mit Ammoniak wieder in (II) zurückgeht. Diese Eigenschaften stimmen mit der mesoiden bzw. racemoiden Konfiguration bei 8 und 9 Kohlenstoffatomen des Dihydronichins bzw. Dihydroepinichins überein.

(Eingegangen am 3. September 1958)

UDC 547.918 : 582.951.6

43. Atsuji Okano, Kazuhiko Hoji, Tosaku Miki, and Akio Sakashita : Studies on the Constituents of *Digitalis purpurea* L. X.[1] Isolation of Several New Glycosides from the Water-soluble Fraction of Digitalis Seeds.

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

It was previously reported in this series, that digitalinum verum,[2] gitostin,[3] glucodigifucoside,[4] and neogitostin[5] had been isolated from the seeds of *Digitalis purpurea*, and the structures of these three new glycosides had been established. Further many unknown glycosides were contained in the easily water-soluble fraction, i.e., fraction Nos. 8~16 in Table I in Part II,[2] which was considered to possess Subst. A-VI, A-VII, B-II, B-III, B-IV, C-II, and C-III besides gitostin (Subst. A-VIII) and neogitostin (Subst. A-IX). Their presence was already indicated by paper chromatography with water-saturated methyl ethyl ketone, as shown in Fig. 1 in Part II.[2]

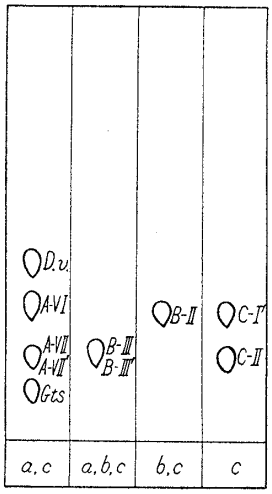

Fig. 1. Paper Partition Chromatography of Easily Water-soluble Fraction
Moving phase : Water-saturated MeCOEt. (solvent system 1)
Paper : Impregnated, with acetone-H_2O(4:1) and acetone evaporated.
Coloring agent : a, 20% $SbCl_3$-$CHCl_3$ solution.
b, 1% HCl-MeOH solution.
c, Raymond reaction.

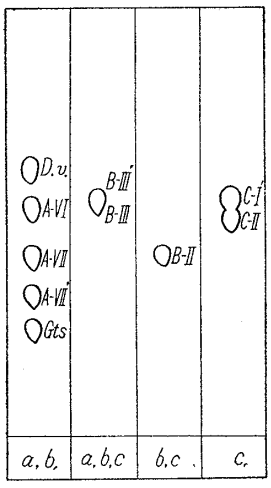

Fig. 2. Paper Partition Chromatography of Easily Water-soluble Fraction
Moving phase : BuOH-toluene-H_2O(6:3:1). (solvent system 2)
Paper : Impregnated, with acetone-H_2O(1:1) and acetone evaporated.

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

1) Part IX. A. Okano : This Bulletin, **6**, 178(1958).
2) Part II. K. Miyatake, *et al.* : *Ibid.*, **5**, 157(1957).
3) Part III. K. Miyatake, *et al.* : *Ibid.*, **5**, 163(1957).
4) Part VI. A. Okano : *Ibid.*, **5**, 272(1957).
5) Part VIII. A. Okano : *Ibid.*, **6**, 173(1958).

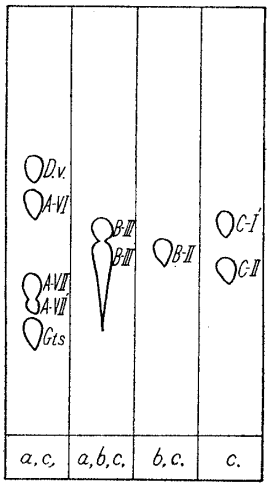


Fig. 3. Paper Partition Chromatography of Easily Water-soluble Fraction
Moving phase : Water-saturated *iso*-AmOH (solvent system 3)
Paper : Impregnated with acetone-H_2O(4:1), and acetone evaporated.

