IS-T-805

I. STRUCTURAL STUDIES OF TERMITE DEFENSE SECRETIONS
II. STRUCTURAL STUDIES OF NATURAL PRODUCTS OF MARINE NUDIBRANCHS

Barbara Ann Solheim

M.S. Thesis Submitted to Iowa State University

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I. Structural studies of termite defense secretions

II. Structural studies of natural products of marine nudibranchs

by

Barbara Ann Solheim

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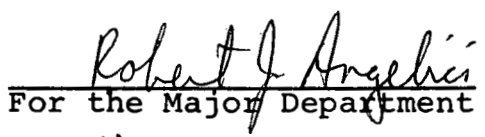
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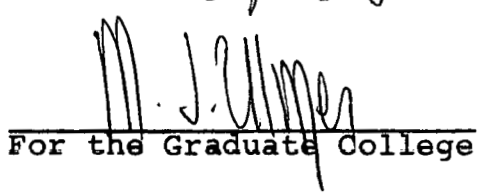
For the Graduate College

Iowa State University
Ames, Iowa

1977

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DEFENSE SECRETIONS OF THE FAMILY TERMITIDAE

General Introduction

Defense is a primary objective among many vertebrates and invertebrates and how a species goes about its defense is sometimes a mystifying subject. It is well-known that some insects mimic the environment around them such as the walking stick or other inedible insects as the viceroy mimics the monarch butterfly, bees have evolved the stinger and the grasshopper has strong jumping legs. In the order Isoptera, certain families of termites have evolved a sticky secretion which tends to envelope and immobilize the enemy.

The most widespread and primitive system of defense in termites is the power behind the soldier caste's mandibles. When the community is threatened, the soldiers gather and mechanically repel the intruder by force. Through evolution, this method of defense has been supplemented by chemical means in three distinct families, the Mastotermitidae, Rhinotermitidae and Termitidae.

The termites of the family Mastotermitidae are classified as primitive among the termite species yet they have evolved an extremely odiferous defense secretion apparently originating from the buccal cavity. The secretion is generally colorless and fluid initially but begins to set and darken after being released until it becomes a dark, rubber-like material which seems to serve as an immobilizer

of the enemy. The chemistry that has been done on this family identifies the major component of the secretion as p-benzoquinone with traces of toluquinone. The biosynthesis of the p-benzoquinone is not known but a prevailing theory suggests that it is formed from the glucoside of its phenolic precursor (1). It is thought that these reactive quinones combine with the protein components of the termite saliva to produce the dark, insoluble sclerotin that forms (2).

In the Rhinotermitidae, soldiers emit from the fontanelle a drop of a milky substance which soon dries to a colorless, resilient film. There appears to be no chemical reaction between other compounds in the development of this film as the material can be reconstituted to its original form merely by adding water to it. Work done on these secretions finds them to be composed of a suspension of lipids of constitution C_{22} through C_{27} most of which are saturated paraffins in an aqueous solution of mucopolysaccharide primarily based on glucosamine and possibly some glucose units (2).

Members of the family Termitidae have the highest level of sophistication in terms of evolutionary progress in means of defense and because of this, elicit a great interest among researchers. Specifically, the subfamily Nasutitermitinae which is both the largest in the order Isoptera and the most specialized has been studied in the greatest detail. This unique specialization has centered around

a gradual reduction of the soldier mandibles to non-functional stubs while simultaneously, a development of a small projection on the front of the head in the form of a long, attenuated snout or nasus at the tip of which is the frontal pore. Contraction of the still present mandibular muscles causes the defensive secretions of the frontal gland to be forcibly ejected through the pore on the nasus (3).

In 1964, Moore investigated the subfamily Nasutitermitinae and said this about their mode of defense (4):

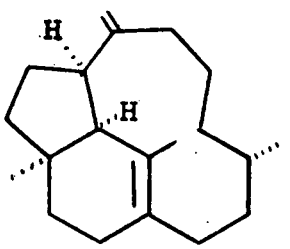
> "Termites of the Nasutitermitinae differ from those of other subfamilies in their complete dependence upon chemical means for defense purposes. The defensive secretion is produced exclusively by the soldiers in a special gland which occupies much of the head cavity and which discharges into a beak-like process, the so-called rostrum, situated on the frons. When stimulated or attacked, the soldiers orientate themselves toward the source of the disturbance and eject a fine stream of mobile secretion, which rapidly forms a sticky resinous thread upon exposure to air. The secretion is believed to function entirely as a mechanical immobilizing agent and to possess no toxic action but no detailed chemical analysis appears to have been recorded."

Moore's investigation of the volatile portion of the secretion found α-pinene, 1, to be the major component with β-pinene, 2, and other monoterpenoid hydrocarbons present in significant amounts. He then theorized that the monoterpenes acted largely as solvent-carriers for resinous constituents of the secretions and possibly as alarm pheromones.

There are two possibilities as to the origin of these compounds; the soldiers concentrate the small amounts in the food material fed to them by the worker caste or they are able to synthesize the compounds internally.

Studies now underway seem to confirm that the defense secretions do elicit alarm response in other members of the community and are both mechanically disabling and systemically toxic to small insects. General concensus considers the alarm behavior to be induced by α-pinene alone or by the mixture of monoterpenes in the volatile portion (5,6). These monoterpenoid compounds also seem to be responsible for the specific scent of each species.

Recently (5), a total chemical analysis of the defense secretions of both major and minor soldiers of the East African termite Trinervitermes gratiosus (Isoptera: Termitidae: Termitinae) was completed. The fluid was found to contain three distinct groups of compounds, monoterpene hydrocarbons, monoterpene alcohols, and polyfunctional diterpenes possessing the novel trinervitene skeleton 3 (7,8).



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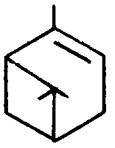
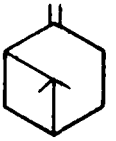
The monoterpene hydrocarbons were identified as α-pinene 1, β-pinene 2, camphene 4, myrcene 5, and limonene 6 by comparison with known samples.

The monocyclic terpene alcohols have been isolated but complete spectral data has not as yet been finished, therefore, structures have not been formally assigned to them.

Most of the polyfunctional diterpenes have been characterized and structures assigned to them from direct spectral analysis of pure samples. They are trinervi-9β-ol 7, trinervi-2β,3α-diol 8, isotrinervi-2β,3α-diol 9, trinervi-2β,3α,9α-triol-9-0-acetate 10 and trinervi-2β,3α,9α-triol-2,3-0-diacetate 11. Three other minor components have not been thoroughly analyzed yet but it is apparent that they also are trinervitene congeners.



1



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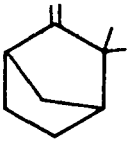

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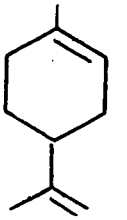

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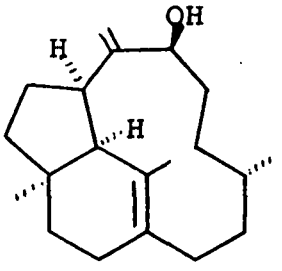

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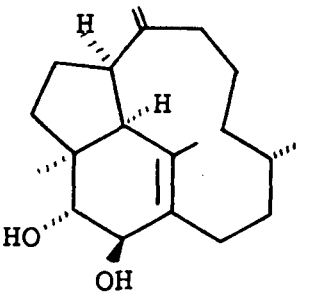

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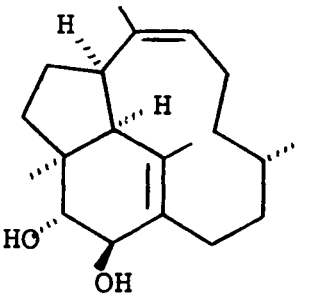

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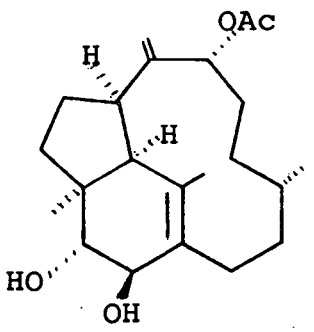

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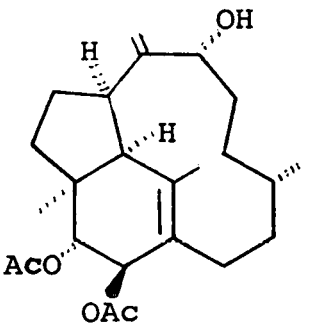

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Eisner has demonstrated that many of the monoterpene hydrocarbons found in the secretions seem to have an irritant effect and it was theorized that addition of the diterpene components would increase that effect. Tests have been run with a solution of 26% trinervi-2β,3α,9α-triol-9-0-acetate 10 in freshly purified α-pinene 1 to substantiate this theory and the results showed no increase in toxicity over the pure α-pinene 1 tested previously in topical applications to formicine ants (Formica exsectoides). There were observed some changes in the physical nature of the α-pinene 1 upon addition of the trinervitene. The viscosity of the solution increased greatly which has been suggested to cause the liquid to stick better and to produce a decreased rate of evaporation of the volatile monoterpene which would prolong the irritating effect of the secretion (5).

The more work that is done with these secretions, the more questions that are raised and for the most part remain

unanswered. The chemical composition of the defense secretion differs from family to family and more surprisingly, from species to species within a family. This fact in itself will take years of research before even a small percentage of the known species will have been examined, the composition of their secretions analyzed and their biosynthetic origins known. The specific functions of these chemicals are now just being guessed at. It is clear that they are defensive in nature but the range of their effectiveness is not known. It is thought that the secretions may protect the colony from such intruders as predators, molds, diseases, parasites and other competitors. The inducement of alarm behavior, the odor of the species and even the control of the caste ratios within the population appears to have some connection with these fluids.

It is the object of the first part of this work to examine the structural characteristics of two diterpenoid hydrocarbons found in the frontal gland secretions of Nasutitermes kempae and Cubitermes umbratus soldiers (Isoptera: Termitidae: Termitinae).

Kempene II

Background

In an attempt to determine the chemical composition of the defense secretions of Nasutitermes kempae soldiers, 5000

heads were crushed under and extracted with hexane. The solvent was then removed in vacuo and the resulting 100 mg. of crude secretion was chromatographed on a Florisil (100-200 mesh) column with increasing percentages of ethyl acetate in benzene as eluent. This procedure provided two uv-active materials, kempene I and kempene II.

The physical constants of kempene II were found to be as follows: mp. 120.5-122.5°; MS, m/e 342 M+ ($C_{22}H_{30}$), 282 (M+ - AcOH), 267 (M+ - AcOH - Me); UV (MeOH), 244 nm (ε 6,330); CD (MeOH), 241 ($\Delta\varepsilon$ + 0.025, diene) and 289 nm ($\Delta\varepsilon$ + 1.46, ketone), IR (CCl_4), 1737 (OAc) and 1702 cm^{-1} (ketone). The nature of all twenty-two carbons was determined by the techniques of PND, selective decoupling, partially relaxed Fourier transform (PRFT) and combined PRFT/selective decoupling (9).

Clarification of the structure except for the linkages between C(1)/C(15), C(12)/C(13) and those extending from C(11) were accomplished by detailed analysis of ^{1}H-NMR spectrum at both 100 and 220 MHz. It was possible to at least partially separate most of the proton signals with the use of $Eu(fod)_3$ and to use decoupling techniques in the correlation of proton signals to carbon signals by selective heteronuclear decoupling.

At this time, it was decided to use x-ray structural analysis to determine the entire structure of kempene II.

Experimental

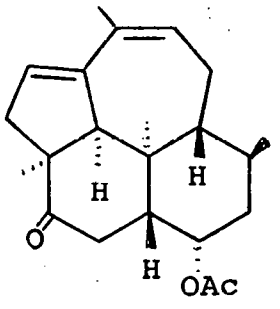
The crystals of kempene II which were used for single-crystal x-ray diffraction analysis were crystallized from olefin-free pentane under an argon atmosphere. Fifteen high angle reflections in least-squares fitting indicated that the compound crystallized in the orthorhombic crystal class with cell constants a = 10.370(3), b = 9.671(2) and c = 19.817(7) Å. Examination of the data collected turned up systematic extinctions which when combined with the chirality of the molecule indicated the space group $P2_12_12_1$ with one molecule per asymmetric unit and a calculated density of 1.14 g/cm^3. All unique data with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using graphite monochromated CuKα (1.54178 Å) x-rays. A total of 1596 reflections were measured with 1258 (78%) considered observed ($F_o^2 \geq 3\sigma(F_o^2)$) after correction for Lorentz, polarization and background effects (10).

Utilization of a multiple solution tangent formula approach gave a reasonable twenty-two atom molecule with the remainder of the molecule being revealed after employing a tangent formula recycling procedure (11). Coordinates of hydrogen atoms were determined and final full-matrix least-squares refinements using anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors

for the hydrogen atoms produced an unweighted crystallographic residual of 0.040. Figure 1 contains a computer generated perspective drawing of kempene II and Tables 1, 2, 3 and 4 contain the fractional coordinates, bond distances, bond angles and observed and calculated structure factors.

Discussion

Kempene II 12 can be described as a dome-shaped tetracyclic array of 5-, 6- and 7-membered rings which appear to be structurally related to the trinervitenes (TG-3 13) (7,8). As in the trinervitene TG-3 13, most of the substituents are on the convex surface with the exceptions of the hydrogens at C(1) and C(11) and the methyl group at C(12).



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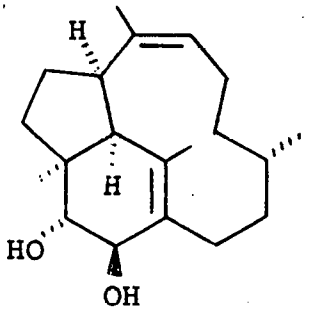

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The absolute configuration of kempene II was not determined by x-ray analysis but since it is structurally related to TG-3 13, we assumed it to have the absolute configuration

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Figure 1. A computer generated perspective drawing from the crystal structure of kempene II with hydrogens omitted for clarity.

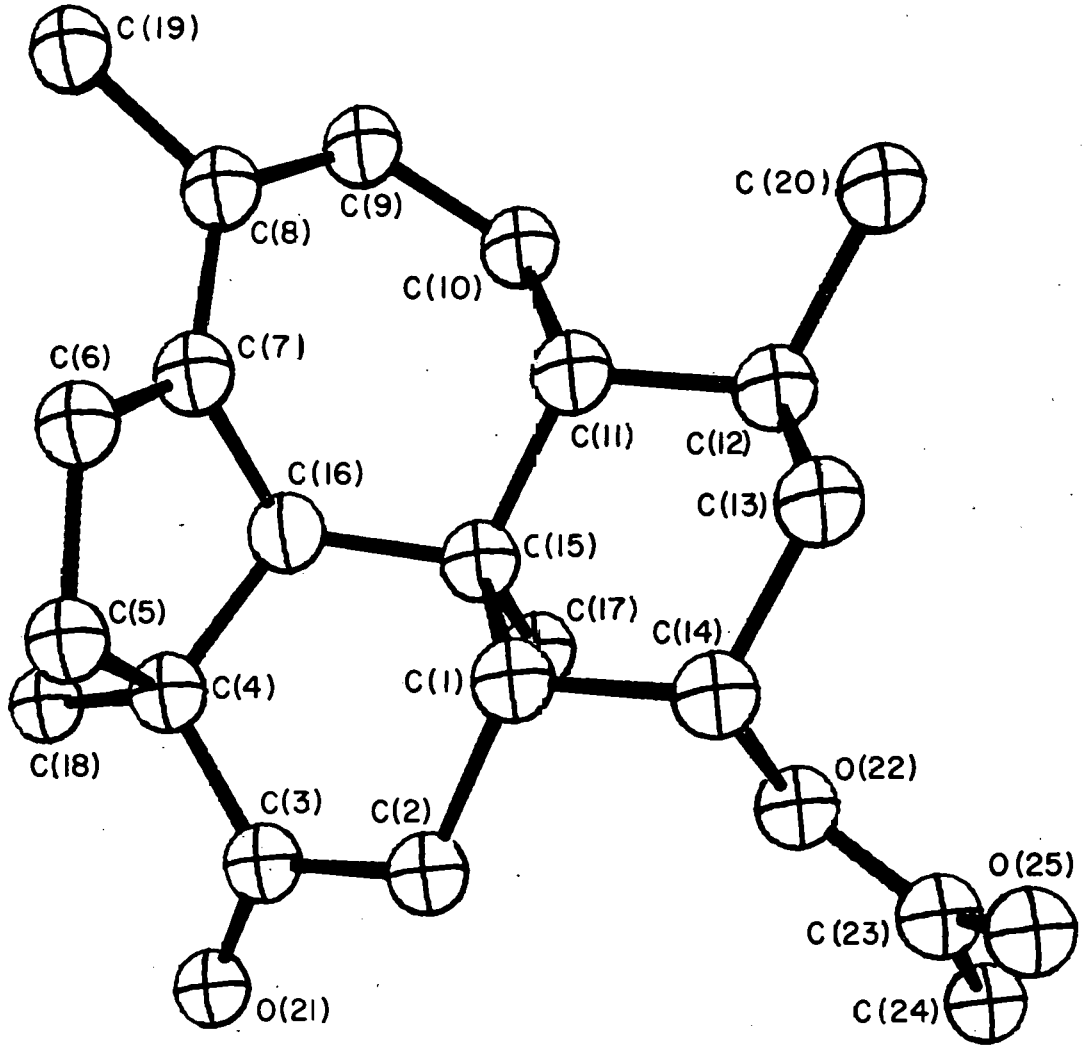

C(19)
C(8)
C(9)
C(10)
C(20)
C(6)
C(7)
C(11)
C(12)
C(16)
C(13)
C(15)
C(5)
C(17)
C(14)
C(4)
C(1)
C(18)
O(22)
C(3)
C(2)
O(25)
C(23)
O(21)
C(24)

Table 1. Final fractional coordinates for kempene II with the estimated standard deviation of the least significant figure given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. The numbering scheme refers to Figure 1.

