do not come merely from a newly cut surface. If the same type of scratch is made on clean glass covered with a thin layer of pure water, and a large volume of soda water immediately poured carefully over the surface, no bubbles arise from the scratch. Bubbles form only during the process of chipping the glass.

Since intense sound waves passing through water cause cavitation and bubbling, we might suppose the phenomenon to be the result of sound waves generated by the scratch. It is difficult to imagine that such sound waves can be intense enough. Moreover, a scratch on the outside of a thin glass container of soda water will not cause bubbles to form inside, provided the scratch does not actually cut through the glass so that an air phase comes in contact with the liquid.

Bubble formation from contact of surfaces becomes more marked in water supersaturated with very high pressures of gas or in water containing air at one atmosphere, evacuated to its vapor pressure. The mere tap of a glass rod on a glass wall will induce bubbles under these conditions. In one experiment, a small glass dish of water covered with cellophane and containing a sphere of plexiglas (5 mm. diameter) was saturated with 80 atmospheres of nitrogen gas and then decompressed to 1 atmosphere. No bubbles formed because the glass dish, water, cellophane and plexiglas sphere had been well cleaned and previously subjected to 16,000 lb./sq. in. hydrostatic pressure (to force gas nuclei into solution).[1] However, when the dish was tipped slightly so that the plexiglas sphere rolled over the glass surface, bubbles arose from its path and a burst of bubbles appeared when it hit the side of the dish.

It is inconceivable that chips of glass can be broken off under a light rolling sphere of plexiglas. It is more likely that when surfaces touch and then separate, the surface layer of water is pushed aside forming a momentary dry spot. Before the water can move in again, a sufficient number of gas molecules accumulate in the space, thereby forming a gas nucleus which immediately grows into a bubble.

[1] Harvey, *et al.*, THIS JOURNAL, **67**, 156 (1945).

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RECEIVED SEPTEMBER 14, 1946

DEGRADATIVE STUDIES ON STREPTOMYCIN

Sir:

Folkers and co-workers[1] have advanced the formula $(C_{21}H_{37-39}O_{12}N_7{\cdot}3HCl)_2{\cdot}CaCl_2$ for the calcium chloride double salt of streptomycin trihydrochloride (I). Our analytical data on purified samples of I, $[\alpha]^{25}D$ −81° (*c* 2, water), support the above formula and establish the presence of one methyl group linked to carbon.

Anal. Calcd. for $(C_{21}H_{37}O_{12}N_7{\cdot}3HCl)_2{\cdot}CaCl_2$: C, 33.88; H, 5.42; N, 13.17; Cl, 19.05; Ca, 2.69. Calcd. for $(C_{21}H_{39}O_{12}N_7{\cdot}3HCl)_2{\cdot}CaCl_2$: C, 33.79; H, 5.67; N, 13.14; Cl, 19.00; Ca, 2.68. Found: C, 33.82; H, 5.69; N, 12.94; Cl, 18.64; Ca, 2.65. A C-methyl determination gave 1.9% CH_3 (calcd. for one C-methyl group, 2.0%).

Hydrogenation of an aqueous solution of I at 100–140 atmospheres and 150° with Raney nickel catalyst, followed by methanolysis and acetylation with acetic anhydride and pyridine yields crystalline methyl dihydrostreptobiosaminide pentaacetate, m. p. 194–195°, $[\alpha]^{28}D$ −117° (*c* 2, chloroform).

Anal. Calcd. for $C_{13}H_{19}O_8N(CH_3CO)_5OCH_3$: C, 51.15; H, 6.61; N, 2.49; OCH_3, 5.51; O-acetyl, 30.5. Found: C, 51.04; H, 6.93; N, 2.50; OCH_3, 5.86; O-acetyl, 30.6.

This compound is unchanged after treatment with hot acetic anhydride and sodium acetate. Since methanolysis and acetylation of streptomycin[2] is known to yield a tetraaacetate containing three methoxyl groups, it appears that in the above compound a carbonyl group of streptomycin has been reduced to an alcohol group.

