PHENOLIC COMPOUNDS FROM SALIX SACHALINENSIS

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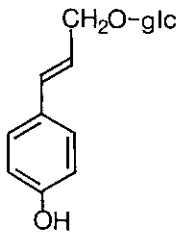
Abstract——Two new glucosides of phenolic compounds, sachalisides 1 (**1**) and 2 (**2**), were isolated from the bark of Salix sachalinensis and their structures were established by the spectroscopic analysis. The aglycone moiety of sachaliside **2** was a new type skeleton consisting of C_6-C_3-C_6-C_3-C_6 units (flavan-3-ol substituted with phenylpropanoid on the A-ring).

In the continuation of our chemotaxonomic studies on Salicaceous plants,[1,2] we have revealed the intraspecific chemical variations in Salix sachalinensis on the basis of the chemical constituents in their leaves.[3] For the advanced characterization of two chemical races in S. sachalinensis, phenolic compounds in the bark and the woods were investigated. Nine compounds including two novel phenolics were isolated and characterized.

Plant materials[4] were collected in November, 1987 at Takane-mura, Ohno-gun, Gifu-prefecture, Japan. From a methanolic extract of the bark, two new compounds (**1** and 2) were isolated together with quercetin, myricetin, taxifolin, (+)-catechin and (+)-gallocatechin. Compound (1) was also obtained from a methanolic extract of the wood besides 2,6-dimethoxy-p-hydroquinone-1-O-β-D-glucopyranoside.[5]

Compound (**1**) was obtained as colorless needles, mp 152-152.5 °C from acetone. In the ^{1}H nmr spectrum, an A_2B_2 system at 7.25 ppm and 6.71 ppm(J = 8.8 Hz) and an ABXY system at 6.53(d, J = 15.8 Hz), 6.11(dt, J = 15.8 and 5.5 Hz), 4.39 and 4.15 ppm (each dd, J = 5.5 and 12.5 Hz) indicated the presence of a p-coumaryl alcohol



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moiety. The ^{13}C nmr[6] not only supported the presence of the moiety, but also showed the presence of a β-D-glucopyranosyl moiety. The position of the glucosyl moiety on p-coumaryl alcohol was determined to be at C-γ, because a singlet (9.49 ppm) of phenolic hydroxyl group was observed in the ^1H nmr spectrum. Therefore, **1** was concluded to be p-coumaryl alcohol-γ-O-β-D-glucopyranoside and named sachaliside 1.

Compound **(2)** was obtained as colorless needles, mp 202-203 °C from methanol. Negative ion fab-ms spectrum of **2** showed $[M-H]^-$ at m/z 583 and $[M-glucose]^-$ at m/z 421, respectively. Other spectral data (Tables 1 and 2) showed **2** to be one of flavan-3-ol derivatives. The configurations of C-2 and C-3 were characterized as 2R and 3S by the cd spectrum[7] and the nmr data. Therefore, 2 was concluded to be a derivative of (+)-catechin. In the ^1H nmr spectrum, a singlet at 6.22 ppm indicated that either C-6 or C-8 in the flavan-3-ol skeleton was substituted. Signals appearing as an ABXY at 6.33, 6.14 and 3.55-3.42 ppm were assigned to a trans-propenyl group, which was confirmed by ^1H-^{13}C COSY spectrum. An A_2B_2 system at 7.13 and 6.69 ppm as doublets in the ^1H nmr spectrum, and signals at 115.3, 126.9, 128.8 and 156.3 ppm in the ^{13}C nmr spectrum were attributable to a para-substituted phenol moiety. The above data suggested the presence of a 1-para-hydroxyphenyl-trans-propenyl moiety in the structure of 2. Six carbon signals at 101.4 and 77.0-60.8 ppm showed the presence of a glucopyranosyl group. In the ^1H nmr spectrum, a broad doublet (J = 7.7 Hz) assignable to β-anomeric proton was observed at 4.74 ppm. In the ^1H-^1H long range COSY and NOESY spectrum, a cross peak was observed between the anomeric proton and

Table 1. ^1H-^1H connectives from COSY and long range COSY spectrum.