C(1)	-.3462(4)	-.2794(4)	.1507(2)
C(2)	-.3084(5)	-.3633(5)	.2137(2)
C(3)	-.2493(5)	-.5025(4)	.1984(2)
C(4)	-.2707(4)	-.5616(4)	.1287(2)
C(5)	-.4145(5)	-.6056(5)	.1208(2)
C(6)	-.4391(4)	-.5777(4)	.0475(2)
C(7)	-.3507(4)	-.4983(3)	.0196(2)
C(8)	-.3347(4)	-.4655(4)	-.0526(2)
C(9)	-.2688(4)	-.3576(4)	-.0750(2)
C(10)	-.2154(4)	-.2410(4)	-.0332(2)
C(11)	-.2930(4)	-.2095(4)	.0313(2)
C(12)	-.3036(4)	-.0557(4)	.0501(2)
C(13)	-.4017(4)	-.0409(4)	.1075(3)
C(14)	-.3734(4)	-.1295(4)	.1687(2)
C(15)	-.2487(3)	-.2998(3)	.0924(2)
C(16)	-.2489(4)	-.4544(3)	.0705(2)
C(17)	-.1102(4)	-.2640(5)	.1150(3)
C(18)	-.1829(6)	-.6863(5)	.1170(3)
C(19)	-.3984(6)	-.5662(6)	-.1017(2)
C(20)	-.3451(7)	.0357(5)	-.0093(3)
O(21)	-.1903(5)	-.5666(4)	.2418(2)
O(22)	-.2599(3)	-.0731(3)	.2032(1)
C(23)	-.2752(5)	.0229(5)	.2509(2)
C(24)	-.1489(6)	.0666(8)	.2801(3)
O(25)	-.3785(4)	.0714(5)	.2650(2)
H(1)	-.067(5)	.318(4)	.632(2)
H(2A)	-.110(7)	.369(7)	.741(3)
H(2B)	-.255(6)	.307(6)	.740(3)
H(5A)	-.026(4)	.545(5)	.647(3)
H(5B)	-.064(4)	.711(5)	.636(2)
H(6)	.016(5)	.620(5)	.526(2)
H(9)	-.247(4)	.354(4)	.375(2)
H(10A)	-.287(3)	.151(4)	.436(2)
H(10B)	-.382(5)	.254(4)	.476(4)
H(11)	-.112(4)	.236(4)	.522(2)
H(12)	-.282(4)	.019(4)	.566(2)
H(13A)	-.009(5)	.068(5)	.584(3)
H(13B)	-.094(4)	-.059(5)	.623(2)
H(14)	-.054(4)	.126(4)	.702(2)
H(16)	-.340(4)	.476(4)	.552(2)
H(17A)	-.446(4)	.283(4)	.582(2)
H(17B)	-.404(4)	.165(6)	.634(2)

Table 1 (Continued)

H(17C)	-.418(4)	.337(5)	.652(2)
H(18A)	-.309(7)	.737(7)	.570(4)
H(18B)	-.304(4)	.756(5)	.647(2)
H(18C)	-.405(7)	.655(6)	.629(3)
H(19A)	-.136(6)	.656(7)	.409(3)
H(19B)	-.114(5)	.530(5)	.350(3)
H(19C)	.003(6)	.568(6)	.403(3)
H(20A)	-.235(8)	-.030(8)	.452(4)
H(20B)	-.135(4)	-.125(6)	.506(2)
H(20C)	-.074(5)	.007(5)	.470(2)
H(24A)	-.371(10)	.013(11)	.799(5)
H(24B)	-.352(9)	-.135(10)	.817(4)
H(24C)	-.425(10)	-.095(12)	.748(6)

Table 2. Bond distances in angstroms for kempene II with the estimated standard deviation of the least significant figure given in parentheses. The numbering scheme refers to Figure 1.

C(1)	- C(2)	1.540(6)
C(1)	- C(14)	1.520(6)
C(1)	- C(15)	1.547(5)
C(2)	- C(3)	1.509(6)
C(3)	- C(4)	1.511(5)
C(3)	- O(21)	1.225(6)
C(4)	- C(5)	1.559(6)
C(4)	- C(16)	1.568(5)
C(4)	- C(18)	1.530(6)
C(5)	- C(6)	1.500(6)
C(6)	- C(7)	1.318(6)
C(7)	- C(8)	1.475(6)
C(7)	- C(16)	1.521(5)
C(8)	- C(9)	1.325(6)
C(8)	- C(19)	1.527(7)
C(9)	- C(10)	1.505(6)
C(10)	- C(11)	1.540(6)
C(11)	- C(12)	1.538(5)
C(11)	- C(15)	1.563(5)
C(12)	- C(13)	1.532(7)
C(12)	- C(20)	1.533(7)
C(13)	- C(14)	1.514(6)
C(14)	- C(22)	1.467(5)
C(15)	- C(16)	1.556(5)
C(15)	- C(17)	1.543(5)
O(22)	- C(23)	1.334(5)
C(23)	- C(24)	1.492(8)
C(23)	- O(25)	1.202(7)

Table 3. Bond angles in degrees of kempene II. Estimated standard deviation of the least significant figures are given in parentheses. The numbering scheme refers to Figure 1.

C(2)	- C(1)	- C(14)	111.1(3)
C(2)	- C(1)	- C(15)	111.8(3)
C(14)	- C(1)	- C(15)	114.7(3)
C(1)	- C(2)	- C(3)	114.3(4)
C(2)	- C(3)	- C(4)	117.5(4)
C(2)	- C(3)	- O(21)	120.9(4)
C(4)	- C(3)	- O(21)	121.6(4)
C(3)	- C(4)	- C(5)	109.6(4)
C(3)	- C(4)	- C(16)	113.7(3)
C(3)	- C(4)	- C(18)	110.5(4)
C(5)	- C(4)	- C(16)	104.1(3)
C(5)	- C(4)	- C(18)	109.8(4)
C(16)	- C(4)	- C(18)	108.9(3)
C(4)	- C(5)	- C(6)	102.2(3)
C(5)	- C(6)	- C(7)	113.1(4)
C(6)	- C(7)	- C(8)	127.6(4)
C(6)	- C(7)	- C(16)	111.6(4)
C(8)	- C(7)	- C(16)	120.4(3)
C(7)	- C(8)	- C(9)	123.5(4)
C(7)	- C(8)	- C(19)	115.7(4)
C(9)	- C(8)	- C(19)	120.8(4)
C(8)	- C(9)	- C(10)	126.5(4)
C(9)	- C(10)	- C(11)	114.4(3)
C(10)	- C(11)	- C(12)	115.5(3)
C(10)	- C(11)	- C(15)	112.2(3)
C(12)	- C(11)	- C(15)	111.9(3)
C(11)	- C(12)	- C(13)	108.5(3)
C(11)	- C(12)	- C(20)	113.0(4)
C(13)	- C(12)	- C(20)	109.2(4)
C(12)	- C(13)	- C(14)	114.4(4)
C(1)	- C(14)	- C(13)	112.8(4)
C(1)	- C(14)	- O(22)	108.4(3)
C(13)	- C(14)	- O(22)	108.6(3)
C(1)	- C(15)	- C(11)	108.4(3)
C(1)	- C(15)	- C(16)	109.3(3)
C(1)	- C(15)	- C(17)	111.3(3)
C(11)	- C(15)	- C(16)	108.6(3)
C(11)	- C(15)	- C(17)	111.9(3)
C(16)	- C(15)	- C(17)	107.3(3)
C(4)	- C(16)	- C(7)	101.7(3)
C(4)	- C(16)	- C(15)	115.4(3)
C(7)	- C(16)	- C(15)	117.0(3)
C(14)	- O(22)	- C(23)	119.6(3)

Table 3 (Continued)

O(22)	- C(23)	- C(24)	111.5(5)
O(22)	- C(23)	- O(25)	122.8(5)
C(24)	- C(23)	- O(25)	125.5(5)

Table 4. The observed and calculated structure factors for kempene II.

H = 0				3	1	45	46	5	18	4	3	0	4	34	34
K	L	FO	FC	3	2	26	25	6	0	25	26	0	5	4	4
0	2	18	19	3	3	29	29	6	1	7	7	0	6	11	12
0	4	25	25	3	4	12	13	6	2	7	8	0	7	32	32
0	6	83	81	3	5	40	38	6	5	15	14	0	8	8	8
0	8	38	38	3	6	51	49	6	6	12	12	0	9	28	28
0	10	9	9	3	7	73	69	6	7	14	14	0	10	22	23
0	12	26	26	3	8	18	18	6	8	10	9	0	12	11	10
0	14	10	10	3	9	15	14	6	9	12	12	0	14	13	13
0	16	3	2	3	10	3	2	6	10	11	11	0	16	6	6
1	0	1	0	3	13	15	15	6	11	14	14	1	0	39	40
1	1	93	96	3	14	10	11	6	12	11	10	1	1	26	28
1	2	20	20	3	15	14	13	6	13	6	6	1	2	41	43
1	3	14	14	3	16	12	12	6	15	9	8	1	3	12	13
1	4	37	36	3	17	3	2	7	1	5	5	1	4	63	66
1	5	39	37	3	18	9	10	7	2	11	11	1	5	26	27
1	6	31	28	3	19	5	6	7	3	5	4	1	6	30	30
1	7	41	40	4	0	42	46	7	4	6	5	1	7	19	18
1	8	6	6	4	1	26	26	7	5	10	10	1	8	6	5
1	9	12	13	4	2	50	49	7	6	18	18	1	9	23	22
1	10	52	52	4	3	22	21	7	7	18	17	1	10	4	5
1	11	5	4	4	4	18	18	7	9	10	9	1	11	15	15
1	12	14	15	4	6	14	13	7	10	6	6	1	12	3	2
1	13	6	6	4	7	16	16	7	12	14	14	1	13	6	6
1	14	9	10	4	8	7	7	7	14	5	5	1	14	11	11
1	15	8	8	4	9	6	6	7	16	5	5	1	15	12	11
1	16	7	6	4	10	2	2	8	0	13	14	1	16	7	7
1	17	13	13	4	11	5	4	8	2	3	1	1	17	9	8
1	18	12	13	4	12	4	4	8	3	10	11	1	18	4	4
1	21	4	3	4	13	10	9	8	4	6	6	1	19	4	3
2	0	124	133	4	14	10	10	8	5	5	6	1	20	3	3
2	1	26	25	4	15	7	6	8	6	15	15	2	0	39	41
2	2	38	38	4	18	7	6	8	8	3	2	2	1	25	24
2	3	68	68	4	19	7	6	8	12	3	3	2	2	24	26
2	4	87	87	5	1	20	21	8	13	5	4	2	3	49	49
2	5	13	12	5	2	31	28	9	1	10	11	2	4	40	39
2	6	41	39	5	3	10	8	9	2	7	8	2	5	18	19
2	7	32	32	5	4	13	12	9	5	10	9	2	6	39	39
2	8	7	6	5	6	3	4	9	7	4	3	2	7	23	23
2	9	18	18	5	7	16	16	9	9	3	3	2	8	12	12
2	11	9	8	5	8	7	7	10	0	4	5	2	9	18	18
2	12	3	1	5	9	3	3	10	6	4	3	2	10	9	9
2	13	10	10	5	10	8	9					2	11	22	22
2	14	4	4	5	11	11	11	H = 1				2	12	9	9
2	15	18	18	5	12	14	14	K	L	FO	FC	2	13	18	18
2	16	17	17	5	13	9	10	0	0	3	0	2	14	14	14
2	17	7	7	5	14	5	6	0	1	34	34	2	15	10	10
2	20	6	6	5	16	10	10	0	2	144	156	2	16	10	9

Table 4 (Continued)

2	17	6	6	5	9	25	24	9	0	3	3	1	15	15	16
2	18	6	7	5	10	13	13	9	1	3	3	1	16	7	7
2	19	3	3	5	11	4	4	9	5	5	7	1	17	12	12
3	0	32	31	5	12	3	2	9	6	5	6	1	18	5	6
3	1	30	32	5	13	8	8	9	7	5	5	1	19	4	4
3	2	21	21	5	14	9	9	9	8	3	3	1	21	3	3
3	3	19	19	5	15	3	2	9	9	2	3	2	0	32	34
3	4	28	25	5	16	3	3	9	10	6	6	2	1	87	92
3	5	8	8	5	17	4	4	10	1	7	7	2	2	51	54
3	6	37	37	6	0	2	3	10	2	4	4	2	3	22	23
3	7	44	46	6	1	4	4	10	3	3	3	2	4	40	41
3	8	36	35	6	2	8	8	10	4	4	4	2	5	21	21
3	9	36	36	6	3	7	7	10	6	3	3	2	6	13	13
3	10	12	12	6	4	5	5					2	7	7	7
3	11	17	17	6	5	9	9		H =	2		2	8	28	26
3	12	9	8	6	6	12	11	K	L	FO	FC	2	9	20	20
3	13	7	6	6	7	9	9	0	0	206	224	2	10	8	8
3	14	9	9	6	9	14	14	0	1	121	128	2	11	4	3
3	15	8	7	6	10	7	6	0	2	14	11	2	13	19	20
3	16	4	4	6	11	11	11	0	4	59	61	2	14	11	12
3	17	5	5	6	12	12	12	0	5	29	30	2	15	4	4
4	0	26	24	6	13	12	12	0	6	38	39	2	16	19	19
4	1	21	21	6	14	7	7	0	7	10	10	2	17	8	8
4	2	24	24	6	15	5	4	0	8	21	21	2	18	4	3
4	3	56	54	7	0	7	7	0	9	9	10	2	19	5	5
4	4	43	41	7	1	5	5	0	10	4	5	2	20	3	2
4	6	13	12	7	2	10	10	0	12	7	6	3	0	2	1
4	7	23	24	7	3	16	16	0	13	4	4	3	1	22	23
4	8	6	6	7	4	26	26	0	14	6	7	3	2	19	19
4	9	23	22	7	5	8	8	0	16	3	3	3	3	16	17
4	10	13	13	7	6	11	12	0	17	6	5	3	4	11	11
4	11	9	9	7	7	8	8	0	18	12	11	3	5	6	6
4	12	12	12	7	8	16	16	0	19	8	8	3	6	9	9
4	13	5	6	7	9	8	7	1	0	21	23	3	7	43	43
4	14	3	3	7	10	11	11	1	1	81	87	3	8	19	18
4	15	9	8	7	12	13	13	1	2	37	37	3	9	8	7
4	16	9	8	7	13	5	5	1	3	25	25	3	10	3	3
4	17	3	3	7	14	6	5	1	4	19	17	3	11	10	10
4	18	4	4	8	0	7	7	1	5	24	25	3	12	4	4
4	19	3	3	8	1	11	11	1	6	28	28	3	13	11	12
5	0	23	24	8	2	11	12	1	7	48	48	3	15	13	13
5	1	17	17	8	3	12	12	1	8	29	29	3	16	7	7
5	2	11	12	8	4	15	15	1	9	11	10	3	17	5	6
5	3	48	48	8	5	9	9	1	10	14	13	3	18	8	8
5	5	18	19	8	7	6	6	1	11	22	22	3	19	8	8
5	6	7	7	8	11	5	4	1	12	4	4	4	0	36	38
5	7	7	6	8	12	4	4	1	13	8	9	4	1	24	23
5	8	12	12	8	13	3	3	1	14	12	12	4	2	30	29

Table 4 (Continued)

4	3	33	33	7	2	8	8	0	15	11	11	3	6	11	12
4	4	17	17	7	3	4	4	0	16	9	9	3	7	24	23
4	5	10	9	7	4	13	14	0	18	4	5	3	8	16	15
4	6	7	7	7	5	14	13	0	19	4	3	3	10	4	4
4	7	13	13	7	6	25	26	0	20	3	3	3	11	9	9
4	8	10	9	7	7	12	12	1	0	26	25	3	12	13	13
4	9	4	5	7	8	4	4	1	1	9	10	3	13	19	20
4	10	10	10	7	9	10	10	1	2	46	47	3	14	4	4
4	11	4	5	7	10	5	5	1	3	23	25	3	15	3	4
4	12	7	7	7	11	11	11	1	4	9	10	3	16	6	6
4	14	14	14	7	12	9	9	1	5	29	29	3	17	4	4
4	17	4	3	7	13	6	5	1	6	23	23	3	18	3	2
4	18	5	5	7	14	9	9	1	7	6	6	3	19	3	3
4	19	5	5	8	0	8	8	1	8	20	19	4	1	15	16
5	0	14	14	8	1	4	4	1	9	9	8	4	2	18	17
5	1	15	16	8	3	10	10	1	10	14	14	4	3	15	15
5	2	21	22	8	4	6	7	1	11	5	4	4	4	35	34
5	3	20	19	8	5	8	7	1	12	13	13	4	5	16	16
5	4	2	2	8	6	4	3	1	13	4	3	4	6	7	6
5	5	11	10	8	7	3	4	1	14	13	13	4	7	5	5
5	6	7	6	8	8	3	3	1	15	6	5	4	8	5	5
5	7	13	14	8	10	5	5	1	16	4	4	4	9	11	11
5	8	13	13	8	13	5	5	1	18	4	4	4	10	18	17
5	9	16	16	9	1	5	6	1	20	5	6	4	11	7	7
5	10	10	10	9	3	5	4	2	0	30	32	4	12	10	10
5	11	10	10	9	4	3	5	2	1	36	37	4	13	6	6
5	12	6	6	9	6	8	9	2	2	35	37	4	14	8	8
5	13	12	12	9	7	3	3	2	3	11	11	4	15	10	10
5	14	5	4	9	8	6	6	2	4	30	31	4	16	4	4
5	15	9	8	9	9	3	3	2	5	38	38	4	17	5	6
5	17	3	4	10	0	3	1	2	6	25	26	4	18	3	3
6	0	5	5	10	1	6	7	2	7	33	32	5	0	6	6
6	1	4	4	10	2	5	5	2	8	16	17	5	1	3	3
6	2	7	6	10	3	3	4	2	9	8	8	5	2	3	4
6	3	11	11	10	4	3	2	2	10	5	5	5	3	3	3
6	4	18	18					2	11	11	10	5	4	18	18
6	5	13	13		H =	3		2	12	7	7	5	5	21	21
6	6	17	17	K	L	FO	FC	2	13	9	9	5	6	9	9
6	7	10	10	0	1	8	8	2	14	11	11	5	7	25	25
6	9	11	11	0	3	18	18	2	15	7	7	5	8	16	16
6	10	9	9	0	4	30	31	2	16	4	5	5	9	18	18
6	11	14	14	0	5	3	3	2	17	6	6	5	10	20	20
6	12	4	4	0	6	47	48	3	0	2	1	5	11	12	12
6	13	6	7	0	7	34	33	3	1	24	24	5	12	8	8
6	14	5	4	0	8	43	41	3	2	7	5	5	13	9	9
6	15	7	7	0	9	15	15	3	3	9	9	5	14	7	7
7	0	13	12	0	11	4	3	3	4	11	12	5	15	6	5
7	1	5	5	0	13	6	6	3	5	23	23	5	18	3	2

Table 4 (Continued)

