

subject to acetylation followed by dehydration. But the presence of 1-hydrazinophthalazine and acetylated 1-hydrazinophthalazine could not be confirmed because of its lability.<sup>3,5)</sup>

M-1 was administered orally to Wistar-strain male rats. In this experiment M-1 gave M-4 and M-5. However, M-1 did not turn over to M-3, indicating no existence of decarboxylation of M-5. This fact suggested that 1-hydrazinophthalazine subjected to formylation took place ring closure accompanied by dehydration to give M-3.

M-6, M-7, and M-8 are thought to have two possible pathways. But we could not confirm it.

Further studies are required on the metabolism of DJ-1461 in order to elucidate quantitatively its absorption, distribution, and excretion.

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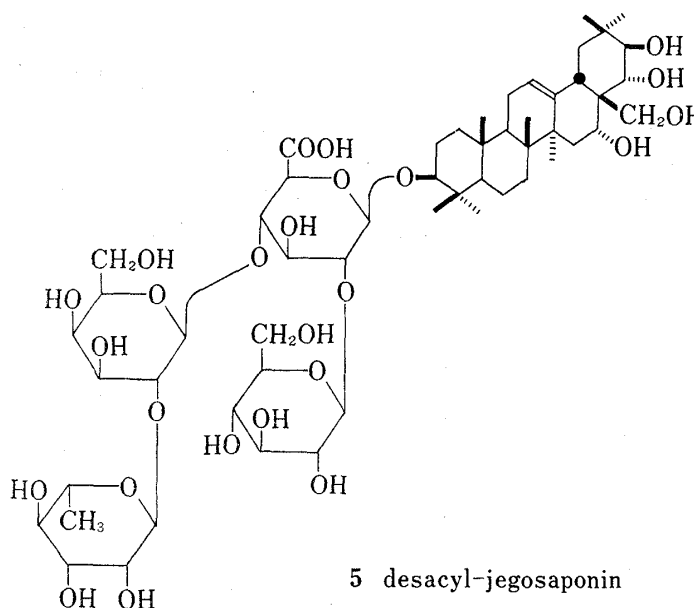
5) Arthur R. Shulert, *Arch. int. Pharmacodyn.*, **132**, 1 (1961).

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### Revised Structure of Desacyl-jegosaponin

Very recently, we proposed the structure of desacyl-jegosaponin, a common desacyl-derivative of jegosaponin which was obtained from the pericarps of *Styrax japonica* SIEB. et Zucc., as barringtogenol C(3)-[ $\beta$ -D-glucopyranosyl (1<sub>glu</sub>→2<sub>glr</sub>)] [ $\alpha$ -L-rhamnopyranosyl(1<sub>rham</sub>→3<sub>gal</sub>)- $\beta$ -D-galactopyranosyl(1<sub>gal</sub>→4<sub>glr</sub>)]- $\beta$ -D-glucuronopyranoside,<sup>1)</sup> in which the location of rhamnose moiety at 3-OH of the galactose moiety was determined on the basis of methanolysis of the LiAlH<sub>4</sub> reduction product of the permethylate of desacyl-jegosaponin. We reported that the methanolysis furnished methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside, methyl 2,4,6-tri-O-methyl-D-galactopyranoside (**1**), and methyl 3-O-methyl-D-glucopyranoside as determined by gas-liquid chromatography (GLC), among which the identification of **1** was a determining evidence for the location of rhamnose on the galactose moiety.



5 desacyl-jegosaponin

1) I. Kitagawa, Y. Imakura, T. Hayashi, and I. Yosioka, *Chem. Pharm. Bull.* (Tokyo), **22**, 1675 (1974).

However, in the course of the structure study on the soybean saponins as described in the following paper,<sup>2)</sup> we have noticed that the above determination of **1** was based on the erroneous GLC operations. The repeated GLC determinations using methyl 2,3,4-tri-O-methyl- (**2**), methyl 2,3,6-tri-O-methyl- (**3**), and methyl 3,4,6-tri-O-methyl-galactopyranoside (**4**) along with **1** for comparison, have finally disclosed that the obtained methyl tri-O-methyl-galactopyranoside was identical with **4** but not with **1**.

