9-Nitro-3-oxojulolidine.—To a solution of 4.0 g. of 3-oxojulolidine in 20 ml. of glacial acetic acid was added 5 ml. of nitric acid (sp. gr. 1.42). After 20 min. at room temperature the product was precipitated by dilution with 200 ml. of water, and recrystallized from hot water; wt. 3.6 g. (73%), m.p. 155–156.5°.

Anal. Calcd. for $C_{12}H_{12}O_3N$: C, 62.06; H, 5.21. Found: C, 62.31; H, 5.21.

Bromination of 3-Oxojulolidine.—Solutions of 3-oxojulolidine in glacial acetic acid reacted with bromine to produce, after dilution with water, a light yellow, amorphous, bromine-containing solid which did not have a definite melting point, and could not be successfully crystallized.

Carbazole-N-β-propionic Acid.—A mixture of 3.0 g. of carbazole-N-β-propionitrile[9] and 20 ml. of concd. hydrochloric acid was refluxed for 14 hr. The solid which separated on cooling was filtered off, dissolved in 10% sodium hydroxide solution, and reprecipitated with hydrochloric acid; wt. 2.8 g. (86%), m.p. 169–170°.

Anal. Calcd. for $C_{15}H_{13}O_2N$: C, 75.28; H, 5.48. Found: C, 75.61; H, 5.44.

N,N-Bis-(β-cyanoethyl)-aniline.—A mixture of 18 g. of aniline, 21 g. of acrylonitrile, 10 ml. of glacial acetic acid and 2.0 g. of cuprous chloride was refluxed for 12 hours. The viscous product was repeatedly extracted with warm ether, from which there separated on cooling 29 g. (75%) of N,N-bis-(β-cyanoethyl)-aniline, m.p. 85°. Details of the preparation and properties of this substance are not available from the original report of it in the literature,[10] but Cookson and Mann[11] report m.p. 80–82° for the compound as prepared in lower yield (23%) by a more drastic procedure.

Anal. Calcd. for $C_{12}H_{13}N_3$: C, 72.34; H, 6.58. Found: C, 72.17; H, 6.58.

This nitrile was recovered unchanged after treatment with dry hydrogen chloride and zinc chloride in anhydrous ether, and after fusion with anhydrous aluminum chloride. The recovered starting material was accompanied by a red lake, which was not further investigated, after the aluminum chloride fusion. We were not successful in obtaining crystalline aniline-N,N-β-propionic acid by alkaline hydrolysis of the nitrile, as were Cookson and Mann.[11]

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[10] I. G. Farbenind., British Patent 404,744 [*C. A.*, **28**, 4068 (1934)]; British Patent 457,621 [*C. A.*, **31**, 3068 (1937)].

[11] R. C. Cookson and F. G. Mann, *J. Chem. Soc.*, 67 (1949).

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The Oxidation of Indium Trisulfide

BY M. F. STUBBS

According to Dupuis and Duval[1] precipitated In_2S_3 loses water up to 94° and then may be weighed without loss from this temperature to 221°. When the sulfide is heated in air between 221–320°, an irregular loss of weight is said to take place with the formation of InS, the reaction being given by the equation

$$In_2S_3 + O_2 \rightleftharpoons 2InS + SO_2$$

The InS is said to be stable in air between 320–544°. On raising the temperature, a second oxidation is said to take place according to the equation

$$2InS + 7/2O_2 \rightleftharpoons In_2O_3 + 2SO_2$$

In view of the fact that no analytical data are given to support the postulates presented, a further study has been made of the effects of heating In_2S_3 in air.

We have found it necessary to heat small quantities of In_2S_3 (approximately 0.2 g.) for several hours at 140–150° to remove moisture, while complete purification requires heating in a vacuum or atmosphere of H_2S for at least an hour at approximately 300°. Such purified samples give a negative test for sulfate ion after digestion with hot water for one hour.

Three samples of In_2S_3, purified as described above, were heated in air in the temperature range 220–280°, with results as shown in Table I. There was no visible change in the color of the sulfides after heating.

TABLE I

EFFECT OF HEATING In_2S_3 IN AIR 220–280°

No.	Wt. of sulfide, g.	Temp. range, °C.	Duration of heating, hrs.	Change in mass, g.	Change in mass theory for InS, g.	Sulfate present after heating
1	0.7869	220–275	12	−0.0027	−0.0775	None
2	.5943	278 ± 5	25	− .0022	− .0585	None
3	.6352	275 ± 2	63	− .0010	− .0626	Trace

Sample No. 1 was next heated for an additional 3.5 hours at 310 ± 5°, gaining 0.40 mg. There was still no visible change in the appearance of the sulfide. The sample was then heated for 89.5 hours between 310–400°, the temperature being raised gradually. During this period the sulfide gained 0.0937 g. A slight odor of SO_2 was detected above 325°. The surface of the product had changed to the light yellow color of In_2O_3. There was no evidence of the dark red brown color of InS.

