# Tannins and Related Compounds. CXXIII.[1a] Chromone, Acetophenone and Phenylpropanoid Glycosides and Their Galloyl and/or Hexahydroxydiphenoyl Esters from the Leaves of *Syzygium aromaticum* MERR. *et* PERRY

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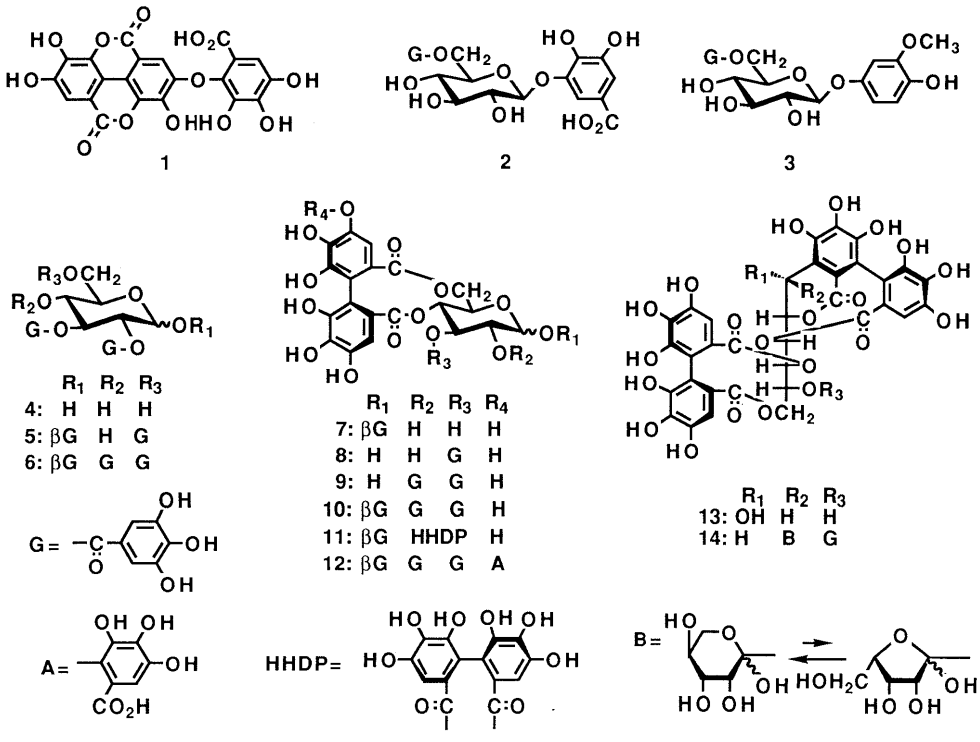
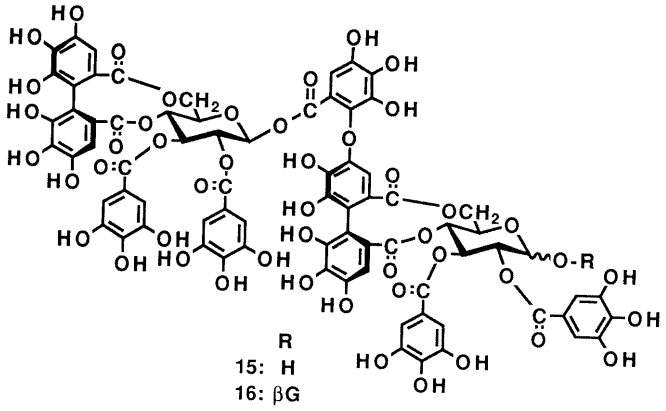
**From the dried leaves of *Syzygium aromaticum* MERR. *et* PERRY (Myrtaceae), eleven new compounds, *i.e.*, eugenol 4-*O*-β-D-(6′-*O*-galloyl)glucopyranoside (17), 2-methyl-5,7-dihydroxychromone 8-*C*-β-D-glucopyranoside (18) and its 6′-*O*-gallate (19), 2,4,6-trihydroxyacetophenone 3-*C*-β-D-glucopyranoside (20) and its 2′-*O*- (21), 6′-*O*- (22), 2′,3′-di-*O*- (23), 2′,6′-di-*O*- (24), 2′,3′,6′-tri-*O*- (25), 2′,3′,4′,6′-tetra-*O*-gallate (26) and 2′,3′-di-*O*-galloyl-4′,6′-*O*-(*S*)-hexahydroxydiphenoyl ester (27) were isolated, together with sixteen known tannins and related compounds. The structures of these compounds were established on the basis of spectroscopic and chemical evidence.**

