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Studies on the Constituents of Palmae Plants. IV.[1a] The Constituents of the Leaves of *Sabal causiarum* BECC.[2]

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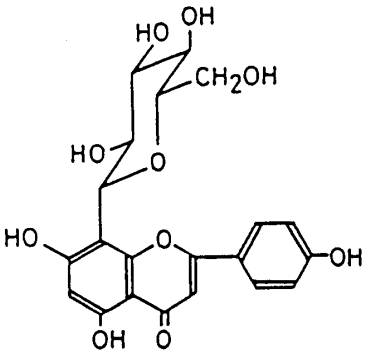
The constituents of the leaves of *Sabal causiarum* BECC. have been investigated. Vitexin, methyl proto-deltonin, methyl proto-causiaroside I(=26-*O*-β-D-glucopyranosyl 22-*O*-methyl-25(*R*)-furost-5-en-3β,26-diol 3-*O*-[α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→4)][α-L-rhamnopyranosyl(1→2)]-β-D-glucopyranoside) and causiaroside II(=3β,16β-dihydroxypregn-5-en-20-one 3-*O*-[α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→4)][α-L-rhamnopyranosyl(1→2)]-β-D-glucopyranosyl 16-*O*-[δ-(β-D-glucopyranosyloxy)-γ-methyl]-valerate) were isolated and identified. This is the first isolation and characterization of the latter two compounds from a natural source, and these results are interesting from the standpoint of the biogenesis of the steroidal glycosides of the Palmae plants.

Keywords——*Sabal causiarum*; Palmae; steroidal saponin; methyl proto-deltonin; methyl proto-causiaroside I; causiaroside II; 20,22-secofurostanol; C-glycosyl flavonoid; vitexin

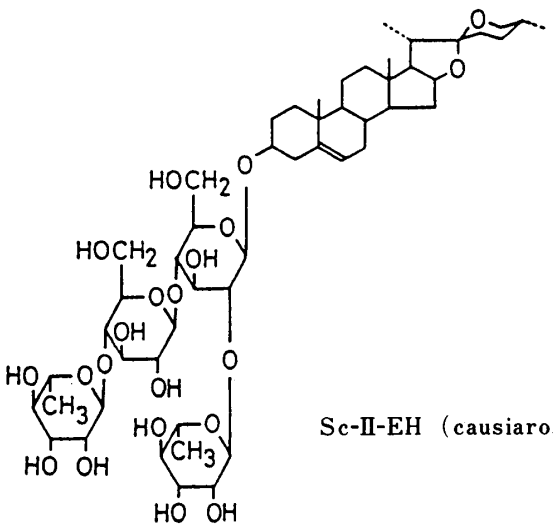
In the previous paper[1] we reported the isolation and structure elucidation of steroidal glycosides and flavonoids from Palmae plants, *Trachycarpus fortunei* (HOOK.) H. WENDL., *T. wagnerianus* BECC., *Rhapis excelsa* HENRY, *R. humilis* BL., and *Chamaerops humilis* L. A series of chemotaxonomical studies on the flavonoids and steroidal glycosides of plants of the Palmae family has been undertaken by us, and intimate relationships have been found between the chemical structures of constituents and the systematic classification of the plants. The present paper is mainly concerned with the studies on the constituents of the leaves of *Sabal causiarum* BECC.

The habitat of *Sabal causiarum* BECC. (Japanese name: onisabal) is Central America and these plants cultivated in Japan as roadside tree or garden plants. The constituents of *S. causiarum* have not been reported, so we started a study on the constituents of this plant.

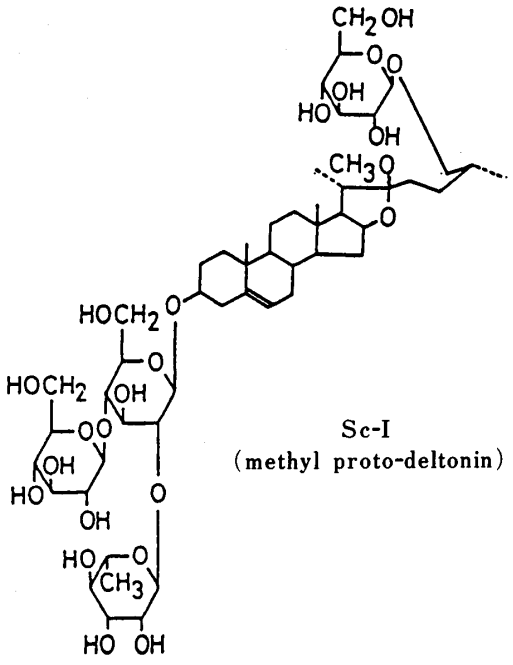
The fresh leaves of *Sabal causiarum* harvested in Chichi island, Ogasawara islands, Tokyo, in January 1985, were chopped and extracted with methanol at room temperature. The methanol extract was suspended in water and the suspension was extracted with ether followed with *n*-butanol saturated with water to afford three fractions, namely ether-soluble, butanol-soluble and water-soluble fractions. The butanol-soluble fraction was chromatographed on a Sephadex LH-20 column to yield three fractions, of which the first fraction gave a positive Ehrlich reaction[3] on a thin layer chromatographic (TLC) plate (Fr. 1), the second fraction gave a negative Ehrlich reaction and ferric trichloride reaction (Fr. 2), and the third fraction gave a positive ferric trichloride reaction (Fr. 3). Three compounds, tentatively named Sc-I, Sc-II, and Sc-III in order of decreasing polarity, were separated from Fr. 1 by column chromatography on Avicel followed by octadecyl silica (ODS) and silica gel. On the other hand, a flavonoid compound tentatively named Sc-f_1, was obtained from Fr. 3 by column chromatography on Avicel. Based on the general properties, Sc-f_1 and Sc-I were deduced to be vitexin[4] and methyl proto-deltonin[5] and they were characterized by comparing the TLC behavior, and the infrared (IR) and nuclear magnetic resonance (NMR)



