UDC 547.918 : 582.951.6

45. Atsuji Okano, Kazuhiko Hoji, Tōsaku Miki, and Akio Sakashita :

Studies on the Constituents of *Digitalis purpurea* L. XII.[1]
New Cardiotonic Glycosides, Gitorocellobioside, Glucogitoroside, and Gitoxin-cellobioside.

(*Research Laboratory, Daiichi Seiyaku Co., Ltd.**)

It was reported in Part X[2] of this series that several new cardiotonic glycosides had been isolated and the structure of substance C–II had been determined, being designated as digifucocellobioside in accordance with its component as described in the preceding paper.[1] The present investigation was undertaken in order to determine the structures of substances B–III and B–III'.

It was shown in Table I of Part X[2] that substance B–III comes as a colorless powder, m.p. 250~254°, $[\alpha]_D^{22}$ +13.5° (MeOH), gives positive Legal and Raymond reactions, and its ultraviolet spectrum exhibits the maximum absorption at 218 mμ (EtOH), indicating the presence of an α,β–unsaturated lactone characteristic to cardiotonic glycosides. Keller–Kiliani reaction gave carmine–red sulfuric acid layer, same as gitoxigenin, and brown glacial acetic acid layer, but Gregg–Gisvold reaction on paper strip gave an intensely blue–gray spot as gitoxin. Therefore, it is reasonable to assume that substance B–III contains 2,6–desoxysugar.

TABLE I.

Substance	$[\alpha]_D$	$[M]_D$ calcd.
Digilanidobiose	+ 30.1°	+ 93.4°
Digilanidotriose	+ 17.6°	+ 83.2°
$\Delta[M]_D$		− 10.2°
α–Methyl–D–glucopyranoside	+158.9°	+270°
β–Methyl–D–glucopyranoside	− 34.2°	− 58°

Mild hydrolysis of substance B–III with 0.05*N* sulfuric acid afforded an aglycone as colorless plates, m.p. 218~222°, which was identified by paper chromatography and the mixed fusion with authentic sample of gitoxigenin.

The syrupy sugar obtained from the foregoing hydrolysate gave a positive Gregg–Gisvold reaction and was submitted to paper chromatography with two developing solvent systems. A single spot appeared on each paper strip. The Rf values in both systems were smaller than those of glucose and digilanidobiose. It was purified on a carbon column and needles (Fig. 1), m.p. 214~219°, $[\alpha]_D^{20}$ +17.6° (H_2O), were obtained. The analytical values and the result of molecular-weight determination agreed closely with the theoretical values for formula $C_{18}H_{32}O_{14}$, calculated for a trisaccharide, composed of two hexoses and one 2,6–desoxysugar.

The state of the enzymatic hydrolysis of this sugar was traced at definite intervals of time by paper chromatography, as described in Part IX,[3] and it was found that this sugar was first hydrolysed to digilanidobiose by elimination of one mole of glucose, during two hours, and then it was finally hydrolysed to digitoxose and glucose after two days.

The difference in molecular rotation between this sugar and digilanidobiose shows that the glucosidic linkage of the terminal glucose in this sugar is in β–configuration, as shown in Table I.

---

* Hirakawabashi, Sumida-ku, Tokyo (岡野淳二, 傍士和彦, 三木藤作, 坂下昭夫).

1) Part XI. A. Okano, *et al.* : This Bulletin, **7**, 222(1959).

2) Part X. A. Okano, *et al.* : *Ibid.*, **7**, 212(1959).

3) Part IX. A. Okano : *Ibid.*, **6**, 178(1958).

Fig. 1.
Digilanidotriose

Since acetolysis of this sugar acetate gave α-octaacetylcellobiose, it was presumed that the sugar is composed of cellobiose and digitoxose, and since a trisaccharide possessing above constitution has never been described in any literature, this trisaccharide was designated as digilanidotriose.

The foregoing results have shown that substance B-Ⅲ is obviously a hitherto unknown glycoside and that it possesses gitoxigenin as aglycone and digilanidotriose as sugar moiety.

