SANGGENONS R, S, AND T, THREE NEW ISOPRENYLATED PHENOLS FROM THE CHINESE CRUDE DRUG "SANG-BAI-PI" (MORUS ROOT BARK)#,[1]

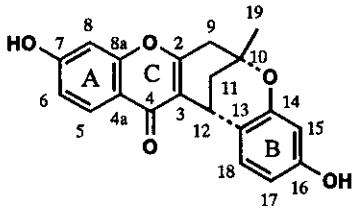
Yoshio Hano, Kohichi Ichikawa, Michiko Okuyama, Juntaro Yamanaka, Tomoko Miyoshi, and Taro Nomura*

Faculty of Pharmaceutical Sciences, Toho University, 2-2-1, Miyama, Funabashi, Chiba 274, Japan

Abstract - *Three new isoprenylated* phenols, sanggenons R (**1**), S (**2**), and T (**3**), were isolated from the Chinese crude drug "Sang-Bai-Pi" (Japanese name "Soha-kuhi"), the root bark of *Morus* sp. (Moraceae). The structures of sanggenons R, S, and T were shown to be **1**, **2**, and **3**, respectively, on the basis of spectral evidence. Sanggenons R (**1**), S (**2**), and T (**3**) are regarded biogenetically as variation of Diels-Alder type adducts between chalcone derivatives and dehydroisoprenylated compounds.

Sanggenon R (**1**), colorless plates, mp 300 °C, $[\alpha]_D^{22}$ + 243°, $C_{20}H_{16}O_5$, gave a brown coloration with methanolic ferric chloride, but was negative to the Gibbs test. The ir spectrum disclosed absorption bands due to hydroxyl, conjugated carbonyl, and benzene ring moieties. The uv spectrum of **1** exhibited maxima at 211, 242, and 288 nm, and was similar to that of daizein (**4**).[2] The ^{1}H nmr spectrum of **1** showed the signals of the following protons (δ in acetone-d_6): two sets of ABC type aromatic protons, δ 6.79 (1H, d, J = 2 Hz), 6.91 (1H, dd, J = 2 and 9 Hz), 7.94 (1H, d, J = 9 Hz), 6.21 (1H, d, J = 2 Hz), 6.22 (1H, dd, J = 2 and 8 Hz), 7.15 (1H, d, J = 8 Hz), two pairs of methylene protons, δ 2.93 (1H, dd, J = 1 and 19 Hz), 3.10 (1H, d, J = 19 Hz), 2.03 (1H, ddd, J = 1, 3, and 13 Hz), 2.19 (1H, dd, J = 3 and 13 Hz), a methine proton, δ 4.28 (1H, t, J = 3

This paper is dedicated to Prof. Rolf Huisgen, Professor of University of Munich, on the occasion of his 75th birthday.



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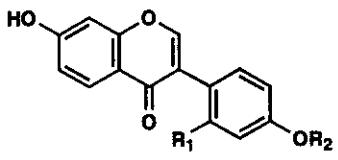

4 : R_1=R_2=H

5 : R_1=OH R_2=CH_3

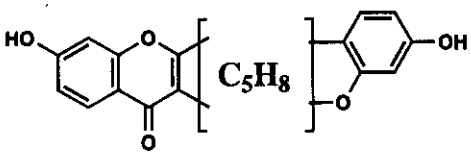

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Figure 1

Table 1. ^{13}C Nmr chemical shifts (ppm) of **1** and **5**

C	1*		5**
C-2	162.1 (Sm)†		154.6
C-3	122.8 (Sm)		121.8
C-4	175.0 (br St, *J* = 4 Hz)		175.4
C-4a	117.1 (Sdd, *J* = 4 and 8 Hz)		116.8
C-5	127.9 (D, *J* = 164 Hz)		127.4
C-6	115.2 (Dd, *J* = 5 and 162 Hz)		115.3
C-7	163.0 (br S)		162.7
C-8	103.1 (Dd, *J* = 4 and 161 Hz)		102.3
C-8a	158.5 (Sdd, *J* = 5 and 9 Hz)		157.7
C-9	43.2 (Ttd, *J* = 4, 6 and *ca.* 129 Hz)		
C-10	75.1 (br S)		
C-11	34.8 (br T, *J* = *ca.*131 Hz)		
C-12	28.7 (br D, *J* = *ca.* 128 Hz)		
C-13	118.7 (br S)	(C-1')	112.2
C-14	155.2 (Std, *J* = 3 and 8 Hz)	(C-2')	156.7
C-15	103.6 (Dd, *J* = 4 and 157 Hz)	(C-3')	101.9
C-16	157.9 (Std, *J* = 2 and 11 Hz)	(C-4')	160.5
C-17	107.5 (Dd, *J* = 4 and 159 Hz)	(C-5')	104.8
C-18	129.2 (Dd, *J* = 4 and 158 Hz)	(C-6')	132.3
C-19	29.0 (br Q, *J* = *ca.* 126 Hz)	OCH_3	55.2

Solvent: * acetone-d_6 ** DMSO-d_6

†: Capital letters refer to the coupling pattern resulting from directly bonded proton(s) and lowercase letters to long-range ^{13}C-^{1}H coupling.

