(Table I) than when it is induced by the $He^3(n,p)H^3$ process. This seems to indicate that the mechanisms are different. In the $He^3(n,p)H^3$ case the formation of each carbon chain presumably is initiated by attack of a tritium ion on a CH_4 molecule.

The many products formed in these reactions offer a valuable source of high specific activity labelled compounds when these non-parent "by-products" can be separated in carrier-free form by gas chromatography or otherwise.

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CHEMICAL REACTION OF RECOIL TRITIUM WITH GASEOUS ALKANES[1]

Sir:

We have studied the reaction of high energy tritium, as produced by nuclear reaction, with gaseous methane and ethane. The reactions $He^3(n,p)H^3$ (0.78 Mev.) and Li^6 $(n,\alpha)H^3$ (4.7 Mev.) were used to supply the "hot" tritium. In the He^3 runs about 0.1 cm. He^3 was sealed with 10–60 cm. CH_4 in a $\sim$ 7 ml. quartz ampoule. In the Li^6 runs a film of normal lithium nitrate formed the inside coating of similar vessels. After irradiation in the Brookhaven reactor, carriers were added and the various tritium labeled species separated and counted, largely as described elsewhere.[2]

A summary of some of our results on the chemical state of the tritium following interaction with methane is shown in Table I. This distribution of

TABLE I

CHEMICAL STATE OF RECOIL TRITIUM STOPPED IN METHANE
Expressed as % of total gaseous activity in absence of I_2

	Irradiation conditions		
Chemical state	$10^{12.6}$ neutrons cm.$^{-2}$ sec.$^{-1}$, no I_2 present	$10^{9.3}$ neutrons cm.$^{-2}$ sec.$^{-1}$, no I_2 present	$10^{9.3}$ neutrons cm.$^{-2}$ sec.$^{-1}$, I_2 present
HT	50.6	61.9	29.8
CH_3T	30.9	29.1	26.0
$C_2H_5T + C_2H_3T$	8.2	2.9	0.1
C_3(T) hydrocarbons	5.0	2.4	0.2
Higher tritiated hydrocarbons and iodides	5.3	3.7	43.9

activity is independent of the source of the tritium, the pressure and the temperature (range 30–200°). However, a drastic reduction of neutron flux, with accompanying decrease in radiation density, although having little effect on the production of CH_3T, seems to reduce significantly the yields of labeled higher hydrocarbons while increasing the amount of HT. The addition of 0.2 mm. of iodine as a radical scavenger has little effect on the yield of CH_3T but virtually eliminates the yield of higher labeled hydrocarbons and reduces the yield of HT.

Studies on the slowing of charged particles passing through matter[3] indicate that the tritium is uncharged on reaching its final reaction site. Taking this into account, our observations suggest two distinct modes of reaction of the tritium atom: (A) Most tritium combines by direct hot replacement reaction. For methane

$$T^* + CH_4 \longrightarrow CH_3T + H$$

$$T^* + CH_4 \longrightarrow HT + CH_3$$

Radical intermediates are definitely ruled out and Walden inversion probably is involved. (B) Some tritium escapes incorporation in stable molecules by hot reaction and becomes thermalized. Its reactions then become sensitive to radical scavengers, such as I_2. In their absence the tritium can react competitively to (1) abstract H to form part of the HT observed, or (2) combine with radiation produced radicals or ions to form the higher labeled hydrocarbons. (Production of the latter probably involves hydrocarbon chains lengthened by ion molecule reactions.[4])

The results observed with ethane are consistent with this picture. Most of the activity appears in HT and C_2H_5T with smaller amounts in CH_3T and higher hydrocarbons. Only C_3 and higher hydrocarbons are eliminated by I_2. This means that degradation products such as CH_3T from ethane are largely formed by direct hot replacement reactions (type A).

It has been demonstrated that neither radical intermediates nor a solvent cage, the central concepts of earlier theories of hot-atom reactions,[5] are necessary for hot reaction of hydrogen. Whether the reaction model postulated here holds also for recoil tritium reactions in the condensed phase remains to be seen. The similar product distributions in gaseous and liquid[2] alkanes are suggestive. But the retention of configuration observed in the solid phase[6] would require further explanation.

(1) Research supported by the Atomic Energy Commission. See also accompanying communication by Gordus, Sauer and Willard, p. 3284.

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DEGRADATION OF BRAIN GANGLIOSIDE TO GLUCOCEREBROSIDE

Sir:

Since Klenk first described the brain gangliosides,[1] evidence has been presented that they are

(1) E. Klenk, *Z. physiol. Chem.*, **273**, 76 (1942).

macromolecular glycolipids[2-4] which contain neuraminic acid, sphingosine,[5] fatty acid (stearic),[6] hexoses, and a hexosamine. Earlier studies have demonstrated the hexoses to be exclusively glucose and galactose and the hexosamine to be exclusively galactosamine.[4,8] However, little is known of the manner in which these constituents are linked. A cerebroside frequently has been postulated to be the basic unit in the structure of the gangliosides. The present communication reports the successful hydrolytic degradation of a purified preparation of brain ganglioside to a glucocerebroside.