Enzymatic hydrolysis of substance B-Ⅲ for three days afforded colorless powder, m.p. 212~215°, $[\alpha]_D^{22}$ +9.9°(MeOH), and it was identified with gitoroside[4]* by paper chromatography and mixed fusion. The sugar portion of this enzymatic hydrolysis was identified with glucose by paper chromatography and it was estimated quantitatively by the Sumner's reagent.

The foregoing results have shown that substance B-Ⅲ is composed of gitoxigenin and digilanidotriose, and its structure is gitoxigenin cellobiosido-digitoxoside. Since this glycoside has never been described in the literature, it was designated as gitorocellobioside in accordance with its structure.

Enzymatic elimination of one mole of glucose from the above triglycoside was effected and the new diglycoside was purified by alumina chromatography. It came as a colorless powder, m.p. 212~216°, $[\alpha]_D^{22}$ +8.3°(MeOH), and gave a coloration similar with gitorocellobioside in Legal, Keller-Kiliani, and Raymond reactions. Its Rf value on paper chromatogram was smaller than that of purpurea glycoside-B. The mild acid hydrolysis of this glycoside gave gitoxigenin and digilanidobiose, and analytical values agreed with those of gitoxigenin glucosido-digitoxoside, $C_{35}H_{54}O_{13} \cdot H_2O$. It has never been described in the literature and it was given the name of glucogitoroside.

It was shown in Table I of Part X[2] that substance B-Ⅲ′ was a colorless powder, m.p. 240~244°, and showed coloration similar to purpurea glycoside-B in Legal and Keller-Kiliani reactions.

Acidic hydrolysis of this substance gave gitoxigenin, digilanidotriose and digitoxose, which were respectively identified with authentic samples by comparisons of Rf values.

Enzymatic hydrolysis of this glycoside for five days afforded needles, m.p. 266~269°,

---

4) D. Satoh, T. Wada, H. Ishii, Y. Oyama, T. Okumura : This Bulletin, 5, 253(1957).

* Grateful acknowledgement is made to Mr. Satoh for kind donation of a valuable sample of gitoroside.

which was identified with authentic sample of gitoxin by mixed fusions of glycosides and of their crystalline acetates, and further by paper chromatographic analysis. Enzymatic decomposition was performed for four hours to eliminate one mole of glucose from substance B–Ⅲ′, and the product was obtained as a colorless amorphous substance, m.p. 208～210°, which was identified with authentic sample of purpurea glycoside–B by the same methods as the above.

It may be concluded from the present results that substance B–Ⅲ′ is gitoxigenin digilanidotriosido–bis–digitoxoside, i.e., cellobiosido–gitoxin, and since it is a new cardiotonic glycoside, it was named gitoxin cellobioside. This glycoside is the first pentaglycoside isolated in the chemistry of cardiotonic glycosides.

Trisaccharides possessing 2,6–desoxysugar have not been obtained in a crystalline form except strophanthotriose,[5,6] and now a new trisaccharide, digilanidotriose, has

