gular widths increase from 20° to 50° with increasing translational energy. The experimental in-plane yield (HgI number density signal per unit density of reactant Hg and I_2) is determined by integration of the angular distributions.

The determination of the threshold energy for an endoergic reaction depends upon a very accurate knowledge of the distribution of relative translational energy and its convolution of the actual cross section functionality.[5] Each angular distribution is fit by convoluting an assumed center-of-mass detailed differential cross section with the known relative velocity distribution. The predicted product yield is obtained by integrating these fits over the laboratory angles.[6]

The resulting experimental and calculated yields are presented as a function of the average relative translational energy in Figure 1, where the circles and squares represent data obtained from separate experimental series with two slightly different translational energy distributions. The experimental data are simulated by including in the differential cross section an Arrhenius translational energy dependence[1] with different values of the translational energy threshold, E_{th}. The value of E_{th} has been systematically varied to achieve a best fit to the data, shown in the figure with $E_{\mathrm{th}} = 1.14$ eV.

Since the average internal energy of the I_2 beam is 0.04 eV, the total energy threshold for reaction is 1.18 ± 0.03 eV. As previously mentioned, the reaction has an inherent endoergicity $\Delta E_0° = 1.15 \pm 0.01$ eV. Thus, the intrinsic activation barrier to the reaction is 0.03 ± 0.03 eV (95% C.L.), i.e., the barrier for the exoergic, reverse reaction of I with HgI is essentially zero (within 1 kcal mol^{-1}).

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(6) Details of this procedure are presented in the Ph.D. Thesis of B. E. Wilcomb, Chemistry Department, The University of Texas at Austin, Texas, 1976.

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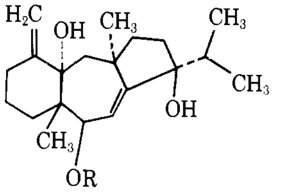
The Isolation and Structure of Dolatriol[1]

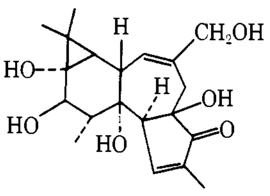
Sir:

Marine Mollusca of the family Aplysiidae (class Gastropoda) are commonly known as sea hares.[2] The poisonous properties of sea hare secretions were already known in pre-Christian times. Indeed, such toxic materials are believed to have been used by Agrippina, mother of Nero (A.D. 37–70) to dispatch relatives blocking his ascent to Roman emperor. The poisonous aspects of an Indian Ocean sea hare were vividly recorded by Grevin in a French work of 1568.[3] Recently, a toxic constituent of the sea hare *Stylocheilus longicauda* was designated aplysiatoxin and its structure was nicely elucidated by the Scheuer group.[4] We have evaluated a small number of such gastropods for antineoplastic constituents and have so far located four species[5] giving extracts with confirmed level activity against the National Cancer Institute's murine P-388 lymphocytic leukemia (PS system). Of special interest has been the Indian Ocean (East Africa) *Dolabella auricularia.* Both ethanol and water extracts from this animal were found to be quite cytotoxic and markedly inhibit growth of the P-388 leukemia.

