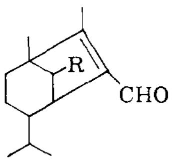
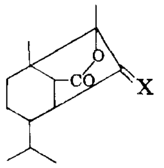
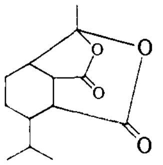
oxidation gave with sodium borohydride a γ-lactone (**2a**) formed with concomitant allylic rearrangement.[1] In agreement with this view no bands in the n.m.r. spectrum attributable to the required methylene hydrogens ($-CH_2-O-$) were present, whereas the expected shift of a singlet methyl (8.0 to 8.61τ) was observed. Reaction of **2a** with osmium tetroxide and then periodate cleavage gave the cyclopentanone (**2b**), m.p. 123–123.5°, ν_{max} 1802, 1767 cm.$^{-1}$, $[\alpha]_D$ +40° [Found: C, 71.16; H, 8.49], reduced to the keto-acid with zinc and acetic acid, m.p. 140–142°, $[\alpha]_D$ −66° ν_{max} 1746, 1703 cm.$^{-1}$ [Found: C, 70.88; H, 9.28].



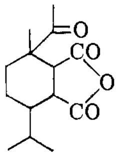
1a. R = CHO
b. R = COOH



2a. X = CH_2
b. X = O



3



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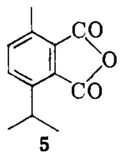

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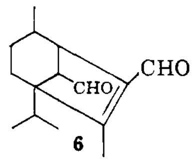

6

Ozonolysis of **2a** gave **2b**, formaldehyde, and the dilactone (**3**) (after heating the crude ozonolysis product), m.p. 76.5–77.5°, ν_{max} 1820, 1790 cm.$^{-1}$, $[\alpha]_D$ +70° [Found: C, 66.66; H, 8.06; mol. wt. (mass spectrum), 252]. The latter, also obtained by the ozonolysis of **1a** or **1b**, was reduced with lithium aluminum hydride to a triol, m.p. 158.5–159.5°, $[\alpha]_D$ ±0° [Found: C, 68.47; H, 11.62] whilst alkaline hydrolysis of the dilactone gave a diacid which, with acetic anhydride, was converted into the keto-anhydride (**4**), m.p. 140 and 156–158°, $[\alpha]_D$ −31° [Found: C, 67.14; H, 8.05]. On heating to a higher temperature than required for its formation the anhydride (**4**) was converted into an equilibrium mixture of **3** and **4**, whilst reduction of **4** with lithium aluminum hydride gave the triol m.p. 158.5–159.5° already described. No rearrangement of the carbon skeleton in the formation of **4** from **3** had, therefore, taken place.

Dehydrogenation of **3** with selenium at 320° gave, presumably *via* **4**, 6-isopropyl-3-methylphthalic anhydride (**5**), m.p. 100.5–101° [Found: C, 70.64; H, 5.69), which was identified by comparison with a synthetic specimen prepared as described. The ylide from triphenylisobutylphosphonium bromide was treated with crotonaldehyde and the diene so obtained subjected to the Diels–Alder reaction with maleic anhydride. Dehydrogenation of the adduct was effected with sulfur at 250° for 45 minutes. The obtention of **5** established the disposition of twelve of the fifteen carbon atoms in helminthosporal. The remaining three atoms form, together with one of the carbonyl carbons of the anhydride (**4**), the unsaturated aldehyde function. Two possibilities (**1a** and **6**) follow for helminthosporal.

The decision in favor of **1a** is indicated clearly by the fact that in all compounds here reported, and in others, a sharp singlet[3] (3H, methyl) (~8.9τ) was observable, in addition to the isopropyl group (two doublets), in the n.m.r. spectrum. The clearly discernible isopropyl group pattern precludes the possibility of ring contraction from a seven-membered ring during the dehydrogenation of **3**.