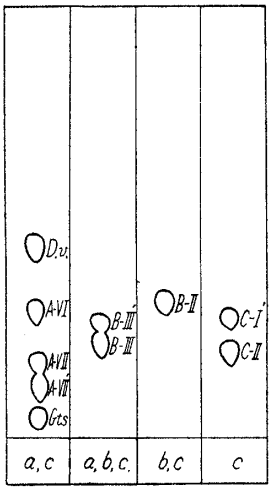


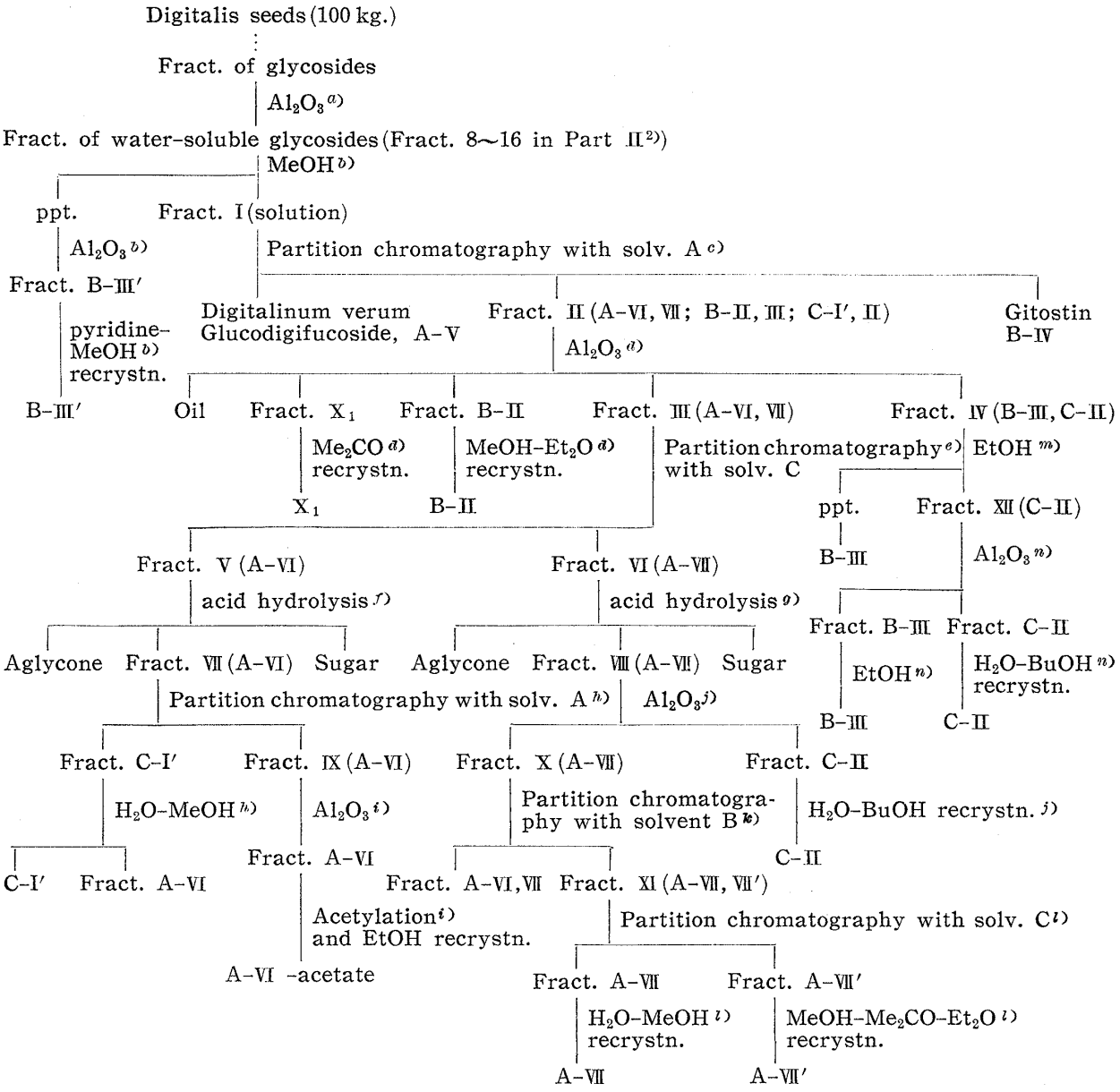
Fig. 4. Paper Partition Chromatography of Easily Water-soluble Fraction
Moving phase : *n*-BuOH-benzene-H_2O(4:6:1). (solvent system 4)
Paper : Impregnated with acetone-H_2O, and acetone evaporated.

Since the amount of these unknown glycosides seemed to be too small to separate, 100 kg. of seeds was extracted, and fractions were separated again by the same method as described in Part II.[2] On the other hand, it was found that these unknown glycosides in the above-mentioned fraction were not sufficiently separated on a filter paper developed with water-saturated methyl ethyl ketone (Solvent system 1, Fig.1). In addition to the system 1, three new solvent mixtures (Solvent systems 2, 3, and 4) were applied to the paper chromatography to effect separation (Figs. 2, 3, and 4). As shown in these figures, three more new spots (A-VII′, B-III′, C-I′) were confirmed in this fraction, but paper chromatography with each of these solvent systems could not always give all of their sharp spots. Therefore, four above-mentioned solvent systems were necessary for the examination of purity and fractionation of the materials.