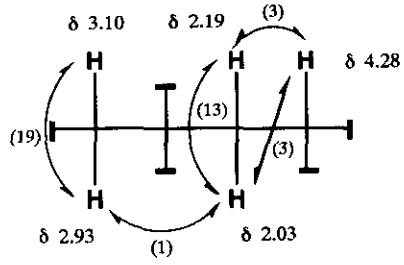


Figure 2a Relationship among the five aliphatic protons (parentheses denote coupling constant)

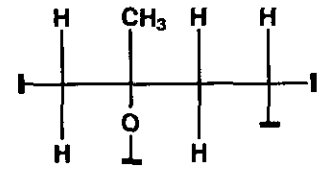
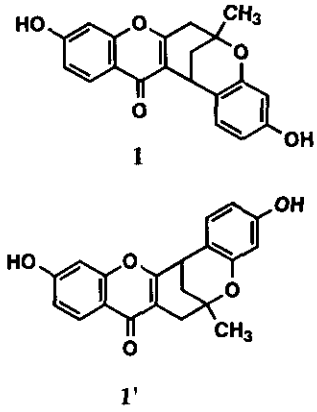


Figure 2b Structure of C_5H_8 moiety



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1'

Figure 2c
Two possible structures for sanggenon R

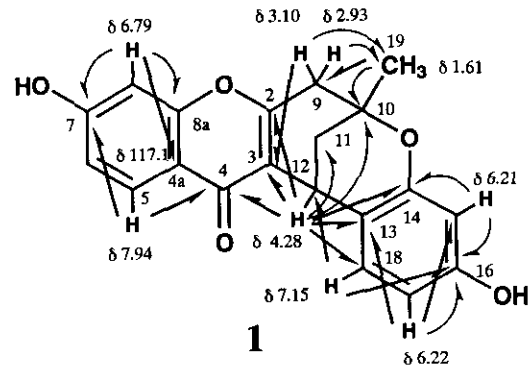

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Figure 3
HMBC spectrum (J_{CCH} ≈ 5 Hz)

Hz), a methyl signal, δ 1.61 (3H, s). The ^{13}C nmr spectrum indicated the presence of twenty carbons and was analysed by comparing with that of 2'-hydroxyformonetin[3] (**5**) (Table 1). In the ^{13}C nmr spectrum of **1**, the chemical shifts of all the carbon atoms in A and C rings except that of C-2 were similar to those of the relevant carbon atoms of **5**. From this result, it was suggested that compound (**1**) has a similar chromone skeleton such as **5**. Furthermore the chemical shifts of the carbon atoms in the B ring of **1** except those of C-13 and C-16 were similar to those of the relevant carbons of **5**. This finding supported the presence of 2, 4-dioxygenated benzene moiety in the structure of **1**. Considering a remaining part consisting of five carbons (Table1) as well as the difference between the nature of C-2 of **1** and that of the relevant carbon of **5**, it was suggested that **1** could not be an isoflavone derivative. Moreover in the ^1H nmr spectrum of **1**, no signal assignable to the characteristic

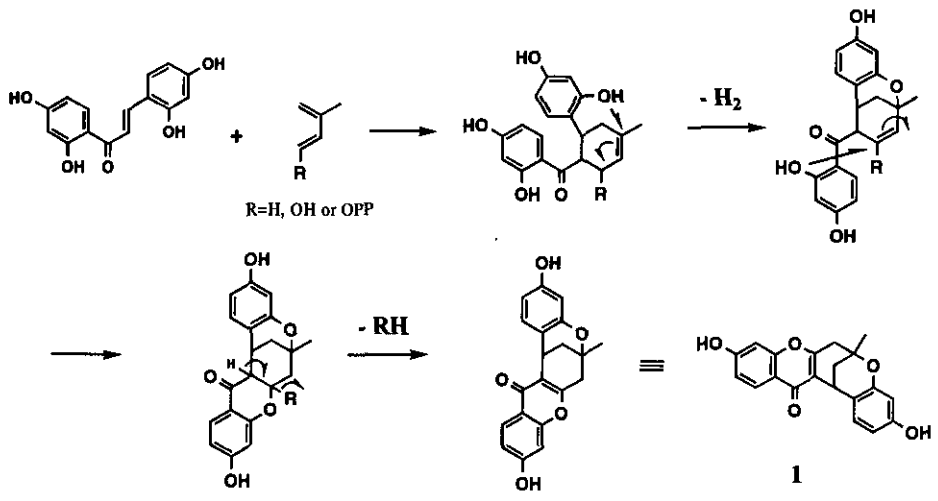


Figure 4 Biogenetic pathway to sanggenon R (1) through Diels-Alder type reaction followed by several oxidation steps

