

REVISED STRUCTURE OF SANGGENON B¹

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Abstract—— The structure of sanggenon B which had been isolated from the extract of the Chinese crude drug "Sang-Bai-Pi" (Japanese name "Sōhakuhi"), the root bark of Morus sp. (Moraceae), was reversed from the structure (1') to (1) on the basis of spectral data.

In the previous paper,² we reported the structure (1') for sanggenon B, which had been isolated from the benzene extract of the Chinese crude drug "Sang-Bai-Pi" (Japanese name "Sōhakuhi"), the root bark of Morus sp. (Moraceae), on the basis of spectral and chemical data. Sanggenon B (1) is regarded biogenetically as a variation of a Diels-Alder type adduct of a chalcone derivative and a dehydroprenylflavanone derivative. Recently, we reported the structure (2) for mulberrofuran H which had been isolated from the root bark of cultivated mulberry tree (a cultivated variety of Morus lhou Koidz.).³ Mulberrofuran H is regarded biogenetically as a derivative induced from the Diels-Alder type adducts, such as chalcomoracin (3),⁴ mulberrofurans C (4),⁵ and J (5),⁶ through a mechanism described in Chart 1.³ The biogenetic pathway of mulberrofuran H (2) being considered, sanggenon B also seems to be a derivative induced from the Diels-Alder type adducts, sanggenons C (6)⁷ and D (7)⁸ through the similar mechanism. This consideration prompted us to reinvestigate the structure of sanggenon B. In this paper, we propose the revised formula (1) for the structure of sanggenon B from the following evidence. Comparison of the ¹H nmr spectra of 1, 1a, and 1b indicates that the acetylation of the hydroxyl group at the C-7 position caused down field shift (-0.19 ppm) of

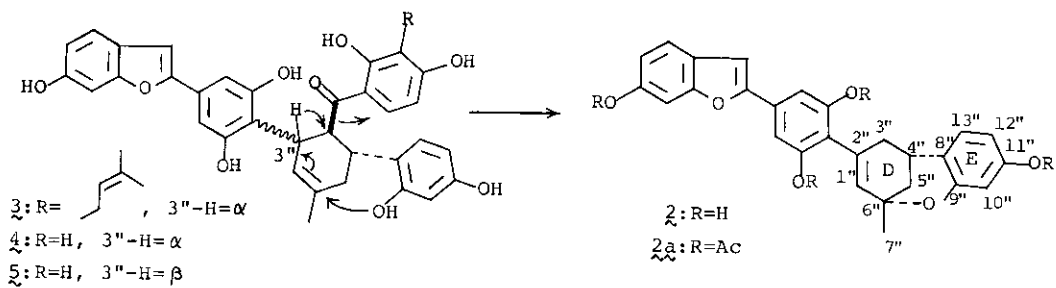
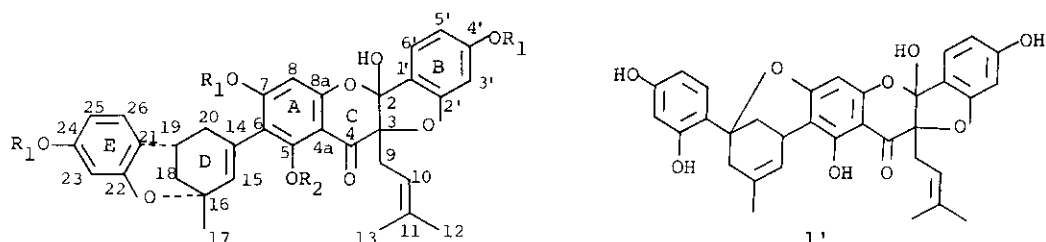


Chart 1



$\underline{1}$: R₁ = R₂ = H
 $\underline{1a}$: R₁ = Ac, R₂ = H
 $\underline{1b}$: R₁ = R₂ = Ac