6	0	9	9	10	0	3	3	2	5	21	21	5	1	3	1
6	1	6	6	10	3	5	5	2	6	8	8	5	2	5	5
6	2	3	3					2	7	6	6	5	3	10	10
6	3	10	10		H =	4		2	8	16	15	5	4	4	5
6	4	5	4	K	L	FO	FC	2	9	4	4	5	5	16	16
6	5	13	12	0	0	11	11	2	10	13	14	5	6	10	10
6	6	7	6	0	1	14	14	2	11	7	7	5	7	4	3
6	7	11	12	0	2	6	5	2	12	5	5	5	8	23	23
6	8	9	9	0	3	12	12	2	13	6	7	5	9	11	11
6	9	3	3	0	4	10	10	2	14	4	5	5	10	10	10
6	10	7	7	0	5	37	37	2	15	5	6	5	11	11	11
6	11	6	6	0	6	27	25	2	16	13	13	5	14	4	4
6	12	9	10	0	7	7	7	2	18	3	4	6	0	3	3
6	13	7	8	0	8	42	42	3	0	26	27	6	1	11	11
6	14	5	5	0	9	9	9	3	1	9	10	6	2	11	12
6	15	4	5	0	11	3	3	3	2	17	17	6	3	12	12
6	16	3	3	0	12	3	2	3	3	27	27	6	4	10	10
7	0	13	13	0	13	7	8	3	4	25	25	6	5	19	19
7	1	11	11	0	14	7	8	3	5	13	12	6	6	19	19
7	2	5	4	0	15	7	6	3	6	22	21	6	7	9	8
7	3	12	13	0	16	5	4	3	7	5	6	6	8	8	8
7	5	8	8	0	17	6	6	3	8	15	14	6	9	8	8
7	6	10	10	0	18	17	17	3	9	4	5	6	10	5	5
7	7	15	15	0	19	3	2	3	10	8	8	6	11	7	7
7	8	16	17	1	0	61	61	3	11	16	16	6	12	5	4
7	9	7	7	1	1	21	23	3	12	9	9	6	13	4	4
7	10	8	7	1	2	21	22	3	13	6	7	6	14	3	4
7	11	5	5	1	3	29	29	3	14	11	11	6	15	3	3
7	12	10	10	1	4	23	23	3	15	11	11	7	1	5	6
7	13	3	3	1	5	36	35	3	17	3	4	7	2	4	4
7	15	4	4	1	6	31	32	3	18	3	3	7	4	21	21
8	0	6	6	1	7	26	26	3	19	5	5	7	5	14	15
8	1	8	8	1	8	5	7	4	1	27	26	7	6	11	11
8	2	17	17	1	9	11	11	4	2	22	22	7	7	10	10
8	4	9	10	1	10	19	19	4	3	19	19	7	8	7	7
8	7	3	4	1	11	20	20	4	5	3	3	7	9	4	5
8	8	3	2	1	12	8	7	4	6	8	7	7	10	4	3
8	9	4	4	1	13	5	6	4	7	13	13	7	11	7	7
8	10	3	3	1	14	6	6	4	8	5	6	7	12	4	4
8	11	3	2	1	15	16	16	4	9	5	4	7	13	4	3
9	0	7	6	1	17	7	7	4	10	7	7	7	14	3	2
9	1	10	10	1	18	3	3	4	11	12	12	8	0	8	8
9	2	5	4	1	19	4	4	4	12	5	4	8	1	9	9
9	3	3	4	2	0	3	4	4	14	8	9	8	2	7	8
9	4	6	6	2	1	26	26	4	16	3	2	8	4	7	7
9	5	6	6	2	2	37	36	4	17	4	4	8	5	5	5
9	6	3	3	2	3	27	27	4	18	4	3	8	6	4	5
9	8	8	8	2	4	32	32	5	0	8	8	8	9	6	6

Table 4 (Continued)

9	0	8	8	2	6	15	15	5	7	5	5		H =	6	
9	2	5	6	2	7	11	12	5	8	15	16	K	L	FO	FC
9	3	5	5	2	8	3	3	5	9	17	17	0	0	33	35
9	4	6	7	2	9	10	9	5	10	16	17	0	1	3	1
9	5	3	3	2	10	6	6	5	11	4	5	0	2	6	7
9	6	8	7	2	11	9	11	5	13	3	3	0	4	27	26
9	7	3	3	2	12	8	9	5	14	4	4	0	6	26	25
9	8	5	5	2	13	13	13	5	15	4	3	0	7	17	17
				2	14	14	14	6	0	3	3	0	10	14	14
	H =	5		2	15	6	6	6	1	7	7	0	11	13	14
K	L	FO	FC	2	18	3	3	6	2	7	7	0	13	5	6
0	1	3	4	3	0	8	9	6	3	14	14	0	14	4	3
0	2	28	27	3	1	15	15	6	4	3	4	0	15	4	4
0	3	5	6	3	2	21	22	6	5	9	9	0	16	5	5
0	5	6	6	3	3	22	21	6	6	10	9	0	18	6	6
0	6	25	24	3	4	8	8	6	7	14	14	1	0	13	13
0	7	17	18	3	5	15	15	6	8	9	9	1	1	12	11
0	8	28	27	3	6	16	15	6	9	8	7	1	2	3	3
0	10	5	5	3	7	11	11	6	10	6	7	1	3	7	7
0	11	15	15	3	9	6	6	6	11	7	6	1	4	20	20
0	13	3	3	3	10	7	7	6	12	4	3	1	5	17	17
0	14	13	13	3	12	11	10	6	13	3	2	1	6	12	12
0	17	5	5	3	13	10	9	6	14	5	5	1	7	9	9
0	18	3	2	3	14	8	8	7	0	4	2	1	8	11	11
0	19	4	4	3	15	3	5	7	1	10	11	1	9	9	8
1	0	22	22	3	16	3	3	7	2	11	11	1	10	13	13
1	1	3	3	4	1	21	21	7	3	11	11	1	11	10	10
1	2	21	21	4	2	7	6	7	4	6	5	1	12	11	11
1	3	14	14	4	3	7	7	7	5	5	5	1	14	10	10
1	4	19	17	4	4	3	3	7	6	10	10	1	16	3	4
1	5	17	16	4	5	6	5	7	7	10	9	1	17	5	5
1	6	10	10	4	6	7	6	7	8	8	7	2	0	7	6
1	7	13	13	4	8	8	8	7	9	3	3	2	1	12	12
1	8	8	6	4	9	10	11	7	10	5	5	2	2	23	23
1	9	12	13	4	10	14	14	8	0	4	5	2	3	8	8
1	10	20	20	4	11	6	5	8	2	11	11	2	4	24	24
1	11	9	9	4	12	4	4	8	3	6	7	2	5	10	10
1	12	7	6	4	13	12	12	8	4	6	6	2	6	6	6
1	14	10	9	4	14	7	7	8	5	4	2	2	7	6	6
1	15	4	4	4	15	7	7	8	6	5	5	2	8	4	4
1	16	3	3	4	16	3	2	8	7	5	5	2	9	10	11
1	18	2	2	5	0	13	14	8	9	3	3	2	11	13	13
2	0	24	25	5	1	9	9	9	0	5	6	2	13	9	10
2	1	7	7	5	2	8	8	9	1	6	5	2	14	4	4
2	2	35	34	5	3	5	5	9	2	6	6	2	16	4	4
2	3	10	10	5	4	7	7	9	3	3	2	3	1	11	11
2	4	21	20	5	5	13	12					3	2	7	7
2	5	18	18	5	6	12	12					3	3	16	16

Table 4 (Continued)

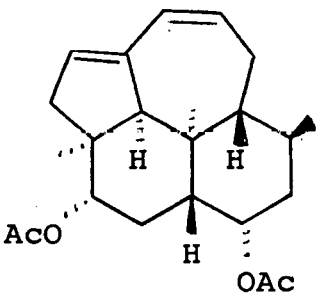
3	4	16	16	7	1	5	6	1	13	4	5	5	5	4	4
3	5	14	13	7	2	6	5	1	14	3	4	5	6	6	7
3	6	9	9	7	3	4	4	1	15	3	3	5	7	5	6
3	9	4	4	7	4	15	14	2	0	8	8	5	8	6	5
3	10	7	6	7	5	4	6	2	1	12	11	5	9	9	9
3	11	6	5	7	6	7	6	2	2	11	12	5	10	3	3
3	12	11	12	7	7	8	7	2	3	14	13	5	11	4	4
3	13	8	8	7	8	4	4	2	4	4	4	5	12	3	3
3	14	8	7	7	9	4	4	2	5	13	13	5	13	3	3
3	17	3	2	7	10	2	2	2	6	7	7	6	0	14	13
4	0	4	5	7	11	3	3	2	7	8	8	6	1	4	4
4	1	10	10	8	1	7	8	2	8	4	4	6	2	7	7
4	2	14	13	8	3	3	3	2	9	7	6	6	3	7	7
4	3	8	7	8	5	6	7	2	11	8	7	6	4	3	2
4	5	10	10	8	6	4	4	2	12	7	8	6	5	4	4
4	6	6	6	8	7	4	4	2	13	7	8	6	6	5	6
4	7	7	7					2	14	6	6	6	7	7	7
4	9	6	4		H =	7		2	15	4	4	6	8	3	4
4	10	6	7	K	L	FO	FC	2	16	6	6	6	10	4	4
4	11	17	17	0	1	9	9	3	0	2	3	6	11	6	6
4	13	3	3	0	2	18	18	3	1	6	7	7	2	7	7
4	14	9	9	0	3	6	6	3	2	7	7	7	3	7	7
4	15	3	2	0	4	4	2	3	3	3	2	7	4	4	3
5	1	8	7	0	5	16	17	3	4	10	9	7	6	3	2
5	2	3	3	0	6	6	5	3	6	9	9	7	7	5	4
5	4	4	4	0	7	3	3	3	7	12	12	8	0	5	5
5	5	6	7	0	8	7	8	3	8	7	7	8	1	4	4
5	6	11	11	0	9	9	9	3	9	6	7	8	3	3	3
5	7	5	5	0	10	3	3	3	10	4	5				
5	8	13	14	0	11	13	13	3	12	4	4		H =	8	
5	9	12	12	0	12	8	8	3	13	3	2	K	L	FO	FC
5	10	5	5	0	13	8	8	4	0	11	11	0	0	21	21
5	11	5	6	0	14	6	6	4	1	10	10	0	2	12	13
5	13	4	4	0	15	9	9	4	2	9	9	0	3	6	6
5	14	3	3	0	16	4	4	4	3	8	8	0	4	6	5
6	0	10	10	1	0	8	8	4	4	7	8	0	5	10	10
6	1	8	8	1	1	8	8	4	5	9	9	0	6	3	4
6	2	9	9	1	2	17	18	4	8	9	9	0	7	6	5
6	3	11	11	1	3	12	12	4	9	13	13	0	9	6	5
6	5	14	13	1	4	16	15	4	11	5	5	0	10	11	12
6	6	8	8	1	5	8	7	4	12	6	6	0	12	10	10
6	7	5	4	1	6	13	14	4	13	7	7	0	13	5	4
6	8	10	11	1	7	8	8	4	14	3	2	0	14	4	3
6	9	3	3	1	8	5	5	5	0	5	5	1	0	9	9
6	10	4	3	1	9	7	7	5	1	15	15	1	1	13	14
6	11	3	3	1	10	10	9	5	2	7	7	1	2	3	2
6	12	7	6	1	11	5	5	5	3	8	8	1	3	9	10
6	13	3	2	1	12	5	6	5	4	7	5	1	4	11	12

Table 4 (Continued)

1	5	11	11	5	11	3	4	4	5	10	9
1	8	5	5	6	1	9	9	4	9	5	4
1	9	4	4	6	2	7	6	4	10	4	3
1	11	4	5	6	3	8	8	5	0	14	14
1	12	5	6	6	4	3	3	5	4	5	5
1	13	7	8	6	5	7	7	5	6	7	8
1	15	3	3	6	8	5	4	6	0	7	7
2	0	7	7	7	0	4	4	6	1	9	9
2	2	13	13	7	1	4	4	6	2	5	5
2	3	18	18	7	2	5	5	6	3	3	3
2	4	5	6	7	4	5	4	6	4	4	3
2	5	16	16								
2	7	7	7		H =	9			H =	10	
2	9	6	6	K	L	FO	FC	K	L	FO	FC
2	10	6	5	0	1	8	8	0	0	7	6
2	11	3	2	0	3	7	7	0	3	3	4
2	13	3	3	0	4	4	3	0	8	7	6
2	14	2	3	0	5	8	8	1	1	6	7
3	0	3	3	0	9	6	6	1	2	7	7
3	2	7	7	0	10	10	9	1	3	7	8
3	3	5	5	0	12	3	4	1	4	8	8
3	4	4	4	1	1	7	7	1	5	4	3
3	5	10	10	1	2	14	15	1	8	4	3
3	6	7	7	1	3	5	5	2	0	8	8
3	7	10	9	1	4	4	4	2	2	6	6
3	8	3	2	1	5	6	6	2	3	6	6
3	9	4	4	1	6	12	11	2	4	9	9
3	11	5	5	1	8	4	5	2	7	3	2
3	12	4	5	1	9	6	5	3	0	3	3
3	13	5	5	1	10	3	3	3	2	3	3
4	0	5	4	2	0	5	4	3	3	4	4
4	1	12	11	2	1	14	14	3	4	3	3
4	4	6	6	2	3	8	7	3	6	3	3
4	5	11	11	2	4	5	6	3	7	4	4
4	6	3	3	2	5	13	12	4	1	3	4
4	7	4	4	2	6	7	7	4	4	5	5
4	8	6	6	2	7	9	8				
4	10	6	5	2	8	3	2		H =	11	
4	11	8	8	2	10	3	3	K	L	FO	FC
4	12	3	3	2	12	3	3	0	1	4	4
5	0	7	6	3	0	5	5	0	2	3	2
5	1	3	3	3	2	8	8	1	0	10	10
5	2	9	9	3	3	4	4	1	2	6	6
5	3	4	4	3	5	3	2	1	3	3	3
5	6	7	7	3	7	5	6	2	1	4	4
5	7	6	6	3	8	3	4	2	2	3	2
5	9	9	9	4	2	5	4				
5	10	4	4	4	3	5	5				

shown 12. This absolute configuration is verified by the positive Cotton effects due to the positively twisted diene system. The diene system is twisted 19.61° out of planarity. All bond distances and angles agree well with generally accepted values and show no pronounced strain effects on the structure (12).

The structure of kempene I 14 was consequently solved by spectral data and comparison to the completed x-ray solution of kempene II.



14

The mass spectra parent peak (m/e 386 M+) corresponds to a molecular formula of $C_{24}H_{34}O_4$, an increase of two carbons, one oxygen and four hydrogen atoms over the formula of kempene II. The ^{13}C-NMR resonances for C(2) and C(4) of kempene I (28.75 and 44.96 ppm) were downfield of the respective resonances in kempene II (36.06 and 53.89 ppm) and an additional carbinyl acetate proton at C(3) appears at 5.08 ppm as a broad doublet with a coupling of 9 Hz,

therefore, the ketone at C(3) of kempene II is now replaced by an acetate unit in kempene I.

Biflora-4,10-19,15-triene

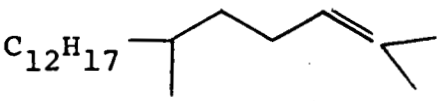
Background

Investigation of the frontal gland secretions of other members of the subfamily Termitinae turned up some surprising data in Cubitermes umbratus soldiers. Examination of the secretions indicated that the major components were four isomeric diterpene hydrocarbons but they were surprisingly not of closely related skeletal structures.

C. umbratus soldier heads were extracted with hexane and then chromatographed over a Florisil column as described previously (13). Biflora-4,10-19,15-triene was isolated as an oil. High resolution mass spectrum data was consistent with a molecular formula of $C_{20}H_{32}$ with M+ found at 272.2499 and calculated as 272.2502. The proton NMR spectrum suggested the presence of a secondary methyl group, a 1,1-disubstituted double bond, a trisubstituted double bond with an adjacent CH_2 and a second trisubstituted double bond with no significant coupling to α-protons (14).

Catalytic hydrogenation, microozonolysis and a ^{13}C NMR spectrum pointed to the 1,1-disubstituted double bond being exocyclic and an eight or nine carbon chain attached to one

of two rings. A partial structure 15 was presented for biflora-4,10-19,15-triene.



15

Because of the small amount of sample available, it was decided to prepare a suitable crystal for x-ray analysis.

Experimental

Sample size was a determining factor in deciding on suitable reaction conditions to change the biflora-4,10-19,15-triene oil to a crystalline derivative. It was desirable to employ a reagent which would selectively react with one of the three double bonds present. After careful consideration of possible reagents, a 5 mg sample of biflora-4,10-19,15-triene was subjected to hydroboration with 9-borabicyclononane (9-BBN). A 2:1 mixture of diastereomeric alcohols in an estimated 85% yield was obtained after oxidative work-up. The major isomer was isolated by a combination of chromatographic methods but failed to crystallize. A 500 µg sample of the major isomer was esterified with p-bromobenzoyl chloride and purified by HPLC on µ-Porasil.

A single crystal was obtained by slow evaporation of a pentane solution at -17°.

A portion of that crystal was received at this lab and x-ray diffraction data was subsequently taken using a fully-automated Syntex $P2_1$ diffractometer. It was found to belong to the monoclinic system with $\underline{a}$ = 7.880(8), $\underline{b}$ = 5.740(4), $\underline{c}$ = 28.19(1) Å and $\underline{\beta}$ = 94.61(6)°. Systematic extinctions indicated the monoclinic space group $P2_1$ with P2 a distinct possibility. A Patterson map was generated and the bromine atom located; its position indicated the space group $P2_1$ as the proper choice.

All unique data was taken with $2\theta \leq 114°$ using a 1°/minute ω-scan and graphite monochromated CuKα (1.54178 Å) x-rays. A total of 2060 reflections were measured with 1666 (81%) considered observed ($F_o^2 \geq 3\sigma(F_o^2)$) after correction for Lorentz, polarization and background effects (10).

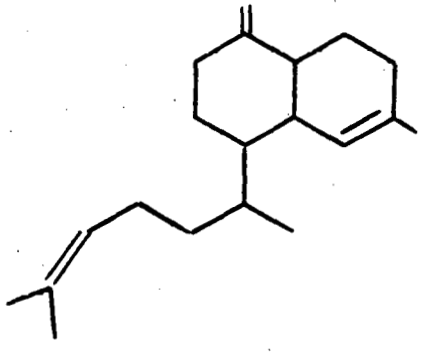
Utilization of a multiple solution tangent formula approach (11) as well as submittal of the bromine position into least squares refinement gave two possible fragments each bonded to the bromine as a result of the pseudosymmetry of the space group. Careful and methodical selection of bonded atoms provided the final structure as in Figure 2. which is a computer generated perspective drawing of biflora-4,10-19,15-triene. Coordinates of the hydrogen atoms were determined and final full-matrix least-squares refinements

using anisotropic temperature factors for all nonhydrogen atoms except C(14), C(15), C(16), C(17) and C(18) which were varied isotropically at a fixed temperature factor gave an unweighted crystallographic residual of 0.114. Tables 5, 6, 7 and 8 contain the fractional coordinates, bond distances, bond angles and observed and calculated structure factors.