The results obtained suggested the possibility that the loss of mass reported by Dupuis and Duval to take place when In_2S_3 is heated between 220–320° might possibly be accounted for by loss of small amounts of water or sulfur, due to incomplete purification of the sulfide used. Our results indicate that only a very slight loss of mass occurs on prolonged heating of purified In_2S_3 in air up to 280°. The small gain in mass, odor of SO_2, and the partial change to a light yellow color observed after prolonged heating between 310–400°, suggested the possibility that the apparent stability observed by Dupuis and Duval between 320–540° might possibly be due to a balance between sulfate and oxide formation.

Accordingly three additional samples of purified In_2S_3 were heated in air between 325–460° and the products analyzed for the presence of sulfate ion. The results are given in Table II.

TABLE II

EFFECT OF HEATING In_2S_3 IN AIR 320–460°

No.	Wt. of sulfide, g.	Temp. range, °C.	Duration of heating, hr.	Change in mass, g.	Sulfate analyses $BaSO_4$, g.	Conversion to sulfate, %
4	0.8321	325–380	138	+0.1782	0.6520	36.44
5	.7191	380 ± 10	135	+ .1210	.5061	32.74
6	.5743	455 ± 5	48	− .0484	.0464	3.76

In each case nearly all of the product changed to the light yellow color of In_2O_3. The odor of SO_2 was detected during the heating.

Three additional samples of purified In_2S_3 were spread out in boats to a very shallow depth, heated in air, and analyzed as shown in Table III.

TABLE III

CONVERSION OF In_2S_3 TO $In_2(SO_4)_3$ AND In_2O_3

No.	Wt. of sulfide, g.	Temp. range, °C.	Duration of heating, hrs.	Change in mass, g.	Sulfate analyses $BaSO_4$, g.
7	0.5651	380 ± 10	110	+0.0502	0.0901
8	.6158	380 ± 10	68	− .0516	.0909
9	.6375	210–380	168	− .0341	.0830

No.	Conversion to sulfate, %	Sulfide analyses $BaSO_4$, g.	Sulfide remaining, %	Conversion to oxide (difference), %
7	7.42	0.0586	4.83	87.75
8	6.86	.0516	3.90	89.24
9	6.24	.2455	18.46	75.30

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[1] T. Dupuis and C. Duval, *Anal. Chim. Acta*, **3**, 331 (1949).

The products were analyzed for the presence of sulfate ion by digesting with 100 ml. of hot distilled water for one hour to dissolve any $In_2(SO_4)_3$ formed. The mixture then was filtered, washed, and the filtrate tested for the presence of sulfate ion by the usual method. Any sulfide remaining in the residues was converted into sulfate by treatment with bromine and nitric acid according to standard procedure.

The results obtained show that pure In_2S_3 may be heated in air up to 280° with only superficial oxidation. In the temperature range 300–460° the sulfide is gradually oxidized to a mixture of sulfate and oxide, the relative amounts depending on the surface exposed, the temperature and the period of heating. There was no evidence of InS formation.

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Isolation of β-Sitosteryl-D-glucoside from the Juice of Florida Valencia Oranges (*Citrus sinensis*, L.)[1]

BY LYLE JAMES SWIFT

Steryl glycosides or phytosterolins have been reported by Matlack in the rinds[2] and in the pulp[3] of California Valencia oranges and by Nolte and von Loesecke[4] in the juice of Florida Valencia oranges. In none of these publications were the glycosides completely identified. Matlack[2] described the sterol from the rind glycoside as sitosterol, but did not identify the sugar component. He surmised that the glycoside was identical with the sitosterol-D-glucoside synthesized by Salway.[5] It is apparent from data in Table I that Matlack's glycoside is very similar, if not identical, with the glucoside described in this paper. Since the various sitosterols were not known when either Salway or Matlack did their work, it seems likely that the former used a mixture of sitosterols in his preparation and the latter, by omitting the specific rotation measurements, failed to detect the discrepancies in rotation between the synthetic glucoside and the β-sitosterol-D-glucoside that he probably had isolated.

TABLE I

COMPARISON OF CONSTANTS OBTAINED IN THE PRESENT WORK WITH THOSE OF SALWAY[5] AND MATLACK[2] ON CORRESPONDING COMPOUNDS

	Present work		Matlack[2]		Salway[5]	
	(α)	M.p., °C.	(α)	M.p., °C.	(α)	M.p., °C.
Sitosterol glucoside	−40.1°	298	..	280	....	295–300
Sitosterol glucoside tetraacetate	−33.7	171	..	164–165	−22.9	166–167
Sitosterol glucoside tetrabenzoate	+15.9	201	..	198	+18.3	198
Sitosterol	−38.2	137–138	..	136–137	−32.2	138
Sitosterol acetate	−40.3	125–126	..	124–125	....	.....
Sitosterol benzoate	−13.6	147–148	..	.....	....	.....

