Communications to the Editor

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RUGOSIN D, E, F AND G, DIMERIC AND TRIMERIC HYDROLYZABLE TANNINS

Takuo Okuda,* Tsutomu Hatano and Noboru Ogawa
Faculty of Pharmaceutical Sciences, Okayama University,
Tsushima, Okayama 700, Japan

Four new hydrolyzable tannins, rugosin D (**1**), E (**2**), F (**3**) and G (**4**), were isolated from *Rosa rugosa*, and their dimeric and trimeric structures, linked *via* a valoneoyl group, were elucidated.

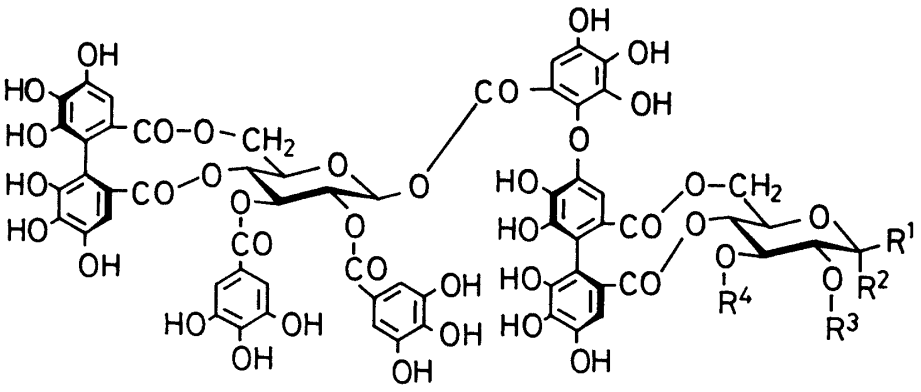
KEYWORDS —— *Rosa rugosa*; Rosaceae; tannin; dimeric hydrolyzable tannin; trimeric hydrolyzable tannin; valoneoyl group; rugosin D; rugosin E; rugosin F; rugosin G

Recently, some dimeric hydrolyzable tannins have been found.[1,2] We now report the isolation and the structures of dimeric tannins of a new type, rugosin D (**1**), E (**2**) and F (**3**), having two monomeric units linked through a valoneoyl group. We report likewise on rugosin G (**4**), the first example of a trimeric hydrolyzable tannin.

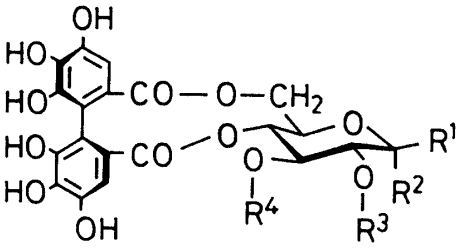
These four tannins, **1**～**4**, have been isolated from the ethyl acetate extract obtained from the crude extract of the flower petal of *Rosa rugosa* Thunb. by column chromatography on Sephadex LH-20, collecting the fractions eluted after monomeric tannins.[3]

Rugosin D (**1**), $C_{82}H_{58}O_{52}\cdot 9H_2O$, $[\alpha]_D$ +118° (c=1, acetone), UV λ_{max}^{MeOH} nm (log ε) 219 (5.17) and 277 (4.84), was obtained as an off-white amorphous powder. Its ^{1}H-NMR spectrum (200 MHz, in acetone-d_6) shows fifteen aromatic protons [δ7.149, 7.032, 7.025, 7.02, 6.99 (s, 2H each, galloyl), 7.146, 6.67, 6.49, 6.47 and 6.26 (s, 1H each, hexahydroxydiphenoyl and valoneoyl)] and fourteen glucose protons [δ6.20 (d, *J*=8 Hz, H-1), 6.15 (d, *J*=8 Hz, H-1), 5.85 (t, *J*=10 Hz, H-3), 5.81 (t, *J*=10 Hz, H-3), 5.61 (dd, *J*=8, 10 Hz, H-2), 5.54 (dd, *J*=8, 10 Hz, H-2), 5.33 (dd, *J*=6, 14 Hz, 2H, H-6), 5.16 (t, *J*=10 Hz, 2H, H-4), 4.54 (dd, *J*=6, 10 Hz, H-5), 4.48 (dd, *J*=6, 10 Hz, H-5), 3.83 (d, *J*=14 Hz, H-6') and 3.79 (d, *J*=14 Hz, H-6')], which indicate that **1** possesses five galloyl, a hexahydroxydiphenoyl and a valoneoyl group, and two glucose cores. The formation of *C1* conformation and β-anomer of the two glucose cores is shown by the coupling constants of the sugar protons.