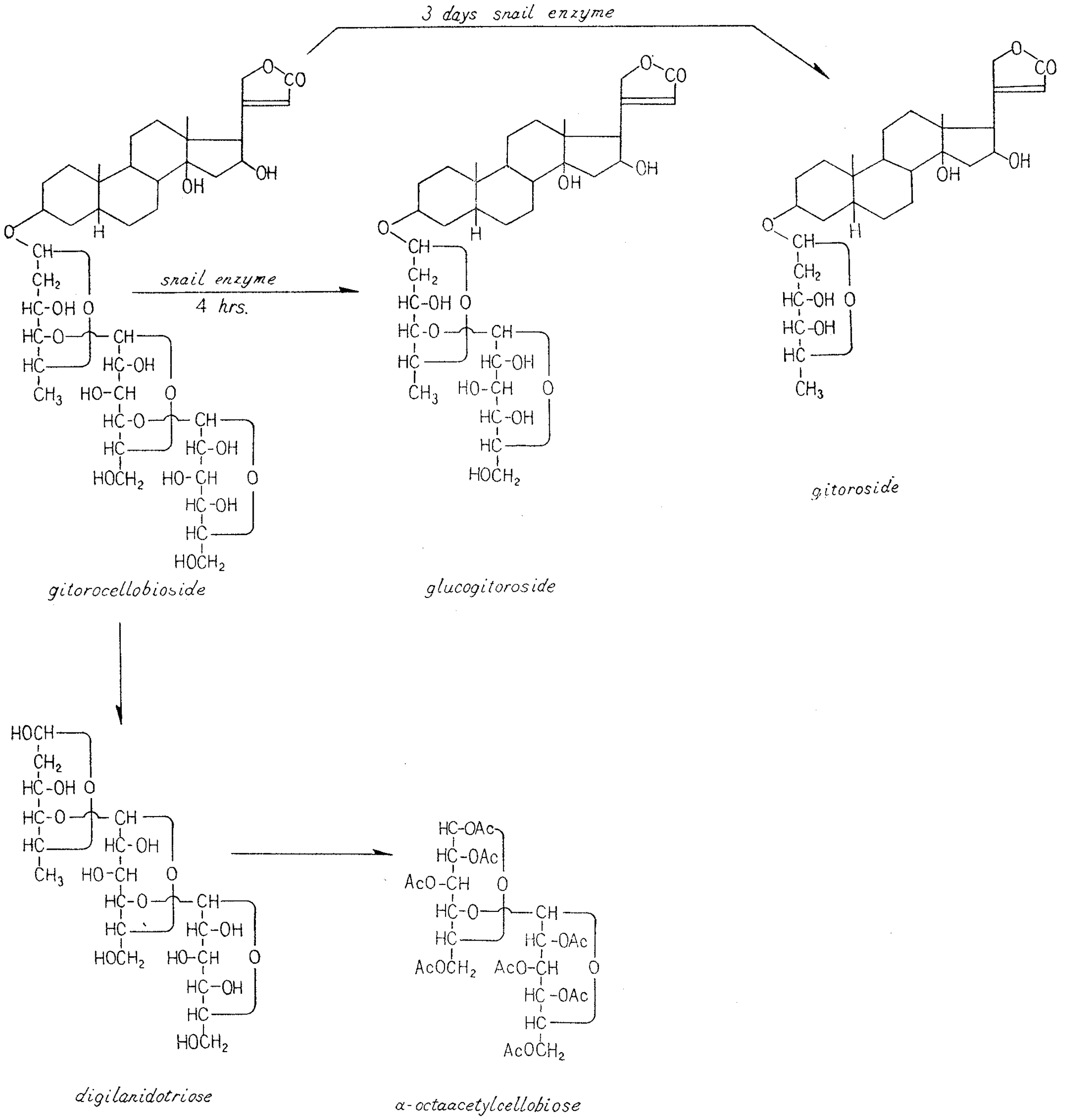


Chart 1.

