Isothiocyanates XXXV. *

Miscellaneous isothiocyanate Glucoside Acetates

ANDERS KJER

Organic Chemical Laboratory of The Royal Veterinary and Agricultural College, Copenhagen, Denmark

Most naturally occurring isothiocyanate glucosides possess poor crystallization properties as apparent from the fact that so far only seven individual glucosides have been reported as crystalline substances (cf. Ref. 1). In contrast herewith, crystalline glucoside O-acetates are frequently obtainable as useful derivatives for purification and characterization purposes. The acetylation procedure used in this laboratory 2 and independently applied to a broader range of glucosides by Schultz and Wagner 3 is similar to that customarily employed in carbohydrate chemistry. It is the purpose of the present note to describe a few isothiocyanate glucoside acetates and, in addition, present some supplementary or correlative data for previously reported derivatives.

Glucoberinger, a crystalline glucoside isolated as a potassium salt from seeds of Iberis amara 4, affords a crystalline tetraacetate on acetylation. A non-analyzed specimen of the latter was characterized by its m. p., 5 (148—149° (decomp.)), optical rotation 5 (D) 20 —12.2° (c 1.4, H2O)) and infra-red spectrum 4. A specimen of potassium tetraoctylglucoberinger prepared in this laboratory separated as a monohydrate in tiny, colourless needles, m. p. 145—147° (decomp.) 6, 9

[α] D 20 —16.6° (c 2.0, H2O). (Found: C 35.50; H 4.87; N 2.13; S 15.25. Calc. for C42H44O14NS2K, H2O: C 35.23; H 4.67; N 2.16; S 14.85.)

The rubidium salt of glucoberinger, desired for special purposes, was prepared from the corresponding potassium salt by percolating a solution of the latter through a column containing

cation exchange resin (Dowex 50) in its rubidium ion form. Rubidium glucosinate separated as a monohydrate from 85% ethanol, m. p. 130—132° (decomp.), [α] D 20 —51.9° (c 2.1, H2O).

(Found: C 24.95; H 4.24; N 2.66; Rb 18.62. Calc. for C15H18O14NS2Rb, H2O: C 25.12; H 4.22; N 2.66; Rb 16.25.)

In 1948 Schmid and Karrer 6 reported on the isolation and structure elucidation of the mustard oil sulphophane, an enzymic hydrolysis product of a glucosidic progenitor in radish seeds. From seeds of Matthiola bicornis, Schultz and Wagner 3 isolated a crystalline glucoside tetraacetate which was tacitly assumed to be identical with the tetraacetate of the radish seed glucoside for which the name glucopharelin was introduced 4. Because no rotation values were reported and analytical data were inconclusive with regard to the contents of water of crystallization 4, a sample of the tetraacetate of the glucosidic progenitor of sulphophane was isolated in this laboratory from radish seed.

A methanolic glucoside extract of crushed and defatted radish seed was purified, first by ion exchange on acid-washed alumina and then by removal of impurities with lead acetate 3. The glassy residue was acetylated in the usual way in pyridine with acetic anhydride. After recrystallization from ethanol, in which the tetraacetate dissolved very slowly, an almost pure product was obtained in amounts corresponding to 3.6 g per 100 g of fresh radish seed. The analytical specimen was recrystallized thrice from ethanol, and separated as a monohydrate in colourless needles, m. p. 155—156° (decomp. 9 [α] D 20 —23.5° (c 1.5, H2O). (Found: C 36.45; H 4.60; N 2.13; S 14.36; K 5.69. Calc. for C42H18O14NS2K, H2O: C 36.41; H 4.58; N 2.12; S 14.68; K 5.93). The infra-red spectrum of our specimen proved identical with that reported elsewhere 5*. Several attempts to prepare the genuine glucoside in crystalline form after deacetylation were unsuccessful.

