TABLE I

SOME HYDROXY PEROXIDES

Peroxide	Formula	Active oxygen, % Calcd.	Found
Hydroxy dicarbethoxymethyl[a]	$C_7H_{12}O_7$	7.7	7.55
Di-[hydroxy dicarbethoxymethyl][b]	$C_{14}H_{22}O_{12}$	4.19	4.24 4.19
α,α′-Dihydroxydiisoamyl	$C_{10}H_{22}O_4$	7.76	7.60
α,α′-Dihydroxydi-*n*-hexyl[c]	$C_{12}H_{26}O_4$	6.84	6.69

[a] d^{29}_{29} 1.226; n^{27}_D 1.4392.
[b] d^{29}_{29} 1.216; n^{27}_D 1.4388.
[c] M. p. 62–63°.

yields from aqueous 30% hydrogen peroxide and *n*-hexaldehyde.

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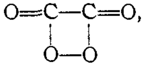
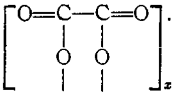
(3) From Part I of Ph.D. Thesis, M. I. T., 1939.

Diperoxalic Acid

When oxalyl chloride[1] was treated at 0° with an ice-sodium peroxide mixture, it was hoped to obtain a carbon peroxide,  $\begin{array}{ccccc} O= & C & - & C & =O \\ & | & & | & \\ & O & - & O & \end{array}$, or one of its polymers,  $\left[\begin{array}{ccccc} O= & C & - & C & =O \\ & | & & | & \\ & O & & O & \\ & | & & | & \end{array}\right]_x$. Neither one of these peroxides was obtained, but instead a small yield of diperoxalic acid. A higher yield of this diperacid was obtained by the following, somewhat different, procedure: To a solution of 19 g. of dry pyridine, 285 cc. of anhydrous ether containing 4 g. of hydrogen peroxide and maintained at −20°, was added, dropwise in the course of two hours and with vigorous stirring, a precooled (−10°) solution of 75 cc. of anhydrous ether containing 14.3 g. of oxalyl chloride. At the end of the reaction, the ether layer was decanted and the solid precipitate, which had separated out, extracted with two 100-cc. portions of anhydrous ether. The residue was then treated with an ice-cold mixture of 60 cc. of saturated sodium sulfate solution and 40 cc. of 85% orthophosphoric acid. The resulting mixture, after adding more solid sodium sulfate, was extracted with three 100-cc. portions of acetone which was combined with an equal volume of ether and the mixture dried and filtered. When the solvent was removed under reduced pressure, a highly viscous residue (2.2 g.) remained which failed to crystallize on standing for some time at 0°. This product was free from chlorine and nitrogenous products, and was found to be very soluble in water and chloroform. Diperoxalic acid is a powerful oxidizing agent, and, when treated with potassium iodide, it is reduced rapidly to oxalic acid.

Anal. Calcd. for $C_2H_2O_6$: (O), 26.3. Found: (O), 25.4, 25.7.

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(1) Prepared according to Staudinger, *Ber.*, **41**, 3563 (1908).

(2) From Part I of Ph.D. Thesis, M. I. T., 1939. Present address: Lowell Textile Institute, Lowell, Mass.

COMMUNICATIONS TO THE EDITOR

3-*n*-PENTADECYLCATECHOL

Sir:

Recently the synthesis of 3-*n*-pentadecylcatechol (Hydrourushiol) was described by H. S. Mason.[1] This compound, the dimethyl ether of which was first synthesized in low yield about thirty years ago by Majima and Tahara,[2] and later by Backer and Haack,[3] has attracted considerable interest in view of its close relationship to poison ivy "urushiol." The scheme of synthesis which Mason found gave the best results was essentially that employed by Backer and Haack for the preparation of the dimethyl ether. However, Mason markedly improved the yields over those reported by Backer and Haack, and carried the synthesis one step further by cleaving the dimethyl ether to obtain the catechol compound.

In view of the current interest in 3-*n*-pentadecylcatechol, because of its possible use as a standard agent for the diagnosis and therapy of poison ivy dermatitis, we are prompted to point out that it was synthesized in our laboratory in minimum over-all yield of 57% from *o*-veratraldehyde over two years ago. The synthesis was not published at that time inasmuch as it was a duplication of the work of Backer and Haack except for the improved yields and the additional ether cleavage step. However, the fact that we had synthesized 3-*n*-pentadecylcatechol was made clear in a later article.[4] Furthermore, the data in this article showing the 100% correlation of hypersensitiveness to poison ivy and to standard acetone solutions of 3-*n*-pentadecylcatechol involving patch tests on 21 patients made obvious the possible use of this synthetic compound as a standard agent for the diagnosis and therapy of poison ivy dermatitis. It would appear that Mason overlooked this article since no reference to it was made in his description of the synthesis nor in his statements in regard to the use of 3-*n*-pentadecylcatechol as a standard allergen.

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(1) Mason, THIS JOURNAL, **67**, 1538 (1945).

