It also follows that intensive boring and encrustation can reverse the primary structural relationship between framework and cavity, so that original framework cavities are filled by encrusters while borers remove the frame. The cavity dwellers have a variety of growth attitudes, and the reef stratigraphy can be modified so that, in places, old skeletons overlie young ones. One reef section revealed 30 cm of successive generations of *Agaricia fragilis*, one on another all pointing downward with the oldest at the top. The reversal of the primary framework-cavity structure is best preserved in reef rock made originally of corals having closely knit upright branches, such as *Madracis decactis* and *Porites porites*. For in these examples an interlocking network of encrusters fills in the space between branches, and this is commonly capable of supporting the overlying living coral once the lower branches are merely bored-out passages. Where borers attack the undersides of massive corals, such as *Diploria*, thick encrustations at the base of the resulting mushroom shape are necessary to support the mass of the coral head. For, with time, intense boring at the base of the skeleton nips off the head. Therefore, early burial causing premature death of borers is necessary to preserve, in situ, the mushroom-shaped form of *Diploria*. If not supported by neighboring skeletons, an undermined coral head either topples over into a valley—where it may continue growth, be destroyed by borers, or be buried—or falls onto the lower part of its own skeleton so that it comes to rest a few centimeters below its former position on an "unconformity" surface, along which (with sufficient water circulation) borers may continue their excavation. Inside prominent knobs, several active excavation surfaces are common under one growing coral surface (Fig. 2).

The rate of growth of massive corals (*3*) and the rate of boring by sponges and bivalves (*4*) are of the same order of magnitude. Under certain conditions where boring is favored, and perhaps coral growth is impeded, coral knobs will diminish. For a knob interior may be disintegrating faster than a (seemingly healthy) growing coral can raise the surface. The relative rates of the processes that operate together to produce reef rock will control the nature of the internal structure. The presence of an elevated reef structure indicates the overall predominance of the building processes, but the depth and water circulation limits for vigorous boring activity and the level of loose sediment on a reef may ultimately control the amount of reef framework preserved.

In summary, the upper 2 m of the interior of these patch reefs is composed chiefly of the massive corals, *Diploria*, *Montastrea*, and *Porites*. Commonly, their skeletons have lost the original structure of both their anchorages and final growth surfaces. Unknown quantities of framework have been removed and converted into loose fine sediment by boring organisms. These phases of erosion are preserved as minor unconformities between corals. The collective time significance of these unconformities may be considerable. Selective boring and the relatively late addition of cavity dwellers to the reef structure can result in a progressive substitution of surface-grown corals by cavity encrustations inside the reef. These changes in composition and structure that happen during the fossilization of Bermuda patch reefs show why students of Recent carbonate sedimentary processes should attempt to follow through to the state of preservation, thus making interpretation from depositional to fossil (and vice versa) more complete.

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## Direct Phase Determination from Neutron Diffraction Data of the Structure of Melampodin

Abstract. *The structure of a large complex molecule,* $C_{21}H_{24}O_9$, *has been solved directly from neutron diffraction data by using sigma-2 and tangent refinement methods. As a consequence, the neutron diffraction technique must be reevaluated as a possible primary tool for crystal structure determination.*

Sikka (*1*) has suggested that "direct methods" of phase determination should be applicable to neutron diffraction data when the amount of scattering from hydrogen atoms, defined by

$$Q_H = 100 \sum_H b_H^2 / \sum_i b_i^2$$

($b_i$ is the neutron scattering length of atom *i*), is less than about 30 percent. He further suggested that the upper limit for the number of atoms in the unit cell is about 100. Subsequently, Verbist *et al.* (*2*) successfully applied the $\Sigma_2$ and tangent refinement methods to the solution of L-proline monohydrate ($Q_H = 27$ percent, 80 atoms in the unit cell). We report here the successful solution by direct methods, involving neutron diffraction data, of a noncentrosymmetric crystal structure containing 216 atoms per unit cell.

Melampodin (*3*) is a sesquiterpenoid lactone derived from a Texas ragweed plant and has the composition $C_{21}H_{24}O_9$ (Fig. 1). Its crystal structure has been determined by x-ray diffraction analysis and reported in a brief communication (*4*). The neutron diffraction analysis was undertaken in order to determine precise internuclear distances and angles in this highly strained, fused-ring natural product (*5*).

The crystal data are as follows. The

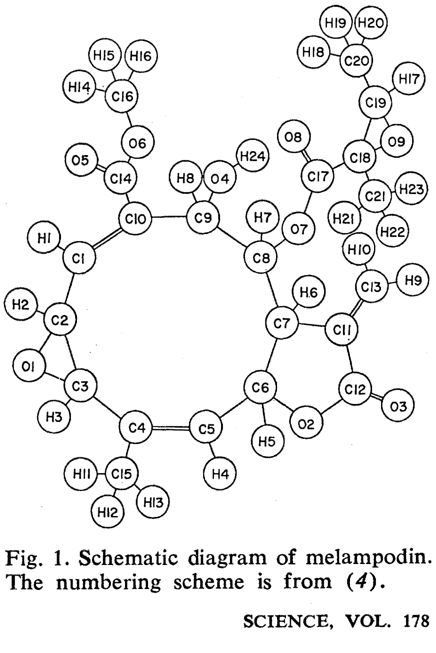

Fig. 1. Schematic diagram of melampodin. The numbering scheme is from (*4*).

