12–31% B_4H_{10}, 6–15% B_5H_9, 17–31% B_6H_{10} and 22–26% non-volatiles; B_5H_{11}-conversion, 34–98%. The yields were not much affected by changes in warming time, per cent. conversion or catalyst history.

The Trimethylamine Reaction.—Warming one B_5H_{11} with 0.924 $(CH_3)_3N$ (−132 to −10°, 10 hr.) gave 13% B_2H_6, 12% B_4H_{10}, 20% B_5H_9, 17% B_6H_{10} and 13% $(CH_3)_3NBH_3$ (no B_5H_{11} recovered). However, 2.06 $(CH_3)_3N$ per B_5H_{11} (−130 to 0°, 12 hr.) gave only 2% B_6H_{10} with 30% $(CH_3)_3NBH_3$, 12% B_5H_9 and traces of B_2H_6, B_4H_{10} and $B_{10}H_{14}$. The previously suggested mechanism $B_5H_{11} + 2R_3N \rightarrow 2R_3NBH_3 + B_3H_5$; $2B_3H_5 \rightarrow B_6H_{10}$[3] seems neither applicable nor heuristically useful.

The Dimethyl-Ether Reaction.—Pentaborane-11 and dimethyl ether (mole ratio 0.64, four experiments) formed a solid at −78°. Warming to −20° (10 min. to 16 hr.) gave 22–28% B_2H_6, 21–22% B_4H_{10}, 0–3.3% B_5H_9, 24.5–27.3% B_6H_{10}, 1.9–2.3% $B_{10}H_{14}$ and about 25% non-volatiles, from the unrecovered B_5H_{11}. The B_5H_{11}-conversion usually was 77–90% and the ether-recovery 96%. One experiment, using one ether per 10 B_5H_{11}, gave 83% conversion but only 10% yield of B_6H_{10}, diborane being favored. Too much ether only slowed the process.

The Diglyme Flow-Method.—Pentaborane-11 was evaporated at −27°, passing through a 12-mm. wide column of 3 mm. beads wet by diglyme, at −20° and under 10 mm. pressure, controlled by a mercury bubbler leading to vacuum. In the first experiment, 0.820 mmole of B_5H_{11} passed a 20-mm. column-length in 8 min., with 40% conversion. Repetition with recovered B_5H_{11} brought the conversion to 65%. The second experiment (0.774 mmole, 40 mm. column-length, one pass, 4 min.) gave 63% conversion. Yields were: 17–18% B_2H_6, 34–32% B_4H_{10}, 1.1–2.8% B_5H_9, 25–23% B_6H_{10} and 23% non-volatile hydrides. Further experimentation with diglyme and other polybases may well increase the per cent. conversion per pass, without serious loss of B_6H_{10} yield.

Discussion.—These syntheses raise interesting questions about borane interconversion mechanisms. Bases remove BH_3 from B_5H_{11}, leading to an over-all disproportionation; and a weak base returns BH_3 to increase the yields of B_2H_6 and B_4H_{10}. Too much strong base permanently removes BH_3 needed to make B_6H_{10}.

Acknowledgment.—The generous support of this work by the Office of Naval Research is gratefully acknowledged. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(3) E. Wiberg and O. Stecher, *Fiat Review*, Inorg. Chem. Part I, 129 (1949).

DEPARTMENT OF CHEMISTRY JAMES L. BOONE
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA ANTON B. BURG

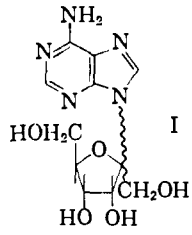
RECEIVED FEBRUARY 7, 1959

A NEW ANTIBIOTIC, 6-AMINO-9-D-PSICOFURANOSYLPURINE

Sir:

The isolation of a new antibiotic having marked antibacterial and antitumor activity *in vivo*, from culture filtrates of *Streptomyces hygroscopicus* var. *decoyinine*, will be reported by T. E. Eble, *et al.*[1]

The findings reported in this communication allow the formulation of the structure 6-amino-9-D-psicofuranosylpurine (I) for this antibiotic (U-9586).



I

Elemental analyses on the crystalline antibiotic [needles m.p. 212–214°d., $[\alpha]^{25}D$ −53.7° (c = 1 in dimethyl sulfoxide) and $[\alpha]^{25}D$ −68° (c = 1 in dimethylformamide)] permitted the assignment of the empirical formula $C_{11}H_{15}N_5O_5$ to I. *Anal.* Calcd. for $C_{11}H_{15}N_5O_5$: C, 44.44; H, 5.08; N, 23.56; O, 26.91. Found: C, 44.25; H, 5.10; N, 23.74; O, 27.02.