The pulp phytosterolin isolated by Matlack he described simply by the necessary classification reactions and a melting point of 250–255°. Nolte and von Loesecke[4] described their phytosterolin also by only the classification reactions.

It was the aim of the present work to establish beyond doubt the identity of the components of the steryl glycoside occurring in orange juice. The glucose was identified by qualitative tests and quantitative determinations after hydrolysis. The identification of the β-sitosterol depends upon the close agreement of its physical properties and those of its derivatives with the values obtained by other investigators.

All melting points determined and reported in this study were taken with a thermometer calibrated by the Bureau of Standards. Correction for stem exposure was also made.

Experimental

Isolation of β-Sitosteryl Glucoside.—About 1100 kg. of pasteurized juice from the 1947 crop of Florida Valencia oranges was filtered in batches through buchner funnels, using a commercial filter-aid. The filter-aid with the retained matter was then extracted with acetone which was subsequently evaporated, leaving the colored lipids of the juice and considerable aqueous solution. Upon extraction of this mixture with petroleum ether (b.p. 35–60°) and subsequent concentration of the extract to recover the lipids, some of the β-sitosteryl glucoside precipitated and was separated, washed with petroleum ether, and recrystallized twice from 90% ethanol. The yield at this point was 26.0 g. of the glucoside from the 1000 g. of lipid matter obtained. A further quantity of the glucoside was isolated from 600 g. of lipid after saponification, extraction of the unsaponifiable matter, and acidification when extraction of the acids was attempted. The glucoside collected at the interface and tended to cause troublesome emulsions. It was separated by filtration, washed with 95% ethanol, and recrystallized from a mixture of ethanol and pyridine. The weight was 8.9 g. of lipid, or 14.8 g. on the basis of the whole 1000 g. Thus, there was obtained a total of 40.8 g. of β-sitosteryl glucoside from 1100 kg. of juice, or a yield of 0.0037%.

The β-sitosteryl glucoside was insoluble in most solvents, was sparingly soluble in 95% ethanol (about 0.06 g. in 100 ml. at 20° and 0.225 g. in 100 ml. in hot), but soluble in pyridine. It gave positive Lieberman–Burchard and Molisch reactions. The melting point was dependent on the rate of heating. In a bath preheated to 298° the glucoside melted in 20 to 30 seconds; $[\alpha]^{20}_{D}$ −40.1° (pyridine, 1.334 g./100 ml., 2-dm. tube).

Anal. Calcd. for $C_{35}H_{60}O_6$: C, 72.85; H, 10.49. Found: C, 72.26, 72.21; H, 10.40, 10.36.

β-Sitosteryl Glucoside Tetraacetate.—A 2.0-g. portion of the glucoside was dissolved in 25 ml. of pyridine and 15 ml. of acetic anhydride was added. The mixture was refluxed for one hour, the solvents were removed by heating under vacuum, and the residue was dissolved in hot 95% ethanol. It was then treated with decolorizing carbon, filtered and allowed to stand. The crystals that formed melted at 170° and the yield was 2.3 g. The m.p. could only be raised to 171° by repeated recrystallization from alcohol. The $[\alpha]^{25}_{D}$ −33.7° (pyridine, 1.3012 g./100 ml. 2-dm. tube) and a Rast determination of the molecular weight using palmitic acid as the solvent gave a value of 787.

Anal. Calcd. for $C_{43}H_{68}O_{10}$: C, 69.30; H, 9.20; CH_3CO, 23.09. Found: C, 69.23, 69.32; H, 9.09, 9.29; CH_3CO, 22.95, 22.86.

The regenerated β-sitosteryl glucoside, which had come out of solution as the saponification proceeded, was separated by filtration, recrystallized from a pyridine–alcohol mixture, and dried. The m.p. was 296° and the $[\alpha]^{27}_{D}$ −41.8° (pyridine, 1.1228 g./100 ml., 2-dm. tube).

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[1] Report of a study made under the Research and Marketing Act of 1946.

[2] M. B. Matlack, *J. Am. Pharm. Assoc.*, **18**, 24 (1929).

[3] M. B. Matlack, *J. Org. Chem.*, **5**, 504 (1940).

[4] A. J. Nolte and H. W. von Loesecke, *Food Research*, **5**, 457 (1940).

[5] A. H. Salway, *J. Chem. Soc.*, **103**, 1022 (1913).