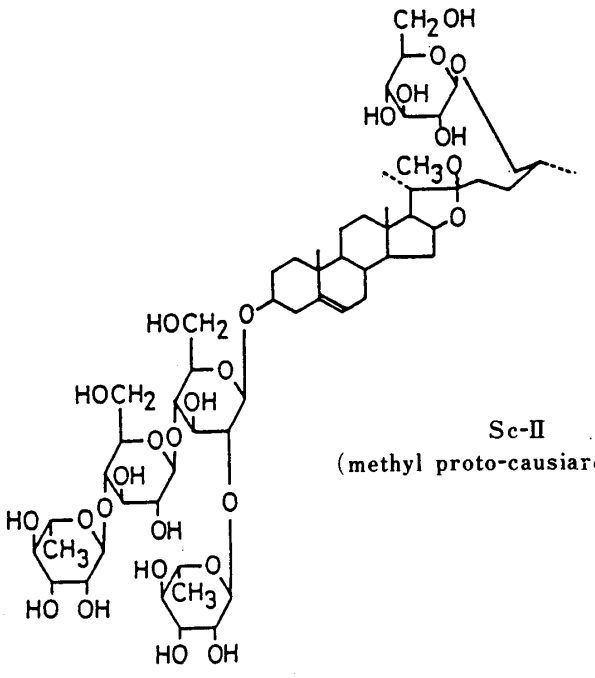
Sc-f_1 (vitexin)



Sc-II-EH (causiaroside I)



Sc-I
(methyl proto-deltonin)



Sc-II
(methyl proto-causiaroside I)

Chart 1

spectra with those of respective authentic samples.

Sc-II, $C_{58}H_{96}O_{27} \cdot H_2O$, was positive in the Liebermann–Burchard reaction and in the Ehrlich reaction. The IR spectrum of Sc-II shows a strong absorption band due to hydroxyl groups and the ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectrum of Sc-II shows five anomeric carbon signals and one methoxyl group signal. On enzymatic hydrolysis with almond emulsin, Sc-II afforded glucose and a prosapogenin (Sc-II-EH), which gave diosgenin, glucose and rhamnose on acidic hydrolysis. The IR spectrum of Sc-II-EH showed strong absorption bands due to hydroxyl and 25(*R*)-spiroketal groups,[6] while the ^{13}C-NMR spectrum of Sc-II-EH showed four anomeric carbon signals at δ 100.4, 101.7, 102.8 and 105.0 ppm, and two methyl signals (δ 19.0, 19.1 ppm) corresponding to C-6 methyl groups of two rhamnoses. Consequently, Sc-II-EH was suggested to be diosgenin tetraoside, which contains 2 mol each of glucose and rhamnose. Methylation of Sc-II-EH by Hakomori's