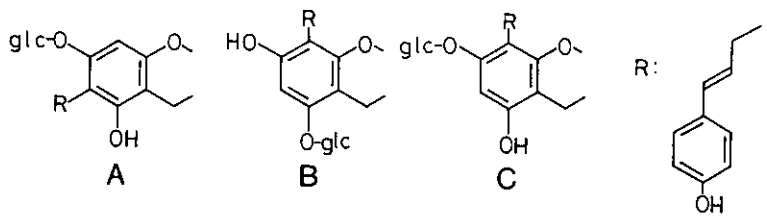
^1H	Chemical shift(δ) J value(Hz)	Coupled to H COSY	long range COSY
H-2	4.56 d (7.3)	H-3	H-2,6
H-3	3.94-3.86 m	H-2,H_2-4	
H-4$_{eq}$	2.78 dd (16.3,5.6)	H-3,H-4$_{ax}$	
H-4$_{ax}$	2.52 dd (16.3,7.7)	H-3,H-4$_{eq}$	
H-8	6.22 s		H-1"'
H-2'	6.76 d (1.3)	H-6'	H-2
H-5'	6.73 d (8.1)	H-6'	
H-6'	6.63 dd (8.1,1.3)	H-2',H-5'	H-2
H-2",6"	7.13 d (8.6)	H-3",5"	H-7"
H-3",5"	6.69 d (8.6)	H-2",6"	
H-7"	6.33 d (15.8)	H-8"	H-2",6" H-9"
H-8"	6.14 dt (15.8,6.8)	H-7",H-9"	
H-9"	3.55-3.42 m	H-8"	H-7"
H-1"'	4.74 br d (7.7)		H-8

These spectra were taken in DMSO-d_6.

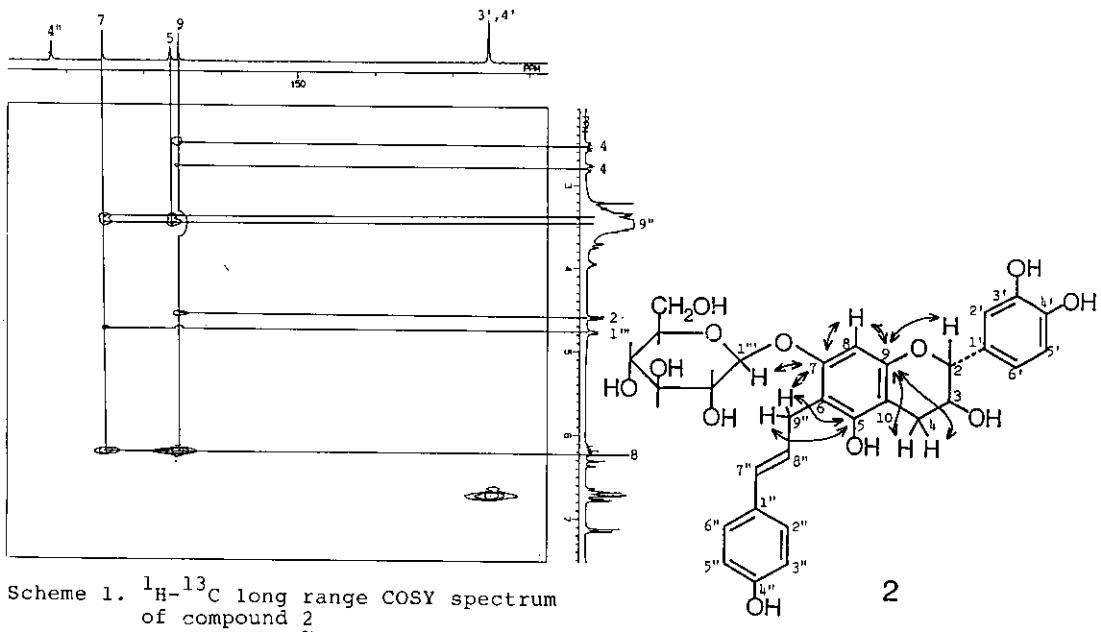
Table 2. ^{13}C nmr and ^{1}H-^{13}C connectives. (measured in DMSO-d_6)