Discussion

Due to the imperfection of the crystal and the thermal movement in the sidechain, the crystallographic residual of the existing data could not be satisfactorily reduced below 0.114.

Biflora-4,10-19,15-triene is a member of the decalin system with a double bond between C(4) and C(5), a double bond connecting C(19) to C(10), a methyl group off C(4) and an unsaturated eight carbon chain off C(7).



Biflora-4,10-19,15-triene

The atoms C(3), C(4), C(5) and C(6) are essentially planar with C(1) and C(2) being -0.462 and 0.335 Å out of the plane respectively. Atoms C(1), C(6), C(7), C(8), C(9) and C(10) form the other half of the decalin system and are in a chair conformation. It is not possible at this time to determine the absolute configuration of the molecule.

Examination of the molecule allows one to divide it into isoprenoid units. From this observation, it is logical to suggest that its biological basis is also isoprene units.

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Figure 2. A computer generated perspective drawing from the crystal structure of biflora-4, 10-19,15-triene with hydrogens omitted for clarity.

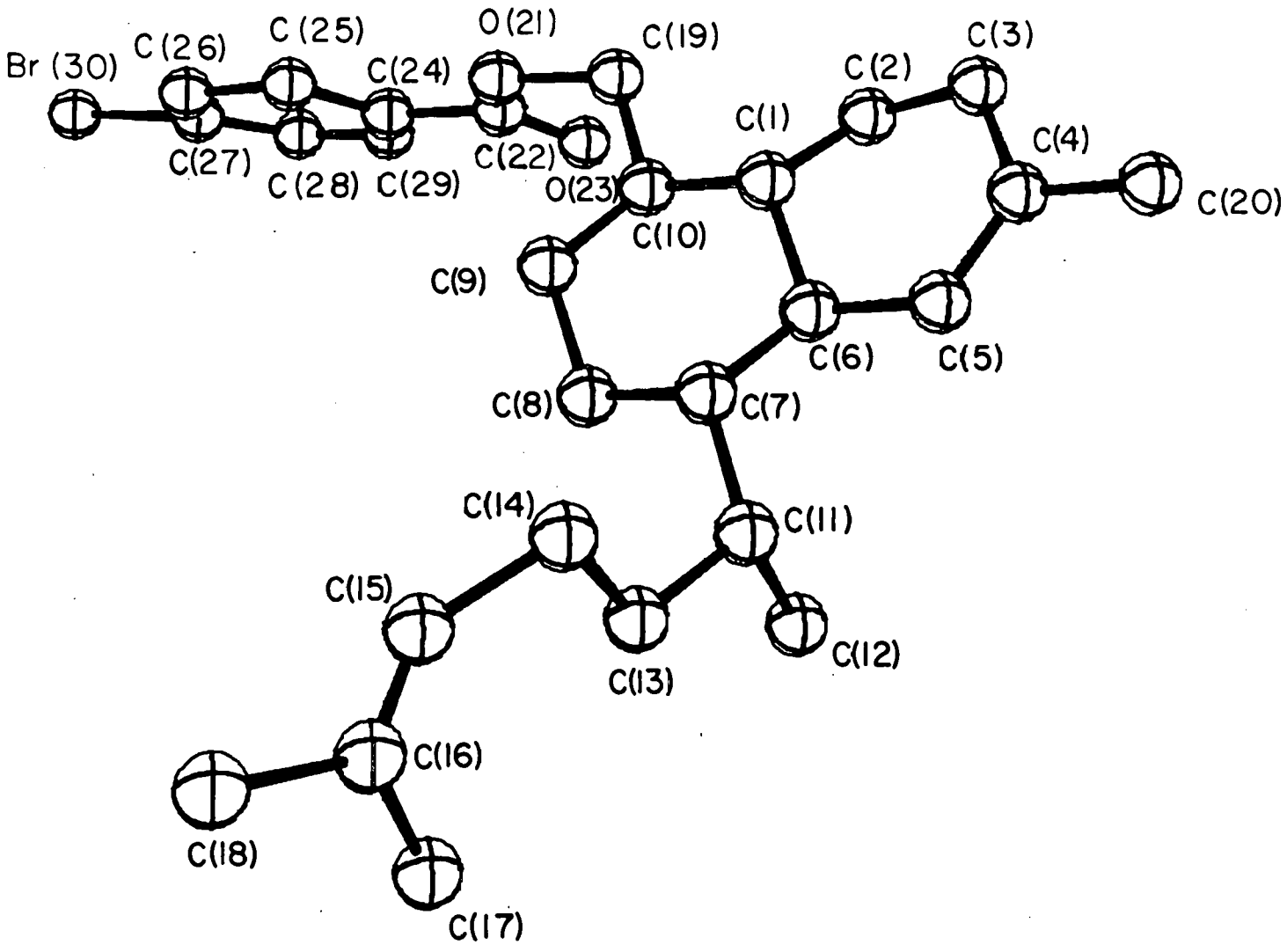
Br (30)
C(26)
C(25)
O(21)
C(19)
C(3)
C(24)
C(2)
C(1)
C(4)
C(27)
C(28)
C(29)
C(22)
O(23)
C(20)
C(10)
C(9)
C(6)
C(5)
C(8)
C(7)
C(14)
C(11)
C(15)
C(12)
C(13)
C(16)
C(18)
C(17)

Table 5. Final fractional coordinates for biflora-4,10-19,15-triene with the estimated standard deviation of the least significant figure given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. The numbering scheme refers to Figure 2.

C(1)	-.4716(21)	-.6795(29)	.2169(7)
C(2)	-.6397(23)	-.7023(45)	.1885(8)
C(3)	-.7413(25)	-.9068(52)	.2064(9)
C(4)	-.7391(23)	-.9066(42)	.2576(11)
C(5)	-.6291(22)	-.7636(60)	.2857(7)
C(6)	-.5013(22)	-.6079(39)	.2665(7)
C(7)	-.3292(26)	-.6014(48)	.3009(8)
C(8)	-.2131(32)	-.4315(65)	.2771(9)
C(9)	-.1840(24)	-.4904(44)	.2271(8)
C(10)	-.3450(23)	-.5103(39)	.1932(7)
C(11)	-.3516(30)	-.5567(53)	.3509(8)
C(12)	-.4536(34)	-.3329(53)	.3614(10)
C(13)	-.1838(35)	-.5467(61)	.3835(8)
C(14)	-.0699(31)	-.7792(64)	.3803(8)
C(15)	.1025(30)	-.6904(52)	.4046(9)
C(16)	.1751(33)	-.6618(51)	.4433(10)
C(17)	.0976(32)	-.4624(59)	.4603(9)
C(18)	.3510(29)	-.7919(58)	.4647(8)
C(19)	-.3230(27)	-.5740(42)	.1471(8)
C(20)	-.8568(26)	-1.0705(49)	.2815(10)
O(21)	-.1797(16)	-.4503(30)	.1262(6)
C(22)	-.2166(26)	-.2492(61)	.1076(6)
O(23)	-.3571(15)	-.1555(34)	.1068(6)
C(24)	-.0647(21)	-.1289(41)	.0885(7)
C(25)	.0916(19)	-.2372(60)	.0939(6)
C(26)	.2293(20)	-.1083(46)	.0775(7)
C(27)	.1982(19)	.0977(34)	.0517(5)
C(28)	.0368(22)	.1882(34)	.0447(7)
C(29)	-.0936(22)	.0764(46)	.0648(7)
Br(30)	.2789(2)	.2500(0)	.0258(1)
H(1)	-.407(0)	-.837(0)	.218(0)
H(2A)	-.621(0)	-.726(0)	.153(0)
H(2B)	-.707(0)	-.557(0)	.191(0)
H(3A)	-.678(0)	-1.063(0)	.197(0)
H(3B)	-.856(0)	-.916(0)	.192(0)
H(5)	-.633(0)	-.798(0)	.321(0)
H(6)	-.556(0)	-.456(0)	.263(0)
H(7)	-.278(0)	-.764(0)	.305(0)
H(8A)	-.271(0)	-.280(0)	.276(0)
H(8B)	-.104(0)	-.430(0)	.296(0)
H(9A)	-.108(0)	-.365(0)	.216(0)
H(9B)	-.120(0)	-.643(0)	.227(0)

Table 5 (Continued)

H(10)	-.404(0)	-.352(0)	.190(0)
H(11)	-.424(0)	-.689(0)	.360(0)
H(12A)	-.398(0)	-.202(0)	.349(0)
H(12B)	-.458(0)	-.329(0)	.397(0)
H(12C)	-.571(0)	-.361(0)	.346(0)
H(13A)	-.209(0)	-.535(0)	.418(0)
H(13B)	-.109(0)	-.423(0)	.375(0)
H(14A)	-.061(0)	-.829(0)	.347(0)
H(14B)	-.131(0)	-.919(0)	.397(0)
H(15)	.201(0)	-.715(0)	.387(0)
H(17A)	.109(0)	-.324(0)	.439(0)
H(17B)	.165(0)	-.428(0)	.493(0)
H(17C)	-.024(0)	-.487(0)	.467(0)
H(18A)	.358(0)	-.858(0)	.471(0)
H(18B)	.331(0)	-.609(0)	.498(0)
H(18C)	.420(0)	-.616(0)	.447(0)
H(19A)	-.294(0)	-.752(0)	.147(0)
H(19B)	-.428(0)	-.555(0)	.125(0)
H(20A)	-.788(0)	-1.187(0)	.303(0)
H(20B)	-.933(0)	-1.160(0)	.259(0)
H(20C)	-.930(0)	-.979(0)	.304(0)
H(25)	.110(0)	-.394(0)	.109(0)
H(26)	.350(0)	-.168(0)	.082(0)
H(28)	.013(0)	.329(0)	.025(0)
H(29)	-.215(0)	.141(0)	.063(0)

Table 6. Bond distances in angstroms for biflora-4,10-19,15-triene with the estimated standard deviation of the least significant figure given in parentheses. The numbering scheme refers to Figure 2.

C(1)	- C(2)	1.498(25)
C(1)	- C(6)	1.495(27)
C(1)	- C(10)	1.579(27)
C(2)	- C(3)	1.529(36)
C(3)	- C(4)	1.443(40)
C(4)	- C(5)	1.393(34)
C(4)	- C(20)	1.518(36)
C(5)	- C(6)	1.480(32)
C(6)	- C(7)	1.603(26)
C(7)	- C(8)	1.528(39)
C(7)	- C(11)	1.458(31)
C(8)	- C(9)	1.483(34)
C(9)	- C(10)	1.531(27)
C(10)	- C(19)	1.372(31)
C(11)	- C(12)	1.556(41)
C(11)	- C(13)	1.550(34)
C(13)	- C(14)	1.615(47)
C(14)	- C(15)	1.557(35)
C(15)	- C(16)	1.201(37)
C(16)	- C(17)	1.400(43)
C(16)	- C(18)	1.646(36)
C(19)	- O(21)	1.494(27)
O(21)	- C(22)	1.292(36)
C(22)	- O(23)	1.230(27)
C(22)	- C(24)	1.517(30)
C(24)	- C(25)	1.377(27)
C(24)	- C(29)	1.365(33)
C(25)	- C(26)	1.421(30)
C(26)	- C(27)	1.399(31)
C(27)	- C(28)	1.373(24)
C(27)	- Br(30)	1.869(17)
C(28)	- C(29)	1.372(28)

Table 7. Bond angles in degrees of biflora-4,10-19,15-triene. Estimated standard deviation of the least significant figures are given in parentheses. The numbering scheme refers to Figure 2.

C(2)	- C(1)	- C(6)	109.0(15)
C(2)	- C(1)	- C(10)	112.9(16)
C(6)	- C(1)	- C(10)	112.3(15)
C(1)	- C(2)	- C(3)	110.8(18)
C(2)	- C(3)	- C(4)	111.4(21)
C(3)	- C(4)	- C(5)	121.8(22)
C(3)	- C(4)	- C(20)	119.1(21)
C(5)	- C(4)	- C(20)	119.2(25)
C(4)	- C(5)	- C(6)	124.0(19)
C(1)	- C(6)	- C(5)	109.7(17)
C(1)	- C(6)	- C(7)	112.5(15)
C(5)	- C(6)	- C(7)	111.2(17)
C(6)	- C(7)	- C(8)	104.9(18)
C(6)	- C(7)	- C(11)	115.2(18)
C(8)	- C(7)	- C(11)	115.8(22)
C(7)	- C(8)	- C(9)	114.5(25)
C(8)	- C(9)	- C(10)	115.3(18)
C(1)	- C(10)	- C(9)	107.5(16)
C(1)	- C(10)	- C(19)	111.6(18)
C(9)	- C(10)	- C(19)	116.8(18)
C(7)	- C(11)	- C(12)	115.7(22)
C(7)	- C(11)	- C(13)	114.6(20)
C(12)	- C(11)	- C(13)	106.6(22)
C(11)	- C(13)	- C(14)	112.9(23)
C(13)	- C(14)	- C(15)	100.1(24)
C(14)	- C(15)	- C(16)	141.2(26)
C(14)	- C(15)	- C(17)	118.5(19)
C(15)	- C(16)	- C(17)	103.6(25)
C(15)	- C(16)	- C(18)	126.6(27)
C(17)	- C(16)	- C(18)	128.5(23)
C(10)	- C(19)	- O(21)	113.8(18)
C(19)	- O(21)	- C(22)	115.6(16)
O(21)	- C(22)	- O(23)	124.8(22)
O(21)	- C(22)	- C(24)	113.1(18)
O(23)	- C(22)	- C(24)	122.0(27)
C(22)	- C(24)	- C(25)	118.7(22)
C(22)	- C(24)	- C(29)	117.5(18)
C(25)	- C(24)	- C(29)	123.8(20)
C(24)	- C(25)	- C(26)	115.5(26)
C(25)	- C(26)	- C(27)	120.1(17)
C(26)	- C(27)	- C(28)	121.1(16)
C(26)	- C(27)	- BR(30)	119.4(12)
C(28)	- C(27)	- BR(30)	119.5(14)
C(27)	- C(28)	- C(29)	118.6(18)
C(24)	- C(29)	- C(28)	120.4(17)

Table 8. The observed and calculated structure factors for biflora-4,10-19,15-triene.

H = 0				1 32 12 16	3 15 25 26	5 5 26 28
K	L	FO	FC	1 33 10 11	3 16 26 26	5 6 24 26
0	2	3	3	1 34 4 5	3 17 35 36	5 7 22 20
0	4	20	22	2 0 6 8	3 18 15 16	5 8 51 54
0	6	50	58	2 1 51 48	3 19 5 3	5 9 17 18
0	8	51	62	2 2 52 44	3 20 3 1	5 10 31 32
0	10	22	26	2 3 9 10	3 21 11 13	5 11 7 8
0	12	36	47	2 4 33 34	3 22 11 12	5 12 35 35
0	14	4	6	2 5 19 15	3 25 27 29	5 13 30 29
0	16	70	92	2 6 37 41	3 26 11 12	5 14 50 50
0	18	41	51	2 7 81 74	3 28 5 2	5 15 29 28
0	20	45	58	2 8 74 76	3 29 16 17	5 16 36 36
0	22	38	51	2 9 44 40	3 30 16 15	5 17 16 17
0	24	9	12	2 10 63 68	3 31 6 7	5 18 63 58
0	26	26	32	2 11 18 23	3 32 11 10	5 21 15 15
0	28	11	15	2 12 8 12	4 0 7 8	5 22 8 9
0	30	25	29	2 13 43 42	4 1 46 45	5 24 7 6
0	32	16	19	2 14 17 21	4 2 68 64	5 25 11 9
0	34	15	14	2 15 6 4	4 3 75 72	5 28 5 4
1	1	11	3	2 16 15 18	4 4 8 8	5 29 11 10
1	2	28	25	2 17 20 18	4 5 19 14	6 2 28 29
1	3	39	46	2 18 28 31	4 6 66 60	6 3 33 31
1	4	104	108	2 19 5 5	4 7 80 77	6 5 50 45
1	5	59	68	2 20 5 1	4 8 3 5	6 6 39 38
1	6	31	37	2 21 13 13	4 9 13 14	6 7 41 38
1	7	35	38	2 22 22 25	4 11 8 7	6 8 15 12
1	8	36	38	2 23 27 29	4 12 32 30	6 9 8 7
1	9	51	56	2 24 40 47	4 14 20 19	6 10 20 18
1	10	3	2	2 25 13 16	4 15 31 31	6 11 11 13
1	11	110	136	2 26 21 23	4 16 6 8	6 12 4 5
1	12	70	81	2 27 22 23	4 17 5 6	6 14 14 14
1	13	18	26	2 28 9 10	4 18 35 36	6 15 13 11
1	14	8	7	2 29 16 20	4 19 65 67	6 17 17 17
1	15	41	50	2 31 5 6	4 20 9 11	6 18 29 28
1	16	6	8	2 32 10 11	4 21 22 21	6 19 5 2
1	17	34	36	3 1 6 10	4 22 9 7	6 20 10 11
1	19	3	2	3 2 39 35	4 23 45 43	6 21 11 11
1	20	39	47	3 3 38 38	4 24 26 25	6 22 16 17
1	21	22	26	3 4 98 94	4 25 11 10	6 23 8 6
1	22	17	21	3 5 31 31	4 26 8 7	6 24 4 8
1	23	8	12	3 6 11 10	4 27 15 13	6 25 11 11
1	24	6	8	3 7 65 62	4 28 6 6	6 26 22 20
1	25	15	17	3 8 39 43	4 29 24 22	6 27 5 5
1	26	10	10	3 9 24 21	4 31 12 10	7 1 9 11
1	27	22	25	3 11 41 34	5 1 15 13	7 2 5 3
1	28	8	8	3 12 94 92	5 2 32 33	7 3 18 18
1	29	5	3	3 13 74 69	5 3 16 14	7 4 5 1
1	31	14	18	3 14 24 23	5 4 58 54	7 5 11 9

Table 8 (Continued)