method[7] afforded a per-*O*-methyl derivative, which was methanolized to afford diosgenin, methyl 2,3,6-tri-*O*-methylglucopyranoside, methyl 3,6-di-*O*-methylglucopyranoside and methyl 2,3,4-tri-*O*-methylrhamnopyranoside. After partial methanolysis of the per-*O*-methyl derivative of Sc-II-EH with methanolic 0.5 N hydrochloric acid, the reaction mixture was further methylated by Hakomori's method to afford two products, tentatively named compounds A and B. The ^{1}H-NMR spectra of compounds A and B suggested these compounds to be permethylates of diglycoside and triglycoside, respectively. On methanolysis with methanolic 1 N hydrochloric acid, diosgenin, methyl 2,3,4,6-tetra-*O*-methylglucopyranoside and methyl 2,3,6-tri-*O*-methylglucopyranoside were formed from the former, and diosgenin, methyl 2,3,4,6-tetra-*O*-methylglucopyranoside, methyl 3,6-di-*O*-methylglucopyranoside, and methyl 2,3,4-tri-*O*-methylrhamnopyranoside from the latter. Accordingly, compounds A and B were concluded to be a permethylate of diosgenin 3-*O*-glucopyranosyl(1→4)-glucopyranoside and a permethylate of diosgenin 3-*O*-[glucopyranosyl(1→4)][rhamnopyranosyl(1→2)]-glucopyranoside (=deltonin),[1c] respectively. Based on the ^{13}C-NMR spectrum of Sc-II, which indicated a furostane skeleton and C-22 methoxyl group, the structure of Sc-II was deduced to be 26-*O*-glucopyranosyl 22-*O*-methyl-25(*R*)-furost-5-en-3β,26-diol 3-*O*-[L-rhamnopyranosyl(1→4)-*O*-glucopyranosyl(1→4)][L-rhamnopyranosyl(1→2)]-D-glucopyranoside. Based on the chemical shifts and C_1–H_1 coupling constants of the four anomeric carbons of Sc-II, 160 Hz (δ 100.1 ppm; glc), 161 Hz (δ 105.0 ppm; glc, glc (C-26)), 172 Hz (δ 101.7 ppm; rha), and 176 Hz (δ 102.7 ppm; rha), the configurations of glucose were assigned to be β, while those of rhamnose were all α.

Finally, the structures of Sc-II and SE-II-EH were characterized to be 26-*O*-β-D-glucopyranosyl 22-*O*-methyl-25(*R*)-furost-5-en-3β,26-diol 3-*O*-[α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→4)][α-L-rhamnopyranosyl(1→2)]-β-D-glucopyranoside and diosgenin 3-*O*-[α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→4)][α-L-rhamnopyranosyl(1→2)]-β-D- glucopyranoside, respectively. The compound Sc-II-EH and its furostanol type compound (Sc-II) described above are new steroidal oligosides and we propose the names of causiaroside I for the former and methyl proto-causiaroside I for the latter.

Sc-III was positive in the Liebermann–Burchard reaction and it was suggested to be a steroidal derivative. The IR spectrum of Sc-III showed strong absorptions due to hydroxyl, ester and carbonyl groups, while the ^{13}C-NMR spectrum of Sc-III showed five anomeric carbon signals. On acidic hydrolysis, Sc-III gave Δ^{16}-pregnenolone, glucose and rhamnose. On the other hand, Sc-III was treated in methanol saturated with potassium carbonate at room temperature to afford two compounds, tentatively named compounds I and II, respectively. The ^{13}C-NMR spectrum of compound I showed four anomeric carbon signals at δ 100.4, 101.8, 105.1, and 102.9 ppm, two C_6-carbon signals of rhamnose at δ 19.1 and 19.0 ppm, and twenty-one carbon signals due to the aglycone. By comparing the ^{13}C-NMR spectra of compound I and Δ^{16}-pregnenolone obtained by acidic hydrolysis of Sc-III, it was revealed that the C_{16}–C_{17} double bond of the latter was not present in the former, and the C_{16}-carbon of the former, which showed the carbon signal at δ 72.0 ppm, was suggested to bear a secondary hydroxyl group. Based on the ^{13}C-NMR spectrometric analysis, compound I was deduced to be 16-hydroxypregnenolone glycoside containing 2 mol each of glucose and rhamnose. The structure of the sugar moiety of compound I was suggested to be identical with that of Sc-II-EH consisting of the same monosaccharide components as compound I, and this was proved by direct comparison of the ^{13}C-NMR spectra. On the other hand, the ^{1}H-NMR spectral analysis of compound II acetate prepared from Sc-III suggested it to be δ-(β-D-glucopyranosyloxy)-γ-methylvaleric acid methyl ester tetraacetate, and this was confirmed by comparing the ^{1}H-NMR spectrum with that of an authentic sample. The ^{13}C-NMR spectrum of Sc-III indicated that the sugar moiety conjugated at the C_3-hydroxyl group was the same as that of Sc-II-EH, and the C_{16}-carbon signal at δ 75.0 ppm was shifted to lower field than