In the process of isolation and fractionation of the glycosides, various separative methods were carried out, such as acetylation, column partition chromatography with various solvents, and alumina adsorption chromatography, etc., as shown in Chart 1. Further, a mild acid hydrolysis was carried out to remove the glycosides containing 2,6-desoxysugar in the sugar portion and attached to B-group,[2] because they were very easily hydrolyzed. By mild hydrolysis, A- and C-groups[2] were freed from contaminating glycosides in B-group. Details of these methods are described in the Experimental section of this paper.

Thus, several new glycosides were successfully isolated. Five substances, A-VI-acetate, C-I′, A-VII, B-II, and X_1, were obtained as crystals, and four substances, B-III, C-II, A-VII′, and B-III′, were obtained as a colorless powder. Their properties are listed in Table I. In accordance with their coloration and absorption spectral data, these substances are classified into the following four groups : (1) Dgt-group : Subst. C-I′ and C-II, composed of digitoxigenin-like aglycones, without 2,6-desoxysugar. (2) Dgl-group : Subst. B-II, composed of digitanol-like aglycone and 2,6-desoxysugar. (3) Gt-group : Subst. A-VI, A-VII and A-VII′, composed of gitoxigenin-like aglycones and no 2,6-desoxysugar. (4) Gt-2,6-ds-group : Subst. B-III and B-III′, composed of gitoxigenin-like aglycones and 2,6-desoxysugar.

The glycosides giving similar Rf values on various paper chromatography are



a, *b* ···· *n* corresponds to numbers in the Experimental section.

Chart 1. Isolation of Glycosides

known to be different from each other in respects to their solubility and their behavior in adsorption column chromatography. They are arranged in the order of decreasing solubility, (a) in water : Gt-group > Dgl-group > Dgt-group > Gt-2,6-ds-group ; (b) in organic solvents : Dgl-group > Gt-group > Dgt-group > Gt-2,6-ds-group. They are arranged in the order of decreasing adsorption affinity on alumina : Dgt-group > Gt-2,6-ds-group > Gt-group > Dgl-group.

From results of studies on seeds of *Digitalis purpurea* L., it was found that eight more new cardiotonic glycosides, Subst. A-VI, A-VII, A-VII', B-II, B-III, B-III', C-I', and C-II, are contained in the easily water-soluble fraction, and an unknown non-cardiotonic, X_1, is also present. Studies on their chemical structures are now in progress and their results will be reported in a subsequent paper.

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 encourage-

TABLE I. Properties of Substances Isolated

Substance	m.p. (°C)	U.V. λ_{max}^{EtOH} (mμ)	Rf value in paper chromatography				Reactions					Yield from seeds (%)
			Solv. 1	Solv. 2	Solv. 3	Solv. 4	$SbCl_3$	Raymond	Gregg-Gisvold	Keller-Kiliani H_2SO_4-layer	Keller-Kiliani AcOH-layer	
A-VI	237~239 acetate[a] (needles)	217	0.32	0.53	0.54	0.30	+	+	−	red	colorless	0.0022
C-I′	251~253 (needles)	218	0.30	0.55	0.50	0.28	−	+	−	brown	〃	0.0005
B-III	250~254 (amorph.)	218	0.23	0.55	0.45	0.22	+	+	+	red	brown	0.0056
C-II	238~242 (amorph.)	217	0.20	0.52	0.39	0.20	−	+	−	brown	colorless	0.0044
A-VII	242~245 (needles)	271[b]	0.19	0.42	0.34	0.17	+	+	−	red	〃	0.00005
A-VII′	221~224 (amorph.)	219	0.19	0.33	0.29	0.11	+	+	−	〃	〃	0.00007
B-II	214~218 (prisms)	310	0.30	0.42	0.43	0.32	−	+	+	brown	〃	0.005
B-III′	240~244 (amorph.)	218	0.23	0.56	0.43	0.27	+	+	+	red	blue	0.0015
X_1	118~120 (needles)						−	−	−	blue	colorless	0.025
Glucodigifucoside	194~197 (needles)	217	0.50	0.79		0.69	−	+	−	brown	〃	0.038
Digitalinum verum	231~234 (needles)	218	0.42	0.62	0.60	0.45	+	+	−	red	〃	0.15
Gitostin	252~254 (needles)	218	0.13	0.25	0.24	0.06	+	+	−	〃	〃	0.05
Neogitostin		218	0.09	0.14			+	+	−	〃	〃	

a) A-VI is a syrupy substance.
b) This maximum is the same as that of anhydrogitoxigenin derivative.

ment 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.