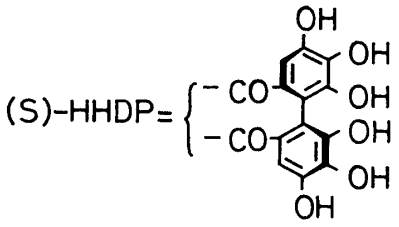
Methylation of **1** with dimethyl sulfate and potassium carbonate in dry acetone afforded nonacosa-*O*-methylrugosin D, $C_{111}H_{116}O_{52}\cdot H_2O$, $[\alpha]_D$ +52° (c=1, acetone) [mass spectrum: m/z 646 and 614 (methylated valoneoyl); 422, 404 and 360 (hexamethoxydiphenoyl); 212, 197 and 195 (trimethylgalloyl)].

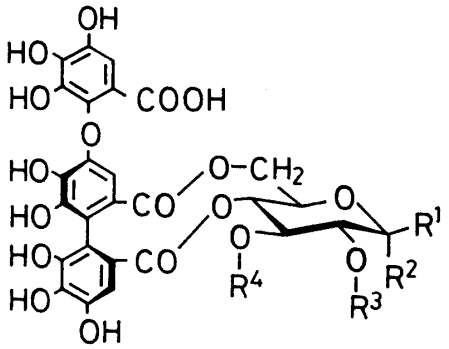


	R^1	R^2	R^3	R^4
1	O-gall	H	gall	gall
2	H, OH		gall	gall
3	O-gall	H	(S)-HHDP	

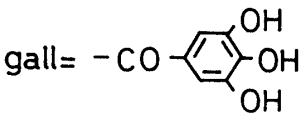


	R^1	R^2	R^3	R^4
5	H, OH		gall	gall
9	O-gall	H	gall	gall
10	O-gall	H	(S)-HHDP	





	R^1	R^2	R^3	R^4
6	O-gall	H	gall	gall
7	H, OH		gall	gall
8	O-gall	H	(S)-HHDP	



Hydrolysis of **1** in hot water gave two products, which were isolated by column chromatography on Sephadex LH-20, and were identified as tellimagrandin I (**5**)[4,5] and rugosin A (**6**),[3] respectively. The structure **1** in which two glucose cores are linked *via* the valoneoyl group is therefore assigned to rugosin D.

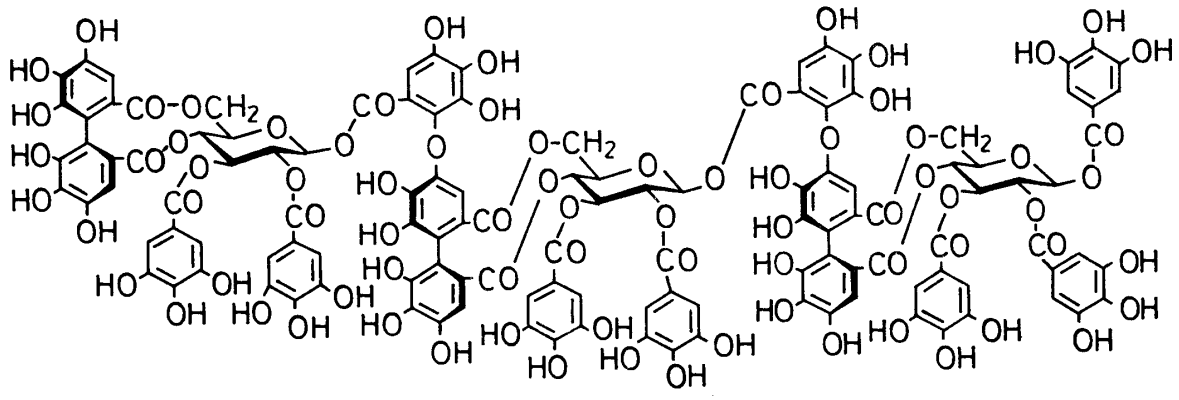
Rugosin E (**2**), $C_{75}H_{54}O_{48}\cdot 5H_2O$, $[\alpha]_D$ +140° (c=1, acetone), was obtained as a light tan amorphous powder, UV λ_{max}^{MeOH} nm (log ε) 220 (5.19) and 275 (4.87), which forms an anomer mixture as indicated by its ^{1}H-NMR spectrum (200 MHz, in acetone-d_6) [δ7.09 (6/5H), 7.08 (4/5H), 7.034 (6/5H), 7.028 (14/5H) and 6.99 (2H) (four galloyl groups); δ7.16 (1H), 6.67 (1H), 6.49 (3/5H), 6.47 (7/5H), 6.251 (3/5H) and 6.245 (2/5H) (a hexahydroxydiphenoyl group and a valoneoyl group); protons of two glucose cores other than H-1 proton (δ6.17, d, *J*=8 Hz) of a glucose core were complicated]. Partial hydrolysis of **2** in hot water afforded **5** and rugosin B (**7**).[3] These results indicate that the structure of rugosin E is **2**.

