However, in the course of the structure study on the soybean saponins as described in the following paper,[2] 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 desacyljegosaponin to barringtogenol C(3)-[β-D-glucopyranosyl($1_{glu}\rightarrow 2_{glr}$)][$\alpha$-L-rhamnopyranosyl ($1_{rham}\rightarrow 2_{gal}$)-$\beta$-D-galactopyranosyl($1_{gal}\rightarrow 4_{glr}$)]-$\beta$-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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UDC 547.597'457.1.02 : 581.192

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

Although the sapogenol compositions of soybean (*Glycine max* Merrill) were elucidated as soyasapogenol A,[1,2] B (**1**, major),[1,2] C,[1,2] D,[1] and E,[3] no report on the structure of soybean saponin has been provided except a few works on the carbohydrate ingredients of the saponin.[4] 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.[5] 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**), $C_{48}H_{78}O_{18}\cdot 2H_2O$,[6] mp 238—240° (MeOH), $[\alpha]_D^{14}$ −8.5° (MeOH), infrared (IR) ν_{max}^{Nujol} cm^{-1}: 3400 (br, OH), 1710 (COOH), afforded soyasapogenol B (**1**), rhamnose, galactose, and an uronic acid, while acid hydrolysis of **3b**, a $NaBH_4$ reduction product of soyasaponin I methyl ester (**3a**) (1740 cm^{-1}: $COOCH_3$, $[\alpha]_D^{27}$ −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_3I–NaH–DMSO[7] yielded an undeca-O-methyl derivative (**3c**), $C_{59}H_{100}O_{18}$, mp 211—214° (MeOH–acetone), $[\alpha]_D^{29}$ −8.2° ($CHCl_3$), which possesses no hydroxyl function as revealed by its IR spectrum (1756 cm^{-1}: $COOCH_3$). The proton magnetic resonance (PMR) spectrum ($CDCl_3$) of **3c** shows the presence of three anomeric protons at δ 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).

(d, J=7 Hz), 4.65 (d, J=7), and 5.22 (br. s) (in C_6D_6: δ 4.44 (d, J=7), 4.89 (d, J=7), and 5.68 (s), respectively), and the coupling patterns of the former two anomeric protons indicate that glucuronic acid and galactose moieties in **3c** are connected with β-orientation. Methanolysis of **3d** (prepared by $LiAlH_4$ reduction of **3c**) furnished 21,24-di-O-methyl-soyasapogenol B (**1a**), methyl 2,3,4-tri-O-methyl-rhamnopyranoside, methyl 3,4,6-tri-O-methyl-galactopyranoside, and methyl 3,4-di-O-methyl-glucopyranoside (identified by gas–liquid and thin-layer chromatography (GLC, TLC)). The structure of **1a**, $C_{32}H_{54}O_3$, mp 194—195° ($CHCl_3$–MeOH), $[\alpha]_D^{29}$ +11.1° ($CHCl_3$), was determined on the basis of its PMR and mass spectra (M^+: *m/e* 486, **i**: *m/e* 238, and **ii**: *m/e* 248 (base peak) derived *via* a reverse Diels–Alder type fragmentation[8,9]) and the similar physical properties of its monoacetate (**1b**) (a characteristic t-like signal at δ 4.56 due to 3α-H in the PMR spectrum[9]).

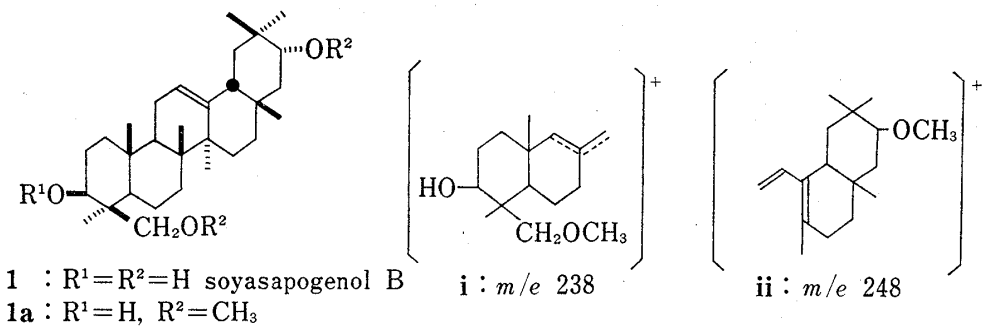
Mild methanolic acid hydrolysis of **3** yielded **1**, prosapogenol (**2a**),[5] and another prosapogenol (**4a**), $C_{43}H_{70}O_{14}\cdot 2H_2O$, mp 262—263° ($CHCl_3$–MeOH), $[\alpha]_D^{14}$ +40.2° (MeOH), IR ν_{max}^{Nujol} cm^{-1}: 3350 (br, OH), 1730 ($COOCH_3$). Further acid hydrolysis of **4a** gave **1**, galactose, and glucuronic acid, the latter being confirmed on the basis of acid hydrolysis of a $NaBH_4$ reduction product (**4b**), $C_{42}H_{70}O_{13}\cdot 2H_2O$, mp 268—269° (MeOH), which furnished galactose and glucose. Methylation of the prosapogenol (**4a**) with CH_3I–NaH–DMSO yielded a fully methylated derivative (**4c**) (IR: no OH, 1754 cm^{-1} ($COOCH_3$); PMR: $OCH_3\times 9$), whose PMR spectrum ($CDCl_3$) shows the presence of two anomeric protons at δ 4.39 (d, J=7) and δ 4.59 (d, J=7) respectively assignable to glucuronic acid and galactose moieties connected with β-orientation.[10] $LiAlH_4$ reduction of **4c** followed by methanolysis afforded **1a**, methyl 2,3,4,6-tetra-O-methyl-galactopyranoside, and methyl 3,4-di-O-methyl-glucopyranoside (TLC, GLC).

