2-Thiophenethiocarboxhydrazide. M.p. 156°.C₅H₆N₂S₂ (158.2)

Calc. C 37.98 H 3.83 N 17.72 S 40.53

Found » 38.11 » 3.58 » 17.83 » 40.42

2-Pyrrolothiocarboxhydrazide. M.p. 122°.C₅H₇N₃S (141.2)

Calc. C 42.55 H 5.00 N 29.78 S 22.67

Found » 42.66 » 5.29 » 29.82 » 22.56

3-Indolethiocarboxhydrazide. M.p. 173°.C₉H₆N₃S (191.2)

Calc. C 56.54 H 4.75 N 21.98 S 16.77

Found » 56.97 » 5.02 » 22.16 » 16.85

A large number of thiohydrazones were prepared by condensation of the thiohydrazides with aldehydes, *e.g.* thiobenzhydrazones of salicylaldehyde (m.p. 155°), 2-methoxybenzaldehyde (m.p. 144°), anisaldehyde (m.p. 84°), 3-hydroxybenzaldehyde (m.p. 158°), 4-nitrobenzaldehyde (m.p. 109°), 4-dimethylaminobenzaldehyde (m.p. 125°), 4-acetamidobenzaldehyde (m.p. 170°), 4-succinylamidobenzaldehyde (m.p. 176° with decomposition), 1-naphthaldehyde (m.p. 126°), 2-naphthaldehyde (m.p. 132°), 2-quinolinecarboxaldehyde (m.p. 138°), 8-quinolinecarboxaldehyde (m.p. 159°), glucose (m.p. 194°); thiophenylacet-hydrazones of 2,4-dichlorobenzaldehyde (m.p. 152°), 4-nitrobenzaldehyde (m.p. 171°), 4-acetamidobenzaldehyde (m.p. 193°) phthaldehydic acid (m.p. 167°), 1-naphthaldehyde (m.p. 160°), furfural (m.p. 98°); 4-methoxythiobenzhydrazone of 4-acetamidobenzaldehyde (m.p. 172°); 2-furanethiocarboxhydrazones of furfural (m.p. 138°), 4-acetamidobenzaldehyde (m.p. 197°) *etc.* Some thioacylated hydrazides were also prepared in the same manner as benzoyl-thiobenzhydrazide (*cf.* Jensen and Miquel ²), *e.g.* nicotinylthiobenzhydrazide (m.p. 142°) and isonicotinyl-thiobenzhydrazide (m.p. 130°).

Further details will be given in a subsequent paper in this journal.

1. Jensen, K. A. *Z. anorg. u. allgem. Chem.* **219** (1934) 243; **221** (1934) 6, 11.
2. Jensen, K. A., and Miquel, J. F. *Acta Chem. Scand.* **6** (1952) 189.
3. Carl, E., and Marquardt, P. *Z. f. Naturforsch.* **4b** (1949) 280; Liebermeister, K. *ibid.* **5b** (1950) 79.

Received June 13, 1952.

On the Atomic Composition of the Mineral Belyankite

A. H. NIELSEN

Chemical Laboratory, "Kryolitselskabet Øresund A/S", Copenhagen, Denmark

The Russian mineralogist Dorfman has recently published a paper ¹ on a new fluorine mineral, belyankite, from Central Kazakhstan. Amongst other things Dorfman has determined some optic constants, thermic data, and the specific weight (2.720) for this mineral. Further Dorfman gives x-ray data (S. S. Kvitka) and a chemical analysis (M. O. Stepan), giving the following weight percentages:

Table 1.

Al ₂ O ₃	21.88
CaO	34.00
F	49.01
H ₂ O+	15.35
H ₂ O-	0.30
	120.54

On the basis of this analysis Dorfman assigns the following formula to belyankite: Ca₂Al₃(F, OH)₁₃ · [H₂O].

If the analysis is recalculated according to the method usually employed for double fluorides (discounting H₂O⁻, as Dorfman himself does), we get:

Table 2.

1.	2.	3.	4.
Weight p.c.	Atomic quot.	Number of atoms and H ₂ O mol.	Ca ₃ Al ₂ F ₁₂ · 4 H ₂ O weight p.c., calc.
Al	11.58	1.00	11.37
Ca	24.30	1.41	25.35
F	49.01	6.01	48.08
H ₂ O+	15.35	1.99	15.20
Total	100.24		100.00

From the values in column 3 we get the ideal formula: $\text{Ca}_3\text{Al}_2\text{F}_{12} \cdot 4 \text{H}_2\text{O}$.

Already a glance at Dorfman's formula shows that it cannot possibly be correct, stating as it does that the percentage content of Ca and Al is about the same.

If we calculate the molecular weight from the figures in column 2, we get $M = 2 \cdot 233.5 = 467.0$.

By inserting Kvitka's cell dimensions, the specific weight and M we get:

$$Z = \frac{13.47 \cdot 8.46 \cdot 9.89 \cdot 2.720}{1.6604 \cdot 467.0} = 3.96$$

That is to say 4 formula units ($\text{Ca}_3\text{Al}_2\text{F}_{12} \cdot 4 \text{H}_2\text{O}$) in the unit cell.

The present author has previously published a paper² in which amongst other things is described a "Ca-cryolite", produced by the wet method, with the formula $\text{Ca}_3\text{Al}_2\text{F}_{12} \cdot 3 \text{H}_2\text{O}$, i.e. chemically closely allied to belyankite, with the same general properties (very readily fusible, easily dissolving in warm diluted hydrochloric acid). Bøgvad³ has determined the specific weight for "Ca-cryolite" at 2.77 in good agreement with Dorfman's value 2.720.

1. Dorfman, M. D. *Doklady Akad. Nauk S.S.S.R.* **75** (1950) 851. Ref. *Chem. Abstr.* **45** (1951) 8943.
2. Nielsen, A. H. Z. *anorg. allg. Chem.* **232** (1937) 155. Ref. *Neues Jahrb. Mineral.* (1937) 595-6.
3. Bøgvad, Z. *anorg. allg. Chem.* **232** (1937) 156.

Received July 5, 1952.

Reaction of Organophosphorus Compounds with Dihydroxyphenyl Derivatives

KLAS-BERTIL AUGUSTINSSON

Institute of Organic Chemistry and Biochemistry, University of Stockholm, Stockholm, Sweden

From both a practical and theoretical point of view we are interested in the reaction mechanism of organophosphorus compounds. We know that these agents inhibit cholinesterases and that this most probably explains their toxic effects. We also know that the inhibitory reaction is a phosphorylation at the so-called esteratic site of the enzyme molecule.

We have tried to protect *in vitro* cholinesterase preparations against inactivation by various organophosphorus compounds. About 120 various compounds have been tested as protectors. The most promising results were obtained with some local anesthetics. It could be demonstrated, for instance, that procaine at a concentration ($5 \times 10^{-5} \text{ M}$) which has no measurable effect on the serum cholinesterase activity protects this enzyme against inactivation by Tabun. In the case of acetylcholinesterases from various sources (erythrocytes, nucleus caudatus, cobra venom) the protective effect is less, but a definite protection has been demonstrated in all cases¹.

The protective action has further been demonstrated when inactivator and protector are simultaneously mixed with the enzyme; in these instances inactivator and protector were mixed together about one hour before mixing with the enzyme. In the procaine experiments, the protective effect was the same, as in those experiments when the enzyme was incubated with the protector prior to the inactivator. With some other compounds tested, however, it was shown that Tabun and DFP react