Bovine brain ganglioside was prepared as an ash-free fraction (I) homogeneous by electrophoretic and ultracentrifuge studies (minimal molecular weight 250,000), completely water-soluble, free of phosphatides (P 0.07%) and of dialyzable contaminants.[4,7,8] (I) contains nitrogen 2.9%, hexose 24.0% (expressed as galactose), and galactosamine 10.0%.

Optimal conditions for the isolation of the constituent glucocerebroside have been defined as follows: a 2% aqueous solution of I is autohydrolyzed at 100° for a critical time interval of 25 minutes, then exhaustively dialyzed. The dialyzate contains 66% of the neuraminic acid and 5.2% of the galactosamine of I. The non-dialyzable residue (II) accounts for 80% by weight of I. II is hydrolyzed with 0.09 *N* HCl (sealed tube, 100°, 16 hours) then exhaustively dialyzed. The resulting non-dialyzable residue (III), still water-soluble, is further hydrolyzed (0.09 *N* HCl, sealed tube, 100°, 5 hours). The hydrolyzate, which now contains a brown insoluble material (IV), is exhaustively dialyzed. IV is separated by centrifugation, dried *in vacuo*, and taken up in clear solution with warm methanol:chloroform (9:1). 12% of IV remains as an insoluble black residue which is discarded. When this solution (40 mg./cc.) is allowed to cool to room temperature, birefringent spherocrystals (MCS) are formed. To date, yields of MCS represent between 26 and 30% by weight of I. MCS crystals contain no neuraminic acid and no galactosamine. The analysis, compared with that expected for a glucostearocerebroside crystallized with one mole of water,[9] is

	N, %	C, %	H, %	Hexose (as glucose), %
Found	1.86	67.13	10.95	21.8
Calcd. for $C_{42}H_{81}O_8N(H_2O)$	1.88	67.65	11.14	22.0

MCS is insoluble in water, slightly soluble in pure chloroform, very soluble in mixtures of chloroform:methanol. MCS shows slight liquefication at 165°, then melts sharply between 172–174°. The iodine number is 23.2. In chloroform:methanol (2:1) (1 mg./cc.), it is levorotatory ($[\alpha]^{20}D$ −2.08°). The infrared spectrum is consistent with that of a cerebroside.[10] A sample of crystalline MCS gave these spacings by X-ray diffraction[11]: 2.41, 4.10, 9.1, 10.4, 15.6, 21.1, 30.6, 49.2, 55.5, and 63.5 Å.

Hydrolysis of MCS in *N* HCl (sealed tube, 100°, 16 hours) liberated the hexose quantitatively. This was shown to be exclusively glucose by paper chromatography. The remaining water-insoluble residue contained 2.3% nitrogen, as expected for a ceramide. It is yet to be established whether the base is sphingosine or dihydrosphingosine.[12]

The melting point, specific rotation, iodine number and the elementary analysis, distinguish MCS from the previously described cerebrosides phrenosine, cerasine and nervone.[13] A glucostearocerebroside has not been described previously. Its presence as the basic constituent of brain ganglioside would be consistent with the demonstration by Klenk that the constituent fatty acid of brain ganglioside is stearic acid.[6] The isolation of this glucocerebroside is of interest with regard to the over-all structure and biosynthesis of the gangliosides.

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SYNTHESIS OF ±-CRYPTOPLEURINE[1]

Sir:

The vesicant alkaloid cryptopleurine[2] has interesting physiological properties[3] and has been stated to possess a skeletal structure of a novel type. Although the alkaloid could not be degraded to compounds of known structure,[3] chemical,[3,4] spectroscopic,[4] and, in particular, crystallographic (X-ray)[5] evidence was adequate to allow the base to be designated as 2′,3′,6′-trimethoxyphenanthro-[9′,10′,2,3]quinolizidine (I).

By the use of the general methods described earlier[6] we have accomplished the first synthesis of ±-cryptopleurine. Condensation of 6-nitroveratraldehyde with homoanisic acid yielded 6-nitro-3,4,4′-trimethoxy-α-phenylcinnamic acid (m.p. 185–186°; *Anal.* Calcd. for $C_{18}H_{17}NO_7 \cdot H_2O$: C,

(1) This investigation was supported by a research grant (H-2170) from the National Heart Institute of the National Institutes of Health, Public Health Service.
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