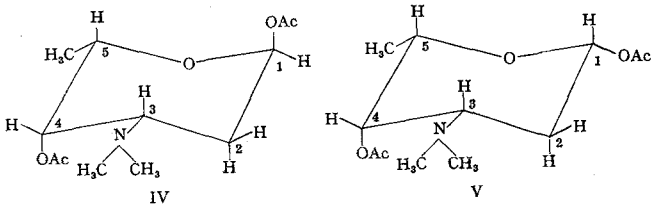
eine spezifische Drehung von $[\alpha]_D^{20}$: $-20° \pm 1°$, für Diacetat II wurde $[\alpha]_D^{20}$: $-109° \pm 3°$ gemessen.

Das KMR-Spektrum der beiden Diacetate wurde mit einem *Varian*-A-60-Spektrometer in $CDCl_3$ mit Tetramethylsilan als internem Standard aufgenommen.

Wie die große Kopplungskonstante $J_{2a,3}$ zeigt, steht das Proton an C-3 axial. Damit ist die äquatoriale Lage der Dimethylaminogruppe bewiesen. Die kleine Kopplungskonstante $J_{3,4}$ ist dann nur durch eine Axial-Äquatorial-Kopplung der Protonen an C-3 und C-4 zu erklären; d.h. die Acetoxygruppe an C-4 steht axial und damit *cis* zur Dimethylaminogruppe an C-3. Daß die kleine Kopplungskonstante $J_{4,5}$ nicht durch äquatorial-äquatoriale, sondern äquatorial-axiale Konstellation bedingt ist, folgt aus der Überführung des Rhodosamins in 2-Desoxy-L-fucose (II) und L-Boivinose (III).

Die Analyse des Protonensignals von C-1 ergibt, daß die beiden Rhodosamin-diacetate Anomere sind. Dem symmetrischen Triplett des Diacetates II ($\tau = 3{,}67$) nach sind die benachbarten Methylen-Protonen gleich weit vom C-1-Proton entfernt, was nur bei axialer Stellung der Acetoxygruppe an C-1 möglich ist. Diacetat II ist daher das α-Anomere IV (wofür auch seine größere Linksdrehung spricht) und Diacetat I das β-Anomere V (bestätigt durch die unterschiedlichen Kopplungskonstanten $J_{1,2a}$ und $J_{1,2e}$).



IV V

Rhodosamin ist somit die 2.3.6-Tridesoxy-3-dimethylamino-L-*lyxo*-hexose.

Herrn Professor Dr. H.H. Inhoffen, Braunschweig, danken wir für die Benutzung des *Varian*-Spektrometers, Fräulein Dipl.-Chem. E. Zühlsdorf und Herrn Dipl.-Chem. E. Ritter für die Durchführung der KMR-Messungen.

Organisch-Chemisches Institut der Universität, Göttingen

Hans Brockmann und Thomas Waehneldt

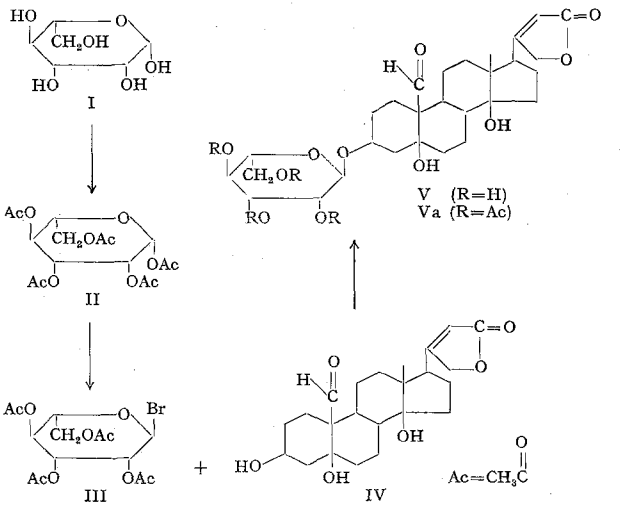
Eingegangen am 17. Dezember 1962

[1]) Brockmann, H., u. E. Spohler: Naturwissenschaften **42**, 154 (1955). — [2]) Brockmann, H., u. E. Spohler: Naturwissenschaften **48**, 716 (1961). — [3]) Brockmann, H., u. Th. Waehneldt: Naturwissenschaften **48**, 717 (1961). — [4]) Brockmann, H., u. W. Lenk: Chem. Ber. **92**, 1904 (1959). — [5]) Prelog, V., u. Mitarb.: Chem. Ber. **92**, 1867 (1959). — [6]) Herrn Professor Dr. T. Reichstein danken wir für Proben der seltenen 2.6-Didesoxy-hexosen.