proton, C-2-H of an isoflavone skeleton was observed. From the above results, the partial structure (**1a**) was supported for the structure of sanggenon R. The structure of the moiety, C_5H_8, was proved by the following nmr experiments. The five aliphatic carbons are composed of one methyl carbon, two methylene carbons, one methine carbon, and one oxygenated quaternary carbon (Table 1). Furthermore the correlation among the five protons (two pairs of methylene protons and one methine proton) was supported by the decoupling experiments as shown in Figure 2a. These findings support the structure of the moiety, C_5H_8, to be shown in Figure 2b and hence the formulas **1** and **1'** were proposed for the structure of sanggenon R (Figure 2c). Discrimination between the two formulas was carried out by the following long-range selective ^1H decoupling (LSPD) experiments. When the signal of the methine proton (δ 4.28) was irradiated, the signal of C-4 at δ 175.0 (triplet like signal J = 4 Hz, Table 1) changed to a doublet (J = 4 Hz) and the signals of the seven carbons also changed their shapes. The HMBC spectrum of **1** also supported the result of the LSPD experiment (Figure 3). From the above results, we proposed the formula **1** for the structure of sanggenon R except the absolute configuration. While sanggenon R (**1**) seems to be a unique chromone derivative, biogenetically **1** may be a derivative induced from the Diels-Alder type adduct between a chalcone derivative and a dehydroisoprenylated compound through the oxidative reaction as described in Figure 4.

Sanggenon S (**2**), yellow crystalline powder, $[\alpha]_D^{20}$ + 58.8°, showed positive reaction to methanolic ferric chloride reaction, magnesium-hydrochloric acid test, and sodiumborohydride test,[4] and gave the protonated

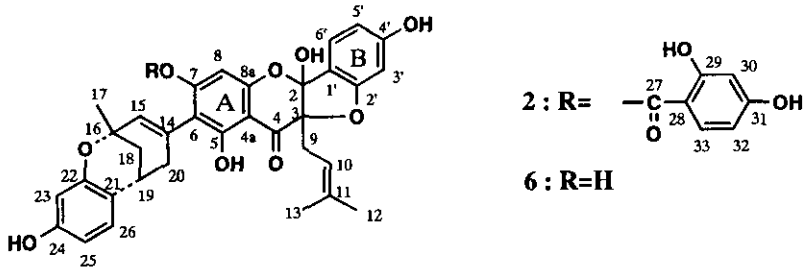


Figure 5

Table 2. ^{1}H Nmr chemical shifts (ppm) of **2** and **6**

	2	**6**
8-H	6.30 (s)	5.87 (s)
3'-H	6.43 (d, J = 2 Hz)	6.42 (d)
5'-H	6.55 (dd, J = 2 and 8 Hz)	6.55 (dd)
6'-H	7.40 (d, J = 8 Hz)	7.35 (d)
5-OH	11.60 (s)	11.95 (s)
9-H	2.78 (dd, J = 6 and 14 Hz)	2.75 (dd)
	3.22 (dd, J = 9 and 14 Hz)	3.15 (dd)
10-H	5.17 (m)	5.23 (m)
11-CH_3	1.48 (3H, br s)	1.45 (3H, br s)
	1.63 (3H, br s)	1.61 (3H, br s)
15-H	5.44 (br s)	5.53 (br s)
16-CH_3	1.20 (3H, s)	1.45 (3H, s)
18-H_2	1.70 ~ 1.75 (2H, br)	1.87 (dd), 1.98 (dd)
19-H	3.07 (m)	3.16 (dd)
20-H	2.46 (br d, J = 16 Hz)	2.35 (br d)
	2.67 (ddd, J = 2, 4 and 16 Hz)	2.71 (ddd)
23-H	6.04 (d, J = 2 Hz)	6.24 (d)
25-H	6.28 (dd, J = 2 and 8 Hz)	6.34 (dd)
26-H	6.88 (d, J = 8 Hz)	6.96 (d)
30-H	6.41 (d, J = 2 Hz)	
32-H	6.51 (dd, J = 2 and 8 Hz)	
33-H	7.63 (d, J = 8 Hz)	
29-OH	10.25 (s)	