Consequently, the accumulated evidence has led us to express the structure of soyasaponin I as 3-O-[α-L-rhamnopyranosyl(1→2)-β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl]-soyasapogenol B (**3**), in which the α-linkage of rhamnose moiety was substantiated by application of the Klyne's rule[11]: $[M]_D$ (**3a**)−$[M]_D$(**4a**)=−538°; $[M]_D$ (methyl α-L-rhamnopyranoside) =−109°[12]; $[M]_D$ (methyl β-L-rhamnopyranoside)=+169°.[12]

Acid hydrolysis of soyasaponin II (**5**), $C_{47}H_{76}O_{17}\cdot 3H_2O$, mp 212—215° (MeOH), $[\alpha]_D^{29}$ −9.6° (MeOH), IR ν_{max}^{Nujol} cm^{-1}: 3400 (br, OH), 1720 (COOH), furnished **1**, rhamnose, arabinose, and glucuronic acid, the latter being confirmed similarly as in the cases of **3** and **4a**. Methylation of **5** gave a deca-O-methyl derivative (**5c**) (IR: no OH, 1760 cm^{-1} ($COOCH_3$)) whose PMR spectrum (C_6D_6) shows the signals due to three anometic protons at δ 4.47 (d, J=8), 4.88 (d, J=6), and 5.44 (s), the former two signals being indicative of the presence of β-glucuronide and α-arabinoside bondings. Methanolysis of a $LiAlH_4$ reduction product (**5d**) furnished **1a**, methyl 2,3,4-tri-O-methyl-rhamnopyranoside, methyl 3,4-di-O-methyl-arabinopyranoside, and methyl 3,4-di-O-methyl glucopyranoside, whereas mild methanolic acid hydrolysis of **5** furnished **1**, **2a**, and a prosapogenol (**6a**), $[\alpha]_D^{29}$ +7.9° (MeOH), IR ν_{max}^{Nujol} cm^{-1}: 3350 (br, OH), 1743 ($COOCH_3$), which, on further acid treatment, was hydrolysed to give **1**, arabinose, and glucuronic acid. Therefore, soyasaponin II has been elucidated to be 3-O-[α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranosyl(1→2)-β-D-glucuronopyranosyl]-soyasapogenol B (**5**), and here again, the α-linkage of terminal rhamnose was proved by application of the Klyne's rule as above.