Mercaptolysis of I with subsequent acetylation[3] yields, after chromatographic purification,[4] two forms of ethyl thiostreptobiosaminide diethyl thioacetal tetraacetate: A, m. p. 80.5–81°, $[\alpha]^{31}D$ −192° (*c* 2, chloroform); B, m. p. 111–111.5°, $[\alpha]^{28}D$ −29° (*c* 3, chloroform).

Anal. Calcd. for $C_{13}H_{18}NO_7(C_2H_5S)_3(CH_3CO)_4$: C, 49.44; H, 6.92; N, 2.14; S, 14.66; CH_3CO, 26.3; mol. wt., 655.9. Found for A: C, 49.63; H, 6.83; N, 2.21. Found for B: C, 49.54; H, 6.71; N, 2.15; S, 14.75; CH_3CO, 26.2; mol. wt. (Rast), 651.

These data indicate that in streptomycin, streptidine is attached to a glycosidic hydroxyl (cyclic hemiacetal) capable of existing in anomeric forms. Formation of a thioglycoside rather than a thioacetal indicates that the cyclic structure concerned in this hemiacetal linkage resists hydrolysis.

Hydrogenolysis of either A or B above with Raney nickel catalyst[5] followed by reacetylation yields didesoxydihydrostreptobiosamine tetraacetate (II), m. p. 158.5–159°, $[\alpha]^{31}D$ −86° (*c* 3, chloroform).

Anal. Calcd. for $C_{13}H_{21}O_7N(CH_3CO)_4$: C, 53.04; H, 7.00; N, 2.94; O-acetyl, 27.2. Found: C, 53.06; H, 7.02; N, 3.04; O-acetyl, 25.4.

An attempted high-pressure hydrogenation of II at 150° with Raney nickel gives unchanged material, demonstrating the absence of an olefinic linkage in the molecule.

[1] R. L. Peck, N. G. Brink, F. A. Kuehl, Jr., E. H. Flynn, A. Walti and K. Folkers, THIS JOURNAL, **67**, 1866 (1945).

[2] N. G. Brink, F. A. Kuehl, Jr., and K. Folkers, *Science*, **102**, 506 (1945).

[3] M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **67**, 500 (1945).

[4] W. H. McNeely, W. W. Binkley and M. L. Wolfrom, *ibid.*, **67**, 527 (1945).

[5] M. L. Wolfrom and J. V. Karabinos, *ibid.*, **66**, 909 (1944).

Acid hydrolysis of II followed by acetylation and chromatographic separation[4] yields N-methyl-α-L-glucosamine pentaacetate, $[\alpha]^{29}\text{D}$ −99 ± 2° (c 1, chloroform), m. p. 158°, unchanged on admixture with an authentic synthetic specimen. These data demonstrate that in streptomycin, the carbonyl group of N-methyl-L-glucosamine is glycosidically joined to the central portion, which is in turn similarly linked to streptidine.

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RECEIVED AUGUST 16, 1946

2,2,5,5-TETRAMETHYL-3-HEXENE

Sir:

The properties of *sym*-di-*t*-butylethylene, as recently reported by Hennion and Banigan,[1] are not in agreement with the properties measured in these laboratories on 2,2,5,5-tetramethyl-3-hexene, nor with those reported by Moersch.[2] However, the properties of the paraffin hydrocarbon (2,2,5,5-tetramethylhexane) prepared from the olefin by each investigator are in close agreement. The properties of the compounds in question are listed in Table I.

TABLE I

	B. p., °C.	F. p., °C.	d^{20}	$n^{20}\text{D}$
2,2,5,5-Me$_4$-3-hexene[a] (*trans*)	125.013[b]	− 4.75	0.71673[c]	1.41148[d]
2,2,5,5-Me$_4$-3-hexene[e] (*trans*)	123.2[f]	.....	.7176	1.4117
2,2,5,5-Me$_4$-3-hexene[g] (*cis*)	144.2–144.4[h]	<−65	.7439	1.4271
2,2,5,5-Me$_4$-hexane[a]	137.457[i]	−12.64	.71875[j]	1.40550[k]
2,2,5,5-Me$_4$-hexane[g]	136.2–136.4[l]	−13	.7189	1.4060
2,2,5,5-Me$_4$-hexane[m]	135.8–136.1[n]	−11.6		1.4057

