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.

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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.

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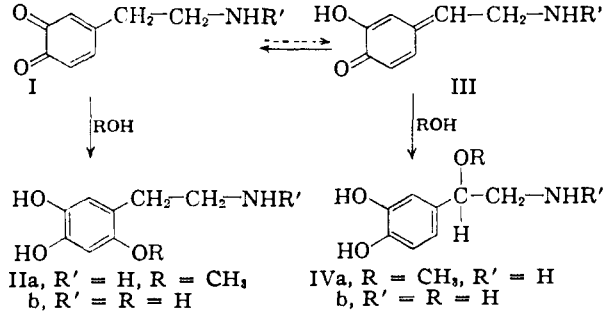
RECEIVED FEBRUARY 6, 1959

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]



IIa, R' = H, R = CH_3 — IVa, R = CH_3, R' = H
b, R' = R = H — b, R' = R = H

(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).

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

We have now demonstrated that IIb is invariably formed from dopamine under conditions of (aut)-oxidation as well as *in vivo*.

A major problem has been the separation of IIb from the isomeric norepinephrine, both compounds having identical R_f values in more than ten different solvent systems. Separation of such mixtures, however, was achieved by treatment with methanolic HCl which methylates IVb quantitatively to IVa[2] but leaves IIb unchanged (Table I).

TABLE I

CHROMATOGRAPHIC RESOLUTION OF MIXTURES OF TRIHYDROXYPHENETHYLAMINE AND NOREPINEPHRINE BY SELECTIVE *O*-METHYLATION

Compound	PhOH:0.02*N* HCl: KCN 80 g.:20 ml.: trace (saturation of SO_2 gas) Anhyd. HCl–CH_3OH Before	After	*sec*-BuOH:HCOOH: H_2O 75:15:10 (N_2 atmosphere) Anhyd. HCl–CH_3OH Before	After
Trihydroxyphenethylamine (IIb)	0.29	0.30	0.25	0.25
Norepinephrine (IVb)	0.29	0.58	0.25	0.51
Mixture of IIb + IVb	0.30	0.30 0.58	0.25	0.25 0.51
β-O-Methylnorepinephrine (IVa)	0.58		0.52	

TABLE II

In Vitro STUDIES WITH H^3 AND C^{14} DOPAMINE

A mixture of dopamine-β,β-H^3 and dopamine-α-C^{14} in the ratio of 3.13 was incubated for 3 hours. The "norepinephrine" was isolated using procedures previously described [*cf. Arch. Biochem. Biophys.*, 74, 252 (1958)].

Incubation with	Counts/min. C^{14}	H^3	H^3/C^{14}	Tritium atoms lost
Dog cerebellum homogenate	248	896	3.60	0
Dog hypothalamus homogenate (boiled)	1,739	5,472	3.13	0
Ascorbic acid–Fe–Versene[3]	8,470	31,200	3.17	0
Enzymatically formed norepinephrine[a]	13,884	24,513	1.75	1
Pure dopamine	...	...	3.13	...

[a] Specific enzymatic side-chain hydroxylation of dopamine occurs in hypothalamus, caudate nucleus, adrenal medulla and similar tissues by the action of an enzyme which may be called "*dopamine β-oxidase*" to differentiate it from any possible *dopamine oxidase* acting on the catechol nucleus.

When a mixture of tritium and carbon labeled dopamines was used for *in vitro* oxidations with various tissues, or with the ascorbic acid–Versene system[3] (Table II), the ratio H^3/C^{14} in the "norepinephrine" fractions was found to be too high except with tissues containing *dopamine β-oxidase*. This suggests that little or no tritium had been lost by hydroxylation of the benzyl position and that norepinephrine was not the product formed. Little or no IVa was detected after treatment with HCl/CH_3OH.

Finally, 800 μg. of dopamine-α-C^{14} (4100 c.p.m./μg.) was administered intraperitoneally to rats, and urine was collected in an all glass system. The "norepinephrine" fraction was found to be largely 2,4,5-trihydroxyphenethylamine, representing from 0.5–1% of the administered radioactivity. These are minimal conversion values, since only 1% of injected IIb could be recovered as such in the urine.

Although it remains to be seen whether IIb has any physiological significance, these findings have an important bearing on the validity of biochemical studies with isotopic precursors of norepinephrine.

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(2) B. F. Tullar, THIS JOURNAL, **70**, 2068 (1948).
(3) S. Udenfriend, *et al.*, *J. Biol. Chem.*, **208**, 731 (1954).

NUCLEAR MAGNETIC RESONANCE SPECTRA. ALLYLMAGNESIUM BROMIDE[1]

Sir:

The proton nuclear magnetic resonance (n.m.r.) spectrum of allylmagnesium bromide (I, Fig. 1)

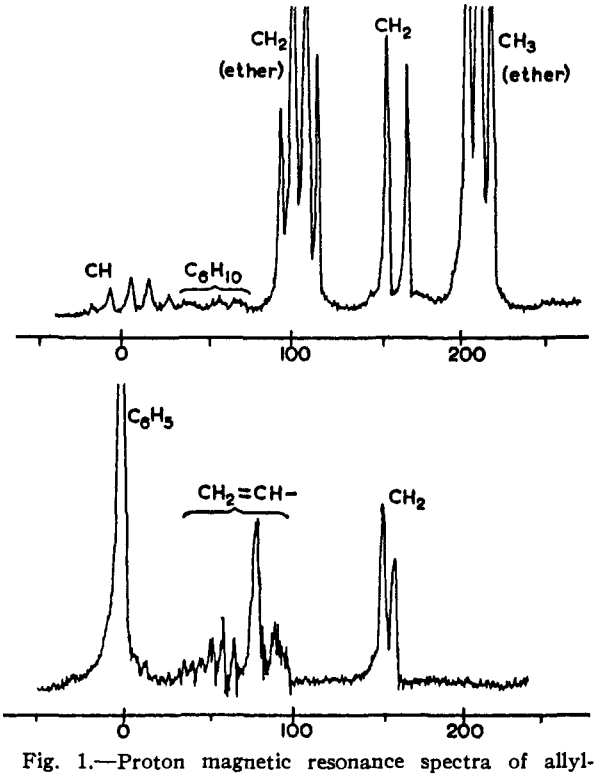

Fig. 1.—Proton magnetic resonance spectra of allylmagnesium bromide in diethyl ether solution (upper) and allylbenzene (lower). The spectra were taken with a Varian Associates High Resolution Spectrometer (V-4300) at 60 Mc. with a 12-inch magnet equipped with a Super-Stabilizer. Chemical shifts are in c.p.s. from benzene (external reference) and were measured by the audio-oscillator sideband superposition method. The signals designated C_6H_{10} in the allylmagnesium bromide spectrum are due to diallyl formed by coupling during preparation of the Grignard reagent, as verified by the spectrum of a sample to which diallyl had been added deliberately.

is extraordinarily revealing with regard to the structure and mobility of this important organometallic compound as ordinarily prepared in diethyl ether solution. In the first place, compared to the

(1) Supported in part by the Office of Naval Research.