Group analysis indicated the absence of methoxyl, C-methyl, alkimide or acetyl ester groupings. Ultraviolet spectra showed maxima at 259 mμ, $E^{1\%}_{1cm.}$ = 508 in 0.01 *N* sulfuric acid, and at 261 mμ, $E^{1\%}_{1cm.}$ = 530 in 0.01 *N* sodium hydroxide.

Compound I gave negative Bial, ninhydrin, and Benedict tests, but the latter was positive after acid hydrolysis. Positive results were obtained with ammoniacal silver nitrate and the Jordan–Pryde[2] test for ketohexoses. Consumption of one equivalent of periodate was complete in 15 minutes at 25° showing two vicinal hydroxyls.[3] Hydrolysis of I with aqueous or ethanolic mineral acids gave the theoretical amounts of adenine salts, identified by analysis and by comparison of the ultraviolet and infrared spectra with those of an authentic sample.

Upon treatment with phenylhydrazine, the deionized filtrate, obtained after separating the adenine sulfate from an aqueous hydrolysis (12 hours at 25° in 0.57 *M* sulfuric acid) afforded a phenylosazone; m.p. 161–163°, $[\alpha]^{25}D$ −75.4° (after 15 minutes, c = 0.557 in pyridine). *Anal.* Calcd. for $C_{18}H_{22}O_4N_4$: C, 60.32; H, 6.19. Found: C, 60.19; H, 6.30. Oxidation of the osazone with copper sulfate gave a phenylosotriazole; m.p. 134–135°, $[\alpha]^{24}D$ 28.5° (c = 0.554 in pyridine). *Anal.* Calcd. for $C_{12}H_{15}O_4N_3$: C, 54.33; H, 5.70. Found: C, 54.71; H, 5.81. These data indicated the sugar to be D-psicose.[4,5,6] The consumption of only one equivalent of periodate requires the furanose ring. The assignment of the glycoside link to the 9-position in adenine is based on a comparison of the ultraviolet spectra with those of 7-

(1) T. E. Eble, H. Hoeksema and G. A. Boyack, to be published.
(2) R. C. Jordan and J. Pryde, *Biochem. J.*, **32**, 279 (1938).
(3) P. F. Fleury and J. Lange, *J. Pharm. Chim.*, **17**, 107 (1933).
(4) M. L. Wolfrom, A. Thompson and E. F. Evans, THIS JOURNAL, **67**, 1793 (1945).
(5) W. T. Haskins, R. M. Hann and C. S. Hudson, *ibid.*, **67**, 939 (1945).
(6) Authentic D-psicosazone was prepared for comparison from D-altrose kindly supplied by N. K. Richtmyer of The National Institutes of Health.

methyl and 9-methyladenine.[7] We believe these findings to be consistent with structure I.[8]

Confirmation of this structure has been obtained by condensing D-psicosyl chloride tetraacetate with chloromercuri-6-acetamidopurine and deacylating the resulting product.[9] Countercurrent distribution of the reaction mixture afforded synthetic 6-amino-9-D-psicofuranosylpurine, identical with the natural material.

The successful extension of this synthetic method to the preparation of other keto nucleosides will be reported in detail at a later date.

D-Psicose has been reported once before[10] to be a naturally occurring sugar, although this claim was subject to question.[11]

The present finding constitutes the first demonstration of a biologically produced ketose nucleoside and provides good evidence that D-psicose can be elaborated by microörganisms.[12]

We wish to thank Dr. W. G. Jackson for his interest in this problem and Mr. W. A. Struck and associates for the microanalyses.

(7) J. M. Gulland and E. R. Holiday, *J. Chem. Soc.*, 765 (1936); J. M. Gulland and L. F. Story, *ibid.*, 259 (1938).

(8) The n.m.r. spectrum, as interpreted by Dr. George Slomp of these laboratories, is also in accord with this proposal.

(9) This general procedure for nucleoside syntheses from aldo sugar halides was developed by J. Davoll and B. A. Lowy, THIS JOURNAL, **73**, 1650 (1951). The present report is the first recorded instance of its use in the synthesis of a keto sugar nucleoside.

(10) F. W. Zerban and L. Sattler, *Ind. Eng. Chem.*, **34**, 1180 (1942); THIS JOURNAL, **64**, 1740 (1942).

(11) L. Hough, J. K. N. Jones and E. L. Richards, *J. Chem. Soc.*, 2005 (1953).

(12) After submission of this paper, we received the paper [Hsü. Yüntsen, *J. Antibiotics (Japan)*, **11A**, 244 (1958)] in which structure I was assigned to angustmycin C.