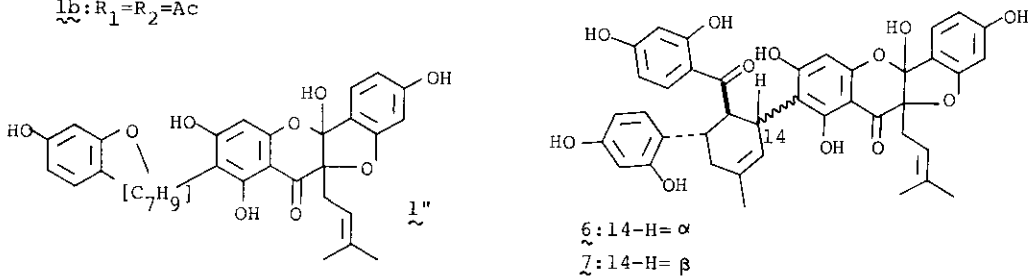


Fig. 1

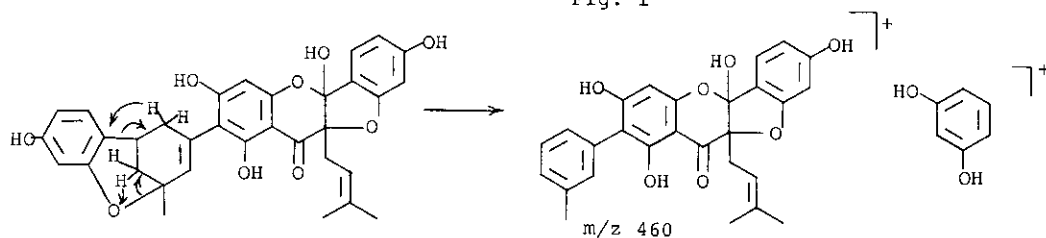


Chart 2

the proton at the C-8 position and that the acetylation of the hydroxyl groups at the C-7 and C-5 positions caused the larger down field shift (-0.69 ppm) of the proton (Table 1). Similar shifts were observed in the case of the proton at the C-8 position of sanggenon N (8) and its acetates (8a, 8b) (Table 1).⁹ On the other hand, the acetylation of the C-5 hydroxyl group of cudraflavone B (9) caused a down field shift (-0.39 ppm) (Table 1).¹⁰ These results suggest that sanggenon B has hydroxyl groups at the C-5 and C-7 positions so that the formula (1') for sanggenon B should be revised.

In the previous paper,² it was clarified that sanggenon B has the same flavanone skeletal structure as sanggenon A (10)¹¹ and that the C-6 side chain consists of a methylcyclohexene ring and a 2,4-dioxygenated phenyl moiety. To confirm the structure of the C-6 side chain, a comparative examination of the ¹H nmr spectra of 1 and 1b was carried out and it was found that acetylation of the C-24 hydroxyl group caused down field shifts (-0.25 ppm) of the protons at C-23 and 25 positions in the E ring. Similar shifts were observed in the cases of the relevant E ring protons of 2 and its acetate (2a),³ and the F ring protons of mulbarrofuran G (11) and its acetate (11a) (Table 2).¹² On the other hand, the acetylation of the 10" and 12" hydroxyl groups of 11 caused larger down field shifts (-0.62~-0.69 ppm) of the protons at C-11" and 13" positions in the E ring.¹² Similar result was also reported in the case of the relevant B ring protons of morusin (12) and its acetate (12a) (Table 3).¹³ These results suggest that the 2,4-dioxygenated phenyl moiety (E ring) in the C-6 side chain of 1 has a hydroxyl group and the other oxygen atom forms an ether linkage. From the above results, the partial structure (1") was proposed. The presence of a tetrasubstituted methylcyclohexene ring (C₇H₉ moiety) was suggested by the following examination of the ¹H nmr spectra of 1. The spectrum was analysed with the aid of sequential decoupling experiments, and the deduced two possible partial structures (A and B) are shown in Fig. 1. In the ¹H nmr spectrum of 1, the chemical shift values and the coupling constants of the protons of the C₇H₉ moiety as well as the E ring were similar to those of the relevant protons of 2 (Fig. 2).³

In the ¹³C nmr spectrum, the chemical shift values of the carbon atoms of the D and E rings of 1 were similar to those of the relevant carbon atoms of 2 except the carbon atom (C-14) which was affected by the additional substituent effect (Table 4).³ From these results, the partial structure (A) seems to be more favorable than the structure (B). Further supporting data for the proposed structure were

obtained by the following long-range selective ^1H decoupling technique: when the signal at δ 1.45 (C-16- CH_3) was weakly irradiated, the signal at δ 70.6 (C-16) increased the area (ca. +23 %). The irradiation of the signal at δ 5.53 (C-15-H) increased the area (ca. +22 %) of the C-16 signal while causing a change in the shape of the signal. The irradiation of the signal at δ 3.16 (C-19-H) also increased the area (ca. +3 %) of the same carbon signal. In the mass spectrum of 1, the characteristic fragment ion at m/z 460 ($\text{M}^+ - \text{C}_6\text{H}_6\text{O}_2$) seems to be formed through the similar route as in the case of mulberrofuran H (Chart 2).³ From these results, we propose the revised formula (1) for the structure of sanggenon B.