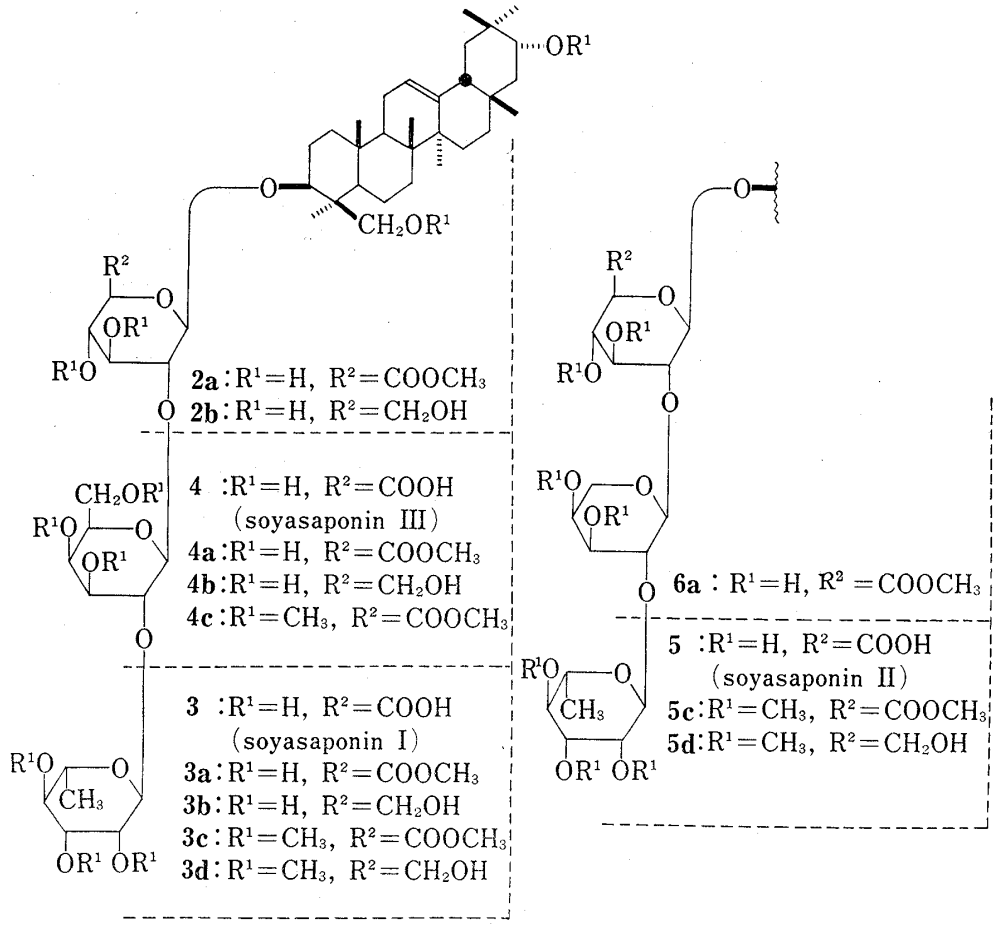
Finally, soyasaponin III (**4**), $C_{41}H_{66}O_{14}\cdot 3/2H_2O$, mp 215—216° (MeOH), $[\alpha]_D^{29}$ +15.0° (MeOH), IR ν_{max}^{Nujol} cm^{-1}: 3350 (br, OH), 1710 (COOH), was hydrolysed with acid to give **1**,

8) H. Budzikiewicz, C. Djerassi, and D.H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 2, Holden-Day Inc., San Francisco, 1964, p. 121.
9) I. Yosioka, T. Nishimura, A. Matsuda, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), **18**, 1610 (1970).
10) The anomeric protons in the permethylates of **2a** and **2b** (in $CDCl_3$) are observed at δ 4.32 (d, J=7) and δ 4.26 (d, J=7), respectively.
11) W. Klyne, *Biochem. J.*, **47**, xli (1950).
12) H. Okabe and T. Kawasaki, *Chem. Pharm. Bull.* (Tokyo), **20**, 514 (1972).



1 : $R^1=R^2=H$ soyasapogenol B
1a : $R^1=H$, $R^2=CH_3$
1b : $R^1=Ac$, $R^2=CH_3$

i : *m/e* 238 **ii** : *m/e* 248



2a : $R^1=H$, $R^2=COOCH_3$
2b : $R^1=H$, $R^2=CH_2OH$

4 : $R^1=H$, $R^2=COOH$ (soyasaponin III)
4a : $R^1=H$, $R^2=COOCH_3$
4b : $R^1=H$, $R^2=CH_2OH$
4c : $R^1=CH_3$, $R^2=COOCH_3$

3 : $R^1=H$, $R^2=COOH$ (soyasaponin I)
3a : $R^1=H$, $R^2=COOCH_3$
3b : $R^1=H$, $R^2=CH_2OH$
3c : $R^1=CH_3$, $R^2=COOCH_3$
3d : $R^1=CH_3$, $R^2=CH_2OH$

6a : $R^1=H$, $R^2=COOCH_3$

5 : $R^1=H$, $R^2=COOH$ (soyasaponin II)
5c : $R^1=CH_3$, $R^2=COOCH_3$
5d : $R^1=CH_3$, $R^2=CH_2OH$

galactose, and glucuronic acid. The PMR spectrum ($CDCl_3$) of a fully methylated nona-O-methyl derivative shows the same signal pattern as that of **4c** (two anomeric proton doublets at δ 4.40 and 4.60 with $J=7$ Hz). Methanolysis of a $LiAlH_4$ reduction product of the per-methylate gave **1a**, methyl 2,3,4,6-tetra-O-methyl-galactopyranoside, and methyl 3,4-di-O-methyl-glucopyranoside. Therefore, soyasaponin III has been elucidated as 3-O-[β-D-galacto-pyranosyl (1→2)-β-D-glucuronopyranosyl]-soyasapogenol B (**4**), which corresponds to alkaline hydrolysis product of the prosapogenol **4a**.