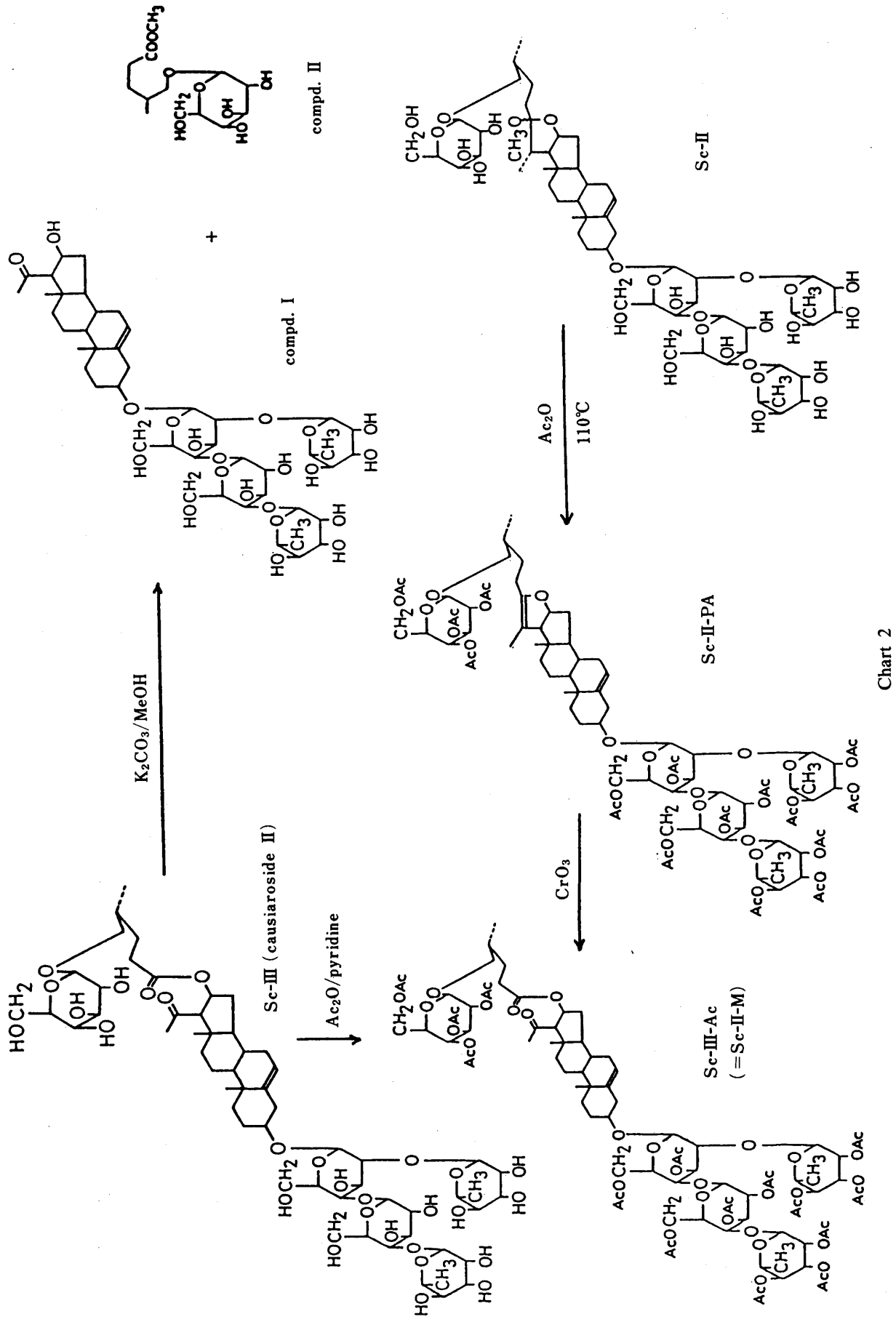


Chart 2

TABLE I. ^{13}C Chemical Shifts of Sc-II, Compd. I and Sc-III in Pyridine-d_5 at 50 °C

Compounds		Sc-II	Compd. I	Sc-III
Aglycone	1	37.9	38.0	38.0
	2	30.6	30.7	30.7
	3	78.8	78.6	78.9
	4	39.4	39.5	39.5
	5	140.7	141.0	141.5
	6	121.8	121.7	121.6
	7	32.6	32.8	32.9
	8	32.1	32.5	32.5
	9	50.7	50.7	51.0
	10	37.5	37.6	37.6
	11	21.5	21.6	21.3
	12	40.2	39.3	38.7
	13	41.2	44.9	42.9
	14	56.9	55.1	54.6
	15	32.7	32.3	31.0
	16	81.5	72.0	75.0
	17	64.5	82.3	75.3
	18	16.8	15.1	14.4
	19	19.9	19.9	20.0
	20	40.9	207.0	204.8
	21	16.8	32.0	31.6
	22	112.7		173.1
	23	31.2		30.5
	24	28.7		29.6
	25	34.7		34.0
	26	75.4		67.1
	27	17.7		17.5
C_{22}-OCH_3		47.7		
C-3 sugars				
Glucose	1	100.1	100.4	100.4
	2	78.4	78.6	78.6
	3	76.3	76.5	76.4
	4	82.0	82.2	82.2
	5	77.8	77.9	77.9
	6	61.3	61.6	61.5
Rhamnose ($\rightarrow^2$glc)	1	101.7	101.8	101.8
	2	72.6	72.7	72.7
	3	72.9	73.1	73.0
	4	74.1	74.3	74.2
	5	69.7	69.7	69.7
	6	19.1	19.1	19.1
Glucose ($\rightarrow^4$glc)	1	105.0	105.1	105.1
	2	75.4	75.4	75.4
	3	77.3	77.4	77.4
	4	77.4	77.6	77.6
	5	76.6	76.8	76.8
	6	62.1	62.4	62.4
Rhamnose ($\rightarrow^4$glc)	1	102.7	102.9	102.9
	2	72.7	72.8	72.8
	3	73.0	73.0	73.0
	4	74.3	74.5	74.5
	5	70.6	70.8	70.8
	6	19.0	19.0	19.0
C-26 sugar				
Glucose	1	105.0		105.0
	2	75.3		75.1
	3	78.1		78.6
	4	72.0		72.2
	5	78.6		78.6
	6	63.2		63.4