Consequently, we would like to revise our previous proposal on the structure of desacyl-jegosaponin to barringtogenol C(3)-[ $\beta$ -D-glucopyranosyl(1<sub>glu</sub>→2<sub>gir</sub>)] [ $\alpha$ -L-rhamnopyranosyl(1<sub>rham</sub>→2<sub>gal</sub>)- $\beta$ -D-galactopyranosyl(1<sub>gal</sub>→4<sub>gir</sub>)]- $\beta$ -D-glucuronopyranoside (**5**).

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2) I. Kitagawa, M. Yoshikawa, and I. Yosioka, *Chem. Pharm. Bull.* (Tokyo), **22**, 3010 (1974).

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### Structures of Three Soybean Saponins: Soyasaponin I, II, and III

Although the sapogenol compositions of soybean (*Glycine max* MERRILL) were elucidated as soyasapogenol A,<sup>1,2)</sup> B (**1**, major),<sup>1,2)</sup> C,<sup>1,2)</sup> D,<sup>1)</sup> and E,<sup>3)</sup> no report on the structure of soybean saponin has been provided except a few works on the carbohydrate ingredients of the saponin.<sup>4)</sup> Recently, we reported the isolation from soybean of three saponins named soyasaponin I, II, and III, in which soyasapogenol B (**1**) was a common triterpenoid aglycone and also elucidated the structure of a prosapogenol (**2a**) of soyasaponin I in conjunction with the photochemical cleavage of the glucuronide linkage.<sup>5)</sup> In this communication, we present the evidence corroborating the structures **3**, **5**, and **4** for soyasaponin I, II, and III, respectively.

On acid hydrolysis, soyasaponin I (**3**), C<sub>48</sub>H<sub>78</sub>O<sub>18</sub>·2H<sub>2</sub>O,<sup>6)</sup> mp 238–240° (MeOH), [ $\alpha$ ]<sub>D</sub><sup>25</sup> –8.5° (MeOH), infrared (IR)  $\nu_{\max}^{\text{Nujol}}$  cm<sup>-1</sup>: 3400 (br, OH), 1710 (COOH), afforded soyasapogenol B (**1**), rhamnose, galactose, and an uronic acid, while acid hydrolysis of **3b**, a NaBH<sub>4</sub> reduction product of soyasaponin I methyl ester (**3a**) (1740 cm<sup>-1</sup>: COOCH<sub>3</sub>, [ $\alpha$ ]<sub>D</sub><sup>27</sup> –22.8° (MeOH)), furnished rhamnose, galactose, and glucose along with **1**, thus the uronic acid in **3** being confirmed as glucuronic acid.

Methylation of **3** with CH<sub>3</sub>I–NaH–DMSO<sup>7)</sup> yielded an undeca-O-methyl derivative (**3c**), C<sub>59</sub>H<sub>100</sub>O<sub>18</sub>, mp 211–214° (MeOH–acetone), [ $\alpha$ ]<sub>D</sub><sup>29</sup> –8.2° (CHCl<sub>3</sub>), which possesses no hydroxyl function as revealed by its IR spectrum (1756 cm<sup>-1</sup>: COOCH<sub>3</sub>). The proton magnetic resonance (PMR) spectrum (CDCl<sub>3</sub>) of **3c** shows the presence of three anomeric protons at  $\delta$  4.28

- 1) G. Cainelli, J.J. Britt, D. Arigoni, and O. Jeger, *Helv. Chim. Acta.*, **41**, 2053 (1958).
- 2) H.M. Smith, J.M. Smith, and F.S. Spring, *Tetrahedron*, **4**, 111 (1958).
- 3) D. Willner, B. Gestetner, D. Lavie, Y. Birk, and A. Bondi, *J. Chem. Soc.*, **1964**, 5885.
- 4) a) A.C. Eldridge and W.J. Wolf, *Cereal Chem.*, **46**, 344 (1969) [*C.A.*, **71**, 87767 (1969)]; b) W.J. Wolf and B.W. Thomas, *J. Chromatog.*, **56**, 281 (1971).
- 5) a) I. Kitagawa, M. Yoshikawa, and I. Yosioka, *Tetrahedron Letters*, **1973**, 3997; b) I. Kitagawa, M. Yoshikawa, Y. Imakura, and I. Yosioka, *Chem. Pharm. Bull.* (Tokyo), **22**, 1339 (1974).
- 6) All the compounds given with the chemical formulae gave the satisfactory analytical values.
- 7) S. Hakomori, *J. Biochem.* (Tokyo), **55**, 205 (1964).