Although (**1a**) is constructed from three isoprene units it represents a new sesquiterpenoid skeleton which, furthermore, cannot be formed by the simple cyclization of a farnesyl precursor. An attractive possibility is that the two aldehyde carbon atoms originally were united and the relevant bond cleaved at a later stage of biogenesis. In such circumstances farnesyl cyclization could lead to the carbon skeleton of the hypothetical precursor, which then would be structurally closely related to the naturally occurring hydrocarbon, longifolene. Labelling experiments to test this hypothesis are in progress.

As originally isolated the purified but non-crystalline toxin shows but weak carbonyl absorption in the infrared depending on the degree of heat treatment. Very mild heat, acid or base treatment generates the ultraviolet spectrum and the carbonyl bands in the infrared. Since biological tests indicate no significant difference in activity, this suggests that helminthosporal exists in the host as an acetal or hemiacetal. The formation of such acetals is unexceptional in dialdehydes,[5,6,7] and in this case could be favored by the conformational disposition and rigidity of the aldehyde functions.

Financial support from the National Research Council of Canada is gratefully acknowledged. The authors wish to thank Dr. J. B. Stothers for the n.m.r. spectra, Dr. K. Biemann (M.I.T.) for the mass spectrometric molecular weight, and Mr. L. G. Crawford for assistance in the isolation of the crude toxin.

(3) The presence of a singlet methyl does not, in itself, exclude the possibility of the presence of a contiguous methine hydrogen,[4] but since the singlet remained sharp in a number of compounds in which the adjacent hydrogens were chemically shifted this possibility can be excluded.

(4) F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961).

(5) G. W. K. Cavill and D. L. Ford, *Austral. J. Chem.*, **13**, 296 (1960).

(6) R. H. Hall, *J. Chem. Soc.*, 4303 1954.

(7) A. N. Starratt, unpublished observations, University of Western Ontario.

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RECEIVED DECEMBER 21, 1961

STRUCTURE OF (RHODIUM(I) CHLORIDE-1,5-CYCLOÖCTADIENE)$_2$

Sir:

A complete X-ray investigation of the dimer of rhodium(I) chloride 1,5-cycloöctadiene has produced a structure which is significantly different from the structure of the dimer of rhodium(I) chloride carbonyl.[1] Whereas the rhodium atoms

(1) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).

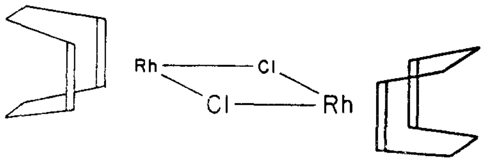

Fig. 1.—Sketch of the $(RhCl\text{-}1,5\text{-cyclooctadiene})_2$ molecule. The rhodiums, chlorines, and double-bond centers are coplanar.

are in an octahedral configuration in the carbonyl they are in a square planar configuration in the cycloöctadiene complex. Thus the close parallelism of bonding often inferred from non-structural studies to hold between olefin complexes and carbonyl halides of low-valence transition metals (*e.g.*[2]) does not exist in this case.

The deep yellow crystals of $(RhClC_8H_{12})_2$ were prepared by D. W. Barnum of these laboratories by the reaction of rhodium chloride trihydrate with the diene, as described by Chatt and Venanzi.[2] (Chatt and Venanzi also note that $(RhClC_8H_{12})_2$ is produced in the reaction of $(RhCl(CO)_2)_2$ with C_8H_{12}.) On the basis of precession and Weissenberg photographs prepared with Mo Kα radiation the crystals are found to belong to the monoclinic system with a = 9.05, b = 25.4, c = 7.28 Å., β = 91.6°. The calculated density of 1.95 g./cm.^{3} for four dimer molecules in the unit cell is in excellent agreement with the density of 1.93 g./cm.^{3} obtained pycnometrically. The systematic absences $0k0$, k odd; $h0l$, $h + l$ odd, are consistent with the space group C_{2h}^5-$P2_1/n$. Since the general positions of this space group are fourfold, the dimeric molecules are not required to possess symmetry, and the solution of the crystal structure involves the location of all atoms in a dimer.