7	6	106	112		H =	1		1	16	30	32	2	31	23	24
7	8	16	15	K	L	FO	FC	1	17	23	26	2	32	7	8
7	9	13	14	0	1	41	43	1	18	27	33	2	33	15	14
7	10	53	51	0	2	45	50	1	19	32	36	3	0	89	78
7	11	8	7	0	3	106	124	1	20	28	32	3	1	38	36
7	12	26	25	0	4	97	116	1	21	16	16	3	2	31	23
7	14	28	28	0	5	20	23	1	22	30	36	3	3	32	25
7	15	12	13	0	6	75	87	1	23	14	13	3	4	84	78
7	16	17	14	0	7	17	20	1	24	10	10	3	5	19	22
7	17	5	5	0	8	14	16	1	25	16	18	3	6	64	63
7	18	18	18	0	9	45	56	1	26	31	35	3	7	87	82
7	20	17	13	0	10	30	36	1	27	14	17	3	8	48	45
7	21	13	12	0	11	7	5	1	28	8	10	3	9	45	42
7	22	13	14	0	12	24	25	1	29	14	13	3	10	14	10
7	23	7	6	0	13	7	8	1	30	5	6	3	11	10	14
7	24	7	5	0	14	25	25	1	31	16	14	3	12	42	40
8	0	27	28	0	15	16	19	1	33	10	12	3	13	12	11
8	1	30	33	0	16	16	23	2	0	101	87	3	14	26	25
8	2	25	25	0	17	14	20	2	1	65	59	3	15	33	32
8	3	9	8	0	18	10	11	2	2	67	65	3	16	23	24
8	4	9	11	0	19	15	20	2	3	53	47	3	17	12	11
8	5	29	31	0	20	5	6	2	4	94	87	3	18	17	16
8	6	46	49	0	21	19	23	2	5	77	70	3	19	19	20
8	7	8	9	0	22	5	6	2	6	26	24	3	20	15	14
8	8	19	16	0	23	5	8	2	7	61	56	3	22	23	20
8	9	26	26	0	24	17	18	2	8	60	61	3	23	25	26
8	10	14	14	0	25	5	7	2	9	39	41	3	24	15	14
8	11	5	6	0	28	19	23	2	10	42	42	3	25	20	19
8	12	22	23	0	29	6	8	2	11	73	73	3	26	13	11
8	13	21	21	0	30	9	11	2	12	29	24	3	28	10	9
8	14	6	5	0	32	5	8	2	13	40	40	3	29	10	11
8	15	5	4	0	33	7	7	2	14	56	62	3	30	11	13
8	16	12	9	1	0	31	26	2	15	29	32	3	31	5	6
8	17	24	24	1	1	60	59	2	16	49	51	3	32	10	9
8	18	11	11	1	2	111	108	2	17	7	8	4	0	30	28
8	19	5	3	1	3	70	68	2	18	47	50	4	1	55	46
9	1	34	37	1	4	104	103	2	19	29	28	4	2	60	54
9	2	4	8	1	5	4	6	2	20	36	36	4	3	38	28
9	4	7	9	1	6	75	75	2	21	8	7	4	4	55	49
9	5	9	10	1	7	56	63	2	22	28	33	4	5	17	16
9	6	8	9	1	8	22	25	2	23	26	27	4	6	47	41
9	7	11	10	1	9	67	71	2	24	14	13	4	7	20	19
9	8	14	14	1	10	38	40	2	25	29	29	4	8	35	33
9	9	9	7	1	11	32	34	2	26	40	41	4	9	10	11
9	10	10	9	1	12	22	23	2	27	14	17	4	10	43	40
9	11	39	38	1	13	29	34	2	28	6	6	4	11	30	27
9	14	7	4	1	14	43	42	2	29	15	15	4	12	28	28
				1	15	42	42	2	30	23	23	4	13	28	27

Table 8 (Continued)

4	14	15	15	6	3	48	46	8	0	20	22	0	16	8	8
4	15	36	35	6	4	14	14	8	1	8	6	0	19	6	6
4	16	23	24	6	5	18	14	8	2	16	18	0	20	15	18
4	17	8	5	6	6	35	29	8	3	22	22	0	22	35	40
4	18	5	7	6	7	11	11	8	4	5	5	0	23	10	11
4	19	6	4	6	8	58	57	8	5	15	17	0	24	12	11
4	20	12	12	6	9	18	19	8	7	25	24	0	25	6	8
4	21	14	13	6	10	40	42	8	9	19	17	0	26	18	21
4	22	16	16	6	11	26	27	8	10	17	14	0	27	25	27
4	23	13	13	6	12	40	40	8	11	21	21	0	29	12	10
4	24	14	13	6	13	23	19	8	12	8	9	0	30	5	6
4	25	13	13	6	14	21	20	8	13	17	18	0	31	16	18
4	26	8	6	6	15	12	15	8	14	7	9	0	32	5	4
4	27	14	11	6	16	33	29	8	15	26	26	1	0	150	140
4	28	17	16	6	17	26	24	8	16	20	17	1	1	44	40
4	29	9	7	6	18	8	9	8	18	8	7	1	2	49	40
4	30	7	6	6	19	42	39	8	19	3	4	1	3	35	34
5	0	8	9	6	20	23	20	9	1	15	16	1	4	60	62
5	1	41	39	6	21	18	18	9	2	25	28	1	5	37	36
5	2	34	37	6	22	8	8	9	3	7	11	1	6	42	42
5	3	37	35	6	23	21	18	9	4	22	24	1	7	39	42
5	4	11	8	6	24	8	6	9	5	28	29	1	8	17	19
5	5	18	19	6	25	18	16	9	6	16	19	1	9	19	17
5	6	45	47	6	26	22	20	9	7	7	7	1	10	42	41
5	7	12	10	7	0	55	59	9	8	17	18	1	11	29	32
5	8	38	36	7	1	20	20	9	9	6	3	1	12	32	33
5	9	17	15	7	2	15	17	9	10	13	15	1	13	13	11
5	10	51	47	7	3	33	32	9	11	12	12	1	14	13	12
5	11	4	4	7	4	34	35	9	12	17	17	1	15	50	52
5	12	36	34	7	5	29	30					1	16	31	35
5	13	29	26	7	6	16	14		H =	2		1	17	12	14
5	14	50	48	7	7	8	7	K	L	FO	FC	1	18	21	24
5	15	6	7	7	8	23	24	0	0	23	20	1	19	7	8
5	16	11	9	7	9	28	29	0	1	43	43	1	20	29	31
5	17	43	42	7	10	35	38	0	2	5	7	1	21	11	11
5	18	10	12	7	11	22	21	0	3	22	23	1	22	41	43
5	19	26	29	7	12	19	18	0	4	66	69	1	23	6	7
5	20	32	30	7	13	9	10	0	5	58	59	1	24	6	10
5	21	24	19	7	14	13	11	0	6	21	23	1	25	19	20
5	22	7	5	7	15	33	33	0	7	59	65	1	26	15	12
5	23	14	11	7	16	16	14	0	8	27	28	1	27	19	21
5	24	18	15	7	17	14	13	0	9	20	18	1	28	10	10
5	25	21	19	7	18	8	9	0	10	33	37	1	29	8	9
5	26	19	19	7	19	31	28	0	11	90	106	1	30	17	16
5	28	20	16	7	20	16	15	0	12	11	11	1	31	15	16
6	0	22	19	7	21	4	3	0	13	17	15	2	0	44	39
6	1	42	38	7	22	23	21	0	14	4	7	2	1	7	8
6	2	37	35	7	23	16	13	0	15	48	52	2	2	47	37

Table 8 (Continued)

2	3	63	55	3	22	30	29	5	9	17	15	7	4	22	24
2	4	26	23	3	23	28	26	5	10	11	9	7	5	29	34
2	5	28	24	3	24	37	34	5	11	6	5	7	6	10	9
2	6	6	8	3	25	9	11	5	12	29	26	7	7	28	27
2	7	14	13	3	26	12	12	5	13	25	23	7	8	18	19
2	8	36	29	3	27	8	7	5	14	32	30	7	9	26	25
2	9	15	14	3	28	17	16	5	15	30	27	7	10	10	9
2	10	15	16	3	29	9	8	5	16	29	29	7	11	14	13
2	11	25	26	3	30	13	12	5	17	8	6	7	12	5	8
2	12	18	17	4	0	35	34	5	18	24	23	7	13	15	17
2	13	17	19	4	1	14	14	5	19	21	18	7	14	10	9
2	14	31	35	4	2	47	41	5	20	26	24	7	15	9	8
2	15	6	8	4	3	53	47	5	21	21	20	7	16	23	22
2	16	21	22	4	4	72	64	5	22	22	20	7	17	33	30
2	18	10	10	4	5	38	34	5	23	14	13	7	18	7	5
2	19	13	12	4	6	19	20	5	24	4	4	7	19	5	1
2	20	18	20	4	7	38	32	5	25	23	19	7	20	7	5
2	21	15	16	4	8	61	56	5	26	17	15	7	21	25	23
2	22	8	12	4	9	31	27	5	27	11	10	8	1	21	25
2	23	6	8	4	10	48	48	6	1	4	3	8	2	6	9
2	24	18	18	4	11	7	9	6	2	16	17	8	3	5	5
2	25	19	20	4	12	59	54	6	3	18	15	8	4	20	20
2	26	17	15	4	13	50	46	6	4	22	22	8	5	18	16
2	27	16	16	4	14	37	35	6	5	8	9	8	6	31	33
2	28	11	12	4	15	30	27	6	6	41	39	8	7	26	28
2	29	5	5	4	16	41	37	6	7	31	31	8	8	10	9
3	0	14	12	4	17	26	25	6	8	16	14	8	9	29	30
3	1	76	70	4	18	42	38	6	9	37	35	8	10	37	40
3	2	55	55	4	19	28	24	6	10	13	11	8	11	12	13
3	3	43	41	4	20	19	19	6	11	22	21	8	12	10	13
3	4	65	58	4	21	9	7	6	12	18	18	8	13	17	17
3	5	22	17	4	22	7	6	6	13	7	6	8	14	18	18
3	6	56	50	4	23	6	8	6	14	11	11	8	15	13	10
3	7	41	36	4	24	10	7	6	15	7	8	8	16	16	14
3	8	61	55	4	25	12	11	6	16	28	28	8	17	20	19
3	9	37	33	4	26	23	22	6	17	15	14	9	0	6	6
3	10	12	12	4	27	13	9	6	18	16	16	9	1	20	22
3	11	18	16	4	28	17	14	6	19	24	21	9	2	15	15
3	12	10	10	4	29	23	20	6	20	14	11	9	4	19	20
3	13	12	16	5	0	19	17	6	21	21	18	9	6	21	22
3	14	38	39	5	1	20	21	6	22	20	17	9	7	11	13
3	15	40	36	5	2	7	8	6	23	13	11	9	8	5	7
3	16	7	3	5	3	41	39	6	24	8	7	9	9	14	14
3	17	7	3	5	4	37	33	6	25	7	6				
3	18	28	29	5	5	13	12	7	0	9	9		H =	3	
3	19	28	27	5	6	13	13	7	1	28	30	K	L	FO	FC
3	20	22	21	5	7	49	45	7	2	13	15	0	1	12	9
3	21	15	15	5	8	25	24	7	3	17	19	0	2	37	34

Table 8 (Continued)

0	3	4	5	1	23	16	17	3	10	32	31	5	2	30	29
0	4	13	14	1	24	16	15	3	11	76	71	5	3	35	34
0	5	5	5	1	25	9	9	3	12	23	21	5	4	18	19
0	6	21	19	1	26	6	9	3	13	12	11	5	5	11	8
0	7	35	36	1	27	12	12	3	14	42	43	5	6	14	11
0	8	13	17	1	28	13	14	3	15	24	21	5	7	12	13
0	10	30	30	1	29	17	20	3	16	33	31	5	8	31	30
0	11	8	7	1	30	14	15	3	17	9	10	5	9	21	21
0	12	12	14	2	0	43	38	3	18	32	30	5	10	45	42
0	14	9	9	2	1	28	25	3	19	23	21	5	12	30	30
0	15	20	22	2	2	53	48	3	20	11	12	5	13	21	18
0	17	28	27	2	3	47	40	3	21	13	11	5	14	26	23
0	18	22	24	2	4	67	61	3	22	26	27	5	15	18	16
0	19	22	22	2	5	13	13	3	23	19	18	5	16	23	20
0	20	7	9	2	6	45	39	3	24	9	8	5	17	11	12
0	21	7	7	2	7	45	39	3	25	5	5	5	18	30	28
0	22	18	21	2	8	11	9	3	26	16	14	5	19	11	9
0	23	14	15	2	9	42	38	3	27	16	15	5	20	26	23
0	24	7	6	2	10	41	41	3	28	5	4	5	21	11	11
0	25	5	6	2	11	18	20	4	0	33	32	5	22	15	13
0	26	10	12	2	12	12	13	4	1	9	7	5	23	16	14
0	27	4	5	2	13	22	22	4	2	36	33	5	24	19	16
0	28	5	5	2	14	18	18	4	3	5	5	6	0	36	38
0	29	7	9	2	15	24	23	4	4	4	4	6	1	39	41
0	30	7	9	2	16	31	29	4	5	34	30	6	2	12	15
1	0	63	54	2	17	16	18	4	7	38	35	6	3	36	36
1	1	45	39	2	18	31	30	4	8	24	21	6	4	5	5
1	2	47	37	2	19	18	17	4	9	7	7	6	5	31	31
1	3	11	8	2	20	32	32	4	10	25	21	6	6	9	8
1	4	69	67	2	21	14	13	4	11	31	31	6	7	17	20
1	5	66	59	2	22	40	38	4	12	22	21	6	8	24	27
1	6	34	29	2	23	11	9	4	13	15	14	6	9	13	12
1	7	31	31	2	24	21	20	4	14	21	19	6	10	35	35
1	8	25	24	2	25	13	13	4	15	16	15	6	11	21	19
1	9	34	33	2	26	23	22	4	16	28	27	6	12	23	20
1	10	9	5	2	27	5	4	4	17	38	36	6	13	9	10
1	11	33	33	2	28	13	11	4	18	12	9	6	14	16	16
1	12	22	21	2	29	20	18	4	19	7	6	6	15	27	25
1	13	17	15	3	0	38	34	4	20	22	20	6	16	24	25
1	14	24	23	3	1	33	31	4	21	6	4	6	17	26	23
1	15	16	19	3	2	12	10	4	22	7	7	6	18	13	11
1	16	15	15	3	3	22	20	4	23	20	17	6	19	12	10
1	17	19	18	3	4	42	40	4	24	16	14	6	20	10	9
1	18	24	25	3	5	39	31	4	25	8	6	6	21	18	17
1	19	9	8	3	6	32	29	4	26	8	6	6	22	25	21
1	20	21	23	3	7	16	15	4	27	8	5	7	0	7	9
1	21	9	11	3	8	32	28	5	0	29	25	7	1	11	13
1	22	22	22	3	9	11	13	5	1	22	24	7	2	13	12

Table 8 (Continued)

7	3	8	8	0	18	25	27	2	13	23	20	4	13	30	30
7	4	11	10	0	19	5	6	2	14	27	27	4	14	36	33
7	5	12	11	0	20	27	28	2	15	34	32	4	15	22	20
7	6	11	15	0	21	29	29	2	16	5	7	4	17	9	8
7	7	18	18	0	22	17	18	2	17	12	12	4	18	21	19
7	8	25	26	0	23	7	8	2	18	5	5	4	19	11	9
7	9	4	5	0	24	26	26	2	19	14	13	4	21	18	17
7	10	12	12	0	25	6	3	2	20	15	14	4	22	17	15
7	11	28	28	0	27	19	21	2	22	9	8	4	23	9	8
7	12	21	20	1	0	73	64	2	23	4	3	5	0	13	15
7	13	15	15	1	1	10	7	2	24	23	21	5	1	8	9
7	14	12	11	1	2	10	6	2	25	9	7	5	2	18	19
7	15	11	12	1	3	20	16	2	26	6	5	5	3	36	41
7	16	6	8	1	4	31	27	3	0	7	7	5	5	14	16
7	18	11	10	1	5	20	19	3	1	24	23	5	6	19	24
8	0	20	22	1	6	21	19	3	2	41	38	5	7	18	19
8	1	10	12	1	7	23	23	3	3	42	38	5	8	7	6
8	2	23	25	1	8	13	12	3	4	18	16	5	9	21	19
8	3	9	8	1	9	30	32	3	5	7	5	5	10	19	18
8	4	20	22	1	10	19	19	3	6	5	8	5	11	24	23
8	5	17	18	1	11	18	18	3	7	33	32	5	12	8	8
8	6	7	8	1	12	35	32	3	8	45	42	5	13	5	7
8	7	8	9	1	13	4	3	3	9	26	27	5	14	22	23
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8	9	4	2	1	15	13	10	3	11	15	13	5	16	4	2
8	10	19	20	1	16	33	32	3	12	25	25	5	17	9	9
8	11	7	9	1	17	5	6	3	13	9	7	5	18	16	14
8	12	14	15	1	18	11	10	3	14	6	5	5	19	34	32
				1	19	8	8	3	15	22	22	5	20	8	7
	H =	4		1	20	26	24	3	16	11	12	6	0	6	6
K	L	FO	FC	1	22	13	14	3	17	20	19	6	1	8	10
0	0	64	61	1	23	8	9	3	18	21	20	6	2	9	11
0	1	4	4	1	24	4	5	3	19	28	23	6	4	6	8
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0	3	7	10	1	26	36	35	3	23	20	17	6	6	16	20
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0	7	32	31	2	3	37	35	4	3	30	30	6	10	10	13
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0	11	41	43	2	7	6	8	4	7	18	20	6	15	9	11
0	12	9	11	2	8	28	28	4	8	47	46	6	16	13	11
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0	14	13	13	2	10	12	13	4	10	6	6	7	2	4	4
0	15	50	51	2	11	15	12	4	11	25	23	7	4	17	22
0	16	24	25	2	12	19	17	4	12	28	27	7	5	13	18

Table 8 (Continued)

7	6	11	14	2	1	4	4	4	12	6	7
7	7	6	9	2	2	14	15	4	13	21	21
7	8	9	10	2	3	7	7	4	14	14	14
7	9	15	17	2	4	25	26	4	15	8	8
7	10	16	18	2	5	24	25	4	16	15	14
7	11	3	4	2	6	13	14	5	1	17	23
				2	7	28	30	5	2	12	13
	H =	5		2	8	11	13	5	3	9	15
K	L	FO	FC	2	9	27	25	5	4	12	16
0	1	16	17	2	10	17	16	5	5	12	15
0	2	9	8	2	11	41	43	5	6	7	8
0	3	10	9	2	12	16	19	5	7	8	11
0	5	9	9	2	13	16	18	5	8	11	14
0	6	27	29	2	14	25	24	5	9	4	3
0	7	9	8	2	15	5	2	5	11	8	8
0	8	13	14	2	16	6	6	6	0	6	12
0	9	21	22	2	17	16	15	6	1	4	5
0	10	8	8	2	18	17	16	6	2	6	10
0	11	19	20	2	19	21	21	6	4	6	11
0	12	11	12	2	20	8	7	6	5	5	9
0	14	23	24	3	0	24	25				
0	15	27	28	3	1	18	19				
0	16	9	10	3	2	13	15				
0	17	18	17	3	3	8	11				
0	19	13	14	3	4	21	22				
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0	21	6	7	3	6	13	15				
1	0	39	40	3	7	26	25				
1	2	37	40	3	8	14	16				
1	3	17	17	3	9	4	7				
1	4	20	20	3	11	21	21				
1	5	10	10	3	14	7	6				
1	6	21	22	3	15	5	5				
1	7	8	6	3	16	14	14				
1	8	11	10	3	17	12	10				
1	9	11	12	3	18	4	3				
1	10	14	12	4	0	17	17				
1	12	9	9	4	1	7	8				
1	13	12	11	4	2	12	16				
1	14	6	5	4	3	5	5				
1	15	8	9	4	4	15	16				
1	16	16	18	4	5	9	9				
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1	18	28	29	4	7	9	10				
1	19	9	7	4	8	12	11				
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2	0	20	21	4	11	10	10				

NATURAL PRODUCTS OF MARINE NUDIBRANCHS

General Introduction

The definition of a symbiont as proposed by Cheng in 1964 states that "any animal or plant that spends a portion or all of its life cycle intimately associated with a different and larger species of animal or plant, during which there is a physiological exchange is considered a symbiont" (15). The phenomenon of movement of soluble photosynthetic products from autotrophic endosymbionts to heterotrophic hosts is now well-established. In fact, the synthesis and secretion of photosynthetically derived materials by animals with autotrophic endosymbionts is widespread and is now being viewed as an important aspect of the recycling of organic matter in coral-reef ecosystems. Examples of symbionic associations with whole algae (Zooxanthellae or Zoochlorellae) can be found in Tridacna, in the sea anemone Anthopleura, in Zoanthus danae, Z. sociatus and Convoluta roscoffensis (16). Marine sea slugs (Opisthobranchia: Sacoglossa) which feed on green algae possess endosymbiotic chloroplasts which contribute photosynthetically fixed carbon to its host.

