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On the Structure of Senegin - III of Senegae Radix

In the previous communication[1] we reported the chemical structure of senegin-II, the main saponin of Senegae Radix (root of *Polygala senega* LINNE var. *latifolia* TORRY et GRAY). The present paper deals with the structure elucidation of Senegin-III (I).

Senegin-III (I), $C_{75}H_{112}O_{35}\cdot 3H_2O$, mp 247—248° (decomp.), white powder from ethanol, $[\alpha]_D^{20}$ −6.6° (c=2.0, methanol), IR ν_{max}^{Nujol} cm^{-1}: 3500—3300 (OH), 1750, 1730 (COOR), 1710 (COOH), 1635(C=C), 1610, 1515 (benzenoid), UV λ_{max}^{EtOH} mμ(log ε): 315(4.30), is composed of presenegenin, 4-methoxycinnamic acid, glucose, galactose, 2-rhamnose, fucose and xylose. The molecular formula, $C_{69}H_{102}O_{31}$, reported in the previous paper[2] is erroneous and it was revised in this paper.

On methylation with diazomethane, I gave a monomethyl ester (II), which was heated with 1N potassium hydroxide under nitrogen atmosphere to afford presenegenin-3-O-β-D-glucopyranoside monomethyl ester (III), $C_{37}H_{58}O_{12}\cdot 2H_2O$, colorless needles from ethyl acetate saturated with water, mp 230—231°, IR ν_{max}^{KBr} cm^{-1}: 3400—3500, 1725, 1690, 1630, 1250, 1050. The compound III was acetylated with acetic anhydride and pyridine to form presenegenin-3-O-β-D-glucopyranoside methyl ester pentaacetate (IV), $C_{47}H_{68}O_{17}\cdot 1/2H_2O$, mp 216—217°, colorless needles from methanol, IR ν_{max}^{KBr} cm^{-1}: 3500, 1740 (with inflection at 1760), 1725, 1250. The product III and it's pentaacetate (IV) were identified with the authentic samples obtained from senegin-II[1] by mixed fusion and comparison of infrared (IR) spectra, respectively. The formation of III from II suggests that one of the two carboxyl groups of presenegenin is present in free form at C-4 and the other at C-17 in ester form.

Permethylation of II by Kuhn's method[3] gave per-O-methylsenegin-III (V), $C_{92}H_{146}O_{35}$, white powder from hexane, mp 142—143°, IR ν_{max}^{Nujol} cm^{-1}: 1730, 1710, 1630, 1600, 1500, 1250, 1100 (broad). On the other hand, II was treated with 0.5% potassium hydroxide over-night to afford des-4-methoxycinnamoyl senegin-III monomethyl ester (VI), which was permethylated by Hakomori's method[4] to give per-O-methyl-des-4-methoxycinnamoyl senegin-III (VII), $C_{83}H_{140}O_{33}$, white powder from hexane, mp 134—136°, IR ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1710, 1620, 1250, 1100 (broad).

On methanolysis with 3N hydrogen chloride in methanol refluxing for 2 hours, V gave methyl 2,3-di-O-methylrhamnoside, methyl 2,3,4-tri-O-methylramnoside, methyl 2,3,4,6-tetra-O-methylgalactoside, methyl 2,3-di-O-methylxyloside, methyl 2,3,4,6-tetra-O-methylglucoside and methyl fucoside, and VII gave methyl 2,3,4,6-tetra-O-methylgalactoside, methyl 2,3-di-O-methylxyloside, methyl 2,3-di-O-methylrhamnoside, methyl 2,3,4-tri-O-methylrhamnoside, methyl 2,3,4,6-tetra-O-methylglucoside and methyl 4-O-methylfucoside, respectively. The partially O-methylated sugars of each methanolysate of V and VII were identified by thin-layer chromatography (TLC) and gas liquid chromatography (GLC). The occurrence of methyl fucoside in the methanolysate of V and methyl 4-O-methylfucoside in that of VII revealed that 4-methoxycinnamic acid is attached on the C-4 hydroxyl group of fucose in ester form.

