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.

(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.

(1) Gerald Pickett, THIS JOURNAL, **67**, 1958 (1945).
(2) S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

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,

(3) T. L. Hill, *J. Chem. Phys.*, in press.

his modification should not be considered a really fundamental improvement over the BET theory.

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STREPTOMYCES ANTIBIOTICS. V. N-METHYL-*l*-GLUCOSAMINE FROM STREPTOMYCIN

Sir:

Streptomycin has been degraded to a new product which has been established as N-methyl-*l*-glucosamine.

Acid hydrolysis of methyl streptobiosaminide dimethyl acetal[1] followed by acetylation yielded a pentaacetyl derivative of a hexosamine; m. p. 160.5–161.5° (micro-block), $[\alpha]^{25}D$ −100° (*c*, 0.7 in chloroform). *Anal.* Calcd. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47; CH_3CO, 53.3; mol. wt., 403. Found: C, 50.51; H, 6.24; N, 3.76; CH_3CO, 49.2; mol. wt., 414 (cryoscopic in benzene). The hydrochloride of the hexosamine was obtained from the pentaacetyl derivative by hydrolysis with hydrochloric acid; m. p. 160–163° (micro-block), $[\alpha]^{25}D$ −103° (initial), −88° (final) (*c*, 0.6 in water). *Anal.* Calcd. for $C_7H_{15}NO_5 \cdot HCl$: C, 36.60; H, 7.02; CH_3N, 6.5. Found: C, 36.65; H, 6.86; CH_3N, 6.8. Treatment of the hydrochloride with silver oxide gave the free base as a colorless gum; $[\alpha]^{25}D$ −65° (*c*, 1.0 in methanol). Acetylation of the free base in the presence of methanol gave the N-acetyl derivative; m. p. 165–166° (micro-block), $[\alpha]^{25}D$ −51° (*c*, 0.4 in water).

The phenylosazone prepared from the hexosamine melted at 205° (capill.).[2] A phenylosotriazole, prepared[3] from this osazone, melted at the same temperature (196–197°) as the corresponding derivative of *d*-glucose, and the specific rotation was of equal magnitude but opposite in sign.

Oxidation of the free hexosamine with mercuric oxide gave an acid which had the same melting point (m. p. 230–232°) reported for N-methyl-*d*-glucosamic acid.[4] Again, the rotation was of the same magnitude but opposite sign.

Hydrolysis of the product of the reaction between *l*-arabinose, methylamine and hydrogen cyanide gave an acid which was identical with the "natural" acid described above. When the synthetic acid was converted to the lactone, reduced and acetylated, the product was found to be identical with the pentaacetyl derivative of the "natural" hexosamine. Thus, the configurations about C_3, C_4, and C_5 of the hexosamine are those at carbons 2, 3, and 4 of *l*-arabinose (or carbons 3, 4 and 5 of *l*-glucose).

Methylation of *d*-glucosamine, followed by acetylation, yielded pentaacetyl-N-methyl-*d*-glucosamine; m. p. 160.5–161.5° (micro-block), $[\alpha]^{25}D$ +101°. The properties of this compound are identical with those of the pentaacetyl derivative described above except for the sign of rotation.

With these data and the reported configuration of carbon atom 2 of *d*-glucosamine,[5] it is concluded that the configuration at carbon atom 2 of the hexosamine is also that of *l*-glucose and the degradation product is N-methyl-*l*-glucosamine.

(1) Brink, Kuehl and Folkers, *Science*, **102**, 506 (1945).

(2) *l*-Glucose phenylosazone, m. p. 205°; Fischer, *Ber.*, **23**, 374 (1890).

(3) Haskins, Hann and Hudson, THIS JOURNAL, **67**, 939 (1945).

(4) Votoček and Lukeš, *Chem. Listy*, **29**, 308 (1935).

(5) Haworth, Lake and Peat, *J. Chem. Soc.*, 271 (1939).

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NEIGHBORING GROUPS AND REACTIVITY

Sir:

Heretofore, we have stressed the stereochemical consequences of participation by neighboring groups[1] such as OAc, Br, OCH_3, etc., in replacement reactions. We have recently completed rate measurements which bring out the striking connection between reactivity and this participation.

First order rate-constants of solvolysis at 75° in glacial acetic acid of a series of 2-substituted cyclohexyl *p*-bromobenzenesulfonates give the following relative reactivities: unsubstituted, 1.00; *trans*-2-OAc, 0.240; *trans*-2-Br, 0.101; *trans*-2-OCH_3, 0.057; *trans*-2-Cl, 4.9×10^{-4}; *cis*-2-OAc, 3.8×10^{-4}; *cis*-2-$OSO_2C_6H_4Br$, 7.7×10^{-5}; *trans*-2-$OSO_2C_6H_4Br$, 6.9×10^{-5}. Similarly, acetolysis rates at 23.6° of cyclohexyl *p*-toluenesulfonates give the relative reactivities: *trans*-2-I, 1800; unsubstituted 1.00.

The effects of a halogen substituent similar to those above are seen also in the rough values of relative reactivities of alcohols to fuming hydrobromic acid or concentrated hydrochloric acid at room temperature. One reactivity sequence obtained in this way is: *trans*-2-iodocyclohexanol 1000; cyclohexanol 1; *trans*-2-bromocyclohexanol 0.08; *trans*-2-chlorocyclohexanol 1.6×10^{-4}.

In the relatively reactive substituted cyclohexyl compounds (which are typical of most of the cases where stereochemical evidence for participation exists) the neighboring group supplies a large driving force for the rate-determining ionization of the departing group. This partially neutralizes or completely overbalances (as for I) the rate-retarding inductive effect. The sequence I > Br > Cl is to be expected. As in the case of the acetoxy group, the driving force is supplied from the *trans*-position and poorly if at all from the *cis*-position. In the case of the

(1) Winstein and Seymour, THIS JOURNAL, **68**, 119 (1946), and previous articles in the series.