Sacoglossans are known to characteristically feed on siphonaceous algae by puncturing single cells and sucking out the fluid contents. Functioning chloroplasts are contained in the cellular contents and are carried intact to

the absorbing tubules of the digestive diverticula (Figure 3). Evidence currently available suggests that the chloroplasts

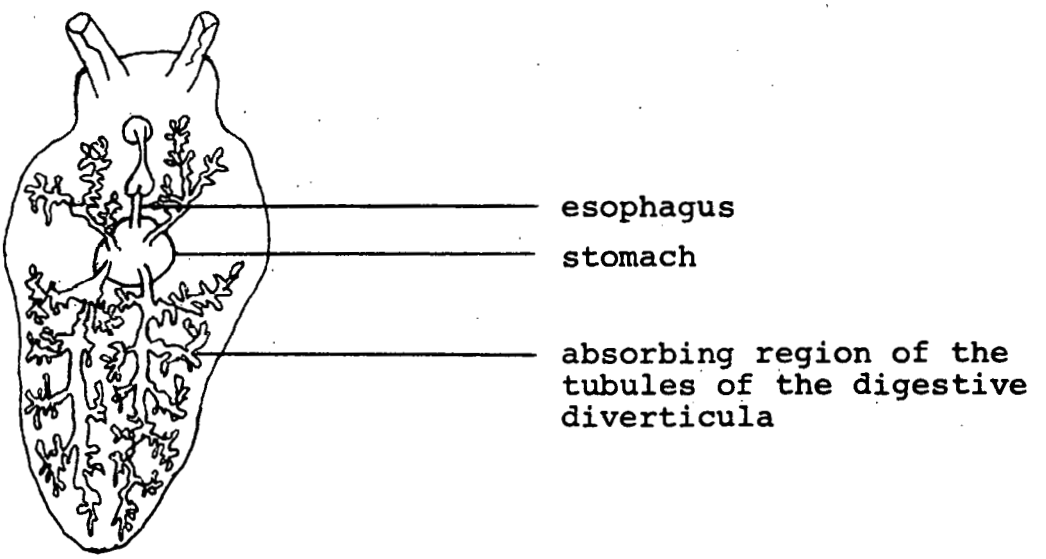


Figure 3. Diagram of the digestive system of a sacoglossan mollusc.

are then engulfed by the phagocytic epithelial cells of the diverticula. Engulfed chloroplasts appear to be free of plant cytoplasm and associated organelles by both morphological and biochemical criteria (17).

Engulfed chloroplasts continue to undergo carbon fixation by photosynthesis. This brings into question whether the chloroplasts are still functioning normally as they would if they were still in the parent plant cells. Trench has proposed the five criteria that he feels defines the normal function of chloroplasts as found in plants: (18)

i) carbon fixation (photosynthesis)

ii) release of organic compounds

iii) synthesis of photosynthetic pigments

iv) synthesis of protein

v) synthesis of RNA and DNA

As will be discussed, the chloroplasts located within the sacoglossans satisfy conditions i and ii but not the others and that they are biochemically stable entities that neither grow nor divide within the animals' cells.

Isolated sea slugs have been kept from their algae source and monitored to determine the period of time that their chloroplasts would continue to function. Surprisingly, these periods have been known to extend up to three months. During this time, chlorophylls and glycolipids are not synthesized but small molecular weight metabolites such as sugars and amino acids are readily produced (19).

When sacoglossans are incubated in sea water containing ^{14}C labeled $NaHCO_3$, ^{14}C fixation by the chloroplasts and its utilization by the slug can be conveniently followed. After a short period of incubation, labeled sugar moieties are found in the gut, If left for longer periods of incubation, ^{14}C labeled materials, primarily glucose and galactose, can be found in chloroplast-free tissues (20,21).

One of the predominant ways in which the slug utilizes chloroplast-derived products is in the synthesis of mucopolysaccharide by the pedal gland. The pedal gland's secretion forms the mucous path over which the slug crawls. Chemical analysis of the secretion shows that it is acidic, sulphated, of large molecular weight (in excess of 2×10^6) and is composed of glucose, gluconic acid, glucosamine, galactosamine and traces of galactose. The protein moiety contains leucine, glutamic acid, aspartic acid, glycine, serine, valine, proline and alanine. Examination of ^{14}C incubated slugs produces labeled sugar moieties. These same sugars can be isolated from unlabeled animals. Using these results as evidence, it has been suggested that photosynthetic products produced by the chloroplasts are used as precursors in the synthesis of mucus by the animal cells (16).

Tridachione

Background

In an attempt to learn more about these unusual molluscs, chemical isolation procedures have been carried out on Tridachiella diomedea, commonly called the Mexican Dancer. It is one of the sacoglossans which form the symbionic relationships with the chloroplasts of the green algae it feeds on.

Tridachione was isolated in the pure state as an oil with a molecular formula of $C_{22}H_{30}O_4$ and a UV maximum at 257 mμ. The oil proved uncrystallizable, therefore other methods were attempted to find a suitable crystallizing analog. The BF_3 etherate rearranged product proved to be formed in high yield and suitable crystals were supplied by the Faulkner group.

Experimental

A clear crystal of the BF_3 etherate rearranged product of tridachione was analyzed by single crystal x-ray diffraction and found to belong to the orthorhombic system. Systematic extinctions (hOO, h = 2N+1; OkO, k = 2N+1; OOl, l = 2N+1) placed it unambiguously in the space group $P2_12_12_1$ with $\underline{a}$ = 7.821(2), $\underline{b}$ = 12.880(3) and $\underline{c}$ = 20.359(5) Å. A total of 1637 unique reflections with $2\theta \leq 114°$ were measured on a fully automated four-circle diffractometer using monochromated CuKα (1.54178 Å) radiation with an ω-scan rate of 1°/minute. After Lorentz, polarization and background corrections were made, 1342 (82%) reflections were judged observed ($F_o^2 \geq 3\sigma(F_o^2)$) (10).

Utilization of a multiple solution tangent formula approach (11) gave the complete structure plus a few extra atoms. Insertion of the two six rings into full-matrix

least-squares refinement cleared up all ambiguities and clearly revealed the entire structure. Assignment of the oxygen atoms was made after a thorough examination of bond distances and isotropic temperature factors. Coordinates of the hydrogen atoms were determined and final full-matrix least-squares refinements using anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms produced an unweighted crystallographic residual of 0.049. Figure 4 contains a computer generated perspective drawing of tridachione and Tables 9, 10, 11 and 12 contain the fractional coordinates, bond distances, bond angles, and observed and calculated structure factors.

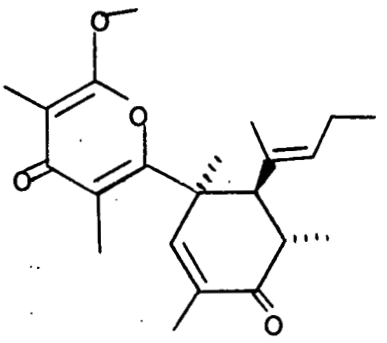
Discussion

Tridachione 16 is a substituted γ-pyrone molecule which appears to be biosynthetically derived entirely from propionate units.

The pyrone ring minus the cyclohexenone substituent is approximately planar with the methyl group of the methoxy substituent being 0.125 Å out of the plane. The cyclohexenone substituent is attached to the γ-pyrone ring from C(6) on the substituent to C(5) on the pyrone ring. As would be expected, C(6) is also in the plane of the pyrone ring with the bond formed between C(11) and C(6) being perpendicular

to the plane of the pyrone ring with dihedral angles of 86.25° for O(24)-C(5)-C(6)-C(11) and -93.84° for C(4)-C(5)-C(6)-C(11).

Atoms C(7), C(8), C(9) and C(10) of the cyclohexenone ring are essentially planar, the dihedral angle being 2.07°. Atom C(6) lies 0.2781 Å above the plane and atom C(11) lies 0.7840 Å above the plane.



16

Tridachione is found to exhibit antibacterial action on a marine bacteria. Other structurally related γ-pyrones can be found in nature which also exhibit antibacterial activity such as spectinabilin 17 from Streptomyces spectabilis and aureothen 18 from both S. thioluteus and S. luteoreticali (22,23).

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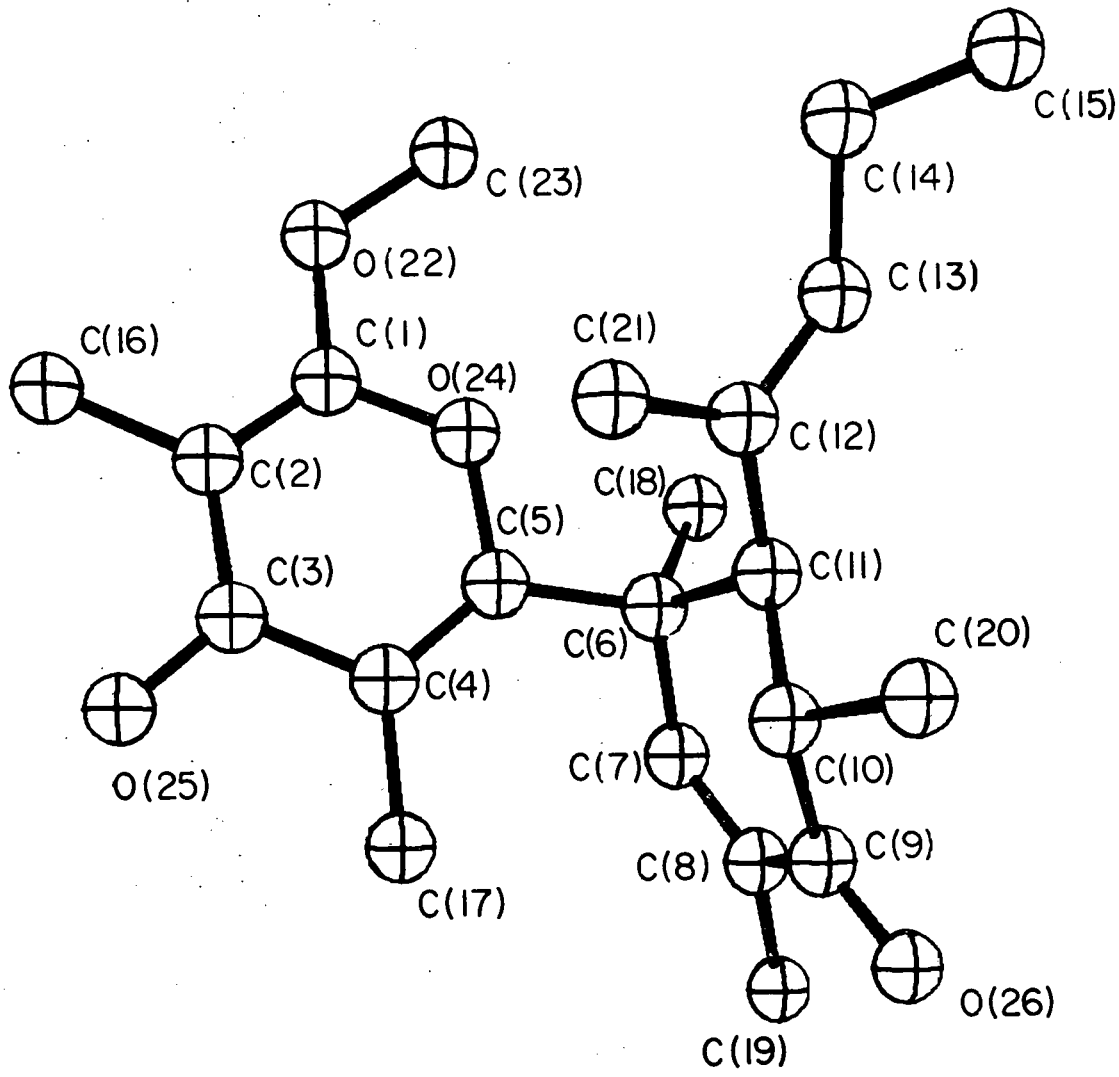
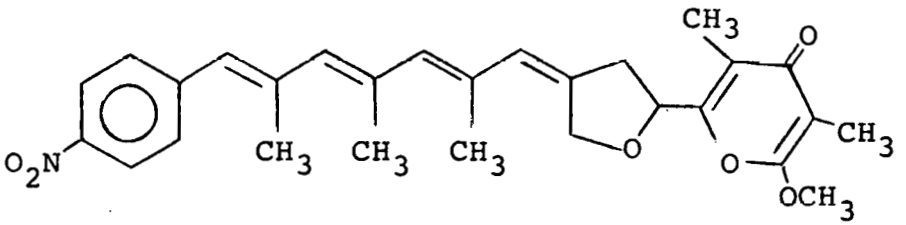
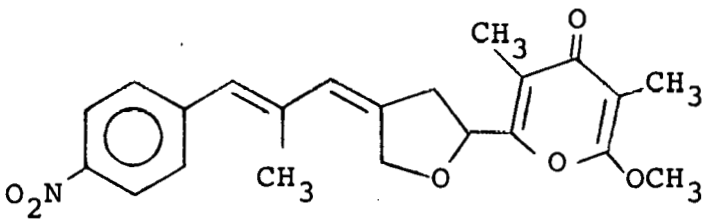
Figure 4. A computer generated perspective drawing from the crystal structure of tridachione with hydrogens omitted for clarity.


C(15)
C(14)
C(23)
C(13)
O(22)
C(21)
C(16)
C(1)
O(24)
C(12)
C(2)
C(18)
C(5)
C(11)
C(3)
C(6)
C(20)
C(4)
C(7)
C(10)
O(25)
C(9)
C(8)
C(17)
O(26)
C(19)



17



18

The proposed biosynthetic pathway of these compounds is also a propionate-acetate sequence such as shown in Figure 5 for aureothin (24).

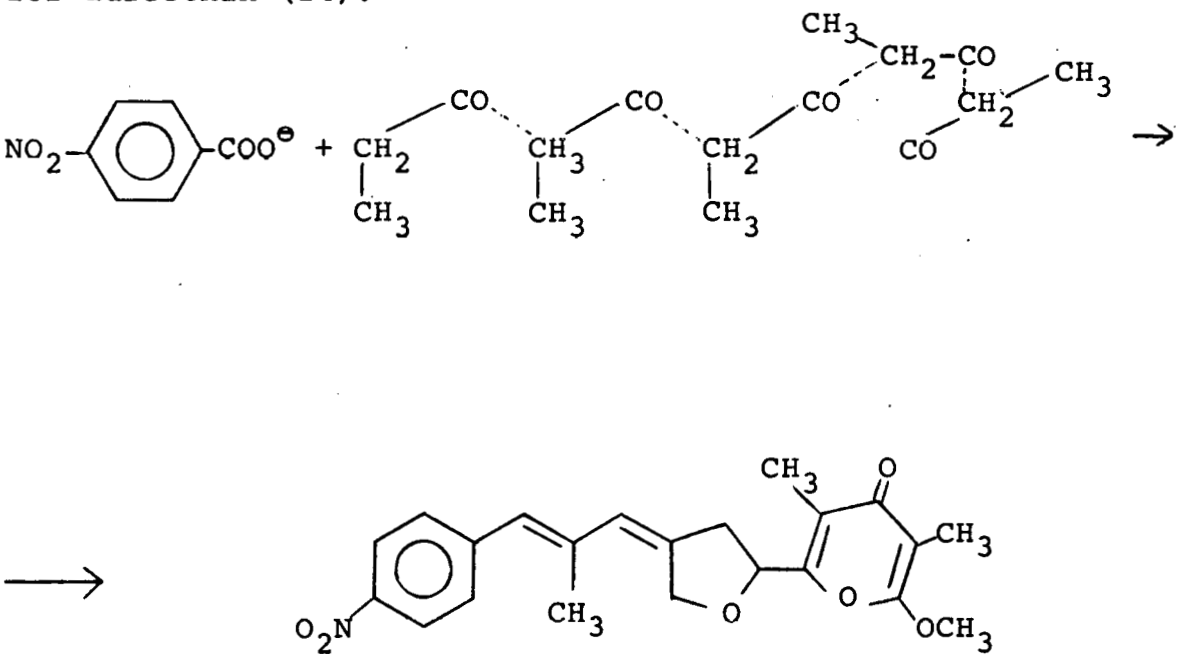


Figure 5. Proposed propionate-acetate biosynthetic sequence for aureothin.

Table 9. Final fractional coordinates for tridachione with the estimated standard deviation of the least significant figure given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. The numbering scheme refers to Figure 4.