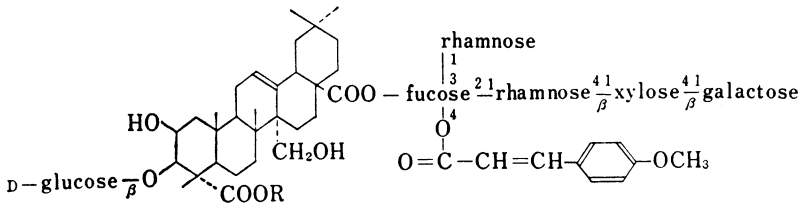
On reduction with lithium aluminium hydride in ether, V gave VIII, $C_{41}H_{68}O_{10}$, white powder from hexane, mp 125°, from the ether extract of the reaction mixture and IX, $C_{40}H_{74}O_{22}\cdot H_2O$, white powder from hexane, mp 68—70°, NMR δ_{TMS}^{Benzen}: 1.28 (3H(d), J= 2 cps, –CH–C$\underline{H}_3$), 1.35 (3H(d), J=2 cps, –CH–C$\underline{H}_3$), 1.55 (3H(broad singlet), –CH–C$\underline{H}_3$), 3.13

1) J. Shoji, S. Kawanishi and Y. Tsukitani, *Chem. Pharm. Bull.* (Tokyo), **19**, 1740 (1971).
2) J. Shoji, S. Kawanishi and Y. Tsukitani, *Yakugaku Zasshi*, **91**, 198 (1971).
3) R. Kuhn, *Angew, Chem.*, **67**, 32 (1955).
4) S. Hakomori, *J. Biochem.* (Tokyo), **55**, 205 (1964).

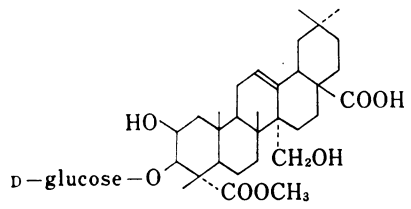
(3H×2(s), 2×OC$\underline{H}_3$), 3.27 (3H×2(s), 2×OC$\underline{H}_3$), 3.33 (3H(s), OC$\underline{H}_3$), 3.41 (3H(s), OC$\underline{H}_3$), 3.45 (3H(s), OC$\underline{H}_3$), 3.46 (3H×2(s), 2×OC$\underline{H}_3$), 3.50 (3H(s), OC$\underline{H}_3$), 3.65 (3H(s), OC$\underline{H}_3$), 4.15 (1H(d), J=7 cps, anomeric H), 4.80 (1H(d), J=7 cps, anomeric H), 5.22 (2H(broad singlet), anomeric H), from the chloroform extract. The product VIII was identified with the compound obtained from per-O-methyl senegin-II by the same reduction by mixed fusion and comparison of IR spectra.

The partially O-methylated sugars of the methanolysate of IX were examined by TLC and GLC to show the presence of methyl 2,3,4,6-tetra-O-methylgalactoside, methyl 2,3-di-O-methylxyloside, methyl 2,3-di-O-methylrhamnoside, methyl 2,3,4-tri-O-methylrhamnoside and fucitol.

