between the trinervitene soldier substances and the Neocembrene-A (natsutene),⁸ reported to be a trail pheromone for an Australian *Nasutitermes* species, implicates cembrene-type intermediates in the biogenesis of the trinervitenes.

Acknowledgment. We are grateful to Professor J. Meinwald for discussions, and to Professor C. Djerassi's group for measurements of the 360-MHz spectrum of TG-2,⁶ and to Ms. V. Parmakovich for MS measurements. We also wish to thank Mr. S. Ogendo for technical assistance, Drs. M. Kaib, O. Bruinsma (ICIPE), and Mr. R. Buxton (Tsavo Research Project, Voi, Kenya) for their help during collections.⁹

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- (2) *T. gratiosus* was collected in Voi and in Kibwezi, Kenya; *T. bettonianus* was collected in Machakos and in Rulru, Kenya. Most studies were carried out on the former species because of its optimal size and abundance as well as the simplicity of its major soldier secretion.
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Inelastic Electron Tunneling Spectroscopy of Carbon Monoxide Chemisorbed on Alumina-Supported Transition Metals

Sir:

The first successful attempt to obtain infrared spectra of carbon monoxide on supported transition metals appears to have been performed by Eischens, Francis, and Pliskin, with the report of CO stretching modes (1800–2100 cm^{-1}).¹ Similar observations on the chemisorption of carbon monoxide with vibrational spectroscopy have been successfully made by other workers.² In most cases, however, the associated metal-carbon stretching vibrations and carbon-oxygen bending modes, which occur at lower frequency (800–200 cm^{-1}) cannot be observed, because the support material interferes strongly in the low frequency region. We wish to report here the successful application of inelastic electron tunneling spectroscopy³ (IETS) for the observation of metal-carbon and carbon-oxygen vibrational modes of carbon monoxide chemisorbed on alumina supported transition metals.

In our experiments, an aluminum electrode is evaporated onto a glass slide and allowed to oxidize in air at 110 °C to form

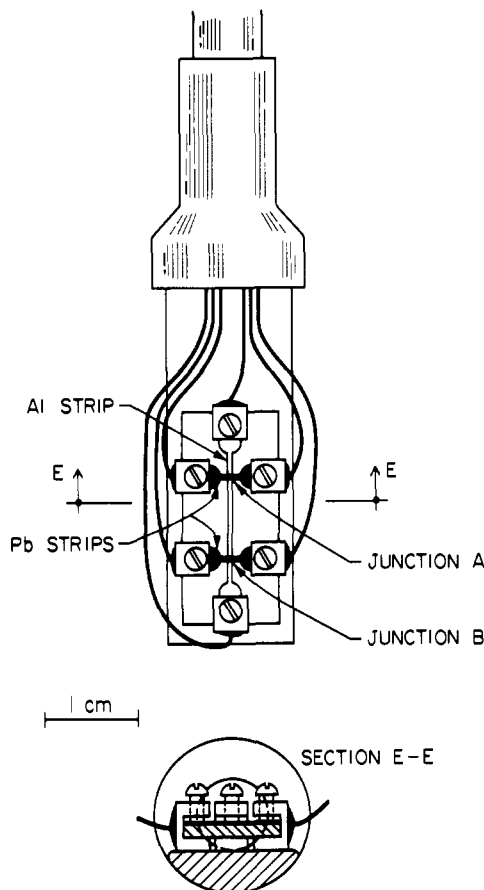


Figure 1. Two Al-oxide-Rh-CO-Pb junctions are formed at the intersections of the crossed metal films. Electrical contact to the junctions is made with brass screw clamps. Tunneling spectra are taken electronically with the sample inserted down the neck of a conventional helium storage Dewar.

the necessary alumina insulating layer. After the alumina is cleaned in an argon glow discharge, a very thin layer of transition metal is evaporated onto it and exposed to carbon monoxide. The junction is completed with an evaporated top metal electrode of lead. The metal-insulator-metal junctions are formed at the intersections of crossed metal electrodes. See Figure 1.

Figure 2 shows a series of tunneling spectra for various coverages of rhodium metal on the alumina. The coverage was determined with an oscillating quartz crystal microbalance and, of course, represents an average over the surface; most of the coverages are submonolayer. The residual gas pressure before the Rh evaporation was in the range 4×10^{-8} to 2×10^{-7} Torr. The pressure was increased to 10^{-5} Torr of CO during the Rh evaporation to ensure that CO would dominate the residual gases. This pressure was maintained for 100 s after the Rh evaporation to give a total exposure of 10^3 Langmuirs of CO. (The spectra were insensitive to exposure >100 Langmuirs.)

The spectrum with Rh = 0 Å is free of any vibrational peaks due to CO; all these peaks are present in junctions not exposed to CO. They are due to vibrational modes of the alumina, OH groups bound to the surface of the alumina, and the aluminum electrode.³

Studies on rhodium carbonyls ($\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$)⁴ suggest that rhodium-carbon stretching modes should be in the range 400–600 cm^{-1} . At low rhodium coverages (0.5 and 1 Å) we observe only one peak in this range: at $408 \pm 5 \text{ cm}^{-1}$. As coverage increases, this peak grows in size and two new peaks appear: a sharp one at $454 \pm 5 \text{ cm}^{-1}$ and a broad one centered at $580 \pm 10 \text{ cm}^{-1}$. The appearance of