that of compound I (δ 72.0 ppm). Accordingly, Sc-III was inferred to have an ester linkage at the C_{16}-hydroxyl group of compound II, namely it is a 20,22-seco derivative of Sc-II. Finally, the structure of Sc-III was established to be 3β,16β-dihydroxypregn-5-en-20-one-3-*O*-[α-L-rhamnopyranosyl(1$\rightarrow$4)-β-D-glucopyranosyl(1$\rightarrow$4)][α-L-rhamnopyranosyl(1$\rightarrow$2)]-β-D-glucopyranosyl 16-*O*-[δ-(β-D-glucopyranosyloxy)-γ-methyl]-valerate by direct comparison of Sc-III acetate with an authentic sample prepared from Sc-II by heating in acetic anhydride followed by oxidation with chromic anhydride. The Sc-III described above is a new steroidal oligoside and we would like to propose the name "causiaroside II."

In this paper we report the isolation and the structure elucidation of a flavonoidal glucoside, vitexin, and three steroidal glycosides, namely methyl proto-deltonin, methyl proto-causiaroside I and causiaroside II, from the leaves of *Sabal causiarum* BECC. Among these steroidal glycosides, methyl proto-causiaroside I is a steroidal saponin which has an additional 1 mol of rhamnose on the oligosaccharide moiety conjugated to the C_3-hydroxyl group of methyl proto-deltonin, and this is the first report of its isolation from a natural source. The isolation of a seco-furostanol compound formed by oxidative fission at C_{20}–C_{22} of the E-ring of furostanol was reported by Kawasaki *et al.* from *Dioscorea tenuipes* FRANCH. *et* SAVAT.[9] (Dioscoreaceae), and the isolation of causiaroside II from *Sabal causiarum* BECC. is the second such example from natural sources. The coexistence of a 20,22-secofurostanol,

causiaroside II, and a furostanol glycoside, causiaroside I, in the same plant is a very interesting finding.

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus (hot-stage type) and are uncorrected. The optical rotations were measured with a JASCO DIP-140 polarimeter at room temperature. The IR spectra were recorded with a JASCO IRA-1 or IR-810, and the ultraviolet (UV) spectra were measured with a Hitachi 340 spectrophotometer. The NMR spectra were recorded with a JEOL JNM-FX 100 (100 MHz for ^{1}H-NMR and 25 MHz for ^{13}C-NMR) or JEOL JNM-GX 400 (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR) and the chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. TLC was performed on precoated Kieselgel 60 F_{254} plates (Merck) using $CHCl_3$–MeOH–H_2O (7 : 3 : 0.4, v/v), and detection was achieved by spraying 10% H_2SO_4 or Ehrlich reagent followed by heating or by spraying ferric chloride reagent. Gas liquid chromatography (GLC) was run on a Shimadzu GC-6A unit equipped with a flame ionization detector. Condition 1: column, 5% SE-52 on Chromosorb W 3 mm × 2 m; column temperature, 200 °C; injection temperature, 220 °C; carrier gas, N_2, 1.0 kg/cm^2. Condition 2: column, 5% neopentylglycol succinate on Shimalite W 3 mm × 2 m; column temperature, 160 °C; injection temperature, 180 °C; carrier gas, N_2, 1.0 kg/cm^2.