We now wish to report that careful chromatographic (prepacked Merck Size B silica gel 60 columns and elution with 70:0.3 heptane-acetone)[1] separation (guided by bioassay) of the ethanol extract has led to the first two members of a uniquely different class of diterpene. The new substances have been designated dolatriol 6-acetate (**1a**) and dolatriol (**1b**). Chromatographic fractions (4 ml volumes) 56–65 afforded (0.001% yield) dolatriol 6-acetate (**1a,** $C_{22}H_{34}O_4$, M^+ 362 *m/e*) as large hexagonal needles (from heptane-acetone) melting at 210–212°: ir (KBr) 3570, 3439, 1733, 1638, and 899 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (d, $J = 7$ Hz, 3 H, isopropyl methyl), 0.89 (s, 3 H, C-5 methyl), 1.03 (d, $J = 7$ Hz, 3 H, isopropyl methyl), 1.19 (s, C-12 methyl), 2.09 (s, acetyl methyl), 2.6 (m, 1 H, isopropyl methine), 4.78 (s, 1 H, C-7 H), 4.93 (s, 1 H, C-6 H), 5.28 (d, $J_{ab} = 6$ Hz, 1 H, methylene), and 6.16 (d, $J_{ab} = 6$ Hz, 1 H, methylene). Dolatriol (**1b,** $C_{20}H_{32}O_3$, M^+ 320 *m/e*) was obtained (0.0005% yield from fractions 95–107) as fine needles, mp 235–236° from heptane-acetone and displayed: ir (KBr) 3500, 3410, 1638, and 909 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3 H, C-5 methyl), 0.84 (d, $J = 7$ Hz, 3 H, isopropyl methyl), 1.01 (d, $J = 7$ Hz, 3 H, isopropyl methyl), 1.19 (s, 3 H, C-12 methyl), 4.73 (s, 1 H, C-7 H), 4.89 (s, 1 H, C-6 H), 4.97 (d, $J_{ab} = 6$ Hz, 1 H, methylene), and 5.45 (d, $J_{ab} = 6$ Hz, 1 H, methylene). Under acidic conditions dolatriol 6-acetate (**1a**) was readily converted to dolatriol.



1a, R = COCH₃
b, R = H



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A single crystal of dolatriol 6-acetate of suitable size was obtained by cleaving one of the hexagonal needles as obtained above. The observed Laue symmetry and extinctions correspond to the very unusual rhombohedral space group $R3$ with: $a = 24.152$ (9), $c = 9.544$ (3) Å; $Z = 9$; $\rho_{\mathrm{calcd}} = 1.124$ for $C_{22}H_{34}O_4$, $\rho_{\mathrm{obsd}} = 1.12$ (2) g/cm^3. Diffraction intensities were measured in the θ–2θ scan mode using graphite monochromated Mo K$\bar{\alpha}$ radiation on a Syntex $P\bar{1}$ diffractometer; of the 2646 reflections examined ($\sin\theta/\lambda \leq 0.6497$), a total of 2020 unique reflections were retained with $|F_o| > 0$. No corrections were applied for either absorption or extinction.

The structure was readily solved by direct methods using the MULTAN-74 system of programs.[6] Large block least-squares refinement[7] of the structure with anisotropic thermal parameters and fixed hydrogen positions (234 independent variables in two blocks) yielded a standard residual $R = 0.1297$ for the 1897 strongest reflections; a weighted residual $R_w = (\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2)^{1/2}$ of 0.0865 was obtained with $w = 1/\sigma_F{}^2$. Many of the hydrogen atoms, including those on both hydroxyl groups, were observed in a difference synthesis based on a refined anisotropic model; for the final refinement both O–H atoms were placed as found and all C–H atoms were placed at idealized positions.

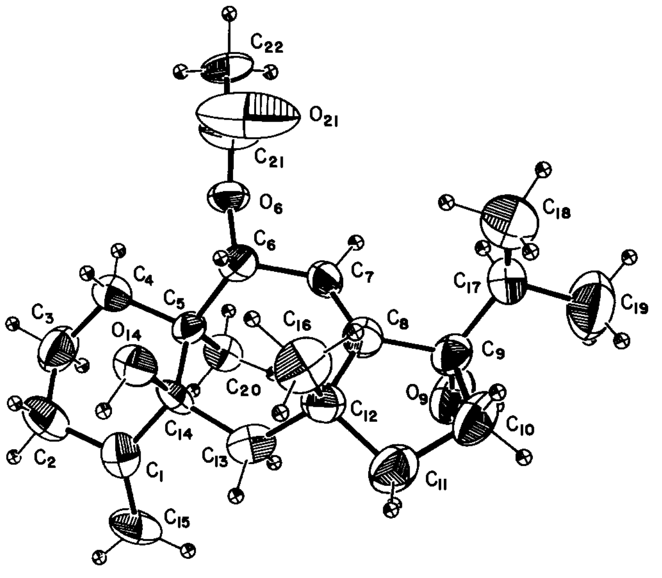

Figure 1.