[a] This work. [b] At 760 mm., dT/dP = 0.048°/mm. range (20–80% distilled) = 0.010°. [c] d^{25} = 0.71223. [d] $n^{25}\text{D}$ = 1.40890. [e] Moersch, ref. 2. [f] At 727.3 mm. [g] Hennion and Banigan, ref. 1. [h] At 748 mm. [i] At 760 mm., dT/dP = 0.050°/mm. range (20–80% distilled) = 0.004°. [j] d^{25} = 0.71480. [k] $n^{25}\text{D}$ = 1.40315. [l] At 739 mm. [m] Buechele, Thesis, Pennsylvania State College, 1937. [n] At 731 mm.

An examination of the experimental evidence reveals that there exists no reasonable doubt concerning the identity of the di-*t*-butylethylene (2,2,5,5-tetramethyl-3-hexene) reported by each investigator. We suggest that the two sets of physical properties may correspond to the two geometric isomers, and that our low-boiling, high-melting olefin is the *trans* isomer, and that of Hennion and Banigan (low-melting, high-boiling) is the *cis* isomer. The methods of preparation strengthen this conjecture. Additional confirmation lies in the fact that the molecular model for *cis*-2,2,5,5-tetramethyl-3-hexene shows very large steric hindrance among four of the methyl groups.

Our synthesis was carried out as follows: 2,2,5,5-Tetramethyl-3-hexanol was prepared by the method described by Moersch.[2] Methyl *t*-butylacetate (6815 g., 52.4 moles) was added to *t*-butylmagnesium chloride (about 300 moles). The product was recovered by orthodox methods and distilled in a 30-plate column. There was obtained 6507 g. (41.2 moles, 79%) of carbinol collected at 166–170°. The carbinol was dehydrated by J. T. Baker Hydralo at 300–305° to a mixture of olefins (4999 g., 86.6%). The mixture was separated into concentrates boiling at 121–127° (2,2,5,5-tetramethyl-3-hexene, 34.5 mole per cent. of product), 139–145° (2,3,5,5-tetramethyl-1-hexene, 35.2%), and 152–158° (2,3,5,5-tetramethyl-2-hexene, 30.2%). The first concentrate was redistilled in a 30-plate column, and the best portion was fractionated in a 6-foot Podbielniak column. Physical constants were measured on a selected best fraction from the latter distillation. Ozonolysis of a sample of 2,2,5,5-tetramethyl-3-hexene gave only trimethylacetaldehyde (m. p. and mixed m. p. of 2,4-dinitrophenylhydrazone, 207–208°).

High-pressure hydrogenation of this olefin gave 2,2,5,5-tetramethylhexane. The other two olefins yielded 2,2,4,5-tetramethylhexane. Purification by distillation in a 6-foot Podbielniak column gave a high-purity sample for measurement[3] of physical constants.

This work was supported by funds from the National Advisory Committee for Aeronautics, the Army Air Forces, and the Navy Bureau of Aeronautics.

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(1) Hennion and Banigan, THIS JOURNAL, **68**, 1202 (1946).

(2) Moersch, Ph. D. Thesis, Pennsylvania State College, 1942.

(3) Brooks, Howard and Crafton, *J. Research Natl. Bur. Standards*, **23**, 637 (1939).

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RECEIVED AUGUST 9, 1946

2,3-DIAMINOQUINOXALINE

Sir:

Our attention has been called to the publication by Gowenlock, Newbold and Spring, *J. Chem. Soc.*, 622 (1945), describing the preparation of 2,3-diaminoquinoxaline by essentially the same procedure as that described in our recent publication, THIS JOURNAL, **68**, 1035 (1946). We are extremely sorry that we neglected to include this reference in our publication.

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RECEIVED SEPTEMBER 18, 1946

PREPARATION OF 2-THIENYLMETHYLCARBINOL AND α-VINYLTHIOPHENE

Sir:

α-Vinylthiophene was obtained in quantitative yields by dehydrating 2-thienylmethylcarbinol