Solvent: acetone-d_6

Table 3. ^{13}C Nmr chemical shifts (ppm) of **2** and **6**

C	**2**	**6**
C-2	93.2 (Sm)†	90.8
C-3	102.3 (Sm)	101.2
C-4	191.0 (br S)	186.6
C-4a	103.9 (Sdd, *J* = 4 and 5 Hz)	98.7
C-5	161.8 (S)	160.8
C-6	117.2 (br S)	109.7
C-7	157.5 (Sd, *J* = 2 Hz)	164.3
C-8	102.9 (D, *J* = 169 Hz)	94.2
C-8a	161.8 (Sd, *J* = 2 Hz)	160.7
C-1'	120.9 (Sdd, *J* = 3 and 4 Hz)	119.8
C-2'	161.2 (Sdd, *J* = 2 and 4 Hz)	159.6
C-3'	99.7 (Dd, *J* = 4 and 163 Hz)	98.3
C-4'	161.4 (Std, *J* = 2 and 4 Hz)	159.7
C-5'	108.6 (Dd, *J* = 4 and 154 Hz)	108.6
C-6'	125.7 (D, *J* = 160 Hz)	124.2
C-9	31.9 (Td, *J* = 4 and 126 Hz)	31.2
C-10	118.3 (Dm, *J* = *ca.* 152 Hz)	117.2
C-11	133.5 (Sm)	135.3
C-12	25.8 (br Q, *J* = *ca.* 126 Hz)	25.1
C-13	18.1 (br Q, *J* = *ca.* 126 Hz)	17.4
C-14	137.9 (Sdd, *J* = 4 and 8 Hz)	135.3
C-15	132.8 (br D, *J* = *ca.* 156 Hz)	132.8
C-16	71.1 (br S)	70.6
C-17	27.6 (br Q, *J* = *ca.* 125 Hz)	27.0
C-18	34.8 (br T, *J* = *ca.* 124 Hz)	33.9
C-19	31.4 (br D, *J* = *ca.* 124 Hz)	30.9
C-20	38.8 (br T, *J* = *ca.* 126 Hz)	38.5
C-21	118.5 (br S)	117.9
C-22	155.1 (Std, *J* = 2 and 4 Hz)	154.0
C-23	103.7 (Dd, *J* = 4 and 157 Hz)	102.5
C-24	157.7 (Std, *J* = 2 and 4 Hz)	156.0
C-25	109.8 (Dd, *J* = 5 and 162 Hz)	107.0
C-26	130.2 (Dd, *J* = 4 and 154 Hz)	129.1
C-27	168.5 (Sd, *J* = 3 Hz)	
C-28	104.1 (Sdd, *J* = 4 and 5 Hz)	
C-29	166.2 (Sd, *J* = 4 Hz)	
C-30	103.6 (br D, *J* = *ca.* 164 Hz)	
C-31	165.3 (Std, *J* = 2 and 4 Hz)	
C-32	110.1 (Dd, *J* = 4 and 162 Hz)	
C-33	133.3 (D, *J* = 164 Hz)	

Solvent: acetone-d6

† : Capital letters refer to the coupling pattern resulting from directly bonded proton(s) and lowercase letters to long-range ^{13}C-^{1}H coupling.

molecular ion peak at *m/z* 707 in the fast-atom bombardment (FAB) ms spectrum. The ^{13}C nmr spectrum indicated the presence of forty carbons (Table 3). These results suggest the molecular formula (**2**) to be $C_{40}H_{34}O_{12}$. The uv spectrum of **2** exhibited the maxima at 208, 273, 282, 288, 293, and 360 nm, and was similar to that of sanggenon B[5] (**6**). The ir spectrum disclosed absorptrion bands due to hydroxyl, ester carbonyl, conjugated carbonyl, and benzene ring moieties. The ^1H nmr spectrum of **2** showed the signals of the following protons: protons in a 3,3-dimethylallyl group, δ 1.48 (3H, s), 1.63 (3H, s), 2.78 (1H, dd, *J* = 6 and 14 Hz), 3.22 (1H, dd, *J* =9 and 14 Hz), 5.17 (1H, m); one methyl protons, δ 1.20 (3H, s), two pairs of methylene protons, δ 1.70 - 1.75 (2H, br), 2.46 (1H, br d, *J* = 16 Hz), 2.67 (1H, ddd, *J* = 2, 4, and 16 Hz), a methine proton, δ 3.07 (1H, m), an olefinic proton, δ 5.44 (1H, br s), protons in three sets of ABC type aromatic protons, δ 6.04 (1H, d, *J* = 2 Hz), 6.28 (1H, dd, *J* = 2 and 8 Hz), 6.88 (1H, d, *J* = 8 Hz), 6.41 (1H, d, *J* = 2 Hz), 6.51 (1H, dd, *J* = 2 and 8 Hz), 7.63 (1H, d, *J* = 8 Hz), 6.43 (1H, d, *J* = 2 Hz), 6.55 (1H, dd, *J* = 2 and 8 Hz), 7.40 (1H, d, *J* = 8 Hz), an aromatic proton, δ 6.30 (1H, s), protons in two hydrogen-bonded hydroxyl groups, δ 10.25 (1H, s), 11.60 (1H, s). A comparative examination of the ^1H nmr spectrum of **2** and **6** was carried out and it was found that the coupling patterns of all the proton signals of **2** except those of a set of the ABC type aromatic protons (δ 6.41, 6.51, 7.63) and the proton in the hydrogen-bonded hydroxyl group (δ 10.25) were in fair agreement with the relevant proton signals of **6** (Table 2). Furthermore the chemical shifts of the proton signals except the above described protons were approximately similar to those of the relevant protons. These findings suggest that sanggenon S (**2**) has a sanggenon B type skeleton. The ^{13}C nmr spectrum of **2** was analysed by comparing with that of **6** as shown in Table 3. In the spectrum, the chemical shifts of all the carbon atoms except those of the A ring carbons and the following seven carbons were approximately similar to those of the relevant carbons of **6** and the seven carbons could be assigned to the relevant carbons of 2,4-dihydroxybenzoyl ester moiety. Furthermore the presence of 2, 4-dihydroxybenzoyl ester moiety in the structure was supported by the ABC type aromatic proton signals in ^1H nmr spectrum (Table 2) and the absorption band at 1690 cm^{-1} in the ir spectrum of **2**. From the above results, sanggenon S (**2**) seems to be 7-*O*-2,4-dihydroxybenzoylsanggenon B. The location of the methylcyclohexene ring moiety in the A ring was confirmed by the following ^{13}C nmr study using the gated decoupling with NOE technique. The CH carbon signal at δ 102.9 in the A ring was observed as a simple doublet (*J* = 169 Hz) coupling with only one proton (δ 6.30) (Table 3), indicating that the carbon signal has no long-range coupling with the C-5-OH (δ 11.60). Therefore, the signal at δ 102.9 could be assigned to the C-8. Based on the above evidence, we proposed the formula (**2**) for