C(1)	-.9603(6)	-.2242(3)	.1602(2)
C(2)	-.9372(6)	-.3075(3)	.1229(2)
C(3)	-.9171(6)	-.2924(3)	.0543(2)
C(4)	-.9233(5)	-.1865(3)	.0285(2)
C(5)	-.9502(5)	-.1068(3)	.0709(2)
C(6)	-.9661(5)	.0105(3)	.0608(2)
C(7)	-1.0421(7)	.0334(3)	-.0058(2)
C(8)	-.9674(7)	.0845(3)	-.0549(2)
C(9)	-.7841(7)	.1073(4)	-.0512(2)
C(10)	-.6836(5)	.0686(3)	.0076(2)
C(11)	-.7934(5)	.0710(3)	.0701(2)
C(12)	-.6938(6)	.0428(3)	.1308(2)
C(13)	-.6945(8)	.1071(4)	.1823(2)
C(14)	-.6031(12)	.0967(6)	.2453(3)
C(15)	-.5055(19)	.1885(9)	.2642(5)
C(16)	-.9291(16)	-.4149(4)	.1523(5)
C(17)	-.8992(9)	-.1775(5)	-.0443(2)
C(18)	-1.0957(7)	.0542(4)	.1107(3)
C(19)	-1.0629(16)	.1134(6)	-.1162(4)
C(20)	-.5180(7)	.1328(5)	.0151(3)
C(21)	-.5893(9)	-.0539(5)	.1311(4)
O(22)	-.9802(6)	-.2314(2)	.2247(1)
C(23)	-.9916(15)	-.1381(5)	.2636(3)
O(24)	-.9690(4)	-.1264(2)	.1376(1)
O(25)	-.8923(5)	-.3677(2)	.0161(2)
O(26)	-.7164(6)	.1559(4)	-.0957(2)
H(7)	.156(7)	.506(4)	.511(2)
H(10)	-.344(4)	.500(3)	.505(2)
H(11)	-.163(4)	.645(3)	.425(2)
H(13)	-.251(6)	.665(4)	.322(2)
H(14A)	-.504(12)	.550(6)	.255(4)
H(14B)	-.334(15)	.588(9)	.209(6)
H(15A)	-.623(13)	.696(7)	.279(5)
H(15B)	-.573(14)	.679(7)	.206(5)
H(15C)	-.371(13)	.746(7)	.232(4)
H(16A)	.002(7)	.051(4)	.364(2)
H(16B)	-.080(8)	.104(4)	.309(3)
H(16C)	-.135(8)	.040(4)	.375(3)
H(17A)	-.191(8)	.281(5)	.554(3)
H(17B)	-.101(7)	.385(4)	.549(2)
H(17C)	-.035(13)	.259(6)	.559(4)
H(18A)	.049(6)	.555(3)	.345(2)

Table 9 (Continued)

H(18B)	.220(8)	.503(4)	.388(2)
H(18C)	.119(5)	.623(4)	.397(2)
H(19A)	.036(10)	.691(6)	.626(3)
H(19B)	.151(14)	.567(9)	.613(5)
H(19C)	.016(11)	.579(7)	.642(4)
H(20A)	-.440(10)	.708(7)	.485(3)
H(20B)	-.540(9)	.619(5)	.524(3)
H(20C)	-.524(8)	.607(5)	.440(3)
H(21A)	-.365(10)	.398(7)	.364(4)
H(21B)	-.488(11)	.442(6)	.335(4)
H(21C)	-.420(13)	.420(8)	.405(5)
H(23A)	-.129(7)	.399(4)	.249(2)
H(23B)	-.026(9)	.334(5)	.185(3)
H(23C)	.090(6)	.368(4)	.233(2)

Table 10. Bond distances in angstroms for tridachione with the estimated standard deviation of the least significant figure given in parentheses. The numbering scheme refers to Figure 4.

C(1)	- C(2)	1.327(5)
C(1)	- O(22)	1.326(5)
C(1)	- O(24)	1.342(4)
C(2)	- C(3)	1.419(6)
C(2)	- C(16)	1.509(7)
C(3)	- C(4)	1.463(5)
C(3)	- O(25)	1.257(5)
C(4)	- C(5)	1.357(5)
C(4)	- C(17)	1.500(6)
C(5)	- C(6)	1.530(5)
C(5)	- O(24)	1.390(4)
C(6)	- C(7)	1.510(6)
C(6)	- C(11)	1.571(6)
C(6)	- C(18)	1.540(7)
C(7)	- C(8)	1.332(7)
C(8)	- C(9)	1.465(8)
C(8)	- C(19)	1.502(10)
C(9)	- C(10)	1.515(6)
C(9)	- O(26)	1.222(7)
C(10)	- C(11)	1.535(6)
C(10)	- C(20)	1.544(7)
C(11)	- C(12)	1.505(6)
C(12)	- C(13)	1.336(7)
C(12)	- C(21)	1.489(8)
C(13)	- C(14)	1.475(9)
C(14)	- C(15)	1.458(15)
O(22)	- C(23)	1.441(7)

Table 11. Bond angles in degrees of tridachione. Estimated standard deviation of the least significant figures are given in parentheses. The numbering scheme refers to Figure 4.

C(2)	- C(1)	- O(22)	121.7(4)
C(2)	- C(1)	- O(24)	124.7(4)
O(22)	- C(1)	- O(24)	113.6(3)
C(1)	- C(2)	- C(3)	117.9(3)
C(1)	- C(2)	- C(16)	121.4(5)
C(3)	- C(2)	- C(16)	120.7(5)
C(2)	- C(3)	- C(4)	118.5(3)
C(2)	- C(3)	- O(25)	121.3(4)
C(4)	- C(3)	- O(25)	120.1(4)
C(3)	- C(4)	- C(5)	118.9(3)
C(3)	- C(4)	- C(17)	115.0(4)
C(5)	- C(4)	- C(17)	126.1(4)
C(4)	- C(5)	- C(6)	132.5(3)
C(4)	- C(5)	- O(24)	120.0(3)
C(6)	- C(5)	- O(24)	107.5(3)
C(5)	- C(6)	- C(7)	110.1(3)
C(5)	- C(6)	- C(11)	113.8(3)
C(5)	- C(6)	- C(18)	109.0(3)
C(7)	- C(6)	- C(11)	110.4(3)
C(7)	- C(6)	- C(18)	105.2(4)
C(11)	- C(6)	- C(18)	107.8(3)
C(6)	- C(7)	- C(8)	126.7(5)
C(7)	- C(8)	- C(9)	119.3(4)
C(7)	- C(8)	- C(19)	121.8(6)
C(9)	- C(8)	- C(19)	118.7(6)
C(8)	- C(9)	- C(10)	118.8(4)
C(8)	- C(9)	- O(26)	119.3(5)
C(10)	- C(9)	- O(26)	121.9(5)
C(9)	- C(10)	- C(11)	111.0(4)
C(9)	- C(10)	- C(20)	109.7(4)
C(11)	- C(10)	- C(20)	112.1(4)
C(6)	- C(11)	- C(10)	111.8(3)
C(6)	- C(11)	- C(12)	115.1(3)
C(10)	- C(11)	- C(12)	112.7(4)
C(11)	- C(12)	- C(13)	119.5(4)
C(11)	- C(12)	- C(21)	119.3(4)
C(13)	- C(12)	- C(21)	121.1(5)
C(12)	- C(13)	- C(14)	128.6(6)
C(13)	- C(14)	- C(15)	114.3(7)
C(1)	- O(22)	- C(23)	119.5(3)
C(1)	- O(24)	- C(5)	120.1(3)

Table 12. The observed and calculated structure factors for tridachione.

H = 0				2 19	4	4	5 9	2	0	8 7	3	3
K	L	FO	FC	2 20	3	4	5 10	9	10	8 12	5	5
0	2	100	112	2 21	3	2	5 13	4	4	8 13	10	10
0	4	18	17	3 1	110	116	5 14	4	4	8 14	3	4
0	6	22	24	3 2	75	75	5 15	20	20	8 17	3	4
0	8	66	59	3 3	24	26	5 16	9	9	9 1	9	10
0	10	46	44	3 4	60	60	5 17	3	3	9 4	15	14
0	12	5	5	3 5	25	24	5 18	8	8	9 5	4	5
0	14	11	11	3 6	3	1	5 20	5	5	9 6	8	8
0	16	22	22	3 7	40	43	6 0	34	37	9 8	5	4
0	18	11	10	3 8	30	27	6 1	32	30	9 9	3	2
0	22	3	2	3 9	16	15	6 2	27	25	9 10	11	11
1	1	36	35	3 10	11	11	6 3	56	52	9 12	8	9
1	2	52	54	3 11	9	10	6 4	14	14	9 13	5	6
1	3	25	25	3 12	6	6	6 5	2	1	9 14	6	6
1	4	8	7	3 14	15	15	6 7	36	36	9 15	4	4
1	5	33	35	3 15	10	9	6 8	8	7	10 0	9	9
1	6	34	35	3 16	14	15	6 9	3	3	10 1	20	21
1	7	15	16	3 17	23	23	6 10	14	14	10 2	5	5
1	8	2	2	3 19	8	7	6 11	8	9	10 5	10	10
1	9	14	14	3 21	2	1	6 12	5	4	10 6	8	8
1	10	12	12	4 0	106	105	6 13	28	28	10 7	8	8
1	11	52	51	4 1	30	30	6 14	8	9	10 8	21	20
1	12	10	10	4 2	31	28	6 15	16	16	10 9	6	6
1	13	9	9	4 3	18	17	6 16	4	4	10 10	14	14
1	14	5	6	4 4	2	2	6 18	5	5	10 11	7	8
1	16	17	16	4 5	26	27	7 1	4	3	10 13	4	4
1	17	8	7	4 6	3	3	7 2	4	4	10 14	4	4
1	18	14	14	4 7	13	14	7 3	13	12	11 1	10	10
1	21	4	4	4 8	11	11	7 4	7	8	11 2	22	21
1	22	4	3	4 9	3	4	7 5	4	2	11 3	3	4
2	0	34	30	4 10	2	3	7 6	3	2	11 4	7	9
2	1	4	2	4 11	2	2	7 7	8	9	11 5	6	6
2	2	61	62	4 12	6	5	7 8	16	16	11 6	14	14
2	3	39	42	4 13	21	21	7 9	10	11	11 7	3	2
2	4	48	51	4 14	9	9	7 10	11	11	11 8	3	4
2	5	15	14	4 15	16	16	7 11	8	8	11 10	6	8
2	6	19	19	4 16	9	8	7 12	12	12	11 12	8	8
2	7	42	40	4 17	3	2	7 13	22	22	11 13	4	3
2	8	16	16	4 18	9	9	7 14	19	19	12 0	12	11
2	9	5	5	5 1	47	42	7 15	7	8	12 1	10	9
2	10	9	9	5 2	10	9	7 17	6	5	12 3	12	11
2	11	8	7	5 3	55	54	7 18	4	4	12 4	5	6
2	12	8	7	5 4	3	5	8 1	5	4	12 5	8	9
2	13	19	19	5 5	2	1	8 2	10	10	12 6	7	7
2	14	12	13	5 6	14	14	8 3	13	13	12 7	3	3
2	16	25	24	5 7	32	30	8 4	13	13	12 8	13	14
2	17	9	9	5 8	15	14	8 5	8	8	12 9	2	2

Table 12 (Continued)

12	10	2	2	2	4	80	83	4	11	10	10	7	1	4	4
12	11	3	3	2	5	16	17	4	12	11	10	7	2	40	40
13	1	3	2	2	6	23	21	4	13	5	6	7	3	17	18
13	4	4	3	2	7	8	8	4	14	5	5	7	4	19	19
13	6	5	4	2	8	6	8	4	15	13	13	7	5	26	25
13	8	3	2	2	9	27	23	4	16	11	11	7	6	12	11
				2	10	22	20	4	17	13	13	7	7	16	16
	H =	1		2	11	21	20	4	18	8	8	7	8	5	5
K	L	FO	FC	2	12	16	16	4	19	6	6	7	9	13	13
0	1	61	63	2	13	6	6	4	21	3	3	7	11	8	7
0	2	61	64	2	15	6	6	5	0	29	28	7	12	16	16
0	3	41	43	2	16	8	8	5	1	9	9	7	13	12	12
0	4	31	31	2	17	6	6	5	2	14	14	7	14	6	6
0	5	18	20	2	18	13	13	5	3	28	26	7	15	14	13
0	6	7	7	2	19	3	3	5	4	21	21	7	16	4	4
0	8	40	38	2	21	4	4	5	5	64	64	7	18	2	1
0	10	10	11	3	0	29	28	5	6	35	32	8	0	10	9
0	11	15	15	3	1	26	26	5	7	8	9	8	1	17	17
0	13	11	10	3	2	14	15	5	8	18	17	8	2	9	8
0	15	20	19	3	3	57	53	5	9	7	7	8	3	7	8
0	16	17	17	3	4	22	25	5	10	8	8	8	4	15	15
0	18	19	19	3	5	18	17	5	11	5	6	8	5	13	13
0	19	4	4	3	6	15	15	5	12	16	15	8	6	6	5
1	0	99	103	3	7	3	4	5	13	12	13	8	8	7	6
1	1	50	51	3	8	35	34	5	14	9	10	8	9	13	13
1	2	89	94	3	9	13	13	5	15	19	19	8	10	8	8
1	3	47	50	3	10	5	5	5	16	17	16	8	11	10	10
1	4	5	6	3	11	26	25	5	17	7	7	8	12	13	13
1	5	43	43	3	12	5	5	5	18	5	4	8	13	8	8
1	6	18	17	3	13	6	6	5	20	2	1	8	14	5	5
1	7	39	39	3	14	11	12	6	0	39	35	8	15	4	4
1	8	46	43	3	15	3	4	6	1	9	10	8	17	4	3
1	9	26	21	3	16	14	14	6	2	26	25	8	18	2	2
1	10	34	29	3	17	13	13	6	3	21	19	9	0	5	5
1	11	13	12	3	18	5	5	6	4	27	25	9	1	7	7
1	12	8	7	3	19	5	6	6	5	23	22	9	2	14	14
1	13	3	3	3	20	3	2	6	6	8	8	9	3	20	20
1	14	6	7	4	0	93	93	6	8	11	11	9	4	9	9
1	15	10	11	4	1	26	22	6	9	4	3	9	5	10	10
1	16	13	13	4	2	6	5	6	10	9	9	9	6	3	3
1	17	8	7	4	3	16	17	6	11	8	8	9	8	7	6
1	18	5	6	4	4	23	22	6	13	4	4	9	10	8	8
1	19	6	6	4	5	36	37	6	14	10	10	9	11	7	7
1	20	6	6	4	6	9	9	6	15	14	14	9	12	5	5
2	0	40	38	4	7	10	9	6	16	14	14	9	13	9	9
2	1	77	77	4	8	7	7	6	17	5	5	9	14	6	6
2	2	57	61	4	9	22	21	6	18	2	2	9	15	5	5
2	3	15	14	4	10	12	12	7	0	13	13	9	16	6	6

Table 12 (Continued)

10	0	12	12	0	2	12	12	2	13	15	15	4	20	3	2
10	1	4	2	0	3	46	47	2	15	3	2	5	0	11	11
10	2	21	20	0	4	35	32	2	16	5	5	5	1	13	14
10	3	14	14	0	5	21	23	2	17	13	12	5	2	21	20
10	4	19	19	0	6	2	2	2	19	4	4	5	3	24	24
10	5	4	3	0	7	41	39	2	20	5	5	5	4	9	8
10	7	6	7	0	8	44	41	2	21	4	4	5	5	17	17
10	8	4	5	0	9	57	56	3	0	36	38	5	6	17	16
10	10	9	10	0	10	43	43	3	1	20	17	5	7	16	16
10	11	5	5	0	11	36	35	3	2	13	14	5	8	7	7
10	12	4	4	0	12	10	10	3	3	11	12	5	9	13	12
10	13	9	9	0	13	5	5	3	4	12	11	5	10	11	11
10	14	5	5	0	14	12	12	3	5	44	43	5	11	7	7
10	15	3	3	0	17	3	4	3	6	23	22	5	12	4	4
11	0	4	4	0	18	4	5	3	7	31	33	5	13	18	18
11	1	8	8	0	20	3	3	3	8	39	36	5	14	7	7
11	2	18	18	0	21	2	3	3	9	19	19	5	15	4	4
11	3	24	24	1	0	136	142	3	10	21	21	5	17	3	3
11	4	13	13	1	1	86	85	3	11	12	12	5	18	3	4
11	5	10	10	1	2	37	35	3	12	15	15	5	19	2	2
11	6	5	5	1	3	46	46	3	13	3	3	5	20	3	3
11	7	10	10	1	4	27	28	3	14	11	11	6	0	3	1
11	8	5	6	1	5	16	16	3	15	16	17	6	1	14	15
11	9	5	5	1	6	13	14	3	16	12	12	6	2	23	20
11	10	3	4	1	7	12	13	3	17	5	5	6	3	8	8
11	11	4	3	1	8	22	20	3	18	5	5	6	4	20	22
11	12	2	2	1	9	31	30	3	19	5	5	6	5	9	8
11	13	5	5	1	10	4	4	3	21	3	2	6	6	9	8
12	0	5	3	1	11	18	18	4	0	2	2	6	7	19	18
12	1	6	6	1	12	5	5	4	1	29	28	6	9	11	11
12	2	6	6	1	13	9	8	4	2	18	16	6	10	11	11
12	3	10	11	1	14	5	5	4	3	50	48	6	11	7	8
12	5	4	5	1	15	7	7	4	4	24	25	6	12	16	15
12	6	3	3	1	16	3	2	4	5	15	15	6	13	13	13
12	8	3	5	1	18	5	6	4	6	12	12	6	14	10	10
12	9	4	4	2	0	38	40	4	7	21	20	6	15	8	8
12	10	2	4	2	1	72	73	4	8	31	31	6	16	7	8
12	11	3	3	2	2	37	36	4	9	5	5	6	17	5	5
13	1	2	2	2	3	4	4	4	10	8	8	6	19	2	2
13	2	4	3	2	4	25	24	4	11	3	3	7	0	2	0
13	3	2	4	2	5	22	23	4	12	5	4	7	1	18	18
13	6	4	4	2	6	4	5	4	13	7	7	7	2	29	30
13	7	5	5	2	7	32	28	4	14	9	9	7	3	16	16
				2	8	13	12	4	15	10	10	7	4	26	26
	H =	2		2	9	23	23	4	16	9	8	7	5	13	13
K	L	FO	FC	2	10	11	10	4	17	9	10	7	6	2	1
0	0	146	179	2	11	15	14	4	18	10	10	7	7	10	10
0	1	45	48	2	12	6	6	4	19	3	3	7	8	8	8

Table 12 (Continued)

