from which it may be readily shown that

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}C_{\mathrm{A}}} = \frac{KC_{\mathrm{B}}}{C_{\mathrm{A}}} - 1$$

This may be integrated to obtain the expression

$$\log \frac{C_{\mathbf{A}}}{C_{\mathbf{A}}^{0}} = \frac{1}{K - 1} \log \left[ 1 - (K - 1) \frac{C_{\mathbf{B}}}{C_{\mathbf{A}}} \right]^{8}$$

where  $C_{\rm A}^{\alpha}$  is the initial concentration of benzilic acid.

(8) The mathematical steps are: 
$$d\frac{C_B}{C_A} = \frac{C_A dC_B - C_B dC_A}{C_A^2}$$

whence  $\frac{dC_B}{dC_A} = \frac{C_A d\frac{C_B}{C_A}}{dC_A} + \frac{C_B}{C_A} = \frac{KC_B}{C_A} - 1$ . Rearranging  $\frac{dC_A}{C_A}$  zero when  $C_A = C_A^0$ , the expression given in the text is obtained. KNOXVILLE, TENNESSEE

Since analysis of the half-hydrogenated mixture gave 65% B, 17.5% A and 17.5% C, starting with 100% A, one may calculate K from these data. The result gives K = 0.22, and  $T_A/T_B$  (which equals  $\sigma_A/\sigma_B$  when  $C_A = C_B$ ) = 4.6. Thus it appears that benzilic acid is 4.6 times more readily adsorbed on the platinum catalyst than phenylcyclohexylglycolic acid.

$$= \frac{d \frac{C_B}{C_A}}{(K-1)\frac{C_B}{C_A} - 1}$$
. When this is integrated, and  $C_B$  set equal to

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

# The Glycosides of the Seeds of Strophanthus amboensis E. and Pax

BY M. R. SALMON, ROBERT FOPPIANO AND W. G. BYWATER

RECEIVED JANUARY 9, 1952

The seeds of Strophanthus amboensis E. and Pax were found to contain sarveroside, intermedioside, panstroside and a new glycoside that has not previously been found in Strophanthus. We also obtained Reichstein's crystallizate 790.

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

The seeds were processed as previously described. We obtained 0.69% crude glycosides from the ether extract and 4.48% of crude product from the chloroform extract. The ether soluble fraction yielded sarveroside<sup>2</sup> and intermedioside (formerly Reichstein's substance 761).<sup>3</sup> The chloroform extract yielded intermedioside and panstroside (formerly Reichstein's substance 762)<sup>4</sup> and a new glycoside which has not previously been found in Strophanthus seeds, as well as a crystallizate 790. We obtained 0.3% of sarveroside, 0.6% of inter-medioside, 0.4% of panstroside, 0.1% of crystalli-zate 790 and 0.05% of the new glycoside.

Crystallizate 790 has recently been described by Euw, Hess, Speiser and Reichstein<sup>4b</sup> as a mixture of three to five difficultly resolvable components which simulate samentocymarin in properties. Sarmentocymarin differs from crystallizate 790 in carbon analysis and ultraviolet absorption spectrum and by crystallizing as a high melting form from acetone and ether.

The new glycoside melted at  $232\text{--}240^\circ$  and had a rotation of  $\left[\alpha\right] D - 25.2^{\circ}$  The Keller-Kiliani test was negative and Legal test positive. The ultraviolet absorption spectrum showed the maximum at 216-218 m $\mu$  which is characteristic of the unsaturated lactone ring of the cardiac glycosides. The analysis does not distinguish between several possible formulas.

We believe that this glycoside is different from substance 792 isolated by Euw and Reichstein<sup>5</sup> from the seeds of S. petersianus. The rotations of the two substances are the same but they differ in melting point, carbon analysis and the color test with 84% sulfuric acid. We failed to obtain a lower melting form by recrystallization from water which appears to be characteristic of substance 792.