The structure elucidation of three soybean saponins, which were already shown to be cleaved photochemically and which possess the glucuronide linkage directly linked to the aglycone, provides with another chemical support for the previously reported photochemical cleavage of the uronide linkage in saponin.[5]

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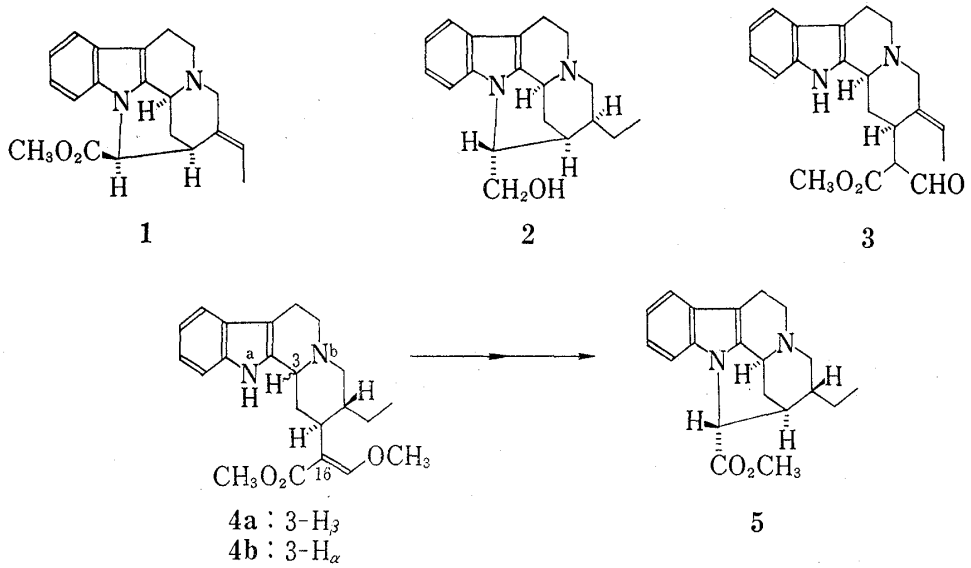
Transformation of Indole Alkaloids. The Chemical Transformation of Corynantheine Type Alkaloids to C-Mavacurine Type Alkaloids

Pleiocarpamine (**1**), an interesting indole alkaloid of apocynaceae plants, has C-mavacurine skeleton.[1] Recently, Boekelheide has reported a synthesis of closely related 19,20-dihydronormavacurine (**2**).[2] We have been interested in the chemical transformation of geissoschizine (**3**) to pleiocarpamine (**1**) through a biomimetic route which involves the formation of bonding between Na and C_{16}.[3,4] In this communication we wish to report that a partial synthesis of 20α-ethyl-19,20-dihydro-16-epipleiocarpamine (**5**) has been accomplished starting either from hirsutine (**4a**) or dihydrocorynantheine (**4b**).



1 **2** **3**

4a : 3-H_β
4b : 3-H_α

5

Chart 1

Very recently, we have described the facile C/D ring opening and regeneration reactions of **4a** and other indole alkaloids.[5] Desmethylhirsutine (**6a**) (mp 116—119°), which was derived from **4a** with acetone–HCl at 0° in 61% yield, was submitted to the C/D ring cleavage reaction using BrCN in 0.6% EtOH–$CHCl_3$. A mixture of 3-(*R*) and (*S*)-ethoxy isomers (**7a**) was obtained as an amorphous powder in 50% yield, which was characterized by the conversion

1) M. Hesse, W. V. Philipsborn, D. Schumann, G. Spiteller, M. Spiteller–Friedmann, W.I. Taylor, H. Schmid, and P. Karrer, *Helv. Chim. Acta.*, **47**, 878 (1964).
2) Dennis D.O'Rell, Fred G.H. Lee, and V. Boekelheide, *J. Am. Chem. Soc.*, **94**, 3205 (1972).
3) E. Wenkert and B. Wickberg, *J. Am. Chem. Soc.*, **87**, 1580 (1965).
4) M. Pinar, M. Hanaoka, M. Hesse, and H. Schmid, *Helv. Chim. Acta.*, **54**, 15 (1971).
5) S. Sakai, A. Kubo, K. Katano, N. Shinma, and K. Sasago, *Yakugaku Zasshi*, **93**, 1165 (1973).