

Fig. 1.—Various of basicity with mole per cent. of water in the following mixed solvents: ●, pyridine–water–tetramethylammonium hydroxide (0.011 *M*); ◐, dimethylsulfoxide–water–tetramethylammonium hydroxide (0.011 *M*); ○, sulfolane–water–tetramethylammonium hydroxide (0.011 *M*); ×, hydrazine–water; △, ethylenediamine–water; □, pyridine–water–benzyltrimethylammonium hydroxide (0.96 *M*)

sulfolane–water, dimethyl sulfoxide–water⁷ (each containing added base), hydrazine–water, and ethylenediamine–water. The H_- values for the latter two systems, which do not contain added hydroxide, were calculated with the optical absorption data of Schaal⁴ but using the pK_a values reported herein. It is interesting to note that the effect of reducing the water concentration in the relatively inert solvents (pyridine, dimethyl sulfoxide, sulfolane), each containing added strong base, is not greatly different from that for the systems containing only a weak base (hydrazine, ethylenediamine) as one of the solvent pairs. Strongly basic solutions also can be obtained using water alone as the solvent. Thus, 2.4 molar aqueous benzyltrimethylammonium hydroxide has an H_- value of 16.2.

We believe the foundations of the present H_- scale are firm for three reasons. First, a great many indicators have been used in establishing the scale. Second, unlike previous investigators we have not based our scale on the acidity of *p*-pyridine–water mixtures, however, the slopes deviated greatly owing, presumably, to the decreased dielectric constant of the media.

(7) The very high basicity of dimethyl sulfoxide–water–base solutions is in accord with the kinetic work of Cram, *et al.* (D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfeld, *J. Am. Chem. Soc.*, **83**, 3678 (1961)).

TABLE I
INDICATOR ACIDITIES

Substituted diphenylamines ^a	pK_a	Substituted anilines	pK_a
2,4,6,2',4',6'-Hexanitro	2.63	2,4,6-Trinitro	12.20
2,4,6,2',4'-Pentanitro	6.72	6-Bromo-2,4-dinitro ^b	13.63
2,4,6,4'-Tetanitro	8.88	2,4-Dinitro ^b	15.00
2,4,6,3'-Tetanitro	9.15	2,6-Dichloro-4-nitro	15.55
2,4,6-Trinitro	10.38	2,5-Dichloro-4-nitro	16.05
2,4,2',4'-Tetanitro	10.82	4-Chloro-2-nitro ^b	17.22
2,4,6-Trinitro-4'-amino	10.82	2-Nitro	17.88
2,4,4'-Trinitro	12.35	4-Nitro ^b	18.37
2,4,3'-Trinitro	12.65		
2,4-Dinitro	13.84		
4,4'-Dinitro	14.08		
2,4-Dinitro-4'-amino	14.64	3-Nitrocarbazole	14.10
4-Nitro ^b	15.90		
2-Nitro	17.57		

^a Diphenylamine, itself, is less than half ionized in 95% dimethyl sulfoxide–5 mole per cent. water containing 0.011 molar tetramethylammonium hydroxide, based on the optical density obtained in anhydrous ethylenediamine containing benzyltrimethylammonium hydroxide. ^b The pK_a values of these five compounds have been determined previously by Langford and Burwell (ref. 5). Except for 2,4-dinitroaniline the agreement is very good (the deviations range from 0.01 to 0.14 pK unit).

nitrobenzyl cyanide which, as will be shown in a subsequent publication, is a most unsatisfactory indicator because of its anomalous ionization equilibria. Third, several solvent systems all yield the same pK_a for a given indicator. This strongly supports the validity of the H_- scale as a measure of solvent basicity.⁸

Acknowledgment.—We are grateful to the Research Corporation for the award of an Unrestricted Venture grant (R.S.) and to the National Research Council of Canada for the award of a Studentship (J.P.O'D.).

(8) All the indicators used in this work were structurally similar and it remains to be seen whether or not the difficulties which appear to occur with the H_a scale when structurally dissimilar indicators are used also occur with H_- . Cf. Ref. 1c and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960).

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THE CONSTITUTION OF HELMINTHOSPORAL

Sir:

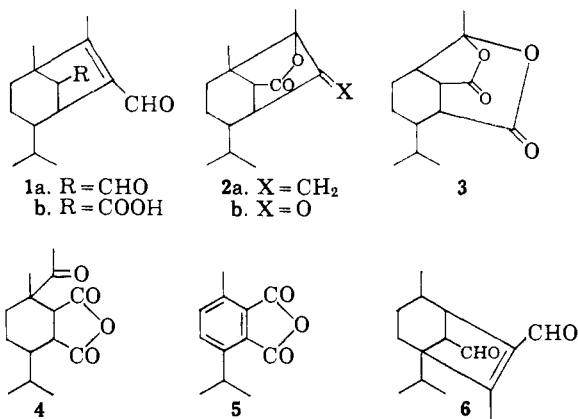
The isolation and characterization of helminthosporal, a toxin produced by the fungus *Helminthosporium sativum*, has been reported recently.¹ This toxin is responsible for a widespread seedling blight, foot and root rot and leaf spot of cereals in North America, which during the last 25 years has resulted, in Western Canada, in an estimated loss of the order of \$50,000,000.² We now wish to report evidence which reveals it to be a modified sesquiterpenoid and leads to the expression (1a) for this substance.

Helminthosporal, $C_{15}H_{22}O_2$, contains two aldehyde functions, one of which is α,β -unsaturated.¹ Since there are no other points of unsaturation in the molecule the substance, is, therefore, bicyclic. The derived acid (1b) obtained by silver oxide

(1) P. de Mayo, E. Y. Spencer and R. W. White, *Can. J. Chem.*, **39**, 1608 (1961); cf. R. A. Ludwig, *Can. J. Botany*, **35**, 291 (1957).

(2) B. J. Sallans, *Can. Plant Disease Survey*, **38**, 11 (1958).

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 ($-\text{CH}_2-\text{O}-$) were present, whereas the expected shift of a singlet methyl (8.0 to 8.61 τ) 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} , $[\alpha]_{\text{D}} +40^\circ$ [Found: C, 71.16; H, 8.49], reduced to the keto-acid with zinc and acetic acid, m.p. 140–142°, $[\alpha]_{\text{D}} -66^\circ$ ν_{max} 1746, 1703 cm^{-1} [Found: C, 70.88; H, 9.28].



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} , $[\alpha]_{\text{D}} +70^\circ$ [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°, $[\alpha]_{\text{D}} \pm 0^\circ$ [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°, $[\alpha]_{\text{D}} -31^\circ$ [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 singlet³ (3H, methyl) ($\sim 8.9\tau$) 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.

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(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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ROBERT W. WHITE

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STRUCTURE OF (RHODIUM(I) CHLORIDE-1,5-CYCLOOCTADIENE)₂ Sir:

A complete X-ray investigation of the dimer of rhodium(I) chloride 1,5-cyclooctadiene 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).