RESEARCH LABORATORIES
THE UPJOHN COMPANY — WILLIAM SCHROEDER
KALAMAZOO, MICHIGAN — HERMAN HOEKSEMA

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ORGANOBORON COMPOUNDS. XI. TRIALKYLBORANES HAVING TWO *t*-BUTYL GROUPS ATTACHED TO BORON[1,2]

Sir:

It is now clear[3] that no authentic organoboron compound having more than one *t*-butyl group attached to the same boron atom has been described previously.

We now report the first trialkylboranes having two *t*-butyl groups attached to boron, *viz.*, di-*t*-butyl-*n*-butylborane (I) and di-*t*-butyl-*n*-amylborane (II). Each of these substances was fractionally distilled at least twice *in vacuo*, below 50°, without evidence of decomposition, rearrangement or disproportionation. Oxidation of I with alkaline hydrogen peroxide gave a 2:1 mixture of *t*-butyl and *n*-butyl alcohols in high yield; II similarly treated produced *t*-butyl and *n*-amyl alcohols in the proper ratio. The infrared spectra of I and II are similar and different from the spectra of related trialkylboranes previously described.[3]

Property		Compd. I	Compd. II
B.p., °C. (mm.)		47.7 (1.7)	42.5–42.7 (0.5)
$n^{25}D$		1.4373	1.4397
d^{25}		0.7608	0.7668
B	Calcd., %	5.94	5.52
	Found, %	6.08	5.56
MR_D	Calcd.	62.67	67.30
	Obsd.	62.76	67.38

When II was heated under nitrogen at 205° for fifteen minutes rearrangement and disproportionation occurred and a 2:1 mixture of triisobutylborane and tri-*n*-amylborane was produced in quantitative yield. It may be noted that the same mixture was produced when *t*-butyl-isobutyl-*n*-amylborane[1] was heated in the same manner.

I was prepared in 41% yield by the alkylation of boron fluoride with *t*-butylmagnesium chloride in anhydrous ether containing a large excess of 1-butene. II was made in the same way (32–39% yields) except that 1-pentene was employed in place of 1-butene. It is noteworthy that attempts to prepare di-*t*-butyl-isobutylborane by this procedure failed. When the reaction of boron fluoride with *t*-butylmagnesium chloride was carried out in the presence of isobutylene, the product proved to be *t*-butyl-diisobutylborane.[3] Furthermore, I did not react with isobutylmagnesium bromide by alkyl exchange.[1] It now appears likely that di-*t*-butyl-isobutylborane, if formed under any conditions, is unstable due to steric hindrance and rearranges rapidly at low temperature to *t*-butyl-diisobutylborane and at high temperature to triisobutylborane.

The mechanisms of the reactions mentioned above are now under investigation in This Laboratory and will be discussed at a later date.

DEPARTMENT OF CHEMISTRY — G. F. HENNION
UNIVERSITY OF NOTRE DAME — P. A. MCCUSKER
NOTRE DAME, INDIANA — J. V. MARRA

RECEIVED FEBRUARY 6, 1959

(1) Previous paper, G. F. Hennion, P. A. McCusker and J. V. Marra, THIS JOURNAL, **80**, 3481 (1958).

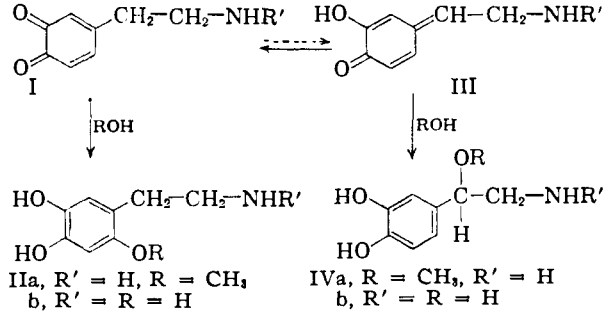
(2) Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38.

(3) G. F. Hennion, P. A. McCusker, *et al.*, THIS JOURNAL, **79**, 5190, 5192, 5194 (1957); **80**, 617 (1958).

2,4,5-TRIHYDROXYPHENETHYLAMINE, A NEW METABOLITE OF 3,4-DIHYDROXYPHENETHYLAMINE

Sir:

The 1,4-addition of nucleophilic agents to *o*-quinones of acylated dopamine derivatives I leads to 6-methoxydopamine (IIa, R = CH_3) and 2,4,5-trihydroxyphenethylamine (IIb, R = H). Concomitant 1,6-addition to the tautomeric quinonemethine III yields <0.1% norepinephrine (IVb).[1]



(1) S. Senoh and B. Witkop, A. C. S. Meeting, Chicago, Sept., 1958, Abstracts p. 64-P.