Experimental[6]

General Method

Paper Partition Chromatography—The easily water-soluble fraction obtained from the seeds of *Digitalis purpurea* L. was submitted to paper chromatography with four solvent systems (Figs. 1, 2, 3, and 4).

1) Apparatus: The same as described in Part II.[2]

2) Mobile phase and time for the solvents to move 25~35 cm.

Solvent system 1: Water-saturated MeCOEt; 4~6 hrs.
2: Upper layer of a mixture of *n*-BuOH : toluene : H_2O (6:3:1); 10~15 hrs.
3: Water-saturated *iso*-AmOH; 15~38 hrs.
4: Upper layer of a mixture of *n*-BuOH : benzene : H_2O (4:6:1); 10~15 hrs.

3) Stationary phase: The filter paper (Toyo Roshi No. 50) was impregnated with water as described in Part II.[2] With the solvent systems 1 and 3, paper impregnated with H_2O-Me_2CO(1:4) was employed, and with the system 2 and 4, the paper was impregnated with H_2O-Me_2CO(1:1).

4) Method of development: Ascending method at 18~22°.

Column Partition Chromatography—Celite 535 (Johns-Manville product) was used as the carrier and water saturated with organic solvent was used as the stationary phase. The mobile phases were the following three solvent systems:

Solvent system A: Water-saturated MeCOEt.
B: Water-saturated *iso*-AmOH.
C: The organic layer of *n*-BuOH-benzene-H_2O(1:2:1).

Ratio of Celite to the stationary phase was about 1:1(g./cc.), and the column was packed and eluted in the same way as described in Part II.[2]

Isolation of Unknown Substances

a) **Water-soluble Glycosides**—By the method described in Part II,[2] 100 kg. of seeds were extracted. The fractions of easily water-soluble glycosides were separated by adsorption chromatography on an alumina column with water-saturated BuOH as the developing solvent. Fractions contained the same crude glycosides shown as Fract. 8~16 in Part II,[2] obtained in 340 g.

b) **Isolation of Substance B-III′**—The above fraction was treated with 3 L. of MeOH and an insoluble material was obtained (7 g.). This material dissolved in a minimal amount of pyridine-MeOH (1:2) mixture was put onto the column (35 g. of Al_2O_3) and eluted with the same mixture. Coloring matter was adsorbed and the eluate was evaporated to dryness under a reduced pressure. The residue (4 g.) was recrystallized from pyridine-MeOH mixture to colorless powder, m.p. 238~241° (1.5 g.).

Paper chromatographic analysis of this material with all solvent systems indicated that it was not contaminated with other glycosides, and it was identified with substance B-III′.

The MeOH-soluble portion (Fraction I) was evaporated to dryness and yielded a residue of 333 g.

c) **Partition Chromatography of Fraction I with Solvent System A**—The above-mentioned Fraction I was dissolved in MeOH, added to 700 g. of Celite 535, and dried. Further 700 cc. of water was added to this mixture, stirred thoroughly, and put on top of a Celite column (7 kg. of Celite 535). The column was eluted with solvent system A and 10-L. fractions were collected. Distribution of this chromatography is shown in Fig. 5, each fraction was examined by paper chromatography, and the results are presented in Fig. 6.

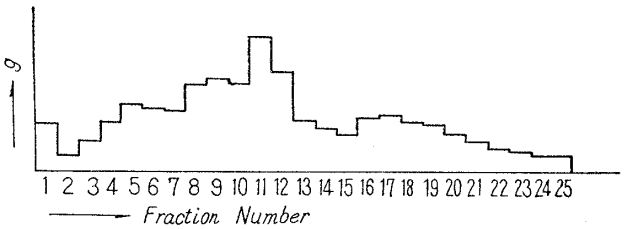


Fig. 5.
Partition Chromatography of Fraction I

Fraction Nos. 1~6 contained the materials corresponding to spots of digitalinum verum, glucodigifucoside, and A-V.

Fraction Nos. 7~12 (142.5 g.) contained majority of materials corresponding to spots of A-VI and

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

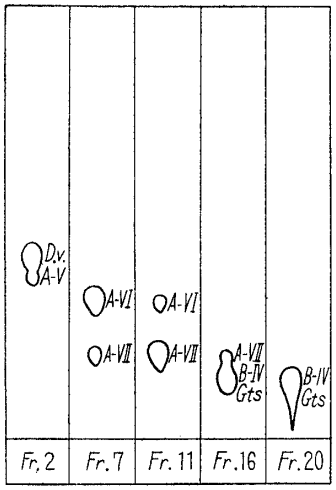


Fig. 6.
Paper Partition Chromatography of Each Fraction from Partition Chromatography of Fraction I
(With solvent system 1)

A-VII. This fraction was designated as Fraction II and further chromatographed. Fraction Nos. 13~20 contained the materials corresponding to spots of gitostin and B-IV.

d) **Alumina Adsorption Chromatography of Fraction II (Isolation of Substances X_1 and B-II)**— The above-mentioned Fraction II was dissolved in MeOH, added to 50~100 mesh silica gel, and dried. This silica gel mixture was suspended in $CHCl_3$ and poured on an alumina column (1 kg. of Al_2O_3). This was successively developed with $CHCl_3$, $CHCl_3$-MeOH mixture, and water-saturated BuOH. The results are given in Table II. Each fraction was examined by paper chromatography and a reproduction of chromatogram is shown in Fig. 7.