Extraction and Isolation of the Compounds from the Leaves——The fresh leaves (14.3 kg) of *Sabal causiarum* Becc. harvested at Tokyo-to Ogasawara Subtropical Agricultural Experiment Station in January 1985 were chopped and extracted with MeOH (40 l × 3) at room temperature. The MeOH extract was evaporated to dryness *in vacuo*. The residue (725 g) was suspended in water (1.5 l) and partitioned with ether (500 ml × 3). The ether layer was concentrated *in vacuo* to afford the ether extract (250 g), and the aqueous layer was partitioned with BuOH saturated with water (500 ml × 3). The BuOH layer was concentrated under reduced pressure to afford the BuOH extract (96 g). The BuOH extract was subjected to column chromatography on Sephadex LH-20 with MeOH to afford four fractions, Fr. 1 (57.4 g), Fr. 2 (20.0 g), Fr. 3 (11.7 g) and Fr. 4 (3.8 g). Fr. 1 was subjected to column chromatography on Avicel with $CHCl_3$–MeOH–H_2O (8 : 2 : 1, v/v, lower layer) followed with (7 : 3 : 1, v/v, lower layer) and (13 : 7 : 2, v/v, lower layer) to yield three fractions (Fr. A (5.2 g), Fr. B (27.5 g) and Fr. C (23.6 g)). Fr. B was subjected to column chromatography on ODS with 80% MeOH to give an Sc-III-rich fraction and Sc-I, Sc-II-rich fraction. The Sc-III-rich fraction was evaporated to dryness *in vacuo* and the residue was dissolved in MeOH (5 ml). AcOEt (200 ml) was added to this solution, and the precipitate (Sc-III, 0.24 g) was collected by filtration. On the other hand, the Sc-I, Sc-II-rich fraction was subjected to column chromatography on silica gel with $CHCl_3$–MeOH–H_2O (13 : 7 : 1, v/v) to afford an Sc-I-rich fraction and an Sc-II-rich fraction. Each fraction was refluxed with MeOH (100 ml) for 1 h and each solution was concentrated to 10 ml. AcOEt (300 ml) was added to each methanolic solution, and the precipitate was collected by filtration to afford Sc-I (0.56 g) and Sc-II (3.53 g), respectively.

Fr. 3 was purified by column chromatography on Avicel with $CHCl_3$–MeOH–H_2O (7 : 3 : 1, v/v, lower layer) to afford Sc-f_1 (0.33 g) as yellow needles from MeOH.

Properties of Sc-f_1, Sc-I, Sc-II and Sc-III——Sc-f_1: Yellow needles from MeOH. mp 264—266 °C (dec.). $[\alpha]_D^{20}$ −21.6° (c=0.23, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3500—3300, 1655, 1610. Sc-f_1 was identified as vitexin by comparing the TLC behavior, and the IR and ^{1}H-NMR spectra with those of an authentic sample. Sc-I: A white powder from MeOH–AcOEt. (mp 186—190 °C (dec.)). $[\alpha]_D^{20}$ −75.1° (c=0.65, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3600—3200 (OH). ^{13}C-NMR (pyridine-d_5) δ: 19.1 (C_1 of rha), 100.5 (C_1 of glc), 101.8 (C_1 of rha), 105.0 (C_1 of glc), 105.2 (C_1 of glc). Sc-I was identified as methyl proto-deltonin by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample. Sc-II: A white powder from MeOH–AcOEt. (mp 192—194 °C (dec.)). $[\alpha]_D^{20}$ −72.6° (c=1.02, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3600—3200 (OH). ^{13}C-NMR (pyridine-d_5) δ: Table I. *Anal.* Calcd for $C_{58}H_{96}O_{27}\cdot H_2O$: C, 56.03; H, 7.94. Found: C, 55.86; H, 7.84. Sc-III: A white powder from MeOH–AcOEt. (mp 172—175 °C (dec.)). $[\alpha]_D^{20}$ −47.2° (c=0.66, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3600—3200, 1740, 1710. ^{13}C-NMR (pyridine-d_5) δ: Table I.

Acetylation of Sc-III——Acetic anhydride (1 ml) was added to a solution of Sc-III (10 mg) in pyridine (2 ml), and the solution was left at room temperature overnight. The reaction mixture was poured into ice water, and the precipitate was collected by filtration to afford a pentadeca-acetate (12 mg) as a white powder from hexane–chloroform. (mp 125—130 °C). *Anal.* Calcd for $C_{87}H_{122}O_{43}$: C, 56.30; H, 6.63. Found: C, 56.57; H, 6.75.

Enzymatic Hydrolysis of Sc-II——A solution of Sc-II (0.25 g) in water (10 ml) was incubated with almond emulsin (0.05 g) at 37 °C for 8 h. The precipitate was collected by filtration to afford Sc-II-EH (0.12 g) as colorless needles from aqueous MeOH. The filtrate was evaporated to dryness *in vacuo* and the residue was derivatized to the trimethylsilyl (TMS) ether, which was examined by GLC (condition 1). t_R (min) 6.2, 8.3 (glucose). Sc-II-EH: Colorless needles from aqueous MeOH. mp 284—287 °C (dec.). $[\alpha]_D^{20}$ −94.2° (c=0.39, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3600—3200 (OH), 980, 920, 900, 860 (intensity 920 < 900, 25(R)-spiroketal). *Anal.* Calcd for $C_{51}H_{82}O_{21}\cdot 1/2H_2O$: C, 58.88; H, 8.04. Found: C, 58.99; H, 8.07.