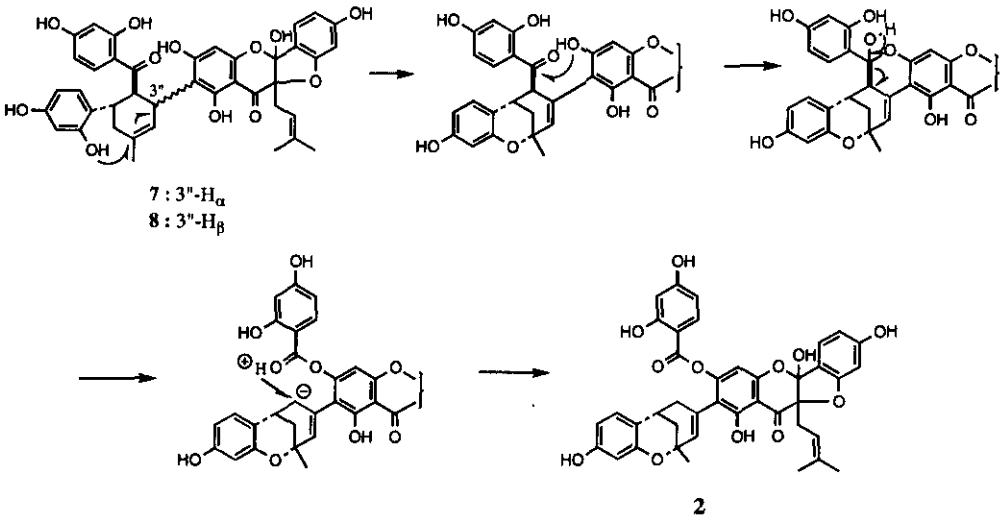


Figure 6 A hypothesis for the biosynthesis of sanggenon S (2)

the structure of sanggenon S. Biogenetically, sanggenon S seems to be a derivative induced from the Diels-Alder type adduct, such as sanggenon C[6] (**7**) or D[7] (**8**), through the mechanism described in Figure 6.

Sanggenon T (**3**), pale yellow crystalline powder, $[\alpha]_D^{22}$ - 194°, showed positive reaction to methanolic ferric chloride test, magnesium-hydrochloric acid test, and sodiumborohydride test,[4] and gave the protonated molecular ion peak at *m/z* 713 in the FAB-ms spectrum. The ^{13}C nmr spectrum indicated the presence of forty carbons. These results suggest that the molecular formula of **3** to be $C_{40}H_{40}O_{12}$. The ^1H nmr spectrum of **3** showed complex patterns and broadened signals at room temperature, which showed the two hydrogen-bonded hydroxyl group [δ in acetone-*d6*, 12.51 (0.5H, br s), 12.91 (0.5H, br s), 13.10 (1H, br s)].[6] The uv spectrum of **3** showed the maxima at 205, 225 (sh), 285, 295 (infl.), 320 (sh) nm, and was similar to those of flavanones.[2] From the uv spectrum and the results of color reaction tests, sanggenon T seems to be a flavanone derivative. In the uv spectrum of **3** in the presence of aluminum chloride ($AlCl_3$), a part of the absorption at 285 nm showed a bathochromic shift immediately after the addition of $AlCl_3$, and the absorption at 290 nm was observed as a shoulder, whereas after 15 minutes the absorption at 285 nm shifted to 310 nm completely. A similar $AlCl_3$-induced bathochromic shift was observed in the uv spectrum of sanggenon G[8] (**9**). Sherif *et al.* reported that $AlCl_3$-induced shift was not observed in the uv spectrum when a prenyl group was located *ortho* to a chelated