Table II. Adsorption Alumina Chromatography of Fraction II

Fract. No.	Solvent	Volume (cc.)	Weight (g.)		
1	$CHCl_3$	1,500	5.0	oil	
2	MeOH-$CHCl_3$ (1:99)	1,500	13.5		
3	〃 (2:98)	2,500	10.5	cryst. X_1	22.5
4	〃 (5:95)	3,000	19.5		
5	〃 (10:90)	2,500	8.0	cryst. B-II	5.1
6	〃 (25:75)	1,000	19.0	Fract. III	58.0
7	〃 (50:50)	3,000	39.0		
8	H_2O-BuOH	5,000	30.0	Fract. IV	

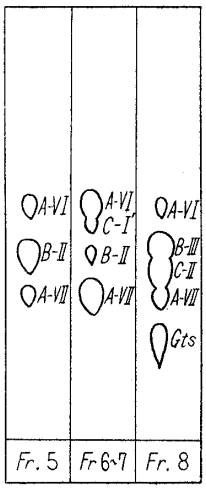


Fig. 7.
Paper Partition Chromatography of Each Fraction from Adsorption Chromatography of Fraction II
(With solvent system 3)

Fraction No. 1 and Fraction Nos. 2~4 did not contain cardiotonic glycoside. Colorless needles, m.p. 90~100°, were obtained by recrystallization from Me_2CO. Yield, 22.5 g. These crystals were tentatively named substance X_1.

Fraction No. 5 gave positive Legal and Raymond reactions. Colorless prisms, m.p. 205~208°, were obtained by recrystallization from MeOH-Et_2O mixture. Yield, 5.1 g. These crystals were a single substance and gave identical spot corresponding to B-II by paper chromatography with various solvent systems.

Fraction Nos. 6 and 7 gave positive Legal and Raymond reactions, and exhibited pale brown glacial AcOH layer and carmine-red H_2SO_4 layer in the Keller-Kiliani reaction. This fraction contained a majority of materials corresponding to A-VI and A-VII together with a small amount of other glycosides. This fraction was designated as Fraction III and further rechromatographed as described in (e).

Fraction No. 8 gave positive Legal and Raymond reactions, and exhibited brown glacial AcOH layer and carmine-red H_2SO_4 layer in the Keller-Kiliani reaction. This fraction contained majority of materials corresponding to B-III and C-II, was designated as Fraction IV, and further rechromatographed as described in (m).

e) **Partition Chromatography of Fraction III with Solvent System C**—The above-mentioned Fraction III was dried with 200 g. of Celite and mixed with 200 cc. of water. This mixture was placed on top of a Celite column (12 kg. of Celite 535), eluted with solvent system C, and fractions of 10 L. each were collected. Distribution of this chromatography is shown in Fig. 8. They were examined by paper chromatography and the results obtained are presented in Fig. 9.

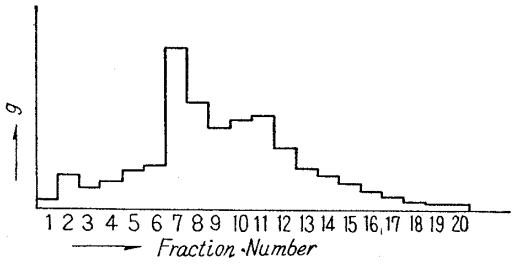


Fig. 8.
Partition Chromatography of Fraction III

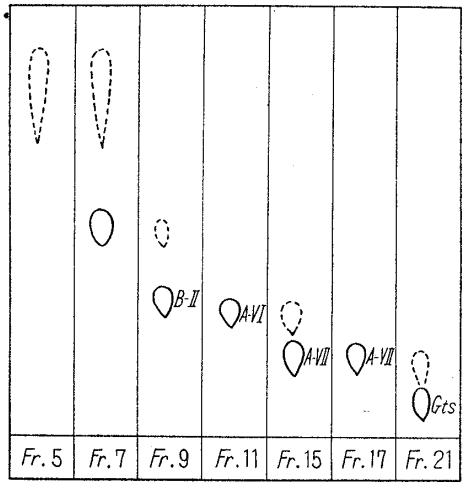


Fig. 9.
Parer Partition Chromatography of Each Fraction from Partition Chromatography of Fraction III
(With solvent system 4)