Acidic Hydrolysis of Sc-II-EH——Sc-II-EH (3.0 mg) was hydrolyzed with 2 N HCl in 50% dioxane (0.5 ml) by refluxing for 2 h on a water bath, then the reaction mixture was cooled, neutralized with $NaHCO_3$, and evaporated to

dryness under reduced pressure. The residue was examined by TLC (solvent: hexane–acetone (3 : 1, v/v)) *Rf* 0.52 (diosgenin). The sugar components in the residue were derivatized to the TMS ether and examined by GLC. GLC (condition 1); t_R (min): 1.9, 2.5 (rhamnose), 6.2, 8.3 (glucose).

Methylation of Sc-II-EH by Hakomori's Method——According to Hakomori's method, NaH (200 mg) was washed with anhydrous benzene followed by petroleum ether, then warmed with dimethylsulfoxide (DMSO, 8 ml) at 65 °C in an oil bath for 1 h with stirring under an N_2 flow. A solution of Sc-II-EH (70 mg) in a small amount of DMSO (0.5 ml) was then added and the mixture was stirred for 1 h under an N_2 flow. CH_3I (10 ml) was added under cooling with ice-water and the reaction mixture was allowed to stand at room temperature for 1 h with stirring. After dilution with water (50 ml), the reaction mixture was extracted with $CHCl_3$ (10 ml × 3) and the organic layer was washed with water, dried and evaporated to dryness. The residue was chromatographed on silica gel with hexane–acetone (3 : 1, v/v) to afford the per-*O*-methylate of Sc-II-EH (70 mg). Per-*O*-methylate of Sc-II-EH: Colorless needles from aqueous MeOH. mp 146—147 °C. IR ν_{max}^{Nujol} cm^{-1}: OH (nil). ^{1}H-NMR ($CDCl_3$) δ: 0.79 (3H, s, CH_3), 1.01 (3H, s, CH_3), 3.38—3.57 (OCH_3), 4.30 (1H, d, J=7 Hz, C_1-H of glc), 4.33 (1H, d, J=7 Hz, C_1-H of glc), 4.99 (1H, br s, C_1-H of rha), 5.23 (1H, br s, C_1-H of rha), 5.34 (1H, m, olefinic H). *Anal.* Calcd for $C_{62}H_{104}O_{21} \cdot 1/2H_2O$: C, 62.34; H, 8.86. Found: C, 62.32; H, 8.87.

Methanolysis of Per-*O*-methylate of Sc-II-EH——The per-*O*-methylate of Sc-II-EH (3 mg) was refluxed with methanolic 5% HCl (1 ml) for 3 h. After cooling, the reaction mixture was neutralized with Ag_2CO_3 and the resulting inorganic precipitate was filtered off. The filtrate was concentrated to dryness *in vacuo*. The residue was derivatized to the TMS ether and examined by GLC. GLC (condition 2); t_R (min): 3.0 (methyl 2,3,4-tri-*O*-methylrhamnopyranoside), 7.1, 10.2 (methyl 2,3,6-tri-*O*-methylglucopyranoside), 8.1, 9.4 (methyl 3,6-di-*O*-methylglucopyranoside).

Partial Methanolysis of Per-*O*-methylate of Sc-II-EH——A solution of the per-*O*-methylate of Sc-II-EH (30 mg) in 10 ml of methanolic 0.5 N HCl was refluxed for 2 h. After cooling, the reaction mixture was neutralized with Ag_2CO_3 and the inorganic precipitate was removed by filtration. The filtrate was evaporated to dryness *in vacuo*. The residue was methylated by Hakomori's method. The reaction mixture was treated in the usual way. The product was chromatographed on silica gel with hexane–acetone (3 : 1, v/v) to afford two compounds, tentatively named compound A (6 mg) and compound B (5 mg). Compound A: A colorless syrup (not crystallized). IR ν_{max}^{Nujol} cm^{-1}: OH (nil). ^{1}H-NMR ($CDCl_3$) δ: 0.72 (3H, s, CH_3), 0.95 (3H, s, CH_3), 3.32—3.56 (OCH_3), 4.30 (2H, d, J=7 Hz, C_1-H of glc × 2). Compound B: A colorless syrup. IR ν_{max}^{Nujol} cm^{-1}: OH (nil). ^{1}H-NMR ($CDCl_3$) δ: 0.78 (3H, s, CH_3), 1.01 (3H, s, CH_3), 3.39—3.64 (OCH_3), 4.34 (1H, d, J=7 Hz, C_1-H of glc), 4.38 (1H, d, J=7 Hz, C_1-H of glc), 5.26 (1H, s, C_1-H of rha). Compound B was identified as deltonin per-*O*-methylate by comparing the TLC behavior, and the ^{1}H-NMR spectrum with those of an authentic sample.