EXPERIMENTAL

Abbreviations: s=singlet, d=doublet, t=triplet, m=multiplet, br=broad, sh=shoulder, infl.=inflection. The general experimental procedures used are described in the previous paper.³

Acetylation of sanggenon B (1) (formation of 1a and 1b)

Sanggenon B (1, 35 mg) was acetylated with acetic anhydride (2 ml) and pyridine (0.5 ml) at room temperature for 2 min, and treated as usual. The product was purified by preparative TLC (hexane:ether=2:3, silica gel) to give triacetate (1a, 9.5 mg) and tetraacetate (1b, 8.2 mg).

Sanggenon B triacetate (1a)

The compound (1a) was obtained as an amorphous powder, positive to FeCl_3 test: green. uv $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 229 (sh 4.12), 280 (sh 3.79), 283 (3.80), 294 (sh 3.62), 366 (3.10). ir $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3590 (sh), 3510 (br), 1760, 1640 (sh), 1630, 1615 (sh), 1590, 1580. EI-MS m/z : 696 (M^+). ^1H nmr (90 MHz, acetone- d_6): δ 1.45 (3H, s, C-11- CH_3), 1.50 (3H, s, C-16- CH_3), 1.57 (3H, s, C-11- CH_3), 1.90 (2H, m, C-18-H x2), 2.03, 2.20, 2.23 (each 3H, s, COCH_3), 2.22 (1H, d, $J=16.5$, C-20-H), 2.55 (1H, br d, $J=16.5$, C-20-H), 2.65-2.85 (1H, m, C-9-H), 3.24 (1H, m, C-19-H), 3.25 (1H, dd, $J=9$ and 15, C-9-H), 5.12 (1H, m, C-10-H), 5.40 (1H, br s, C-15-H), 6.07 (1H, s, C-8-H), 6.47 (1H, d, $J=3$, C-23-H), 6.56 (1H, 1H, dd, $J=3$ and 9, C-25-H), 6.74 (1H, d, $J=2$, C-3'-H), 6.78 (1H, dd, $J=2$ and 9, C-5'-H), 7.12 (1H, d, $J=9$, C-26-H), 7.57 (1H, d, $J=9$, C-6'-H), 11.53 (1H, s, C-5-OH).

Sanggenon B tetraacetate (1b)

The compound (1b) was obtained as an amorphous powder, negative to FeCl_3 . uv $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 228 (4.16), 275 (3.69), 282 (sh 3.64), 335 (2.90). ir $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3490, 1765, 1690, 1655 (sh), 1613, 1587. EI-MS m/z : 738 (M^+). ^1H nmr (90 MHz, acetone- d_6): δ 1.46 (3H, s, C-11- CH_3), 1.50 (3H, s, C-16- CH_3), 1.60 (3H, s, C-11-

CH₃), 1.90 (2H, m, C-18-H x2), 2.04, 2.23 (each 6H, s, COCH₃ x2), 2.25 (1H, d, J=16.5, C-20-H), 2.59 (1H, br d, J=16.5, C-20-H), 2.80-2.95 (1H, m, C-9-H), 3.26 (1H, dd, J=9 and 15, C-9-H), 3.28 (1H, m, C-19-H), 5.08 (1H, m, C-10-H), 5.36 (1H, br s, C-15-H), 6.49 (1H, d, J=2.5, C-23-H), 6.57 (1H, s, C-8-H), 6.61 (1H, dd, J=2.5 and 9, C-25-H), 6.71 (1H, d, J=2, C-3'-H), 6.79 (1H, dd, J=2 and 9, C-5'-H), 7.18 (1H, d, J=9, C-26-H), 7.58 (1H, d, J=9, C-6'-H).

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