On partial methanolysis with 0.2N hydrogen chloride–methanol at room temperature, VII gave an O-methyl-pentasaccharide (X) which was refluxed for 1 hour with 1N hydrogen chloride–methanol afforded an O-methyl-trisaccharide (XI) composed of 4-O-methylfucase, 2,3,4-tri-O-methylrhamnose, and 2,3-di-O-methylrhamnose. The O-methyl-trisaccharide (XI), preparatively isolated by TLC, was methylated by Hakomori's method to give a per-O-methyl-trisaccharide (XII), which affords methyl 4-O-methylfucoside and methyl 2,3,4-tri-O-methyl-rhamnside by refluxing with 3N hydrogen chloride–methanol for 2 hours.
Furthermore, O-methyl-trisaccharide (XI) was kept for over-night in 3N hydrogen chloride–methanol to afford an O-methyl-disaccharide (XIII) composed of 2,3-di-O-methylrhamnose and 4-O-methylfucose. The O-methyl-disaccharide (XIII), preparatively isolated by TLC, was methylated by Hakomori's method to give a per-O-methyl-disaccharide (XIV) which affords methyl 2,3,4-tri-O-methylrhamnoside and methyl 3,4-di-O-methylfucoside by refluxing with 3N hydrogen chloride–methanol for 2 hours.



I : R=H
II : R=CH₃



III

Thus the structure of senegin-III is formulated as I. The nuclear magnetic resonance spectra of VIII revealed that glucose, xylose and galactose in the saponin are linked with β configuration. The configurations of the other sugars are now under investigation.

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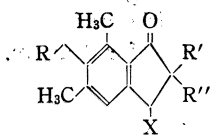
Further Characterization of 1-Indanone Derivatives from Bracken, *Pteridium aquilinum* var. *latiusculum*

In the previous communication[1] structures (I—VI) of six sesquiterpenoids having 1-indanone nucleus from methanol extract of air-dried young leaves of *Pteridium aquilinum* KUHN var. *latiusculum* UNDERWOOD (Pteridaceae) (Japanese name, warabi) were reported. This communication concerns further characterization of four derivatives from more polar fractions of the extract.

TABLE I



		R	R′	R″	X	Trivial name[2]
I	BI-2[1]	CH_2OH	CH_3	H	H	petrosin B
II	BH-4[1]	COOH	CH_3	H	H	pterosin E
III	HJ-5[1]	CH_2Cl	CH_3	H	H	pterosin F
IV	HQ-2[1] (hypolepin B[3])	CH_2OH	CH_3	CH_3	H	pterosin Z
V	BJ-4[1]	CH_2OH	CH_3	CH_3	OH	pterosin D
VI	BK-3[1]	CH_2OH	CH_3	CH_2OH	H	pterosin A
VII	Ac-3	CH_2OH	CH_3	H	OH	pterosin C
VIII	BM-5	CH_2OH	CH_2OH	H	H	pterosin G
X	pteroside C[4,5]	CH_2O-gl	CH_3	H	OH	
XI	pteroside B[6]	CH_2O-gl	CH_3	H	H	
XII	pteroside A[4,5]	CH_2O-gl	CH_3	CH_2OH	H	
XIII	pteroside D[5]	CH_2O-gl	CH_3	CH_3	OH	
XIV	pteroside Z[5]	CH_2O-gl	CH_3	CH_3	H	
XV	hypolepin A[3]	CH_2Cl	CH_3	CH_3	H	pterosin H
XVI	hypolepin C[3]	CH_2OCH_3	CH_3	CH_3	H	pterosin I

(gl=β-D-glucopyranose)

1) K. Yoshihira, M. Fukuoka, M. Kuroyanagi, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **19**, 1491 (1971).
2) The decision was made by the agreement by Professor T. Takemoto and Dr. H. Hikino, Tohoku University, Dr. Y. Hayashi, Osaka City University, and the authors at Nagoya, October 18, 1971.
3) Dr. Y. Hayashi, Osaka City University, private commuication; *cf.* M. Nishizawa, Y. Hayashi, and T. Sakan, The paper presented at the 15th Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics, Osaka, November 1971, Abstracts of Papers, p. 141.
4) H. Hikino, T. Takahashi, and T. Takemoto, The paper presented at the Annual Meeting of Pharmaceutical Society of Japan, Fukuoka, April 1971, Abstracts of Papers, p. 777.
5) H. Hikino, T. Takahashi, and T. Takemoto, The paper presented at the 40th Meeting of Tohoku Branch, Pharmaceutical Society of Japan, Sendai, July 1971.
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