In addition to S. amboensis, sarveroside, intermedioside and panstroside have been found in S. schuchardti,<sup>1b</sup> sarmentosus,<sup>6</sup> courmontii<sup>7</sup> and gerrardi<sup>3</sup> and the latter two glycosides are also found in S. intermedius.<sup>1,4b</sup> The occurrence of intermedioside in S. amboensis has previously been mentioned briefly.3

#### Experimental

The light brown seeds had 4.1% moisture and 26% fat. Slices of seeds treated with 84% sulfuric acid became tan (2 nin.), brown (5 nin.), and then purple (30 min.). The seeds (200 g.) were extracted and sarveroside, inter-

neiloside and paustroside were isolated, purified and char-acterized as previously described.<sup>1</sup> The yield and physical constants of these glycosides are shown in Table I. Each of these glycosides showed no melting point depression when inised with the corresponding glycoside isolated from S. sarmentosus or S. intermedius and the color tests with 84% sulfuric acid were identical with those previously described.

A major portion of the intermedioside and panstroside rystallized when the chloroforn soluble fraction was taken up in acetone. The mother liquor from these crystals was

<sup>(1) (</sup>a) M. R. Salmon, Eric Smith and W. G. Bywater, THIS JOUR-NAL, 73, 3824 (1951); (b) Robert Foppiano, M. R. Salmon and W. G. Bywater, ibid., 74, 4537 (1952).

<sup>(2)</sup> A. Buzas, J. v. Euw and T. Reichstein, Helv. Chim. Acta, 33, 465 (1950).

<sup>(3)</sup> J. P. Rosselet and A. Hunger, ibid., 34, 1036 (1951).

<sup>(4) (</sup>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).

<sup>(5)</sup> J. v. Euw and T. Reichstein, ibid., 83, 1551 (1950).

<sup>(6) (</sup>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, 83, 2153 (1950); (c) intermedioside: mentioned briefly in reference 3 and confirmed by Smith and Salmon (unpublished).

<sup>(7)</sup> J. v. Euw and T. Reichstein, ibid., 33, 1006 (1950).

<sup>(8)</sup> J. v. Euw and T. Reichstein, ibid., 33, 522 (1950).

### 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.

	Ultraviolet absorption spectrum												
Glycoside	Crude yield, mg.	[α]D	Pure yield, mg.	[ <b>α</b> ]D	M.p., °C.		Max mµ	-	Car- bonyl absorp- tion	C Calcd.	arbon, % Found	Hydr Caled.	ogen, % 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
<b>Cry</b> stallizate 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.

tion eluted with chlorororm 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.;  $[\alpha]D - 12.5^{\circ}$ . 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  $615 \pm 20$  calculated on the assumption that  $\log \epsilon$  is 4.22-4.25at 216–218 mµ. For analysis it was dried at  $140^\circ$  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.

JERSEY CITY 6, N. J.

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

## The Glycosides of the Seeds of Strophanthus schuchardti Pax

BY ROBERT FOPPIANO, M. R. SALMON AND W. G. BYWATER RECEIVED MARCH 1, 1952

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

Continuing our examination of the glycosides of *Strophanthus*<sup>1</sup> 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 coöperation.

The seeds (200 g.) were processed as previously described.<sup>1a</sup> 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 sarveroside<sup>2</sup> after crystallization from methanol, and dilution of the methanolic mother liquors with ether yielded intermedioside.<sup>3</sup> 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 panstroside<sup>4</sup> which were subse-

(1) (a) M. R. Salmon, Eric Smith and W. G. Bywater, THIS JOUR-NAL, **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 (1930).

(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).

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*,<sup>1b</sup> sarmentosus,<sup>5</sup> courmontii<sup>6</sup> and gerrardi<sup>7</sup> and the latter two glycosides have also been found in *S. intermedius*.<sup>1a,8</sup>

#### 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.<sup>1</sup>

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

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

(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).

<sup>(3)</sup> J. P. Rosselet and A. Hunger, ibid., 34, 1036 (1951).