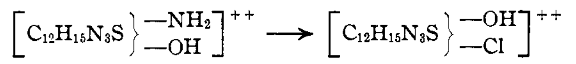
two substances are so similar it must be inferred that no rearrangement has taken place in the transformation. From a comparison of the two empirical formulas, it is evident that in addition to the hydrolysis of the amino group present in the original vitamin, we have replaced an —OH by non-ionic Cl.



$$\left[C_{12}H_{15}N_3S\begin{cases}-NH_2\\-OH\end{cases}\right]^{++} \longrightarrow \left[C_{12}H_{15}N_3S\begin{cases}-OH\\-Cl\end{cases}\right]^{++}$$

Vitamin "Chlorooxyvitamin" (IV)

The ultraviolet absorption spectrum of (IV) contrasted with that of the vitamin is shown in the accompanying chart. The peak at 267 mμ in the vitamin curve persists in the curve for our compound, while the absorption maximum at 235 mμ is shifted to 220 mμ. In a recent paper[6] from the University of Göttingen dealing with ultraviolet absorption spectra of compounds related to vitamin B_1, there is mention of a "hydrolysis product of the vitamin probably $C_{12}H_{15}N_3O_2S$." Its curve exhibits maxima at 265 and 219 mμ so that we may assume that structurally it resembles (IV). Judging from the tentative empirical formula, Windaus and collaborators have hydrolyzed the aminopyrimidine grouping, leaving the aliphatic hydroxyl intact. The chief value of our own work lies in the fact that it is the first evidence of the presence of a free hydroxyl group in the vitamin.

(IV) has no vitamin B_1 activity when injected into polyneuritic rats.

We wish to thank Miss Marion Ammerman for the bio-essays, Mr. A. E. Ruehle for the spectrograms, Drs. H. T. Clarke and O. Wintersteiner for securing the microanalyses, and the Carnegie Corporation for financial aid rendered through the Carnegie Institution of Washington.

Summary

1. Vitamin B_1 is converted by the action of concentrated hydrochloric acid into a compound $[C_{12}H_{16}N_3SOCl]^{++}Cl_2^{=}$ (IV).

2. This is interpreted as evidence for the presence of an aliphatic hydroxyl group in the vitamin.

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[6] A. Smakula, *Z. physiol. Chem.*, **230**, 232 (1934).

NOTES

2-Methyl- and 2-Ethyl-4-(*p*-fluorophenyl) Thiazoles and Some of their Derivatives

BY J. P. WETHERILL AND RAYMOND M. HANN

In a recent communication[1] the synthesis of 2-methyl and 2-ethyl thiazoles containing a *p*-chlorinated, brominated or iodinated phenyl group in the 4-position was reported. Subsequent preparation of *p*-fluorophenacyl chloride[2] (ω-chloro-*p*-fluoroacetophenone) now allows completion of the series of halogenated derivatives.

Experimental

The thiazoles were obtained by the interaction of ω-chloro-*p*-fluoroacetophenone with thioacetamide and thiopropionamide under conditions similar to those previously employed. The properties of the new compounds and of some simple derivatives are summarized in Table I.

TABLE I

2-METHYL- AND 2-ETHYL-4-*p*-(FLUOROPHENYL) THIAZOLES AND DERIVATIVES

	4-*p*-Fluorophenyl thiazole	Appearance	M. p., °C. (corr.)	Formula	N analyses, % Calcd.	N analyses, % Found
1	2-Methyl	Colorless glistening plates	81	$C_{10}H_8NSF$	7.25	7.24
2	2-Methyl, hydrochloride	Colorless glistening needles	131	$C_{10}H_8NSF\cdot HCl$	6.10	5.96
3	2-Methyl, picrate	Light yellow platelets	161	$C_{16}H_{11}O_7N_4SF$	13.27	13.19
4	2-Methyl, mercuri-chloride	Long colorless needles	160	$C_{10}H_8NSF\cdot HgCl_2$	3.01	3.09
5	2-Ethyl	Colorless plates	15–16	$C_{11}H_{10}NSF$	6.76	6.61
6	2-Ethyl, picrate	Thin yellow platelets	154	$C_{17}H_{13}O_7N_4SF$	12.84	12.71
7	2-Ethyl, mercuri-chloride	Long colorless needles	160[a]	$C_{11}H_{10}NSF\cdot HgCl_2$	2.93	2.55

[a] Decomposition with melting point lowering on recrystallization.