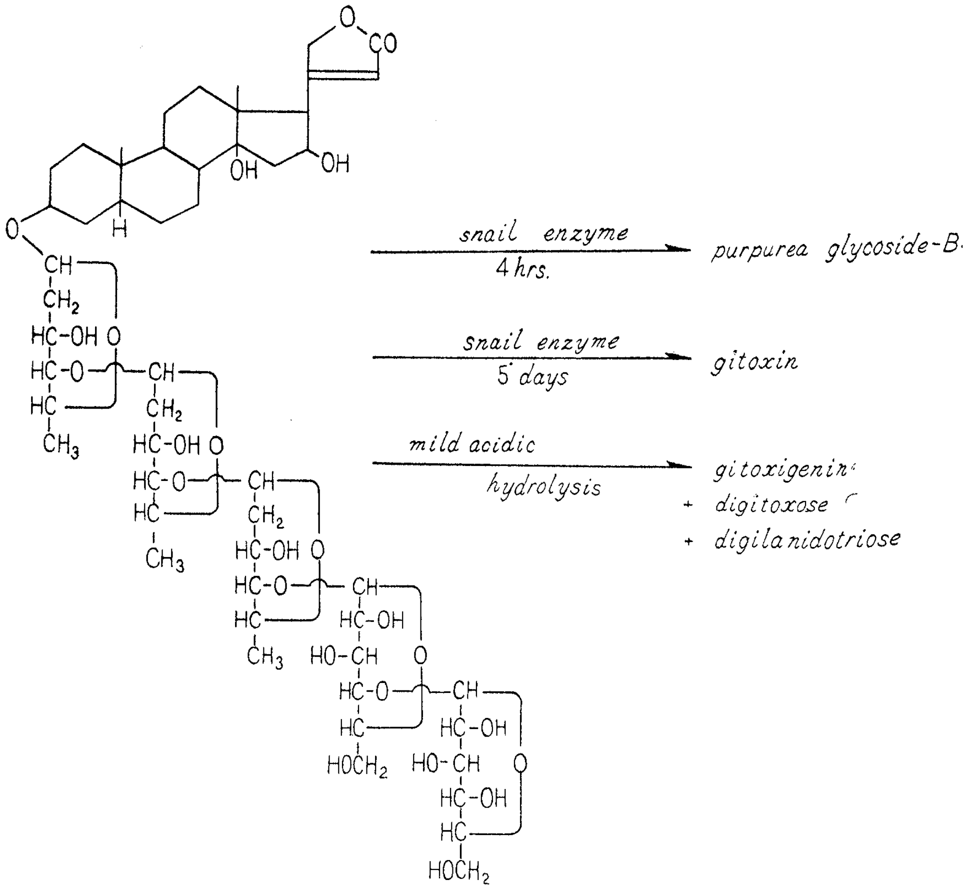
---

5) A. Stoll, J. Renz, W. Kreis : Helv. Chim. Acta, **20**, 1484(1937).

6) J.C. Hess, A. Hunger, T. Reichstein : *Ibid.*, **35**, 2202(1952).

been added to this group. It is interesting that new glycosides from digitalis seeds, gitostin, neogitostin, digifucocellobioside, gitorocellobioside, and gitoxin-cellobioside, which have been isolated in this laboratory, do not contain gentiobiose residue, but cellobiose residue, except neogitostin.

The writers express their deep gratitude to Prof. S. Shibata of the University of Tokyo for reviewing this manuscript, to Dr. Junzo Shinoda, President of this Company, to Mr. Sakan Hashimoto, Director, and to Dr. Masao Shimizu, Acting Director, of this Laboratory, for kind encouragement during the course of this work, and to Dr. Kazuo Miyatake, Director of the Yanagishima Factory, for continued guidance. The writers are much indebted to Messrs. Kurihara and Abe for elemental analyses.



gitoxin cellobioside

Chart 2.

Experimental[7]

Gitorocellobioside (Substance B-III)—The manner of isolation was reported in Part X.[2] This substance was recrystallized from MeOH-Me_2CO to colorless powder, m.p. 250~254°, $[\alpha]_D^{22}$ +13.5°(c=0.266, MeOH), $[\alpha]_D^{22}$ −19.3°(c=0.826, pyridine), U.V. λ_{max}^{EtOH} 218 mμ (log ε 4.26). *Anal.* Calcd. for $C_{41}H_{64}O_{18}$: C, 58.28; H, 7.63; glucose, 42.64. Calcd. for $C_{41}H_{64}O_{18} \cdot H_2O$: C, 57.06; H, 7.71; glucose, 41.66. Found: C, 56.88; H, 8.05; glucose, 37.69.*

Acid Hydrolysis of Gitorocellobioside—A solution of 200 mg. of gitorocellobioside dissolved in a mixture of 30 cc. of MeOH and 30 cc. of 0.1*N* H_2SO_4 was refluxed for 1 hr. MeOH was distilled off under a reduced pressure and the residue was extracted 5 times with 20 cc. each of $CHCl_3$.

i) Aglycone : The combined $CHCl_3$ extract was washed with two 20-cc. portions of water and was evaporated to dryness (75 mg.). The residue was recrystallized from hydr. EtOH to plates, m.p. 216~

---

7) All m.p.s were measured on a Kofler block and are uncorrected.