Fraction Nos. 10~14 (20.46 g.) contained majority of material corresponding to spot of A-VI and this fraction was designated as Fraction V. Fraction Nos. 15~20 (14.10 g.) contained majority of material corresponding to spot of A-VII and was designated as Fraction VI.

f) **Acid Hydrolysis of Fraction V**—To a solution of Fraction V (20.46 g.) dissolved in 500 cc. of MeOH, 250 cc. of 0.1*N* H_2SO_4 was added, the solution was refluxed on a water bath for 1 hr., MeOH was distilled off under a reduced pressure, the concentrated solution was extracted with four 300-cc. portions of $CHCl_3$, and $CHCl_3$ layer was washed twice with 100 cc. each of water. The aqueous layer was further extracted with five 300-cc. portions of BuOH-$CHCl_3$ (2:1) mixture and the organic layer was washed twice with 200 cc. each of water. The residual aqueous layer was deacidified with Amberlite IR-4B and evaporated to a syrup (3.24 g.). This syrup contained sugars which gave positive Gregg-Gisvold reaction, and exhibited dark blue glacial AcOH layer and pale brown H_2SO_4 layer in the Keller-Kiliani reaction. The $CHCl_3$ layer contained aglycones which were derived from glycosides containing 2,6-desoxysugar.

The BuOH-$CHCl_3$ layer was evaporated under a reduced pressure and the residue (Fraction VII, 11.31 g.) gave positive Legal and Raymond reactions, negative Gregg-Gisvold reaction, and exhibited brown glacial AcOH layer and carmine red H_2SO_4 layer in the Keller-Kiliani reaction. It consisted of the material corresponding to A-VI evidenced by paper chromatography.

g) **Acid Hydrolysis of Fraction VI**—Fraction VI (14.10 g.) was treated as in the above experiment (f). The $CHCl_3$ layer was evaporated and 6.29 g. of aglycones was obtained. The aqueous layer was evaporated to a syrup (1.36 g.), which gave positive Gregg-Gisvold reaction, and exhibited dark

blue glacial AcOH layer and pale brown H_2SO_4 layer in the Keller-Kiliani reaction.

The BuOH-$CHCl_3$ layer was evaporated and the residue (Fraction Ⅷ, 10.81 g.) gave positive Legal and Raymond reactions, negative Gregg-Gisvold reaction, and exhibited brown glacial AcOH layer and carmine-red H_2SO_4 layer in the Keller-Kiliani reaction. It consisted mostly of the material corresponding to A-Ⅶ.

h) **Partition Chromatography of Fraction VII with Solvent System A (Isolation of Substance C-I′)**—The above-mentioned Fraction Ⅶ (11.31 g.) was dried with 50 g. of Celite and mixed with 50 cc. of water. This mixture was placed on top of a column (600 g. of Celite 535), eluted with solvent system A, and fractions of 500 cc. each were collected. Each fraction was examined by paper chromatography and the results obtained are presented in Fig. 10.

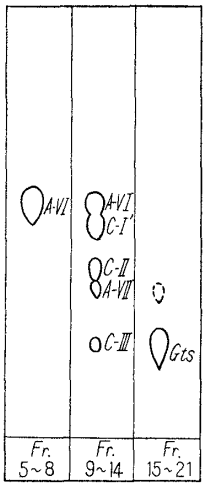


Fig. 10.
Paper Partition Chromatography of Each Fraction from Partition Chromatography of Fraction Ⅶ
(With solvent system 2)

Fraction Nos. 5~8 (6.76 g.) mostly contained the material corresponding to spot of A-VI and was designated as Fraction Ⅸ.

Fraction Nos. 9~14 (2.91 g.) contained the materials corresponding to spots of A-VI and C-I′. This fraction was dissolved in 20 cc. of MeOH and 20 cc. of H_2O was added to it. MeOH was distilled off under a reduced pressure and colorless precipitate was obtained. This material was identified with C-I′ by paper chromatography.

i) **Alumina-adsorption Chromatography of Fraction IX (Isolation of Substance A-VI Acetate)**—The above-mentioned Fraction Ⅸ (6.76 g.) was purified by chromatography (50 g. of Al_2O_3). This column was developed with 500 cc. of $CHCl_3$-MeOH (1:1) mixture, the eluate was evaporated, and colorless syrupy substance was obtained (2.49 g.). This syrupy substance gave a single spot corresponding to A-VI by paper chromatography. It was acetylated by the usual method with 50 cc. of Ac_2O by leaving at room temperature for 2 days and the reaction mixture was evaporated under a reduced pressure. The residue was recrystallized from EtOH to needles, m.p. 235~239°. Yield, 2.18 g. This substance was considered to be the acetate of A-VI.

j) **Alumina-adsorption Chromatography of Fraction VIII (Isolation of Substance C-II)**—The above-mentioned Fraction Ⅷ (10.81) was chromatographed over 100 g. of Al_2O_3, and this column was successively eluted with 500 cc. of $CHCl_3$-MeOH (5:1) mixture, 900 cc. of $CHCl_3$-MeOH (1:1) mixture, and 1000 cc. of water-saturated BuOH.

