

Figure 2. The double reciprocal plot of the rate of decomposition of the complex: — $[RH_2, A]$; - - - $[RH_2-4-d_1, A]$; ···· $[RH_2-4-d_2, A]$. The concentration of the oxidant was fixed at 1×10^{-3} M and the reaction was followed at 550 nm. The lowest curve (- - -) corresponds to the reciprocal $A_0 - A_\infty$ determined from the kinetic runs for each concentration of dihydronicotinamide used.

namide derivatives indicate that the concentration of dihydronicotinamide at which the rate is half maximal is identical with that for the dihydro form. Since this parameter is independent of the isotopic form of the dihydronicotinamide used and is the same as that obtained from plotting the initial absorbance increase as a function of dihydronicotinamide, this concentration must represent the dissociation constant of the charge-transfer complex. Of perhaps greater significance is that the pseudo-first-order rate constant extrapolated at infinite dihydronicotinamide concentration does not exhibit a substantial primary isotope effect even though a substantial isotope partitioning ratio is observed in the product *N*-methylacridan when monodeutero *N*-benzyl dihydronicotinamide-4- d_1 is used as the reducing agent (Table I). Therefore these data obtained at saturating concentrations of dihydronicotinamide exhibit the same divergence of the kinetic isotope effect and the isotope partitioning ratio as was observed previously under strict bimolecular conditions for *N*-propyl dihydronicotinamide.¹

The most definitive statement that can be made from these data is that the charge-transfer complex observed cannot be the intermediate indicated in eq 1, as in this case a pronounced isotope effect would be expected on the extrapolated pseudo-first-order rate constant. Although the scheme summarized in eq 3 cannot be absolutely excluded, it must be indicated that if the kinetically competent charge-transfer complex is considered to be Z of that scheme, the problems of postulating the existence of a single noncovalent complex such as X, which have been discussed above, still remain.

In view of the recent suggestion of (a) the likely importance of radical ion pairs in flavin and dihydronicotinamide reductions,¹¹ (b) the expectation that such intermediates might form via complexes of the nature identified here, and (c) the a priori argument favoring the formation of two intermediates in any case, we consider that the scheme summarized in eq 2 most accurately represents the detailed mechanism of the dihydronicotinamide reduction of *N*-methylacridinium ion. The direct demonstration of intermediate Y_2 and the elucidation of its chemical nature should be valuable in understanding the mechanisms of chemical and enzymic dihydronicotinamide reductions.

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Nasute Termite Soldier Frontal Gland Secretions. 1. Structure of Trinervi-2 β ,3 α ,9 α -triol 9-*O*-Acetate, a Novel Diterpene from *Trinervitermes* Soldiers

Sir:

The defensive secretions ejected from the nozzle-like frontal glands of *Trinervitermes* and *Nasutitermes* soldiers (Isoptera: Termitidae: Nasutitermitinae) have been reported¹⁻⁵ to contain polyisoprenoids of unknown structure dissolved in monoterpene hydrocarbons. These sticky secretions mechanically disable ant predators,⁶ and also appear to possess some systemic toxicity to the ants.^{4,7-9}

We wish to report the results of x-ray crystallographic studies carried out on one of the major constituents, "TG-2", of the soldier secretions of *Trinervitermes gratosus* Sjoestedt. It is a novel diterpene skeleton with a bridgehead double bond in an 11-membered ring.

Trinervi-2 β ,3 α ,9 α -triol 9-*O*-acetate crystallized upon slow evaporation of an ether solution under an argon atmosphere. The crystals formed in the monoclinic space group *C*2 with $a = 15.726$ (3) Å, $b = 10.903$ (2) Å, $c = 25.749$ (5) Å, and $\beta = 106.52$ (1)°. The volume indicated that the asymmetric unit consisted of two complete molecules of $C_{22}H_{34}O_4$ for a physically reasonable calculated density of 1.14 g cm⁻³. All unique diffraction maxima within a 2θ sphere of 114° were measured on a fully automated four-circle diffractometer using graphite monochromated Cu K α radiation (1.5418 Å). The crystal was sealed in a Lindemann capillary. Of the 3092 reflections measured, 2297 (74%) were considered to be observed ($F_o^2 \geq 3\sigma(F_o^2)$) after correction for polarization, background, and Lorentz effects.

An initial phasing of the normalized structure factors was done with a weighted, multiple solution tangent formula approach.¹⁰ Among the solutions with the lowest figures of merit was one displaying a chemically reasonable eight atom fragment. When this fragment was displaced 1.25 Å in the z direction and used to calculate starting phases for tangent formula recycling, additional chemically reasonable atoms appeared which eventually were elaborated into a complete trial structure. Full-matrix least-squares refinements¹¹ with anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogens lowered the

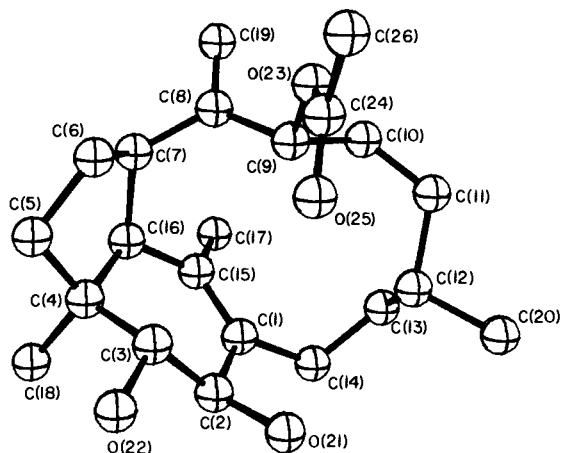
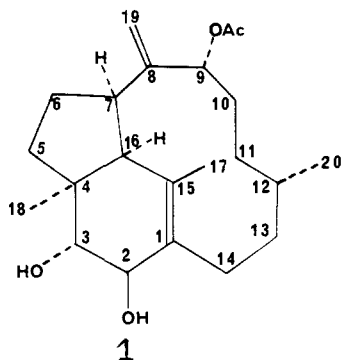


Figure 1. A computer generated perspective drawing of trinervi-2 β ,3 α ,9 α -triol 9-*O*-acetate (**1**). Hydrogens are not shown for clarity, and the absolute configuration is deduced from spectral measurements.

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

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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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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 gratosus* (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