Intensity data were collected at room temperature with the use of Mo Kα radiation from a very small crystal (average dimension, 0.2 mm.), and were estimated visually. The rhodium and chlorine atoms were located without difficulty on a three-dimensional Patterson map and the carbon atoms were located subsequently on a difference Fourier. The structure has been refined by least-squares techniques. The present reliability factor R_1 is 9.7% for the 800 observed reflections; it is 16% if the carbon atom contributions to the structure factors are omitted. The limits of error at this stage of the refinement are approximately 0.004, 0.014, and 0.07 Å. for Rh, Cl, and C.

The structure of the molecule is sketched in Fig. 1; some of the bond distances and angles are shown in Fig. 2. All distances and angles are normal. There are no significant differences among bond lengths of a given type. The C–C distances in the ring average 1.52 ± 0.10 Å., the C=C distances 1.44 ± 0.06. The closest atoms in other molecules to a given rhodium are carbons at about 3.8 Å. away. Thus a given rhodium atom is bonded only to two chlorine atoms and to two double-bond centers of a cycloöctadiene ring (boat configuration). Within the limits of error of this study the four double-bond centers, the two rhodiums, and the two chlorine atoms in a given molecule are coplanar. Accordingly a given rhodium atom is in a square-planar configuration and the structure of the molecule is that envisioned by Chatt and Venanzi.[2] In the rhodium chloride carbonyl dimer the two planar $Rh(CO)_2Cl$ groups intersect at an angle of 124° and Dahl, *et al.*,[1] describe the configuration of a given rhodium as octahedral and the bonding to involve bent metal–metal bonds. Thus there are striking differences between the bonding in the carbonyl and in the cycloöctadiene complexes of rhodium(I) chloride.

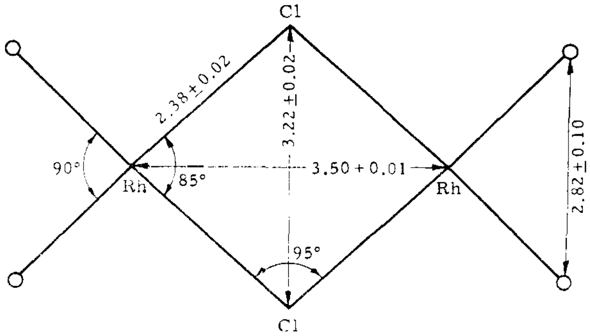

Fig. 2.—Principal bond distances and angles in the plane of the Rh, Cl, and double-bond centers (symbolized by ○)

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[2] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

[3] Department of Chemistry, Brookhaven National Laboratory, Upton, L.I., N.Y.

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RECEIVED OCTOBER 30, 1961

THE ISOLATION AND CHARACTERIZATION OF A FULLY DEUTERIATED PROTEIN[1]

Sir:

The successful culturing of fully deuteriated micro-organisms has been reported by Katz, Crespi and co-workers,[2] and it now has been possible for the first time to isolate, purify and characterize a fully deuteriated protein containing deuterium in both exchangeable and non-exchangeable positions from one of these organisms. An algal chromoprotein, phycocyanin, has been isolated from the blue-green alga *Plectonema calothricoides* now cultured in D_2O for two years. The harvested algae were frozen and thawed twice, and the water-soluble protein then was extracted at 5° in aqueous acetate buffer (pH 4.7, μ = 0.1) for a period of a week. The extracted protein then was purified by ammonium sulfate reprecipitation and fractionation in ordinary water. An identical purification procedure was used to isolate phycocyanin from ordinary water-grown *P. calothricoides*. Consistent with cytological observations of the deuterio-algal cell which indicate a difference in cell walls,[2] cell lysis and extraction of the deuterio-protein is considerably faster than for the H_2O-grown organism.

To establish unambiguously the fully-deuteriated nature of the protein, the deuterium content has been ascertained by direct analysis. The protein isolated from the completely deuteriated algae was dialyzed against D_2O for three days with daily

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. L. Crespi, S. M. Conrad, R. G. Uphaus and J. J. Katz, *Ann. New York Acad. Sci.*, **84**, 648 (1960).