*iso*Thiocyanates XXXV.*

Miscellaneous *iso*Thiocyanate Glucoside Acetates

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Most naturally occurring *iso*thiocyanate 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 *iso*thiocyanate glucoside acetates and, in addition, present some supplementary or corrective data for previously reported derivatives.

Glucoiberin, 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.[3,5] (148−149° (decomp.)), optical rotation[5] $[\alpha]_D^{20}$ $-12.2°$ (c 1.4, H_2O)) and infra-red spectrum[5]. A specimen of *potassium tetraacetylglucoiberate* prepared in this laboratory separated from 96 % ethanol as a *monohydrate* in tiny, colourless needles, m. p. 145−147° (decomp.) **, $[\alpha]_D^{23}$ $-16.6°$ (c 2.0, H_2O). (Found: C 35.50; H 4.87; N 2.13; S 15.25. Calc. for $C_{19}H_{28}O_{14}NS_3K, H_2O$: C 35.23; H 4.67; N 2.16; S 14.85).

The rubidium salt of glucoiberin, desired for special purposes, was prepared from the corresponding potassium salt by percolating a solution of the latter through a column containing a cation exchange resin (Dowex 50) in its rubidium ion form. *Rubidium glucoiberate* separated as a *monohydrate* from 85 % ethanol, m. p. 130−132° (decomp.), $[\alpha]_D^{23}$ $-51.9°$ (c 2.1, H_2O). (Found: C 24.95; H 4.24; N 2.66; Rb 16.62. Calc. for $C_{11}H_{20}O_{10}NS_3Rb,H_2O$: 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 sulphoraphene, an enzymic hydrolysis product of a glycosidic progenitor in radish seeds. From seeds of *Matthiola bicornis*, Schultz and Wagner[3] isolated a crystalline glycoside tetraacetate which was tacitly assumed to be identical with the tetraacetate of the radish seed glucoside for which the name glucoraphenin was introduced[5]. Because no rotation values were reported and analytical data were inconclusive with regard to the contents of water of crystallization[5], a sample of the tetraacetate of the glucosidic progenitor of sulphoraphene 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.) $[\alpha]_D^{27}$ $-23.5°$ (c 1.5, H_2O). (Found: C 36.45; H 4.50; N 2.13; S 14.36; K 5.69; Calc. for $C_{20}H_{28}O_{14}NS_3K, H_2O$: C 36.41; H 4.58; N 2.12; S 14.58; 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 *iso*thiocyanate glucoside glucocheirolin as a crystalline potassium salt, affording 3-methylsulphonylpropyl 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 glucocheirolin monohydrate with

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** All melting points reported are uncorrected and determined in capillary tubes in an electrically heated block. Microanalyses were performed by Mr. P. Hansen at the Chemical Laboratory of the University of Copenhagen.

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

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 thiocyanate caused the precipitation of the quaternary base sinapine as the slightly soluble thiocyanate. The dried residue from the filtrate was subjected to acetylation in the usual way [3] 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, glucocheirolin monohydrate separated as colourless needles, purified for analysis by two additional recrystallizations.

The intermediate, anhydrous *potassium tetraacetylglucocheirolinate* was obtained from water as thin colourless needles, m. p. 193—194° (decomp.), $[\alpha]_D^{24}$ $-18.0°$ (c 1.0, H_2O). (Found: C 35.32; H 4.26; N 2.04; S 14.78. Calc. for $C_{19}H_{28}O_{15}NS_3K$: C 35.33; H 4.37; N 2.17; S 14.89.)

Seeds of *Lunaria annua* L. (= *L. biennis Moench)* have formerly served in this laboratory as a source of *iso*propyl *iso*thiocyanate [8]. The hypothetical glucosidic progenitor of this mustard oil, *glucoputranjivin*, which was independently suggested by Puntambekar [9] as a constituent of the Indian plant *Putranjiva Roxburghii* 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 tetraacetylglucoputranjivate* with m.p. 180—190° (decomp.), highly dependent on the rate of heating; $[\alpha]_D^{23}$ $-15.4°$ (*c* 1.2, H_2O). (Found: C 38.20; H 4.77; N 2.54. Calc. for $C_{18}H_{26}O_{13}NS_2K$: C 38.08; H 4.62; N 2.47.)

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

Electrical Conductivity of Some Palladium Sulfides and of Silver Palladium Sulfide

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The System Pd-S has recently been examined by Grønvold and Røst [1] who found the following compounds stable at room temperature: Pd_4S, $Pd_{2,2}S$, PdS and PdS_2. The system Ag—Pd—S was studied, in 1954, by Raub, Wullhorst and Plate [2]. Only one ternary compound, Ag_2Pd_3S, was detected.

Specimens of $Pd_{2,2}S$ and PdS were kindly supplied by Dr. Grønvold. Pd_4S and Ag_2Pd_3S were prepared by heating briquetted mixtures of the finely powdered elements (c.p. grade) in evacuated, sealed-off silica tubes to 630°C for several days, in accordance with the conditions of formation indicated by the phase studies [1,2]. The samples were crushed, X-ray powder patterns recorded to confirm the completeness of the reaction, and the powders rebriquetted 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 600°C. X-Ray patterns recorded

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