From seeds of the wall-flower (Cheiranthus cheiri) Schneider and Schütz 7 isolated, many years ago, the isothiocyanate glucoside glucoberingin as a crystalline potassium salt, affording 3-methylsulphophynpropyl mustard oil upon enzymic hydrolysis. Failure to repeat the isolation of crystalline glucoside by the reported procedure prompted the development of the following modification which has afforded crystalline glucoberingin monohydrate with

* The author is grateful to Dr. W. Wagner for kindly placing the original spectrum at his disposal for comparison.

Acta Chem. Scand. 13 (1959) No. 4
correct analysis and a rotation value in agreement with that reported *. A methanolic extract of commercial wallflower seeds was concentrated, dissolved in water and filtered. Addition of potassium thio-cyanate caused the precipitation of the quaternary base sinapine as the slightly soluble thio-cyanate. The dried residue from the filtrate was subjected to acetylation in the usual way and the crude tetraacetate, in turn, subjected to deacetylation with ammonia in methanol to give the oily glucoside. On recrystallization of this from 80 % ethanol, glucosechoerin monohydrate separated as colourless needles, purified for analysis by two additional recrystallizations.

The intermediate, anhydrous potassium tetracetylethylenechoerinolate was obtained from water as thin colourless needles, m. p. 193–194° (decomp.), [α] D20 –18.0° (c 1.0, H2O). (Found: C 35.32; H 4.26; N 2.04; S 14.78. Cals. for C10H14O12NS2K: C 35.33; H 4.37; N 2.17; S 14.68.)

Seeds of Lunaria annua L. (= L. biennis Moench) have formerly served in this laboratory as a source of isopropyl isothiocyanate. The hypothetical glucosidic progenitor of this mustard oil, glucoputranjavin, which was independently suggested by Puntambekar * as a constituent of the Indian plant Putranjiva Rozburghii Wall. (Euphorbiaceae), has now been isolated in form of its crystalline tetraacetate. A crude specimen, isolated from Lunaria seeds and acetylated in the usual way, was repeatedly recrystallized from 96 % ethanol to give colourless needles of the anhydrous potassium tetracetylethylenechoerinite with m. p. 180–190° (decomp.), highly dependent on the rate of heating: [α] D20 –15.4° (c 1.2, H2O). (Found: C 38.20; H 4.77; N 2.54. Cals. for C19H34O14NS2K: C 38.08; H 4.62; N 2.47.)

Valuable assistance of Dr. R. Gmelin, Mr. Bo W. Christensen and Mrs. Dortho Hansen in the present work is gratefully acknowledged. The work is part of investigations supported by The Danish State Research Foundation, The Carlsberg Foundation and Kai Hansen’s Fond.


* For our preparation a decomposition range from 140–160° was observed, rather than the m. p. 158–160° reported 7.

5. Wagner, W. Papierchromatographische Analyse der Senföllglucoside, preparative Darstellung ihrer Acetylderivate und ein Beitrag zu ihrer allgemeinen Struktur (Diss.) University, Tübingen 1956.
7. Schneider, W. and Schütz, L. A. Ber. 46 (1913) 2634.

Received April 2, 1959.

Electrical Conductivity of Some Palladium Sulfides and of Silver Palladium Sulfide

H. FISCHMEISTER

Institute of Chemistry, University of Uppsala, Sweden *

The System Pd-S has recently been examined by Grønvold and Rost 1 who found the following compounds stable at room temperature: Pd,S, Pd,S,S, Pd,S and Pd,S. The system Ag-Pd-S was studied, in 1954, by Raub, Wullhorst and Plate 4. Only one ternary compound, Ag,Pd,S, was detected.

Specimens of Pd,S and Pd,S were kindly supplied by Dr. Grønvold. Pd,S and Ag,Pd,S were prepared by heating briquetted mixtures of the finely powdered elements (c.p. grade) in evacuated, sealed-off silica tubes to 650°C for several days, in accordance with the conditions of formation indicated by the phase studies 5, 6. The samples were crushed, X-ray powder patterns recorded to confirm the completeness of the reaction, and the powders re-briquetted at ca. 250 kg/cm² in the form of small bars of 15 × 4 × 3 mm. These were sintered for a week in evacuated silica tubes at 800°C. X-ray patterns recorded...