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[1] Wetherill and Hann, THIS JOURNAL, **56**, 970 (1934).

[2] Hann and Wetherill, *J. Wash. Acad. Sci.*, **24**, 526 (1934).

Summary

The series of 2-methyl and 2-ethyl-4-(*p*-halogenated phenyl) thiazoles has been completed by preparation of the fluorine analogs.

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Emil Fischer's Assignment of Configuration to *d*-Glucose. The Pentaacetates of *d*-Arabitol and *d*-Xylitol[1]

BY R. C. HOCKETT AND C. S. HUDSON

To decide between two alternative configurations for *d*-glucose, Fischer investigated the trihydroxyglutaric acids derived from *l*-arabinose and *d*-xylose[2] and found the former to show $[\alpha]^{20}_{\mathrm{D}}$ $-22.7°$ in water, while the latter was inactive and must therefore contain the symmetrical configuration. Theoretically, the same conclusions could have been drawn from the properties of the corresponding pentitols which must contain the same symmetries, respectively, as the acids, and it is therefore remarkable to note that, in 1891, the literature recorded *l*-arabitol as optically inactive[3] and *d*-xylitol as active,[4] or just the opposite situation to that obtaining with the acids. Fischer resolved the anomaly by augmenting the rotation of arabitol just to the visible with borax, and satisfied himself as to the inactivity of xylitol by partially purifying the sirupy alcohol by its conversion to dibenzalxylitol, which, however, proved to be too insoluble to recrystallize.

The true optical nature of these pentitols can, however, be shown very readily and quite conclusively by converting them to the corresponding acetates, which are formed in quantitative yields, crystallize well and can easily be purified. The rotation of the active isomer (*d*-arabitol) is thus augmented to an easily read value of $[\alpha]^{20}_{\mathrm{D}}$ in $CHCl_3$ $+37.2°$, while the acetate of the inactive xylitol remains inactive. Thus any possibility that xylitol could be inactive through *fortuitous* internal compensation without a true plane of symmetry is removed. (*Cf.* β-methyl-*d*-galactoside, which is asymmetric yet nearly inactive. Its acetate shows $[\alpha]^{20}_{\mathrm{D}}$ in $CHCl_3$ $-13°$, however.)

We believe that this method of proof is pedagogically superior to that of Fischer, based upon the properties of the acids, since the yields are more nearly quantitative and the rotation of the active isomer actually greater. The necessary reactions could readily be carried out by advanced students as part of a laboratory exercise to prove the configuration of *d*-glucose. The pentitols were acetylated by warming with four parts of acetic anhydride and one-quarter part of fused sodium acetate.

d-Arabitol pentaacetate separates from water–methanol mixtures as large, clear, tabular prisms, m. p. 74–75° (corr.) and $[\alpha]^{20}_{\mathrm{D}}$ in $CHCl_3$ $+37.2°$ (*c*, 7.31; 4-dm. tube). *d*-Xylitol pentaacetate crystallizes from water–methanol mixtures as large, clear, tabular prisms which melt at 61.5–62.5° (corr.) and are wholly inactive (*c*, 1.61 in $CHCl_3$; 2-dm. tube).

Several investigators[5] have recently isolated *d*-arabitol from lichens. Several of them also prepared the acetate and found it to melt at 75° but did not record the rotation. Dr. Asahina informs us that a sample of authentic *d*-arabitol pentaacetate which we sent him gives an undepressed m. p. of 76° when mixed with the pentaacetate of his natural pentitol.

NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service. A paper containing this material was read by R. C. H. before the Division of Chemical Education at the St. Petersburg, Florida, Meeting of the American Chemical Society in March, 1934.

(2) Fischer, *Ber.*, **24**, 1836, 2683 (1891).

(3) Kiliani, *ibid.*, **20**, 1234 (1887).

(4) Bertrand, *Bull. soc. chim.*, **5**, 556 (1891).

(5) Nolan and Keane, *Nature*, **132**, 281 (1933); Yabuta and Sumiki, *J. Agr. Chem. Soc. Japan*, **9**, 492 (1933); Asahina and Yanagita *Ber.*, **67**, 799 (1934); Klima, *Monatsh.*, **62**, 209 (1933).