

TABLE I

All rotations are in methanol at 1–1.5% concentration. All melting points were taken with a hot-stage microscope and are uncorrected. Carbonyl absorption refers to a plateau or inflection in the ultraviolet absorption spectrum in the region 270–300 $m\mu$. All glycosides had positive Legal tests.

Glycoside	Crude yield, mg.	[α] _D	Pure yield, mg.	[α] _D	M.p., °C.	Keller-Kiliani	Ultraviolet absorption spectrum			Carbon, %		Hydrogen, %	
							Max. $m\mu$	log ϵ	Carbonyl absorption	Calcd.	Found	Calcd.	Found
Sarveroside	590	+7.6	394	+11.9	119–125	+	216	4.22	+	63.81	63.31, 63.95	7.85	7.37, 8.00
Intermedioside	1200	+20	941	+20.0	189–193	+	218	4.25	+	63.81	63.98, 63.86	7.85	7.71, 7.45
Panstroside	847	+26	579	+29.7	227–230	–	216	4.23	+	62.06	62.52, 62.30	7.64	7.54, 7.60
New glycoside	112	–23	86	–25.2	232–240	–	217		–	64.52, 64.55		7.96, 8.21	
Crystallizate 790	184			–12.5	136–141				±	64.38, 64.31		8.10, 8.29	

chromatographed as described in Table I of reference 1b. The fifth and sixth fractions eluted with ether–chloroform (60:40 and 40:60) contained intermedioside. The seventh and eighth fractions eluted with ether–chloroform (20:80) and chloroform contained crystallizate 790. The ninth fraction eluted with chloroform containing 1% methanol contained panstroside, and the tenth fraction eluted with chloroform containing 2% methanol contained the new glycoside.

Crystallizate 790 from fraction 8 was recrystallized from methanol and ether; yield 114 mg.; [α]_D –12.5°. The melting point was 136–141° or if finely ground in a mortar it melted at 133–138°. The color test with 84% sulfuric acid was brown developing an olive tinge but not becoming green. The ultraviolet absorption spectrum showed a plateau at 275–290 $m\mu$ with an intensity about 35–40% of that of pure intermedioside and/or panstroside.

The new glycoside from fraction 10 was recrystallized

from methanol and ether; color test with 84% sulfuric acid brownish orange becoming brownish red in 5–10 min., then bluish-green in 1 hour. The probable molecular weight is 615 ± 20 calculated on the assumption that log ϵ is 4.22–4.25 at 216–218 $m\mu$. For analysis it was dried at 140° and 0.2 mm. for five hours.

Anal. Found: C, 64.52, 64.55; H, 7.96, 8.21.

This analysis is in agreement with several formulas.

We wish to thank Drs. Eric Smith and Robert W. Price for advice and suggestions and The Upjohn Company for encouragement and support. Microanalyses were done by the Schwarzkopf Microanalytical Laboratories.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF S. B. PENICK & COMPANY]

The Glycosides of the Seeds of *Strophanthus schuchardti* Pax

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The seeds of *Strophanthus schuchardti* Pax were found to contain sarveroside, intermedioside, panstroside and sarverogenin.

Continuing our examination of the glycosides of *Strophanthus*¹ we wish to report our investigations on the seeds of another species which has not previously been described. The seeds were collected in the extreme south of Angola. The collection was supervised and samples identified as *Strophanthus schuchardti* Pax by John Gossweiler, botanist, Service of Agriculture, Luanda, Angola, whom we wish to thank for his cooperation.

The seeds (200 g.) were processed as previously described.^{1a} We obtained 2.08 g. (1.04%) of crude glycosides from the ether extract and 12.63 g. (6.31%) of crude glycosides from the chloroform extract. The ether-soluble fraction yielded sarveroside² after crystallization from methanol, and dilution of the methanolic mother liquors with ether yielded intermedioside.³ Chromatography of the mother liquors resulting from the separation of intermedioside gave additional sarveroside.

The chloroform soluble glycosides after solution in acetone and cooling yielded a mixture of intermedioside and panstroside⁴ which were subse-

quently separated by chromatography. The mother liquors from these crystals were also chromatographed and yielded sarveroside, sarverogenin and an additional quantity of panstroside.

From 200 g. of seeds we obtained 1.27 g. of sarveroside, 1.09 g. of intermedioside, 780 mg. of sarverogenin and 620 mg. of panstroside.

In addition to *S. schuchardti*, sarveroside, intermedioside and panstroside have been found in *amboensis*,^{1b} *sarmentosus*,⁵ *courmontii*³ and *gerrardi*⁷ and the latter two glycosides have also been found in *S. intermedius*.^{1a,8}

Experimental

All rotations are in methanol at 1–1.5% concentration. All melting points were taken with a hot-stage microscope and are uncorrected. The color tests and the preparation of the alumina have been described.¹

The light brown seeds had 4.6% moisture and 22% fat. Slices of seeds treated with 84% sulfuric acid became tan (2 min.), brown (5 min.), reddish-brown (10 min.) and brownish-purple (30 min.).