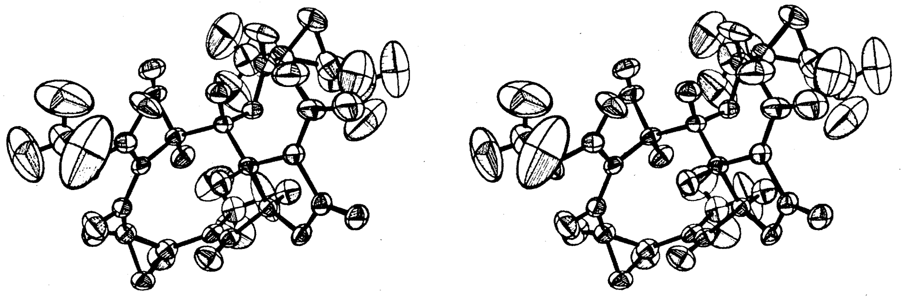

Fig. 2. Stereopair diagram of melampodin.

unit cell parameters are $a = 8.990$, $b = 14.352$, and $c = 16.294$ Å; the number of molecules in the unit cell, $Z$, is 4; the space group is $P2_12_12_1$; $Q_H$ is 21.9 percent; and the wavelength of incident neutrons is 1.0142 Å. A total of 2884 independent reflections were measured and converted to normalized structure factors ($E$'s). Of these, 414 were in the range 1.40 to 3.21 and were used to generate 2000 $\Sigma_2$ relationships. The computer program MULTAN *(6)* automatically selected three reflections (11,0,3; 4,0,3; 0,3,1) for origin definition, and assigned a phase of 90° to each. Another reflection (3,2,1) was assigned, in turn, the phases 45°, 135°, 225°, and 315°, while the reflection which fixed the enantiomorph (6,8,4) was assigned alternately the phases +45° and −45°. These eight combinations were used as starting phases in the tangent formula *(7)* as implemented by Germain *et al.* *(6)* to produce eight sets of refined phases for all 414 reflections. These eight sets actually represent only four unique possible solutions, since the sets are equivalent in pairs and differ only in the enantiomorph assignment. The associated figures of merit (*6*) range from 1.86 to 1.39.

The only $E$-map computed was that with the set of phases having the highest figure of merit and the angle $\alpha(6,8,4)$ equal to +45°. A model of the 22 largest maxima on the $E$-map showed all 13 of the skeletal atoms in the two fused rings (Figs. 1 and 2), three peripheral atoms, and only four spurious peaks. In all, 16 of the 21 carbon atoms and 5 of the 9 oxygen atoms were located directly from the $E$-map. Subsequent comparison with the atomic positions found in the x-ray analysis (*8*) revealed that the x-ray and neutron solutions differed only in the assignment of the enantiomorph. Since our experiment is not sensitive to the absolute configuration, we reversed the sign of the phase of the 6,8,4 reflection to conform to the x-ray assignment.

A standard analysis of the 2303 observed intensities produced a refined model of melampodin, all 54 atoms of which were allowed to vibrate anisotropically, with an agreement index, $R$, of 0.050; a weighted agreement index, $R_w$, of 0.041; and an error of fit of 1.082.

We must conclude that Sikka's upper limit of 100 atoms per unit cell for direct solution of neutron data is far too conservative. Under the conditions of our experiment (availability of good crystalline material, a complete set of high-quality data, and a relatively large contribution from "randomly" located positive scatters) it should be possible to solve nearly any neutron diffraction structure without recourse to x-ray diffraction results. Indeed, we have shown that neutron diffraction may be used as a primary tool in the structural investigation of moderately complex molecules, a fact which is of particular importance when hydrogen plays a prominent role in stereochemistry. Examples of interest to molecular biologists include hydrogen bonding, bond torsion angles in strained rings, hindered rotations, zwitterion structure, and protonation and hydrogenation products. These structural problems can be accurately elucidated only by neutron diffraction, since neither the atomic positions nor the thermal motion of hydrogen atoms can be detected with sufficient accuracy by means of x-ray analysis.

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## A New Newton's Law of Cooling?

Abstract. *Several physiologists confuse Fourier's law of animal heat flow with Newton's law of cooling. A critique of this error in 1932 remained ineffective. In 1969 Molnar tested Newton's cooling law. In 1971 Strunk found Newtonian cooling unrealistic for animals. Unfortunately, he called the Fourier formulation of animal heat flow, requiring post-Newtonian observations, a "contemporary Newtonian law of cooling."*

A warm body without internal heating surrounded by a cold environment loses temperature faster, the greater the difference between the body temperature $T_b$ and the ambient temperature $T_a$. This is Newton's law of cooling, published in the year 1701 (*1*). It can be formulated as follows:

$$dT_b/dt = k_N(T_b - T_a) \qquad (1)$$

where $k_N$ is Newton's cooling constant.

Molnar (*2*) reproduced Newton's thermometer with linseed oil as the expanding liquid. He used this thermometer itself as the cooling body in order to investigate the conditions under which the temperature loss by cooling, $\Delta T_b$, follows the logarithmic form of Newton's law of cooling:

$$\ln(T_b - T_a)_t = \ln(T_b - T_a)_0 - k_N t \qquad (2)$$

where 0 is the start of the measurement and $t$ is the time from start.

An instrument for measuring the cooling effect of a cold environment on a warm body is called a katathermometer (*3*). The simplest form of it is a true Newtonian coolometer. Count Rumford called it a "passage thermom-