* Same as determination of glucose from neogitostin monoacetate by enzymatic decomposition, in Part IX.[3]

220°, which did not show any depression on admixture with gitoxigenin, m.p. 218~222°. The aglycone was further identified with gitoxigenin by paper chromatography (Toyo Roshi No. 50 used) in two different solvent systems, xylene : MeCOEt(1:1) saturated with formamide, and cyclohexane: AcOH:$CHCl_3$:H_2O(100:30:20:1), by ascending method. *Anal.* Calcd. for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78. Found : C, 70.60; H, 8.92.

ii) Sugar moiety : The aqueous solution was deionized by Amberlite IR-4B (3 cc.), evaporated to dryness, and the syrupy sugar was obtained (145 mg.).

Digilanidotriose—The above syrupy sugar was placed on a carbon column (1 g. of Edocol, 2 g. of Celite 535) and eluted with 100 cc. each of water, 1%, 2%, 5%, 10%, and 20% EtOH. The 20% EtOH fraction was evaporated and the residue was repeatedly recrystallized from hydr. MeOH-Et_2O to needles (15 mg. of digilanidotriose), m.p. 215~219°; $[\alpha]^{20}_{D}$ +17.6°(c=1.206, H_2O). This sugar was examined on paper chromatogram using the following two solvent systems and detection with 1% HCl-MeOH spray showed one spot on each strip. (a) BuOH:AcOH:H_2O(4:1:5), Rf 0.09; (b) BuOH:pyridine:H_2O (4:3:3), Rf 0.28.

This sugar gave positive Gregg-Gisvold and Fehling reactions, and negative Keller-Kiliani reaction. Easily soluble in water, sparingly soluble in MeOH, and insoluble in Et_2O. *Anal.* Calcd. for $C_{18}H_{32}O_{14}$: C, 45.76; H, 6.83; mol. wt., 472.44. Found : C, 45.60; H, 6.88; mol. wt.(Barger-Akiya), 462.

Formation of Glucogitoroside from Gitorocellobioside—To a solution of 330 mg. of gitorocellobioside dissolved in 50 cc. of MeOH, 250 cc. of distilled water was added, MeOH was removed under a reduced pressure, and distilled water was added until 500 cc. A filtrate obtained from 70 mg. of the enzyme powder treated 3 times with 25 cc. each of distilled water was added to this solution, together with 10 cc. of toluene, and the mixture was allowed to stand in a thermostat of 32° for 4 hrs. The mixture was evaporated in vacuum, the residue was treated with 50 cc. of MeOH-$CHCl_3$(1:1), and filtered. The filtrate was evaporated, the residue was placed on a column containing 10 g. of alumina, and eluted with 50 cc. each of MeOH-$CHCl_3$(1:9), (1:4), (1:1), and 200 cc. of water-saturated BuOH. The fraction eluted with H_2O-BuOH was evaporated to colorless powder (glucogitoroside).

The insoluble material was submitted to paper chromatography with BuOH:AcOH:H_2O(4:1:5), and a spot corresponding to glucose alone was obtained.

Glucogitoroside—The crude glucogitoroside was recrystallized from MeOH-Me_2CO to colorless powder, m.p. 212~216°; $[\alpha]^{22}_{D}$ +19.9°(c=0.691, EtOH), $[\alpha]^{20}_{D}$ +8.3°(c=0.987, MeOH). It gave positive Legal, Raymond, and Gregg-Gisvold reactions. Keller-Kiliani reaction gave carmine-red H_2SO_4 layer and brown glacial AcOH layer. Easily soluble in MeOH and EtOH, sparingly soluble in Me_2CO and water, and insoluble in Et_2O. *Anal.* Calcd. for $C_{35}H_{54}O_{13}$: C, 61.56; H, 7.97. Calcd. for $C_{35}H_{54}O_{13}\cdot H_2O$: C, 59.98; H, 8.05. Found : C, 59.86; H, 7.88. U.V. λ^{EtOH}_{max} 219 mμ (log ε 4.15).