The perspective view shown in Figure 1 displays the essential conformational features of the molecule. Since the absolute configuration has not been determined only the relative configuration can be shown.

While diterpenes with an angular 6-7-5 ring system such as phorbol (2) are characteristic of the Euphorbiaceae plant family,[8] dolatriol represents the first member of a hitherto unknown linear system.[9,10] Also of interest in respect to dolatriol is the allylic positioning of each oxygen substituent.

The detailed structural features of this molecule as well as the unusual packing scheme will be discussed in a complete presentation of the structure. Evaluation of dolatriol and related substances from *Dolabella* species is presently in progress.

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References and Notes

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(7) All calculations other than data reduction and direct methods were performed with the "CRYSTALS" computing package adapted to the UNIVAC 1110: R. S. Rollett and J. R. Carruthers, personal communication.

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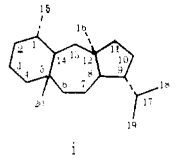
(9) We recommend that the hydrocarbon system of this new class of diterpenes be designated dolastane and numbered as illustrated in structure i.



i

(10) Interestingly, some of the phorbol-type diterpenes are very toxic and cocarcinogenic. L. Crombie, M. L. Games, and D. L. Pointer, *J. Chem. Soc. C*, 1347 (1968). More recently two members of this series have been found to display antineoplastic activity: M. S. Kupchan, I. Ucheda, A. R. Branfman, R. G. Dailey, Jr., and B. Yu Fei, *Science*, **191**, 571 (1976).

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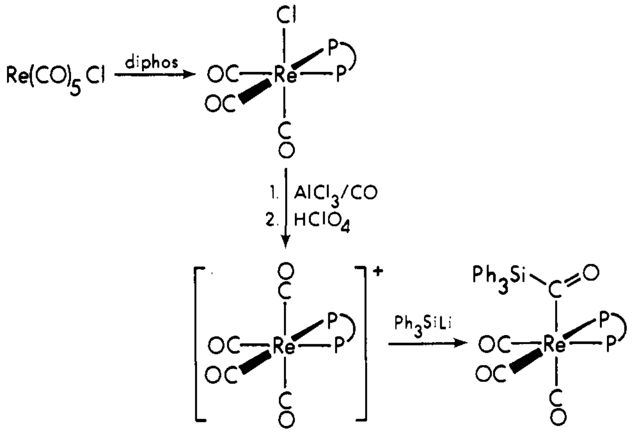
An Acylsilane Derivative of a Transition Metal

Sir:

The physical and chemical properties of acylsilanes, acylgermanes, and acylstannanes are known to differ markedly from those of their carbon analogues.[1-4] As an extension of our interest in transition metal-group 4 chemistry, we have undertaken the preparation of group 4 acyl derivatives of transition metals. We report here the synthesis and characterization of the first transition metal bonded acylsilane, *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**).

Compound **1** was prepared by adding a THF solution of Ph_3SiLi[5] to a slurry of $[Re(CO)_4(diphos)][ClO_4]$[6] (**2**) in THF at 25°. After 90 min, the mixture was concentrated and treated with acetone to precipitate the crude product, which was then recrystallized from methylene chloride-acetone to yield air-stable purple crystals of **1** in 25-30% yield.[7] Upon melting (182-184°), **1** decolorizes and evolves CO, and the mass spectrum, obtainable only above 180°, corresponds to that of the product of thermal decarbonylation *mer*-$Re(CO)_3(diphos)SiPh_3$.

Samples of ^{13}C enriched **1** for spectroscopic studies were prepared using two enrichment procedures. In one, $Re(CO)_5Cl$



(2) **(1)**