Rugosin F (**3**), $C_{82}H_{56}O_{52}\cdot 12H_2O$, $[\alpha]_D$ +88° (c=1, acetone), UV λ_{max}^{MeOH} nm (log ε) 218 (5.18) and 273 (4.85), was obtained as a light tan amorphous powder. The ^{1}H-NMR spectrum (200 MHz, in acetone-d_6) shows the presence of three galloyl (δ7.17, 7.00 and 6.97; 2H each), a valoneoyl and two hexahydroxydiphenoyl (δ7.12, 6.65, 6.54, 6.47, 6.46, 6.42 and 6.26; 1H each) groups and two glucose cores [δ6.19 (d, *J*=8.5 Hz, H-1), 6.13 (d, *J*=8 Hz, H-1), 5.80 (t, *J*=10 Hz, H-3), 5.51 (dd, *J*=8, 10 Hz, H-2), 5.44 (dd, *J*=9, 10 Hz, H-3), 5.32 (dd, *J*=6, 14 Hz, H-6), 5.29 (dd, *J*=6, 13 Hz, H-6), 5.16 (t, *J*=10 Hz, H-4), 5.15 (dd, *J*=8.5, 9 Hz, H-2), 5.09 (t, *J*=10 Hz, H-4), 4.48 (dd, *J*=6, 10 Hz, H-5), 4.47 (dd, *J*=6, 10 Hz, H-5), 3.83 (d, *J*=14 Hz, H-6') and 3.78 (d, *J*=13 Hz, H-6')] forming *C1* conformation and the β-anomer, as shown by the coupling constants.

Methylation of **3** afforded nonacosa-*O*-methylrugosin F, $C_{111}H_{114}O_{52}\cdot 3/2H_2O$, $[\alpha]_D$ +26° (c=1, acetone) [mass spectrum: m/z 646 and 614 (methylated valoneoyl); 422, 404 and 360 (hexamethoxydiphenoyl); 212, 197 and 195 (trimethylgalloyl)].

Hydrolysis of **3** afforded **5** and rugosin C (**8**)[3] in an analogous way to the partial hydrolysis of **1** and **2**. Thus structure **3** was assigned to rugosin F.

Rugosin G (**4**), $C_{123}H_{86}O_{78}\cdot 18H_2O$, $[\alpha]_D$ +109° (c=1, acetone), UV λ_{max}^{MeOH} nm (log ε) 218 (5.37) and 276 (5.05), was obtained as a light tan amorphous powder. This tannin was pure and homogeneous on TLC, HPLC, and in the ^{1}H-NMR spectrum. The retention volume on gel permeation chromatography on a co-polymer of styrene and divinylbenzene is consistent with the molecular weight of the trimeric version of the other rugosins. The ^{1}H-NMR spectrum (200 MHz, in acetone-d_6) shows that



4

it has twenty-two aromatic protons [δ7.15 (3H), 7.14 (1H), 7.03 (2H), 7.02 (2H), 7.009 (2H), 7.006 (2H), 7.00 (2H), 6.98 (2H), 6.68 (1H), 6.48 (1H), 6.47 (2H), 6.23 (1H) and 6.22 (1H)] corresponding to seven galloyl, a hexahydroxydiphenoyl and two valoneoyl groups, and twenty-one glucose protons [δ6.19, 6.11 and 6.08 (d, J=8 Hz, H-1); 5.85, 5.78 and 5.77 (t, J=10 Hz, H-3); 5.62, 5.58 and 5.54 (dd, J=8, 10 Hz, H-2); 5.32, 5.31 and 5.27 (dd, J=6, 14 Hz, H-6); 5.17, 5.16 and 5.10 (t, J=10 Hz, H-4); 4.53, 4.47 and 4.43 (dd, J=6, 10 Hz, H-5); 3.79, 3.76 and 3.70 (d, J=14 Hz, H-6')]. The coupling constants of glucose protons indicate three glucose cores form *C1* conformation and β-anomer.

Partial hydrolysis of **4** gave **5**, **6** and **7** in approximately the same amount. Therefore, rugosin G has the structure **4** having three tellimagrandin II (**9**)[4~6] units.

Among the tannins of this flower, **9** is the most abundant component (ca. 15% of the extract of fresh flower petal). The dimeric tannins (and also the trimer) may have been produced by ether linkage formation between the galloyl group of **9** and the hexahydroxydiphenoyl group of **5**, casuarictin (**10**),[4] or another molecule of **9**, although another biosynthetic route, esterification of the valoneoyl group of **6**, **7** or **8** with anomeric hydroxyl group of **5**, is also conceivable.

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