Formation of Gitoroside from Gitorocellobioside—To a solution of 200 mg. of gitorocellobioside dissolved in 30 cc. of MeOH, 400 cc. of distilled water was added and MeOH was evaporated from this solution under a reduced pressure. A filtrate obtained from 200 mg. of the enzyme powder treated 3 times with 50 cc. each of distilled water and filtered, was added to this solution, together with 10 cc. of toluene, and the mixture was allowed to stand in a thermostat of 32° for 3 days. The mixture was evaporated and the residue was treated with MeOH-$CHCl_3$ (1:1). This MeOH-$CHCl_3$ solution was evaporated to dryness (160 mg.) and it was chromatographed on 6 g. of alumina with 2% MeOH-$CHCl_3$. The colorless material (150 mg.) obtained was recrystallized from Me_2CO-petr. ether to colorless powder, m.p. 212~215°; $[\alpha]^{22}_{D}$ +9.9°(c=0.978, MeOH), $[\alpha]^{22}_{D}$ +18.3°(c=0.718, EtOH); U.V. λ^{EtOH}_{max} 219 mμ (log ε 4.17; Calcd. for $C_{29}H_{44}O_8$). It gave positive Legal, Raymond, and Gregg-Gisvold reactions. Keller-Kiliani reaction gave carmine-red H_2SO_4 layer and dark blue glacial AcOH layer. Easily soluble in MeOH, soluble in Me_2CO and $CHCl_3$, and insoluble in water, Et_2O, and petr. ether. Mixed fusion of this powder with gitoroside,[4] m.p. 209~214°, melted at 209~214°. Paper chromatography was carried out on these glycosides, using a mixture of toluene:BuOH(9:1) saturated with formamide on a formamide-impregnated paper, and Rf values obtained were 0.59 for this powder and 0.585 for gitoroside.

Acid Hydrolysis of Glucogitoroside—A solution of 100 mg. of glucogitoroside in 30 cc. of 0.05*N* H_2SO_4 (50% MeOH) was refluxed for 1 hr. About 50 mg. of crude aglycone extracted with $CHCl_3$ was recrystallized from hydr. EtOH to plates, m.p. 210~217°. This was identified with gitoxigenin by a mixed fusion and paper chromatographic analysis.

The residue (ca. 60 mg.) obtained from sugar portion was chromatographed on a carbon column (1 g. of Edocol and 2 g. of Celite 535) and eluted with 100 cc. each of water, 1%, 5%, 10%, and 20% EtOH. The fraction eluted with 10% EtOH was recrystallized from hydr. EtOH to colorless needles, m.p. 226~227°, which gave a mixed m.p. 224~227° with digilanidobiose, m.p. 224~226°. Paper chromatography was carried out on these two sugars, using a mixture of BuOH:AcOH:H_2O(4:1:5) and the Rf values obtained were 0.23 for the sugar from glucogitoroside and 0.23 for digilanidobiose. *Anal.* Calcd. for $C_{12}H_{22}O_9$: C, 46.45; H, 7.15. Found : C, 46.57; H, 6.67.

Acid Hydrolysis of Gitoroside—From 100 mg. of gitoroside obtained from gitorocellobioside, about 80 mg. of aglycone was obtained by the same treatment as in the above case, and recrystallized from hydr. EtOH to plates, m.p. 208~212°, which were identified with gitoxigenin.

The syrupy sugar (42 mg.) obtained from sugar portion was identified with digitoxose by paper chromatographic analysis.

Acetolysis of Digilanidotriose—Acetylation of 30 mg. of digilanidotriose by the usual method was carried out by standing with 2 cc. of pyridine and 1 cc. of Ac_2O for 2 days.

To a solution of amorphous digilanidotriose acetate in 1 cc. of Ac_2O, 15 mg. of $ZnCl_2$ was added and the mixture was heated at 100° for 30 mins. The mixture was cooled, poured into 70 cc. of ice water, allowed to stand for 3 hrs., and this was extracted 5 times with 20 cc. each of $CHCl_3$. The combined $CHCl_3$ extract was washed twice with water and evaporated to 55 mg. of a syrupy material. It was chromatographed on a mixture of 1 g. of Florisil and 0.2 g. of Celite 535, and eluted with 50 cc. of benzene and 50 cc. of EtOH-benzene(1:99). The fraction of EtOH-benzene was evaporated and the residue was recrystallized from $CHCl_3$-MeOH to colorless needles, m.p. 221~224°, which gave a mixed m.p. 220~224° with α-octaacetylcellobiose, m.p. 223~225°.