6'-Hydroxyconvallatoxin

In order to provide precise information in an attempt to relate the structure of the glycosidically bound sugar to the cardiotonic activity of a particular cardenolide, we prepared previously the 2-deoxy-β-D-glucopyranoside of digitoxigenin[1]). Although highly potent, the new cardenolide was shown to have a toxicity somewhat less than the corresponding β-D-glucopyranoside, prepared by Elderfield and coworkers[2]). This fact suggested to us that deoxygenation in the pyranoside ring is perhaps an unfavorable change, and it was in this connection that we investigated the preparation of the 6'-hydroxy analog of the highly potent convallatoxin (6-deoxy-α-L-mannopyranoside of strophanthidin), having MLD = 0·079 mg kg^{-1} as measured in 10 cats. This communication describes summarily the partial synthesis of 6'-hydroxyconvallatoxin (α-L-mannopyranoside of strophanthidin) (V), having MLD = 0·069 mg. $kg.^{-1}$ as measured in 10 cats. The new glycoside V is therefore the *most potent of all known cardenolides*.

The non-naturally occuring β-L-mannose[3]) (I) was acetylated at 0° under the usual conditions to give 51% of 1,2,3,4,6-penta-O-acetyl-β-L-mannose (II), m.p. 116—7°, $[\alpha]_D^{16} + 28{\cdot}6°$ (*c* 0·90, $CHCl_3$). Calcd. for $C_{16}H_{22}O_{11}$: C 49·23; H 5·67. Found: C 49·49; H 5·75. Treatment of II with hydrogen bromide-acetic acid gave 91% of 2,3,4,6-tetra-O-acetyl-α-L-mannosyl bromide (III), m.p. 56—8°, $[\alpha]_D^{17} - 138{\cdot}9°$ (*c* 0·80, $CHCl_3$). When strophanthidin (3β, 5β, 14β-trihydroxy-19-oxocard-20,22-enolide) (IV) was treated with the bromide III in the presence of silver carbonate using an azeotropic distillation technique, there was obtained an O-acetylated intermediate which was not isolated. Instead, the reaction products were saponified *in toto* and extraction with chloroform-methanol (9:1 and 9:2) gave 24% of 6'-hydroxyconvallatoxin monohydrate (V), m.p. 262—5°, $[\alpha]_D^{20} + 6{\cdot}28°$ (*c* 0·42, 90% aq. methanol), λ_{max}^{EtOH} 218 mμ (4·19). Calcd. for $C_{29}fH_{42}O_{11} \cdot H_2O$: C 59·60; H 7·53. Found: C 59·70; H 7·54. For analytic purposes, a sample of V was obtained as anhydrous material,



I II III IV V (R=H) Va (R=Ac)

m.p. 265—9°. Calcd. for $C_{29}H_{42}O_{11}$: C 61·46; H 7·47. Found: C 61·72; H 7·76. Acetylation of V gave the expected tetra-O-acetylated derivative Va which was obtained only as amorphous powder, m.p. 128—133°. Calcd. for $C_{37}H_{50}O_{15}$: C 60·50; H 6·86. Found: C 60·43; H 7·17.

The authors gratefully acknowledge support by the U.S. Public Health Service (Grant H-5839) and are much indebted to Drs. K.K. Chen and Francis G. Henderson, Eli Lilly and Co., Indianapolis, Indiana, for the pharmacological evaluation of the new cardenolide V.

Department of Chemistry, Georgetown University, Washington 7, D. C., U.S.A.

W. Werner Zorbach and Seitaro Saeki

Eingegangen am 29. September 1962

[1]) Zorbach, W.W., and G. Pietsch: Liebigs Ann. Chem. **655**, 26 (1962). — [2]) Elderfield, R.C., F.C. Uhle and J. Fried: J. Amer. Chem. Soc. **69**, 2235 (1947). — [3]) Sowden, J.C., and H.O.L. Fischer: J. Amer. Chem. Soc. **69**, 1963 (1947).

Vincaminoridine and Vincoridine, Two New Alkaloids from Vinca minor L.

Eleven alkaloids have already been isolated from Vinca minor L. [see[1])]. We have obtained two further alkaloids, for which we proposed the names vincaminoridine and vincoridine.

The weak-alkaloid fraction U[2]), obtained by countercurrent distribution of the "yellow fraction B" of the crude alkaloids[3]) was separated by chromatography on alumina. [Thinlayer chromatography on alumina (benzene) gives *Rf* values for vincaminorine 0·75 for vincaminoridine 0·58 and for vincoridine 0·34].

Light petrolether-benzene (1:1) eluates afforded a crystaline alkaloid, identical with vincaminorine[4]) in all respects. According to its total formula and the values of its UV spectrum we assume its fundamental skeleton to be tetracyclic, probably of quebrachamine type.

From the fraction eluated by benzene we obtained the mixture of two alkaloids, which by rechromatography on alumina light petrolether-benzene (1:1) afforded vincaminoridine m.p. 99—100° (from heptane), $[\alpha]_D^{20} + 57{\cdot}7°$ (c = 1·05; $CHCl_3$). Found: C 71·55, H 8·36, N 7·54, OCH_3 16·45, N-CH_3 7·69. $C_{22}H_{30}N_2O_3$ requires C 71·32, H 8·16, N 7·56, 2 OCH_3 16·75, 1 $^N CH_3$ 4·06. The characteristic maxima of vincaminoridine in ultraviolet light at λ_{max} 232 (log ε = 4·57) and 300 mμ (log ε = 3·84), λ_{inflex} 288 mμ (log ε = 3·79) and λ_{min} 262 mμ (log ε = 3·50) indicate the indole grouping. The shift