**Keywords** *Syzygium aromaticum*; Myrtaceae; tannin; *C*-glycoside; phenol *C*-glucoside; eugenol glucoside gallate

As a part of our chemical studies on tannins in Myrtaceous plants,[2] we previously reported the occurrence of an ellagitannin[2a] in cloves (dried flower-buds of *Syzygium aromaticum* MERR. *et* PERRY). In a continuation of that work, we have examined the leaves of *S. aromaticum* and isolated eleven new compounds consisting of chromone, acetophenone and phenylpropanoid glycosides and their gallic acid and/or hexahydroxydiphenic acid esters, together with sixteen known tannins and related compounds. This paper deals with the isolation and structure elucidation of these compounds.

The air-dried leaves collected in Indonesia were extracted with 70% aqueous acetone. The extract was initially subjected to Sephadex LH-20 column chromatography with water containing increasing proportions of methanol to afford six fractions. Each fraction was repeatedly chromatographed on Sephadex LH-20 with ethanol or water–methanol, on various reversed-phase gels such as MCI-gel CHP 20P, Bondapak $C_{18}$/Porasil B and Toyopearl HW 40F with water–methanol, and on Avicel cellulose with 2% acetic acid to afford twenty-seven compounds (**1**—**27**). Among them, compounds **1**—**16** were shown by physical and spectral comparisons to be valoneic acid bislactone (**1**),[3] phenol glucoside gallates [gallic acid 3-*O*-β-D-(6′-*O*-galloyl)-glucopyranoside (**2**)[4] and 4-hydroxy-3-methoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)-glucopyranoside (**3**)[5]], galloylglucoses [2,3-di-*O*- (**4**),[6] 1,2,3,6-tetra-*O*- (**5**)[7] and 1,2,3,4,6-penta-*O*-galloyl-β-D-glucose (**6**)[7]] and ellagitannins [strictinin (**7**),[8] gemin D (**8**),[9] 1-desgalloyleugeniin (**9**),[10] eugeniin (**10**),[2a] 1(β)-*O*-galloylpedunculagin (**11**),[11] rugosin A (**12**),[12] casuariin (**13**),[8,13] pterocarinin A (**14**)[14] and rugosins E (**15**) and D (**16**)[15]].





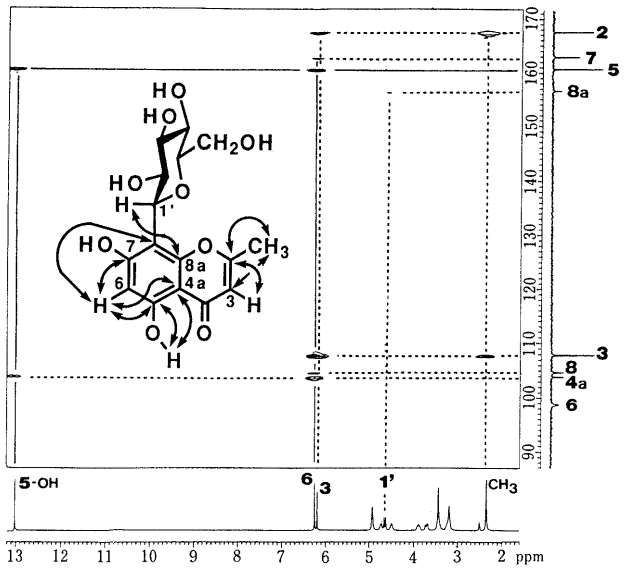
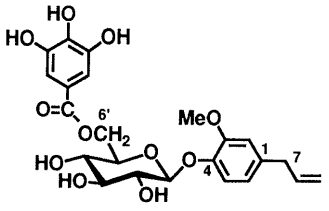