Carbon No.	Chemical shift(δ)	Multiplicity (INEPT 3/4J)	Connect. to H	Carbon No.	Chemical shift(δ)	Multiplicity (INEPT 3/4J)	Connect. to H
2	80.8	CH		1"	128.8	-C-	H-3",5"
3	66.2	CH		2",6"	126.9	CH	
4	28.3	CH_2		3",5"	115.3	CH	H-2",6"
5	152.9	-C-	H-9",H-8	4"	156.3	-C-	H-2",6"
6	108.9	-C-	H-8	7"	128.7	CH	H-2",6"
7	154.9	-C-	H-8,H-9",H-1"'	8"	126.2	CH	
8	95.0	CH		9"	26.3	CH_2	
9	153.1	-C-	H-8,H-2,H_2-4	1"'	101.4	CH	
10	102.9	-C-	H-4,H-8	2"'	73.5	CH	
1'	130.4	-C-		3"'	77.0	CH	
2'	114.4	CH		4"'	69.8	CH	
3'	144.9	-C-	H-2',H-5',H-6'	5"'	76.8	CH	
4'				6"'	60.8	CH_2	
5'	115.1	CH					
6'	118.4	CH					

the A ring proton. These results suggested that the glucose was linked with a hydroxyl group being adjacent to the A ring proton. Consequentry, three possible partial structures (**A**, **B** and **C**) could be considered as follows.

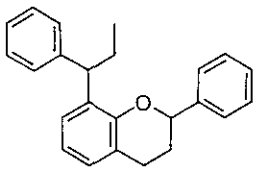


The ^{1}H-^{13}C long range COSY spectrum (J_{CH} = 8 Hz) showed cross peaks of H-2, H_2-4



Scheme 1. ^{1}H-^{13}C long range COSY spectrum of compound 2

and H-8 with C-9; H-8, H_2-9" and H-1"' with C-7; H_2-9" with C-5 (in Scheme 1); and H_2-4 with C-10. These data indicated that the glucosyl moiety was attached to the hydroxyl group at C-7 and the 1-para-hydroxyphenyl-trans-propenyl moiety was attached to C-6 such as **A**. On the basis of above data, **2** was concluded to be 6-(1-para-hydroxyphenyl-trans-propenyl)catechin-7-O-β-D-glucopyranoside and named sachaliside 2.



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To the best of our knowledge, natural products with a C_6-C_3-C_6-C_3-C_6 skeleton are very rare. The C-C bond sequence between a C_6-C_3 moiety (phenylpropene) and a C_6-C_3-C_6 moiety (catechin) is different from that of the cognate (**3**) *in* Cinchona[8].

Further investigation on the chemotaxonomy of the genus Salix is now in progress.

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3. M. Mizuno, M. Kato, M. Iinuma, T. Tanaka, A. Kimura, H. Ohashi, H. Sakai, and T. Kajita, Bot. Mag. Tokyo, 1989, **102**, 403.
4. Plant materials used in this study were the individuals belonging to the flavonoid race that contains considerable amounts of myricetin and dihydromyricetin in their leaves.
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6. ^{13}C nmr(DMSO-d_6) δ : 61.1(C-6'), 68.8(C-γ), 70.1(C-4'), 73.4(C-2'), 76.7(C-5'), 76.9(C-3'), 101.9(C-1'), 115.3(C-3,5), 122.6(C-α), 127.5(C-β), 127.6(C-2,6), 131.7(C-1), 157.1(C-4).
7. Cd spectrum of compound **2** (MeOH) λ_{ext}(nm) : 223(Δε -3.0), 245(+2.3), 273 (-0.76); (+)-catechin (MeOH) λ_{ext}(nm) : 232(-0.88), 245(+0.088), 277(-0.75).
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Received, 24th April, 1990