Enzymatic Decomposition of Digilanidotriose—About 10 mg. of digilanidotriose was dissolved in 5 cc. of distilled water. A filtrate from 2 mg. of enzyme powder treated with 2 cc. of distilled water was added to this solution, together with 0.5 cc. of toluene, and the mixture was allowed to stand in a thermostat of 32°. The state of hydrolysis of this sugar was examined by paper chromatography at intervals of 0.5, 1, 2, 4, 24, and 72 hrs.

The hydrolysis of this sugar proceeded stepwise, first to digilanidobiose by the rapid hydrolysis of 1 mole of glucose, and further to digitoxose by liberation of 1 mole of glucose.

Gitoxin Cellobioside (Substance B-III′)—The isolation was reported in Part X[2] and this substance was recrystallized from pyridine-MeOH to colorless powder, m.p. 240~244°. *Anal.* Calcd. for $C_{53}H_{84}O_{24}$: C, 57.59; H, 7.66. Calcd. for $C_{53}H_{84}O_{24}\cdot 2H_2O$: C, 55.78; H, 7.77. Found: C, 55.82; H, 7.50.

Acid Hydrolysis of Gitoxin Cellobioside—To a mixture of 5 mg. of gitoxin cellobioside in 1 cc. of MeOH, 1 cc. of 0.1*N* H_2SO_4 was added and the mixture was refluxed on a water bath for 45 mins. MeOH was distilled off under a reduced pressure, the residue was extracted 3 times with 5 cc. each of $CHCl_3$, combined extract was washed with 5 cc. of water, evaporated, and the residue was recrystallized from hydr. EtOH to colorless plates which were identified with gitoxigenin.

The aqueous solution was deacidified through Amberlite IR-4B, evaporated, and the residue was submitted to paper chromatography with BuOH:AcOH:H_2O(4:1:5). Coloration with 1% HCl-MeOH solution (Gregg-Gisvold reaction) revealed two spots at Rf 0.54 and Rf 0.09 which were respectively identified with digitoxose (Rf 0.54) and digilanidotriose (Rf 0.09).

Formation of Purpurea Glycoside-B from Gitoxin Cellobioside—To a solution of 100 mg. of gitoxin cellobioside dissolved in 200 cc. of MeOH, 500 cc. of distilled water was added and MeOH was evaporated from this solution under a reduced pressure. A filtrate, obtained from 25 mg. of the enzyme powder treated 3 times with 10 cc. each of distilled water, was added to this solution, together with 20 cc. of toluene, and the mixture was allowed to stand in a thermostat of 32° for 4 hrs. After evaporation to dryness, the mixture was treated with MeOH-$CHCl_3$(1:1) and filtered. MeOH-$CHCl_3$ solution was evaporated in vacuum and the residue was purified on 5 g. of alumina. The column was eluted with 50 cc. each of MeOH-$CHCl_3$(1:9), (1:4), and (1:1), and 200 cc. of water-saturated BuOH. The fraction eluted with H_2O-BuOH was evaporated in vacuum and the residue was recrystallized to colorless powder, m.p. 208~210°. This powder was submitted to paper chromatography with water-saturated MeCOEt, and coloration with 20% $SbCl_3$-$CHCl_3$ solution revealed a single spot which was found to agree with the Rf value of purpurea glycoside-B. This powder was acetylated by the usual method and was recrystallized to colorless needles, m.p. 145~151°/215~221°, which melted at 146~150° with an authentic sample of purpurea glycoside-B acetate,[8] m.p. 147~149°.

Formation of Gitoxin from Gitoxin Cellobioside—To a solution of 100 mg. of gitoxin cellobioside dissolved in 250 cc. of MeOH, 600 cc. of distilled water was added and MeOH was distilled off under a reduced pressure. A filtrate, obtained from 40 mg. of the enzyme powder treated 3 times with 10 cc. each of distilled water, was added to this solution, together with 20 cc. of toluene, and the mixture was allowed to stand in a thermostat of 32° for 5 days. The reaction mixture was evaporated and the separated glycoside was recrystallized from MeOH to m.p. 260~262°. It was further recrystallized from pyridine-MeOH to needles, m.p. 266~269°, melted at 267~270° with authentic gitoxin, m.p. 269~272°.