The portion eluted with $CHCl_3$-MeOH mixture contained the material corresponding to the spot of A-Ⅶ. The portion eluted with water-saturated BuOH contained the material corresponding to the spot of C-Ⅱ and colorless powder was obtained by recrystallization from hydr. BuOH. Yield, 0.83 g. It was identified with C-Ⅱ by paper chromatography with various solvent systems.

k) **Partition Chromatography of Fraction X with Solvent System B**—The above-mentioned Fraction Ⅹ (8.37 g.) was dried with 50 g. of Celite and mixed with 50 cc. of water. The mixture was put on top of a Celite column (1.5 kg. of Celite 535), eluted with solvent system B, and fractions of 500 cc. each were collected. Each fraction was examined by paper chromatography and a reproduction of its chromatogram is shown in Fig. 11.

Fraction Nos. 4~7 contained the materials corresponding to spots of A-VI and A-Ⅶ, and fraction Nos. 8~13 (Fraction Ⅺ, 2.65 g.) contained the materials corresponding to spots of A-Ⅶ and A-Ⅶ′.

l) **Partition Chromatography of Fraction XI with Solvent System C (Isolation of Substance A-VII and A-VII′)**—The above-mentioned Fraction Ⅺ (2.65 g.) was dried with 30 g. of Celite and mixed with 30 cc. of water. This was placed on top of a Celite column (600 g. of Celite 535), eluted with solvent system C, and fractions of 800 cc. each were collected.

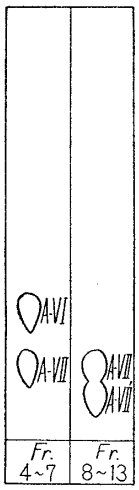


Fig. 11.
Paper Partition Chromatography of Each Fraction from Partition Chromatography of Fraction X
(With solvent system 4)

Fraction Nos. 7~9 contained the material corresponding to spot of A-IV. Fraction Nos. 10~14 contained the material corresponding to spot of A-VII, and was recrystallized from hydr. MeOH to needles, m.p. 238~240°. Yield, 0.07 g. They were identified with A-VII by paper chromatography.

Fraction Nos. 17~21 contained the material corresponding to the spot of A-VII′ and was recystallized from MeOH-Me_2CO-Et_2O to colorless powder, m.p. 213~219°. Yield, 0.05 g. It was identified with A-VII′ by paper chromatography.

m) **Isolation of Substance B-III from Fraction IV**—The above-mentioned Fraction IV (30 g.) was treated with 300 cc. of EtOH and the precipitate (m.p. 244~247°) was collected. Yield, 3.59 g. It was identified with B-III by paper chromatography. The EtOH-soluble portion was designated as Fraction XII (26 g.).

n) **Alumina-adsorption Chromatography of Fraction XII (Isolation of Substances B-III and C-II)**—The above-mentioned Fraction XII (26 g.) was chromatographed over 500 g. of alumina, developed with water-saturated BuOH, and fractions of 250 cc. each were collected. Each fraction was examined by paper chromatography and the results are presented in Fig. 12.

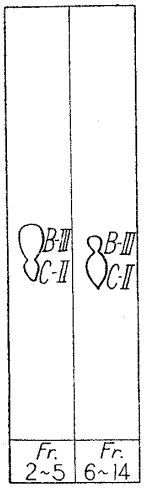


Fig. 12.
Paper Partition Chromatography of Each Fraction from Adsorption Chromatography of Fraction XII
(With solvent system 3)

Fraction Nos. 2~5 was treated with 200 cc. of EtOH, and the precipitate (m.p. 244~249°) (2.06 g.) was identified with B-III by paper chromatography.

Fraction Nos. 6~14 was heated with 100 cc. of water-saturated BuOH until in solution and 100 cc. of BuOH was added. After one day, the precipitate (m.p. 231~235°; 3.80 g.) obtained was identified with C-II by paper chromatography.