Methanolyses of Compounds A and B——Compounds A and B were individually refluxed with methanolic 5% HCl in the same way as described above. Each product was derivatized to the TMS ether and examined by GLC. GLC (condition 2); Compound A: t_R (min): 6.2, 9.6 (methyl 2,3,4,6-tetra-*O*-methylglucopyranoside), 7.1, 10.2 (methyl 2,3,6-tri-*O*-methylglucopyranoside). Compound B: t_R (min): 3.0 (methyl 2,3,4-tri-*O*-methylrhamnopyranoside), 6.2, 9.6 (methyl 2,3,4,6-tetra-*O*-methylglucopyranoside), 8.1, 9.4 (methyl 3,6-di-*O*-methylglucopyranoside).

Acidic Hydrolysis of Sc-III——Sc-III (3.0 mg) was hydrolyzed with 2 N HCl in 50% dioxane (0.5 ml) in the same way as described above and the product was examined by TLC and GLC. TLC (solvent: hexane–acetone (3 : 1, v/v)), *Rf* 0.51 (Δ^{16}-pregnenolone). GLC (condition 1; the products were derivatized to the TMS ethers): t_R (min): 1.9, 2.5 (rhamnose), 6.2, 8.3 (glucose).

Methanolysis of Sc-III——Sc-III (30 mg) was treated with methanol (10 ml) saturated with potassium carbonate at room temperature for 2 h with stirring. After dilution with water (45 ml), the reaction mixture was extracted with BuOH saturated with water (15 ml × 3) and the organic layer was evaporated to dryness.

The residue was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (7 : 3 : 0.4, v/v) to afford two products, tentatively named compound I (8 mg) and compound II (1 mg). Compound II was acetylated in the usual way to afford an acetate (compound IIa, 1 mg). Compound I: A white powder from aqueous methanol. (mp 236—239 °C (dec.)). ^{13}C-NMR (pyridine-d_5) δ: Table I. Compound IIa: A colorless syrup. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (3H, d, J=6 Hz, >CH–CH_3), 2.04 (3H, s, OAc), 2.05 (3H, s, OAc), 2.07 (3H, s, OAc), 2.11 (3H, s, OAc), 3.69 (3H, s, $COOCH_3$), 4.52 (1H, d, J=7 Hz, anomeric H). Compound IIa was identified as δ-(β-D-glucopyranosyloxy)-γ-methylvaleric acid methyl ether tetraacetate by comparing the ^{1}H-NMR spectrum with that of an authentic sample.

Preparation of Pseudo-Compound of Sc-II——Sc-II (0.50 g) was dissolved in acetic anhydride (3 ml) and the solution was heated at 110 °C for 2 h in a sealed tube. After cooling, the reaction mixture was poured into ice water and the precipitate was collected by filtration. The product was chromatographed on silica gel with benzene–acetone (4 : 1, v/v) to afford an acetate of pseudo-Sc-II (Sc-II-PA, 0.21 g). Sc-II-PA: A white powder from hexane–ether. (mp 126—129 °C). IR ν_{max}^{Nujol} cm^{-1}: OH (nil). ^{1}H-NMR ($CDCl_3$) δ: 0.67 (3H, s, CH_3), 0.88 (3H, d, J=7 Hz, CH_3), 1.01 (3H, s, CH_3), 1.12 (3H, d, J=6 Hz, CH_3 of rha), 1.18 (3H, d, J=6 Hz, CH_3 of rha), 1.57 (3H, s, CH_3), 1.98—2.13 (OAc), 5.36 (1H, br s, olefinic H). *Anal.* Calcd for $C_{87}H_{122}O_{41}$: C, 57.29; H, 6.74. Found: C, 57.00; H, 6.70.

Oxidation of Sc-II-PA with Chromic Anhydride——A solution of chromic anhydride (80 mg) in 95% acetic acid

was added dropwise to a solution of Sc-II-PA (0.75 g) in 95% acetic acid (20 ml) under stirring at room temperature. The reaction mixture was treated with methanol to degrade the excess chromic anhydride. The solution was diluted with water (100 ml) and then extracted with ether (40 ml × 4). The ether extract was evaporated *in vacuo* and the residue was chromatographed on silica gel with benzene–acetone (4 : 1, v/v). The product (150 mg), obtained as a white powder from hexane–chloroform, (mp 126—130°C), was identified as Sc-III-Ac by comparing the TLC behavior and the ^{13}C-NMR spectrum with those of an authentic sample.

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