The seeds (200 g.) were extracted as previously de-

(1) (a) M. R. Salmon, Eric Smith and W. G. Bywater, THIS JOURNAL, **73**, 3824 (1951); (b) M. R. Salmon, Robert Foppiano and W. G. Bywater, *ibid.*, **74**, 4546 (1952).

(2) A. Buzas, J. v. Euw and T. Reichstein, *Helv. Chim. Acta*, **33**, 465 (1950).

(3) J. P. Rosselet and A. Hunger, *ibid.*, **34**, 1036 (1951).

(4) (a) J. v. Euw and T. Reichstein, *ibid.*, **33**, 522 (1950); (b) J. v. Euw, H. Hess, P. Speiser and T. Reichstein, *ibid.*, **34**, 1821 (1951).

(5) (a) Sarveroside: J. v. Euw, A. Katz, J. Schmutz and T. Reichstein, *Pharm. Acta Helv.*, **24**, 178 (1949), and reference 2; (b) panstroside: J. v. Euw and T. Reichstein, *Helv. Chim. Acta*, **33**, 2153 (1950); (c) intermedioside: mentioned briefly in reference 3 and confirmed by Smith and Salmon (unpublished).

(6) J. v. Euw and T. Reichstein, *ibid.*, **33**, 1006 (1950).

(7) J. v. Euw and T. Reichstein, *ibid.*, **33**, 522 (1950).

(8) J. v. Euw, H. Hess, P. Speiser and T. Reichstein, *ibid.*, **34**, 1821 (1951).

scribed.^{1a} The aqueous solution of the crude glycosides was extracted successively with ether and with chloroform.

Ether Extract.—The ether extract on concentration gave 2.08 g. of crude glycosides that crystallized immediately when stirred with 3 cc. of methanol. It was allowed to stand in the refrigerator for 5 days and then filtered and washed with methanol. The product was 904 mg. of crude sarveroside, $[\alpha]_D +11.2^\circ$; m.p. 110–117°.

The mother liquors from the sarveroside were concentrated to a small volume and diluted with ether (10 cc.). Intermedioside crystallized in a yield of 114 mg.; $[\alpha]_D +20.2^\circ$; m.p. 184–193°. A second crop of intermedioside was obtained by reworking the mother liquors; 28 mg.; m.p. 170–188°.

The mother liquors were chromatographed on alumina and from the second and third fractions eluted with benzene-ether (75:25 and 50:50) an additional 53 mg. of sarveroside was obtained after crystallization from methanol; m.p. 114–123°; $[\alpha]_D +9.4^\circ$. No additional crystals were obtained from the later fractions of the chromatogram.

The two crops of sarveroside were combined and recrystallized four times from methanol; yield 514 mg.; m.p. 119–125°; $[\alpha]_D +12.5^\circ$; Keller-Kiliani test positive; Legal test positive; color test with 84% sulfuric acid brown becoming red-brown immediately, developing a blue edge in 5 min., and becoming blue-green in 20–30 min. Ultraviolet absorption spectrum maximum at 218 μ , $\log \epsilon$ 4.20; plateau at 265–280 μ , $\log \epsilon$ 1.84. There was no melting point depression when mixed with sarveroside from *S. amboensis*. For analysis it was dried at 100° and 0.1 mm. for four hours. We have prepared sarveroside a number of times from several species and have never been able to obtain a satisfactory analysis for this glycoside.

Anal. Calcd. for $C_{30}H_{44}O_{10}$: C, 63.81; H, 7.85. Found: C, 62.80; H, 7.61.

The two crops of intermedioside were combined and recrystallized three times from a mixture of methanol and ether; yield 58 mg.; m.p. 191–195°; $[\alpha]_D +23.7^\circ$; Keller-Kiliani test positive; Legal test positive; color test with 84% sulfuric acid brown becoming red-brown immediately and developing a blue-green edge in 5 min., becoming blue-green in 20 min., and then blue in 40 min. The slightly higher rotation and melting point may be due to the presence of a small amount of panstroside.

Chloroform Extract.—The chloroform extract after concentration yielded 12.63 g. of crude glycosides which were dissolved in acetone and allowed to stand 3–4 days in the refrigerator, giving 3.04 g. of crystals, m.p. 191–203°; $[\alpha]_D +24.3^\circ$. When recrystallization from methanol and ether did not effect purification this crop was chromatographed on 120 g. of alumina using 250 cc. of solvent for each fraction. The same solvent mixtures were employed as described in Table I of our previous report,^{1a} and the results were similar. The four fractions eluted with benzene-chloroform (60:40; 50:50; 40:60 and 30:70) contained intermedioside which crystallized from methanol and ether in a yield of 953 mg.; $[\alpha]_D +20^\circ$; m.p. 185–190°. Chloroform containing 20% benzene eluted a mixture of intermedioside and panstroside. Chloroform containing 10% benzene, chloroform, and chloroform containing 1% methanol eluted panstroside which crystallized from methanol and ether in a yield of 466 mg.; $[\alpha]_D +26^\circ$; m.p. 224–228°.