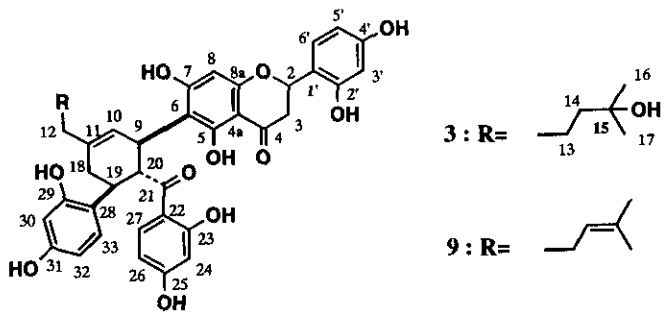


Figure 7

Table 4. ^{13}C Nmr chemical shifts (ppm) of **3** and **9**

C	3*	9**	C	3*	9**
C-2	73.9br	75.9br	C-18	37.4	38.5
C-3	43.3	43.1	C-19	37.4	36.3
C-4	196.7	198.4	C-20	45.3br	47.1
C-4a	103.9	103.8	C-21	208.6	210.8
C-5	161.5	165.9	C-22	115.0br	116.2
C-6	109.0	110.4	C-23	164.2	165.5
C-7	164.2	165.9	C-24	101.9br	103.8
C-8	94.5br	97.1br	C-25	164.1	165.5
C-8a	161.2	163.3	C-26	106.2br	107.4
C-1'	120.8	119.7	C-27	132.4	134.1
C-2'	155.7	156.6	C-28	123.6br	122.9
C-3'	103.0	102.9	C-29	155.7	157.0
C-4'	158.6	159.5	C-30	103.1br	103.4
C-5'	106.9	107.9	C-31	156.1	157.0
C-6'	128.0	132.0	C-32	107.1br	107.8
C-9	37.4	38.5	C-33	128.8	128.8
C-10	124.0br	125.5			
C-11	135.8br	137.0br			
C-12	39.5	38.5			
C-13	22.1	27.3			
C-14	40.1	125.2			
C-15	68.9	130.4			
C-16	29.4	25.9			
C-17	29.4	17.8			

Solvent: * DMSO-d_6 at 80 °C ** CD_3OD

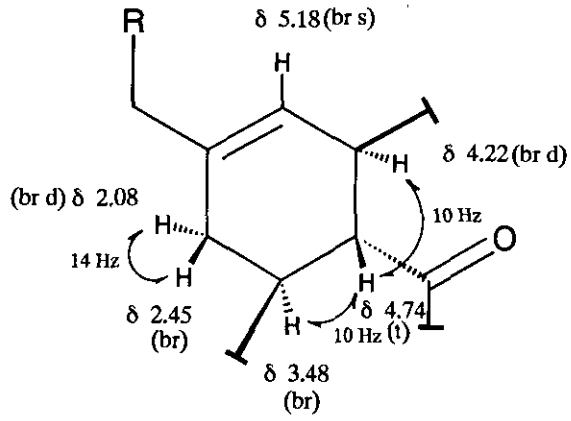
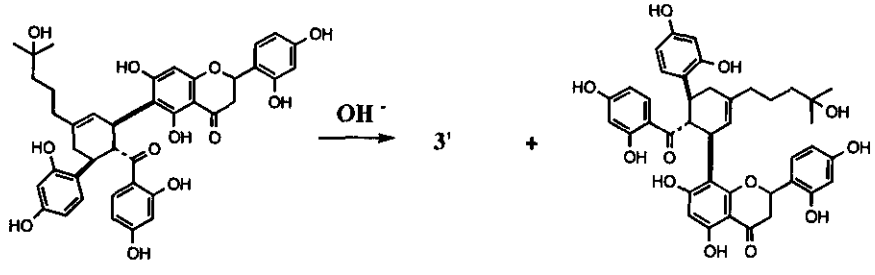


Figure 8 ^{1}H Nmr data for cyclohexene ring moiety of 3

Table 5. ^{1}H Nmr data of hydrogen-bonded hydroxyl groups

comp.	5-OH	23-OH
3	12.50, 12.91 (each 0.5H)	13.10 (1H)
9	12.51, 12.91 (each 0.5H)	13.12 (1H)