Properties of Unknown Substances

1) **Substance A-VI Acetate**: Repeatedly recrystallized from EtOH to needles, m.p. 237~239°; U.V. λ_{max}^{EtOH} 217 mμ. It gives positive Legal and Raymond reactions, negative Gregg-Gisvold reaction, and exhibits colorless glacial AcOH layer and carmine-red H_2SO_4 layer in the Keller-Kiliani reaction. It is easily soluble in $CHCl_3$, soluble in Et_2O and EtOH, and insoluble in water.

2) **Substance C-I′**: Recrystallized from hydr. *iso*-PrOH to needles, m.p. 251~253°; U.V. λ_{max}^{EtOH} 218 mμ. It gives positive Legal and Raymond reactions, negative Gregg-Gisvold reaction, and

exhibits colorless glacial AcOH layer and pale brown H_2SO_4 layer in the Keller-Kiliani reaction. It is easily soluble in MeOH-$CHCl_3$(1:1) mixture, soluble in MeOH, and insoluble in Me_2CO, Et_2O, and water.

3) **Substance B-III**: Repeatedly recrystallized from MeOH-Me_2CO to colorless powder, m.p. 250~254°; U. V. λ_{max}^{EtOH} 218 mμ. It gives positive Legal, Raymond, and Gregg-Gisvold reactions, and exhibits brown glacial AcOH layer and carmine-red H_2SO_4 layer in the Keller-Kiliani reaction. It is easily soluble in MeOH-$CHCl_3$(1:1) mixture, soluble in MeOH, sparingly soluble in EtOH and water, and insoluble in Me_2CO and Et_2O.

4) **Substance C-II**: Repeatedly recrystallized from hydr. *n*-BuOH to colorless powder, m.p. 238~242°; U. V. λ_{max}^{EtOH} 217 mμ. It gives positive Legal and Raymond reactions, negative Gregg-Gisvold reaction, and exhibits colorless glacial AcOH layer and pale brown H_2SO_4 layer in the Keller-Kiliani reaction. It is easily soluble in MeOH and EtOH, soluble in water, and insoluble in Me_2CO and Et_2O.

5) **Substance A-VII**: Recrystallized from hydr. MeOH to needles, m.p. 242~245°; U. V. λ_{max}^{EtOH} 271 mμ. It gives positive Legal and Raymond reactions, and negative Gregg-Gisvold reaction, and exhibits colorless glacial AcOH layer and carmine-red H_2SO_4 layer in the Keller-Kiliani reaction. It is soluble in MeOH-$CHCl_3$(1:1) mixture, and sparingly soluble in MeOH and water.

6) **Substance A-VII′**: Recrystallized from MeOH-Me_2CO-Et_2O to colorless powder, m.p. 221~224°; U. V. λ_{max}^{EtOH} 219 mμ. It gives positive Legal and Raymond reactions, negative Gregg-Gisvold reaction, and exhibits colorless glacial AcOH layer and carmine-red H_2SO_4 layer in the Keller-Kiliani reaction. It is easily soluble in MeOH and water, and insoluble in Me_2CO and Et_2O.

7) **Substance B-II**: Repeatedly recrystallized from MeOH and MeOH-Et_2O to prisms, m.p. 214~218°; U. V. λ_{max}^{EtOH} 310 mμ. It gives positive Legal, Raymond, and Gregg-Gisvold reactions, and negative Keller-Kiliani reaction. It is easily soluble in MeOH and EtOH, soluble in water, and insoluble in Et_2O.

8) **Substance B-III′**: Repeatedly recrystallized from pyridine-MeOH to colorless powder, m.p. 240~244°; U. V. λ_{max}^{EtOH} 218 mμ. It gives positive Legal, Raymond, and Gregg-Gisvold reactions, and exhibits dark blue glacial AcOH layer and carmine-red H_2SO_4 layer in the Keller-Kiliani reaction. It is easily soluble in pyridine, soluble in MeOH-$CHCl_3$(1:1) mixture, sparingly soluble in MeOH, and insoluble in Me_2CO, Et_2O, and water.

9) **Substance X_1**: Repeatedly recystallized from Me_2CO to prisms, m.p. 118~120°. It is negative to Legal, Raymond, Gregg-Gisvold, and Keller-Kiliani reactions. It is easily soluble in MeOH, EtOH, and water, soluble in Me_2CO, and insoluble in Et_2O.

Summary

Several new glycosides were isolated from digitalis seeds. Five substances, A-VI acetate, C-I′, A-VII, B-II, and X_1, were obtained as crystals, and four substances, B-III, C-II, A-VII′, and B-III′, were obtained as a colorless powder. In accordance with their colorations and absorption spectra, it was assumed that A-VI, A-VII′, B-III, and B-III′ belong to gitoxigenin series, C-I′ and C-II to digitoxigenin series, and B-II to digitanol series.

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