(2) Majima and Tahara, *Ber.*, **48**, 1606 (1915).

(3) Backer and Haack, *Rec. trav. chim.*, **57**, 225 (1938).

(4) Keil, Wasserman and Dawson, *J. Exptl. Med.*, **80**, 275 (1944.)

Since our method of cleaving the dimethyl ether gives comparable, if not better, yields of pure 3-*n*-pentadecylcatechol, and takes less time and effort than the procedure described by Mason, it seems worth while to outline it here in some detail.

The cleavage of the 3-*n*-pentadecylveratrole to yield pure 3-*n*-pentadecylcatechol was best accomplished in the following way. Three grams of the veratrole compound, 3 g. of anhydrous aluminum chloride and 30 cc. of dry chlorobenzene were refluxed for three hours, cooled, poured on ice, washed with 50% methanol solution, and the chlorobenzene layer evaporated under vacuum. The residue on molecular distillation yielded 2.5 g. (91%) of crude catechol compound melting at 52–59°. After three recrystallizations from petroleum ether, 2.1 g. (76%) of pure 3-*n*-pentadecylcatechol melting at 59–60° was obtained in the form of short white needles.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78.97; H, 11.30.

In the conversion of *o*-veratraldehyde to pure 3-*n*-pentadecylcatechol, an over-all yield of 57% was obtained.

During the past two years we have been using 3-*n*-pentadecylcatechol as a standard agent for the diagnosis of poison ivy hypersensitiveness and for demonstrating cross reactivity between poison ivy and other members of the anacardiaceae.[4,5,6,7] The optimal concentrations for these tests were found to lie between 0.1 and 1.0% in a suitable non-irritating carrier such as acetone or isoamyl acetate.

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(5) Keil, Wasserman and Dawson, *Science*, **102**, 279 (1945).

(6) Keil, Wasserman and Dawson, *Indust. Med.*, **14**, 285 (1945).

(7) Keil, Wasserman and Dawson, *J. Allergy*, **16**, 275 (1945).

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RECEIVED SEPTEMBER 24, 1945

CONCERNING A PROPOSED MODIFICATION OF THE BRUNAUER-EMMETT-TELLER THEORY OF MULTIMOLECULAR ADSORPTION

Sir:

In a recent paper, Pickett[1] proposed a modification of the BET[2] theory of multimolecular adsorption. This modification does not affect the familiar equation

$$\frac{v}{v_m} = \frac{cx}{(1 - x)(1 - x + cx)} \qquad (1)$$

which holds for adsorption on a free surface. It applies, rather, to adsorption in those cases where the maximum number of adsorbed layers (n) is restricted.

When n is finite, the BET theory does not predict complete filling of capillaries at saturation pressure. This is generally considered to be an unsatisfactory feature of the theory. Pickett's modification eliminates this feature and seems to improve the range of agreement with experimental data in a number of cases.

The equations obtained by Pickett follow from his assumption that there is a "decrease in probability of escape from an elemental area covered with n layers (the maximum number possible in the limited space) as adjacent elemental areas also become covered with n layers." Specifically, he assumes that the probability of escape from the n-th layer is reduced by a factor of $1 - x$. It is pointed out that there is an alternative but logically equivalent way of expressing this assumption. Since the two alternatives are equivalent we shall confine our attention to the first statement, given above, as it is more amenable to analysis (the second statement has a certain intuitive appeal but is more difficult to interpret).

It appears to the present writer that Pickett's assumption can be criticized on the following grounds:

(1) If there is a decrease in probability of escape from an elemental area covered with n layers as adjacent elemental areas become covered with n layers, there is also a decrease in probability of escape from elemental areas covered with 1, 2, 3 . . ., layers as adjacent elemental areas become covered with n layers.

(2) If there is a decrease in probability of escape (rate of evaporation) as adjacent elemental areas become covered with n layers, there is also an identical decrease in the rate of condensation, according to the principle of microscopic reversibility. Hence, multiplying only the right-hand member of the equation

$$as_{n-1}p = bs_n e^{-E_L/RT} \qquad (2)$$

by the factor $1 - x$ is not justified. The same is true if, in Equation (2), n is replaced by 1, 2, 3, . . . (when n is replaced by 1, E_L is replaced by E_1).

(3) Even if the multiplication of the right-hand member of Equation (2) by a factor were justified, the function $1 - x$ seems to be advantageous only because it has (a) simplicity, (b) "correct" boundary values, and (c) it allows the fundamental assumption to be restated in the alternative form mentioned above.

(4) A treatment of the problem, using statistical mechanics,[3] leads to the BET result rather than to the result obtained by Pickett. In the statistical treatment, no assumptions regarding mechanism need be made. It suffices to consider only possible states of the system.

The conclusion of the present writer is that, although Pickett's equations may improve the agreement with experimental data in some cases,

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[1] Gerald Pickett, THIS JOURNAL, **67**, 1958 (1945).

[2] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

[3] T. L. Hill, *J. Chem. Phys.*, in press.