3 3a

Figure 9

hydroxyl group.[9] These data led us to presume that one of the *ortho* positions of the two hydrogen-bonded hydroxyl groups is replaced by an isoprenyl moiety, and another position is not. The ^{1}H nmr spectrum of **3** was resolved and sharpened at higher temperature (in DMSO-*d6*, 100 °C), which showed the signals of the following protons: protons in two methyl groups, δ 1.09 (6H, s), three pairs of methylene protons, δ 1.38 - 1.48 (4H, m), 1.98 (2H, br t, *J* = 7 Hz), ABX type protons, δ 2.57 (1H, br d, *J* =17 Hz), 3.03 (1H, dd, *J* =13 and 17 Hz), 5.44 (1H, br s), protons in tetrasubstituted cyclohexene ring described in Figure 8, an aromatic proton, δ 5.78 (1H, br s), protons in three sets of ABC type aromatic protons, δ 6.25 (1H, dd, *J* = 2 and 8 Hz), 6.33 (1H, d, *J* = 2 Hz), 7.08 (1H, d, *J* = 8 Hz), 5.96 (1H, dd, *J* = 2 and 8 Hz), 6.12 (1H, d, *J* = 2 Hz), 6.73 (1H, d, *J* = 8 Hz), 5.95 (1H, d, *J* =2 Hz), 6.02 (0.5H, dd, *J* = 2 and 8 Hz), 6.05 (0.5H, dd, *J* = 2 and 8 Hz), 7.53 (1H, d, *J* = 8 Hz). Comparing the ^{1}H nmr spectrum of **3** with that of **9**, it was found that all the signal patterns of **3** except those of the two methyl groups and three pairs of methylene protons were similar to those of the relevant protons of **9**. The ^{13}C nmr spectrum of **3** was analysed by comparing with that of **9** as shown in Table 4. In the spectrum, the chemical shifts of all the carbon atoms except those of the six carbons of the side chain located at the C-11 position were good agreement with those of the relevant carbons of **9**. Taking the ^{1}H nmr, ^{13}C nmr spectra, and molecular formula into account, sanggenon T (**3**) seems to be a hydrate of sanggenon G (**9**). The location of the cyclohexene ring on the A ring was confirmed by the following results. Fukai *et al.*[10] reported that the signal of hydrogen-bonded hydroxyl proton (C-5-OH) of 6-isoprenoid substituted flavonoid appeared at more down field (0.25 - 0.30 ppm) than that of the 6-nonsubstituted flavonoids. In contrast, the signal of C-5-OH of the 8-isoprenoid substituted flavonoid shows upfield shift (0.04 - 0.10 ppm) compared with that of the flavonoid having no side chain.[10] The chemical shifts of hydrogen-bonded hydroxyl protons of **3** were in good agreement with the relevant protons of **9** (Table 5). While the uv spectrum of **3a** derived from **3** by alkaline treatment showed a bathochromic shift immediately after the addition of $AlCl_3$. These results supported that the cyclohexene ring should be located at the C-6 position. Considering the relative configuration among the three chiral centers in the cyclohexene ring and the negative optical rotation value ($[\alpha]^{22}$ - 194°), the absolute configurations of the three chiral centers were assigned to be 9*R*, 20*R*, and 19*S*.[11-13] Thus, the structure of sanggenon T is proposed as the formula **3** except for the absolute configuration at C-2 position. Biogenetically, sanggenon T is the second example of a natural product which is considered to be formed by a Diels-Alder type of enzymatic reaction process of a chalcone derivative and a dehydrogeranylflavanone derivative.

EXPERIMENTAL

Abbreviations: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, br = broad, sh = shoulder, infl. = inflection. The general procedures and instruments used in our previous paper.[14]

Plant material

"Sang-Bai-Pi" (Japanese name "Sohakuhi"), a species of *Morus* (Moraceae), imported from People's Republic of China, was purchased from Uchida Wakanyaku Co., Tokyo, in 1984, October.

Isolation of Sanggenon R (1), S (2), and T (3)

The crude drug "Sang-Bai-Pi" (50 kg) was finely cut and extracted at room temperature with *n*-hexane (180 *l*, three times), benzene (180 *l* x 3), and acetone (180 *l* x 3), successively (each 3 days). Evaporation of the *n*-hexane, benzene, and acetone solutions to dryness yielded 1260 g, 210 g, and 500 g of the residue, respectively. The acetone extract (285 g) was chromatographed over silica gel (1200 g) using benzene - methanol (1 : 0 → 83 : 17). The fraction eluted with benzene - methanol (97 : 3) was evaporated to give the residue (16 g), which was rechromatographed over silica gel (250 g) using benzene - acetone (1 : 0 → 9 : 1). The fraction eluted with benzene - acetone (9 : 1) was evaporated to give the residue (7.7 g), which was rechromatographed over silica gel (200 g) using *n*-hexane - acetone (1 : 0 → 8 : 2). From the fraction eluted with *n*-hexane - acetone (8 : 2), sanggenon R (**1**, 16 mg) was obtained by preparative hplc [solvent, *n*-hexane - ethyl acetate (1 : 1), column, Senshu Pak SSC Silica 4251-N, 10 ϕ x 250 mm, detector, uv 254 nm], and sanggenon S (**2**, 8 mg) was obtained by preparative tlc [chloroform - ether (1 : 1)] followed by preparative hplc [solvent, *n*-hexane - ethyl acetate (1 : 1) and chloroform - ethyl acetate (5 : 4)]. The fraction eluted with benzene - methanol (83 : 17) was evaporated to give the residue (30 g), which was rechromatographed over silica gel (270 g) using chloroform - methanol (1 : 0 → 5 : 1). The fraction eluted with chloroform - methanol (95 : 5) was fractionated by preparative tlc [chloroform - methanol (5 : 1)] and followed by preparative hplc [*n*-hexane - ethyl acetate (1 : 3)] to give sanggenon T (**3**, 13 mg).