The crystals were acetylated by the usual method and the acetate obtained was recrystallized to colorless prisms, m.p. 152~156°, which gave mixed m.p. 150~155° with authentic gitoxin acetate,[8] m.p. 150~156°. By paper chromatographic analysis, these substances were identified with gitoxin and its acetate.

---

[8] Part V. A. Okano, *et al.*: This Bulletin, **5**, 171(1957).

Summary

The structures of substance B–Ⅲ and B–Ⅲ′, newly isolated from digitalis seeds,[2] were examined. It was found that enzymatic hydrolysis of substance B–Ⅲ afforded gitoroside, and a mild acid hydrolysis afforded gitoxigenin and new trisaccharide which consists of cellobiose and digitoxose. This sugar was named digilanidotriose. Therefore, substance B–Ⅲ is formulated as gitoxigenin cellobiosido–digitoxoside, and was designated as gitorocellobioside. The partial decomposition of gitorocellobioside with a snail enzyme afforded a new diglycoside which is gitoxigenin glucosido–digitoxoside and this was designated as glucogitoroside.

Substance B–Ⅲ′ was examined by the same method and was shown to be a new cardiotonic pentaglycoside which has a structure of gitoxigenin cellobiosido–tridigitoxoside, and was named gitoxin cellobioside.

(Received September 3, 1958)

UDC 547.92.07

46. **Kyosuke Tsuda and Shigeo Nozoe**: Steroid Studies. XI.[1] On the Methylation of 3–Oxosteroids. (1).

(*Institute of Applied Microbiology,* University of Tokyo*)

2–Substituted analogs of steroidal hormones possess glucocorticoidal activity[2] and 4–substituted analogs of testosterone show anabolic activity.[3] The present paper deals with the synthesis of 3–oxosteroids possessing a methyl group in 2– or 4–position.

Methyl group can be introduced into the 2–position of 3–oxosteroids by ethoxyoxalylation with ethyl oxalate, followed by methylation and deoxalylation,[2,4] while methyl derivative of testosterone is obtained by its direct methylation.[3]

The methylation of 3–oxosteroid carried out in the present series of work consisted of introduction of a hydroxymethylene group with ethyl formate, followed by methylation of its product and deformylation. Shortly before this work was completed, Quartey[5] published reports on the methylation of 2–position of cholest–4–en–3–one according to the same principle.

Formylation of 4,6,22–ergostatrien–3–one (I) affords a hydroxymethylene compound (Ⅱ) of m.p. 138°, which shows ultraviolet absorption maxima at 292 and 331 mμ (in MeOH) and an absorption for α,β–unsaturated β–hydroxy ketone at 1637 cm^{-1} in its infrared absorption spectrum.[6] (Ⅱ) easily undergoes conversion by hydrochloric acid to a formyl compound (Ⅲ) of m.p. 169°, which shows ultraviolet absorption maxima (in MeOH) at 294 and 323 mμ, and an absorption for α,β–unsaturated β–hydroxy aldehyde at 1667 cm^{-1} in its infrared spectrum[6] (Fig. 1).

The infrared spectra of (Ⅱ) and (Ⅲ) are entirely devoid of free O–H stretching absorption in the fundamental region. This is a characteristic of enolic β–diketone

---

* Yayoi–cho, Hongo, Bunkyo–ku, Tokyo (津田恭介, 野副重男).

[1] Part X: J. Am. Chem. Soc., in press.

[2] J.A. Hogg, F.H. Lincoln, R.W. Jackson, W.P. Schneider: J. Am. Chem. Soc., **77**, 6401(1955).

[3] B. Camerino, B. Patelli, A. Vercellone: *Ibid.*, **78**, 3540(1956).

[4] S. Bernstein: *Ibid.*, **79**, 4555(1957).

[5] J.A.K. Quartey: J. Chem. Soc., **1958**, 1710.

[6] L.J. Bellamy: "The Infra-red Spectra of Complex Molecules," 114(1954). John Wiley & Sons, Inc., New York.