The oily mother liquor (9.59 g.) was separately chromatographed on 479 g. of alumina using 1 liter of solvent for each fraction. The chromatogram and results are shown in Table I.

Sarveroside from fractions 2, 3 and 4 of Table I was combined and recrystallized four times from methanol; yield 122 mg.; m.p. 117–122°; $[\alpha]_D +11.9^\circ$; Keller-Kiliani test positive; Legal test positive; ultraviolet absorption spectrum maximum at 216 μ , $\log \epsilon$ 4.20; plateau at 265–280 μ , $\log \epsilon$ 1.85; color test with 84% sulfuric acid brown becoming red-brown immediately and developing a blue

TABLE I

Fraction	Solvent, %	Crude yield, mg.	Crystals		Identification
			Yield, mg.	$[\alpha]_D$	
1	100B	43			
2	50B	50E	216	+ 9°	Sarveroside
3	100E	104	16	+15	Sarveroside
4	80E	20C	443	+13	Sarveroside
5	60E	40C	791	+42	Sarverogenin
6	40E	60C	1122	+42	Sarverogenin
7	20E	80C	1028	+43	Sarverogenin
8	100C	984			
9	99C	1M	1956	+29	Panstroside
10	98C	2M	432		
11	50C	50M	780		

edge (5 min.) and becoming blue-green (30 min.). The mixed melting point with sarveroside from *S. amboensis* showed no depression. For analysis it was dried at 100° and 0.1 mm. for four hours.

Anal. Calcd. for $C_{30}H_{44}O_{10}$: C, 63.81; H, 7.85. Found: C, 62.57; H, 7.64.

Sarverogenin from fractions 5, 6 and 7 of Table I was combined and recrystallized four times from a mixture of methanol and ether; yield 396 mg.; m.p. 216–222°; $[\alpha]_D +49.7^\circ$; Keller-Kiliani test negative; Legal test positive; ultraviolet absorption spectrum maximum at 216 μ , $\log \epsilon$ 4.21; plateau at 265–280 μ , $\log \epsilon$ 1.84. Color test with 84% sulfuric acid pink becoming red (2 min.) developing blue edges (5 min.) and becoming blue in 10–15 min. The mixed melting point with sarverogenin from *S. amboensis* showed no depression. For analysis it was dried at 140° and 0.1 mm. for four hours.

Anal. Calcd. for $C_{23}H_{32}O_7$: C, 65.69; H, 7.67. Found: C, 66.13; H, 7.27.

Panstroside from the two chromatograms was combined and recrystallized four times from a mixture of methanol and ether; yield 326 mg.; m.p. 229–233°; $[\alpha]_D +30.4^\circ$; Keller-Kiliani test negative; Legal test positive; ultraviolet absorption spectrum maximum at 216 μ , $\log \epsilon$ 4.25; plateau at 265–280 μ , $\log \epsilon$ 1.98; color test with 84% sulfuric acid pink becoming red in 2 min., developing blue edges in 3 min., and becoming blue in 10–15 min. The mixed melting point with panstroside from *S. intermedius* showed no depression. A sample for analysis was dried at 140° and 0.1 mm. for four hours.

Anal. Calcd. for $C_{30}H_{44}O_{11}$: C, 62.06; H, 7.64. Found: C, 61.79; H, 7.25.

Intermedioside from the first chromatogram was recrystallized four times from methanol and ether; yield 700 mg., m.p. 188–192°; $[\alpha]_D +19.1^\circ$; Keller-Kiliani test positive; Legal test positive; ultraviolet absorption spectrum maximum at 216 μ , $\log \epsilon$ 4.23; plateau at 270–280 μ , $\log \epsilon$ 1.82; color test with 84% sulfuric acid brown becoming red-brown in 1 min., developing a blue-green edge in 5 min., and becoming blue-green in 30 min. The mixed melting point with intermedioside from *S. intermedius* showed no depression. For analysis it was dried at 140° and 0.1 mm. for four hours.

Anal. Calcd. for $C_{30}H_{44}O_{10}$: C, 63.81; H, 7.85. Found: C, 63.97; H, 7.36.

We wish to thank Drs. Eric Smith and Robert W. Price for advice and suggestions and The Upjohn Company for encouragement and support. Microanalyses were done by the Schwarzkopf Micro-analytical Laboratories.

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