Sanggeno R (1)

Compound (**1**) was recrystallized from *n*-hexane - acetone to give colorless plates, mp 300 ℃, $[\alpha]_D^{22}$ + 243° (*c* = 0.06, MeOH). $FeCl_3$ test: positive (brown). Gibbs test: negative. EI-ms: *m/z* (rel. int.) 336 (M^+, 82 %), 321 (53), 227 (100). HR-ms: *m/z* 336.0971 (M^+, $C_{20}H_{16}O_5$ requires 336.0997). Ir ν_{max}^{KBr} cm^{-1}: 3150 (br), 1653, 1600, 1590 (sh), 1460. Uv λ_{max}^{EtOH} nm (log ε): 228 (4.15), 242 (4.34), 211 (4.50).

Sanggenon S (2)

Compound (**2**) was obtained as a yellow powder from benzene. $FeCl_3$ test: positive (brown). Mg - HCl test: positive (orange). $NaBH_4$ test: positive (violet). $[\alpha]_D^{22}$ + 58.8° (*c* = 0.10, MeOH). FAB-ms: *m/z* (rel. int.) 707 [$(M+H)^+$, 20 %], 571 (14), 503 (10). Ir ν_{max}^{KBr} cm^{-1}: 3380 (br), 1660 (sh), 1648 (sh), 1638, 1618. Uv λ_{max}^{MeOH} nm (log ε): 208 (3.36), 273 (2.87), 282 (2.87), 288 (2.87),298 (2.82), 360 (2.07).

Sanggenon T (3)

Compound (**3**) was obtained as a yellow powder from n-hexane - acetone. $FeCl_3$ test: positive (brown). Mg - HCl test: positive (orange). $NaBH_4$ test: positive (violet). $[\alpha]_D^{22}$ - 194° (*c* = 0.08, EtOH). FAB-ms: *m/z* 713 $(M+H)^+$. Ir ν_{max}^{KBr} cm^{-1}: 3380 (br), 1660 (sh), 1648 (sh), 1638 (sh), 1618. Uv λ_{max}^{MeOH} nm (log ε): 205 (3.85), 225 (sh 3.56), 285 (3.37), 295 (infl. 3.32), 320 (sh, 2.99).

Treatment of Sanggenon T (3) with Alkaline Solution

A mixture of **3** (3 mg) and 5 % K_2CO_3 solution (10 ml) was kept for 5 min at room temperature and treated as usual. The product was purified by preparative hplc [solvent, chloroform - MeOH (13 : 1)] to give **3'** (2 mg) and **3a** (0.8 mg). **3'**, FAB-ms: m/z 713 $[M+H]^+$. $[\alpha]_D^{22}$ - 140° (*c* = 0.02, EtOH). The ^1H nmr spectrum of **3'** was in fair agreement with that of **3**. **3a**, FAB-ms: *m/z* 713

$(M+H)^+$. $[\alpha]_D^{22}$ - 70° (c = 0.08, EtOH). ^{1}H Nmr (acetone-d_6): δ 1.12, 1.15, 1.18 (6H in total, 15-CH_3 x 2), 1.4 - 1.5 (4H, br, 13-H x 2 and 14-H x 2), 1.9 - 2.0 (1H, br, 18-H), 2.0 - 2.5 (3H, br, 12-H x 2 and 18-H), 2.7 - 3.2 (3-H, overlapping with H_2O signal), 3.7 (1H, br, 19-H), 4.43 (1H, br, 9-H), 4.8 (1H, br, 20-H), 5.18, 5.32 (1H in total, br s, 10-H), 5.65 (1H, br d, J = 12, 2-H), 5.77, 5.81 (1H in total, 6-H), 6.0 - 6.3 (4H, br, 24-, 26-, 30-, and 32-H), 6.4 - 6.6 (2H, br, 3'- and 5'-H), 6.89 (1H, br d, J = 8, 33-H), 7.54 (1H, br d, J = 8, 27-H), 7.63 (1H, br d, J = 8, 6'-H), 12.10 (1H, br s, 5-OH), 13.12 (1H, br s, 23-OH).

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