7	9	10	10	10	8	3	3	0	16	5	5	3	4	32	32
7	10	5	5	10	9	6	6	0	18	2	2	3	5	20	21
7	11	3	2	10	10	6	6	0	20	3	2	3	6	18	18
7	12	10	10	10	11	6	7	1	0	30	28	3	7	3	3
7	13	11	11	10	12	7	8	1	1	56	54	3	8	6	4
7	14	10	9	10	14	4	3	1	2	45	44	3	9	5	4
7	15	6	6	11	0	10	10	1	3	21	20	3	10	10	10
7	16	6	6	11	1	3	3	1	4	17	17	3	11	3	1
7	18	2	2	11	2	9	10	1	5	11	12	3	12	4	5
8	0	17	16	11	3	8	8	1	6	16	16	3	13	7	6
8	1	10	11	11	4	9	9	1	7	27	26	3	14	6	7
8	2	4	4	11	5	3	4	1	8	13	12	3	15	8	8
8	3	5	5	11	6	5	5	1	9	16	15	3	16	8	8
8	4	2	3	11	9	6	6	1	10	25	24	3	17	9	9
8	5	8	8	11	10	3	3	1	11	3	2	3	18	3	3
8	6	11	11	11	11	7	8	1	12	10	10	3	19	2	2
8	7	10	9	11	12	2	3	1	13	7	7	4	0	35	31
8	8	5	5	12	0	7	7	1	14	5	4	4	1	25	22
8	9	14	13	12	1	7	7	1	15	12	12	4	2	17	17
8	10	5	5	12	2	3	3	1	16	2	4	4	3	11	10
8	11	5	5	12	3	4	5	1	17	7	7	4	4	25	25
8	12	5	6	12	5	4	4	1	18	5	5	4	5	22	23
8	13	6	6	12	6	5	5	1	19	4	4	4	6	26	26
8	14	13	14	12	8	6	7	1	20	2	2	4	7	10	10
8	15	4	5	12	10	4	5	2	0	23	21	4	8	16	16
9	1	16	15	13	0	2	2	2	1	49	47	4	9	14	14
9	2	12	12	13	1	5	5	2	2	22	20	4	10	13	13
9	3	17	17	13	2	4	4	2	3	22	23	4	11	6	6
9	4	4	5	13	4	6	6	2	4	15	15	4	12	7	7
9	5	13	13	13	6	3	3	2	5	30	32	4	14	3	3
9	6	9	9					2	6	10	10	4	15	16	16
9	7	8	8		H =	3		2	7	7	7	4	16	5	5
9	8	5	5	K	L	FO	FC	2	8	4	5	4	17	10	10
9	9	4	4	0	1	48	52	2	10	13	13	4	18	3	3
9	10	6	6	0	2	64	68	2	11	2	2	4	19	4	5
9	11	7	6	0	3	12	12	2	12	4	4	5	0	13	12
9	12	14	15	0	4	25	23	2	13	6	7	5	1	18	20
9	13	6	6	0	5	23	21	2	14	8	9	5	2	14	14
9	14	4	4	0	6	6	7	2	15	2	2	5	3	24	25
9	16	2	2	0	7	6	6	2	16	3	2	5	4	13	12
10	0	9	9	0	8	21	20	2	17	7	7	5	5	8	8
10	1	23	23	0	9	18	18	2	18	2	3	5	6	27	26
10	2	11	12	0	10	22	22	2	19	2	2	5	7	17	17
10	3	8	8	0	11	11	12	2	20	3	3	5	8	11	11
10	4	9	10	0	12	2	2	3	0	5	5	5	9	2	2
10	5	19	19	0	13	16	16	3	1	15	16	5	10	4	4
10	6	9	10	0	14	5	6	3	2	6	6	5	11	3	4
10	7	10	9	0	15	3	2	3	3	39	38	5	12	7	7

Table 12 (Continued)

5	13	10	10	8	7	6	6	12	5	7	8	2	4	17	17
5	14	9	8	8	9	6	5	12	6	3	4	2	5	11	11
5	15	6	7	8	11	13	14	12	7	2	3	2	6	3	2
5	16	11	11	8	12	3	4	12	8	3	4	2	7	3	2
5	17	6	6	8	13	8	8	13	0	3	3	2	8	19	18
6	0	26	24	8	14	4	5	13	1	4	4	2	9	11	11
6	1	13	13	8	15	3	2	13	2	2	3	2	10	11	11
6	2	30	29	9	0	6	6					2	11	4	5
6	3	15	16	9	1	5	5		H =	4		2	12	7	7
6	4	16	16	9	2	5	5	K	L	FO	FC	2	14	8	8
6	5	21	21	9	3	16	16	0	0	27	32	2	15	7	7
6	6	11	12	9	4	10	10	0	1	46	49	2	16	7	7
6	7	17	17	9	5	5	4	0	2	7	8	3	0	5	4
6	8	16	15	9	6	6	5	0	3	9	8	3	1	17	18
6	9	14	14	9	7	7	8	0	4	2	3	3	2	8	9
6	11	6	6	9	8	3	3	0	5	5	6	3	3	13	14
6	12	8	9	9	9	6	7	0	6	8	8	3	4	6	5
6	13	11	11	9	10	5	5	0	7	3	3	3	5	18	19
6	14	9	9	9	11	3	3	0	8	8	8	3	6	13	12
6	15	8	8	9	12	9	10	0	9	15	15	3	7	3	3
6	16	7	7	9	14	6	7	0	10	8	9	3	8	14	15
6	17	3	3	10	0	13	13	0	11	11	10	3	9	2	2
6	18	3	4	10	1	4	4	0	12	3	3	3	10	8	7
7	0	7	6	10	2	12	11	0	14	10	10	3	11	6	6
7	1	2	3	10	3	17	17	0	18	3	2	3	12	6	6
7	2	13	13	10	4	10	10	1	0	54	53	3	13	5	5
7	3	4	4	10	5	4	4	1	1	29	29	3	14	5	4
7	4	11	12	10	6	6	6	1	2	16	15	3	16	4	4
7	5	19	18	10	7	6	6	1	3	30	30	3	17	3	3
7	6	7	7	10	8	5	6	1	4	2	3	4	0	4	4
7	7	12	12	10	9	4	4	1	5	7	7	4	1	7	7
7	8	6	5	10	11	3	3	1	6	8	8	4	2	6	5
7	9	12	11	10	12	3	3	1	7	9	9	4	3	5	6
7	10	8	7	10	13	2	3	1	8	9	9	4	4	19	19
7	11	9	9	11	0	5	4	1	9	6	7	4	5	4	2
7	12	12	12	11	2	12	12	1	10	16	15	4	6	5	6
7	13	3	4	11	3	7	7	1	11	4	4	4	7	9	8
7	14	5	6	11	4	12	11	1	12	9	9	4	8	14	14
7	15	8	9	11	6	6	7	1	13	8	9	4	10	8	8
7	16	5	6	11	7	8	9	1	14	3	4	4	11	10	10
7	17	2	2	11	8	3	3	1	16	6	7	4	12	11	10
8	0	8	8	11	9	3	3	1	17	4	5	4	13	5	5
8	1	15	14	11	10	4	5	1	18	3	3	4	14	7	7
8	2	11	11	12	0	8	8	1	19	2	2	4	16	5	5
8	3	2	1	12	1	4	4	2	0	2	3	4	17	4	4
8	4	11	11	12	2	5	5	2	1	27	28	5	0	10	11
8	5	8	7	12	3	10	10	2	2	29	27	5	1	8	9
8	6	7	7	12	4	6	6	2	3	17	17	5	2	13	12

Table 12 (Continued)

5	3	10	10	8	1	4	6	0	4	3	2	3	8	12	13
5	4	6	5	8	3	10	10	0	6	2	2	3	9	4	4
5	5	11	11	8	4	5	5	0	7	18	19	3	10	9	8
5	6	13	13	8	5	7	7	0	8	6	7	3	11	6	6
5	7	2	3	8	7	7	7	0	9	10	10	3	12	5	4
5	8	11	11	8	9	4	4	0	11	14	15	3	13	4	4
5	9	11	10	8	10	4	4	0	12	7	7	3	14	8	8
5	10	5	5	8	11	5	6	0	13	4	5	3	15	3	3
5	11	5	6	8	12	8	9	0	15	3	2	3	16	3	4
5	12	13	13	8	13	4	6	0	16	4	4	3	17	3	4
5	13	6	5	8	14	2	0	1	0	12	12	4	1	6	6
5	14	6	7	9	0	5	5	1	1	21	21	4	2	2	2
5	15	9	10	9	1	12	12	1	2	7	8	4	4	9	9
5	16	9	10	9	2	9	9	1	3	14	14	4	5	6	7
6	0	3	3	9	3	13	13	1	4	11	11	4	6	19	19
6	1	10	9	9	4	9	9	1	5	3	3	4	7	15	16
6	2	14	14	9	5	5	6	1	6	13	12	4	8	13	13
6	3	6	6	9	6	9	9	1	7	8	8	4	9	10	10
6	4	8	8	9	7	4	4	1	8	15	14	4	10	7	7
6	5	15	15	9	8	5	5	1	9	15	14	4	11	5	6
6	6	10	11	9	9	7	8	1	10	10	9	4	12	6	6
6	7	7	7	9	10	7	7	1	11	11	11	4	14	2	2
6	8	8	8	9	11	7	8	1	12	4	4	4	15	5	5
6	9	7	7	9	12	4	5	1	13	6	7	4	16	4	5
6	10	7	7	9	13	4	4	1	14	4	5	5	0	4	4
6	11	7	7	10	1	13	13	1	15	5	5	5	1	3	3
6	12	8	8	10	2	2	2	2	0	27	29	5	2	13	12
6	13	8	8	10	4	10	10	2	1	9	8	5	3	6	5
6	14	5	6	10	6	6	7	2	2	5	6	5	4	3	5
6	16	5	5	10	7	3	3	2	3	5	6	5	5	4	4
6	17	4	5	10	8	3	3	2	4	11	11	5	6	9	9
7	0	8	8	10	9	6	5	2	5	8	7	5	7	2	2
7	1	12	12	11	0	9	8	2	6	13	13	5	8	3	4
7	2	6	6	11	1	5	5	2	7	9	9	5	9	4	4
7	3	14	14	11	2	8	8	2	8	22	22	5	10	12	11
7	4	14	13	11	3	5	5	2	9	2	3	5	11	6	6
7	5	3	2	11	4	3	3	2	10	13	14	5	12	4	5
7	6	7	7	11	5	7	8	2	11	5	5	5	14	5	5
7	7	4	5	11	7	2	2	2	13	4	4	5	16	5	5
7	8	8	8	11	8	5	6	2	15	3	4	6	2	6	6
7	10	9	9	12	2	7	7	2	17	3	3	6	3	7	7
7	11	7	7	12	3	5	5	3	0	13	13	6	4	12	12
7	12	4	4					3	1	3	3	6	5	12	12
7	13	12	12		H =	5		3	2	16	16	6	6	8	8
7	14	7	7	K	L	FO	FC	3	3	11	11	6	7	7	7
7	15	6	6	0	1	2	4	3	4	7	8	6	8	7	7
7	16	3	3	0	2	25	26	3	6	13	14	6	9	5	5
8	0	14	14	0	3	8	8	3	7	7	7	6	10	5	5

Table 12 (Continued)

6	11	3	3		H =	6		3	4	5	4	9	5	2	2
6	12	4	5	K	L	FO	FC	3	5	8	8				
6	14	3	4	0	0	6	7	3	6	11	10		H =	7	
6	15	5	6	0	1	7	7	3	7	4	4	K	L	FO	FC
7	0	7	7	0	2	7	7	3	8	9	8	0	2	13	14
7	1	3	4	0	3	9	9	3	9	4	4	0	3	8	8
7	2	5	5	0	4	8	8	3	10	6	6	0	5	7	6
7	3	4	4	0	5	16	16	3	13	4	4	0	6	3	3
7	5	4	5	0	6	5	4	3	14	4	4	0	7	3	2
7	6	8	8	0	7	15	15	4	1	3	3	1	0	15	15
7	7	10	11	0	9	18	18	4	3	3	3	1	1	4	5
7	8	3	3	0	11	13	13	4	5	6	6	1	2	8	8
7	9	5	6	0	12	7	7	4	6	4	5	1	3	7	7
7	10	4	4	0	13	3	3	4	9	2	2	1	4	3	4
7	11	8	9	0	14	6	6	4	11	4	4	1	6	4	3
8	0	2	2	0	15	2	2	4	13	5	5	1	7	4	4
8	1	5	5	1	0	16	15	4	14	2	3	1	8	4	4
8	2	4	4	1	1	15	16	5	3	4	4	1	11	5	5
8	3	4	4	1	2	5	5	5	4	7	7	2	0	4	4
8	4	3	3	1	3	14	15	5	5	5	5	2	1	3	3
8	5	2	3	1	4	9	9	5	6	9	9	2	2	3	3
8	6	4	3	1	5	8	7	5	7	10	10	2	3	3	4
8	7	6	7	1	6	7	6	5	8	7	8	2	4	6	6
8	8	4	4	1	7	5	4	5	12	5	6	2	6	2	2
8	9	4	4	1	8	8	8	6	1	6	7	2	9	4	4
8	10	2	1	1	9	4	4	6	2	7	6	3	1	3	3
8	11	3	2	1	11	5	5	6	3	4	3	3	3	3	3
8	12	4	4	1	13	2	2	6	4	7	8	3	4	4	4
9	0	8	7	1	14	4	4	6	5	4	4	3	5	5	5
9	1	9	9	1	15	3	3	6	6	5	5	3	6	6	5
9	2	5	6	2	0	7	7	6	7	5	5	3	8	3	3
9	3	7	7	2	1	2	3	6	9	4	5	3	9	2	2
9	5	5	5	2	2	14	14	7	1	5	4	3	11	5	5
9	7	4	4	2	3	6	6	7	2	4	4	4	0	3	2
9	10	3	4	2	4	5	4	7	3	3	3	4	1	6	5
10	0	9	9	2	5	8	8	7	4	4	4	4	2	4	3
10	1	4	4	2	6	7	7	7	6	3	3	4	3	4	4
10	2	5	5	2	7	14	13	7	8	4	5	4	5	2	2
10	3	6	6	2	8	12	12	7	10	2	2	5	0	5	5
10	4	4	4	2	9	9	8	7	11	5	6	5	1	6	6
10	5	3	3	2	10	2	3	8	0	9	9	5	2	5	5
10	7	4	5	2	11	3	3	8	2	3	3	5	3	5	5
11	2	6	6	2	12	4	4	8	4	4	4	5	5	5	5
11	3	2	3	2	13	3	3	8	6	3	5	5	6	2	3
11	4	5	5	2	15	2	2	8	9	3	3	5	7	5	5
				3	0	2	0	9	0	4	4	6	1	5	5
				3	1	5	6	9	1	4	4	6	3	3	2
				3	2	7	8	9	2	4	5	6	4	4	4

Table 12 (Continued)

6	5	6	6
6	6	3	4
7	1	4	5
7	3	4	5

H = 8

K	L	FO	FC
0	0	7	10
0	2	4	5
0	3	11	11
0	4	3	3
0	5	8	8
1	1	5	5
1	2	4	4
1	3	4	4
1	5	3	1
1	6	2	2
2	0	3	2
2	1	4	3
2	2	4	4
2	4	2	2
2	5	4	4
3	0	3	3
3	1	3	4
3	2	4	5
4	3	2	1

ACKNOWLEDGMENT

Last, but not least, I'd like to thank the man who taught me this very invaluable lesson:

Life

is easier than you think-
all you have to do is
accept the impossible,
do without the indispensable
and bear the intolerable
(and be able to smile at anything).

Thanks, Boss.

REFERENCES

1. R. C. Potts and P. H. Hewitt, Insect Biochem., 2, 400 (1972).

2. B. P. Moore, J. Insect Physiol., 14, 33 (1968).

3. W. L. Nutting, M. S. Blum and H. M. Fales, Psyche, 81, 167 (1974).

4. B. P. Moore, J. Insect Physiol., 10, 371 (1964).

5. Glenn D. Prestwich, Insect Biochem., 7, 91 (1977).

6. Jan Vrkoc, Karel Ubik, Ladislav Dolejs and Ivan Hrdy, Acta Ent. Bohemoslaw, 70, 74 (1973).

7. Glenn D. Prestwich, Steven P. Tanis, James P. Springer and Jon Clardy, J. Amer. Chem. Soc., 98, 6061 (1976).

8. Glenn D. Prestwich, Steven P. Tanis, Frank G. Pilkiewicz, Iwao Miura and Koji Nakanishi, J. Amer. Chem. Soc., 98, 6062 (1976).

9. Glenn D. Prestwich, Barbara A. Solheim, Jon Clardy, Steven P. Tanis, Frank G. Pilkiewicz, Iwao Miura and Koji Nakanishi, "Kempene I and II, Unusual Tetrecyclic Diterpenes from Nasutitermes Termite Soldiers" (to be published).

10. $|Frel| = (I/Lp)^{\frac{1}{2}}$ with $L = 1/\sin 2\theta$ and $\rho = .5(1 + \cos^2\chi \cos^2 2\theta)/(1 + \cos^2\chi) + .5(1 + \cos\chi \cos^2 2\theta)/(1 + \cos\chi)$ where 2θ is the Bragg angle of the reflection and χ is the angle between the x-ray beam off the target and the x-ray beam off the monochrometer. All x-ray data were collected with a Syntex $P2_1$ diffractometer using 1° ω scans.

11. The following library of crystallographic programs was used: G. Germain, P. Main and M. M. Woolfson, Acta Cryst., A27, 368 (1971); C. R. Hubbard, C. O. Quicksall and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT and Friedel", USAEC Report IS-2625, Iowa State University, Institute for Atomic Research, Ames, Iowa, 1971; W. R. Busing, K. O. Martin and H. A. Levy, "A Fortran Crystallographic Least Squares Program", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program", USAEC

Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

12. K. Lonsdale, "International Tables for X-Ray Crystallography, Vol. III", Kynoch Press, Birmingham, England, 1962.

13. See background material for kempene II.

14. Glenn D. Prestwich, David F. Wiener, Jerrold Meinwald, Barbara A. Solheim and Jon Clardy, "Structure of Biflora-4,10-19,15-triene, a New Diterpene from a Termite Soldier" (to be published).

15. T. C. Cheng, in Current Topics in Comparative Pathobiology, edited by Thomas C. Cheng (Academic Press, New York, 1973), p. 215.

16. Robert K. Trench, Bull. Mar. Sci., 23, 299 (1973).

17. Robert K. Trench, Richard W. Greene and Barbara G. Bystrom, J. Cell. Biol., 42, 404 (1969).

18. Robert K. Trench and David C. Smith, Nature, 227, 196 (1970).

19. Robert K. Trench and Sharon Ochlhorst, New Phytol., 76, 99 (1976).

20. R. K. Trench, J. Elizabeth Boyle and D. C. Smith, Proc. Ray. Soc. London, Series B., 185, 453 (1974).

21. Robert K. Trench, Merriley E. Trench and Leonard Muscatine, Biol. Bull., 142, 335 (1972).

22. K. Kakinuma, C. A. Hanson and K. L. Rinehart, Jr., Tet., 32, 217 (1976).

23. Yoshimasa Hirata, Hisao Nakata, Kiyoyuki Yamada, Kunio Okuhara and Takayuki Naito, Tet., 14, 252 (1961).

24. Mikio Yamazaki, Tet. Let., 2701 (1972).