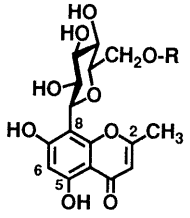

Fig. 1. $^{1}H$–$^{13}C$ Long-Range COSY Spectrum of **18** in DMSO-$d_6$ ($J_{CH}=8$ Hz)

Compound **17** gave a dark blue coloration with the ferric chloride reagent, and showed the $[M-H]^-$ peak at $m/z$ 477 in the negative ion FAB-MS. The $^{1}H$-NMR spectrum showed signals due to a tri-substituted aromatic ring [$\delta$ 6.69 (dd, $J=2$, 8 Hz), 6.82 (d, $J=2$ Hz) and 7.12 (d, $J=8$ Hz)], three olefinic protons [$\delta$ 5.94 (m), 5.01 (br d, $J=10$ Hz) and 5.04 (br d, $J=17$ Hz)], a methoxyl [$\delta$ 3.81 (3H, s)] and a methylene [$\delta$ 3.29 (2H, d, $J=7$ Hz)], suggesting the presence of a eugenol framework in the molecule. The $^{13}C$-NMR spectrum showed, together with the signals arising from the eugenol moiety, signals due to a $\beta$-glucopyranosyl residue ($\delta$ 102.3, 77.4, 75.0, 74.4, 71.2 and 64.5) and a galloyl group ($\delta$ 166.9, 146.0, 138.8, 121.5 and 109.9). The chemical shifts of the signals due to the eugenol and glucosyl moieties were closely related to those of eugenol 4-*O*-$\beta$-D-glucopyranoside (citrusin C),[16] except for the lowfield shift of the glucose C-6 signal in **17**. These observations, combined with the appearance of the glucose C-6 proton signals at lower field [$\delta$ 4.36 (dd, $J=6$, 12 Hz) and 4.64 (dd, $J=2$, 12 Hz)] in the $^{1}H$-NMR spectrum, indicated the galloyl group to be located at this position. Thus, **17** was characterized as eugenol 4-*O*-$\beta$-D-(6′-*O*-galloyl)glucopyranoside.

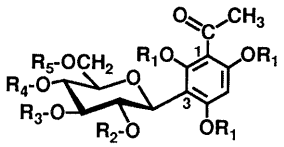
Compound **18** was obtained as colorless needles, mp 183—184 °C. The $^{13}C$-NMR spectrum showed the presence of a phloroglucinol-type aromatic ring [$\delta$ 98.4 (d), 103.5 (s), 104.4 (s), 156.2 (s), 160.4 (s) and 162.6 (s)], a tri-substituted double bond [$\delta$ 107.5 (d) and 167.3 (s)], a carbonyl ($\delta$ 182.0) and a methyl group [$\delta$ 19.7 (q)], suggesting **18** to have a 2-methyl-5,7-dihydroxychromone skeleton. Furthermore, the appearance of six aliphatic carbon signals at $\delta$ 81.2 (d), 78.5 (d), 73.1 (d), 70.8 (d), 70.4 (d) and 61.3 (t), whose chemical shifts were closely related to those of the *C*-glucosyl residue of 6-*C*-glucosylquercetin [$\delta$ 73.0 (C-1), 70.5 (C-2), 78.9 (C-3), 70.3 (C-4), 81.3 (C-5) and 61.4 (C-6)],[17] indicated that **18** is a *C*-glucoside of 2-methyl-5,7-dihydroxychromone. In the $^{1}H$-NMR spectrum, the observation of a chelated hydroxyl proton signal



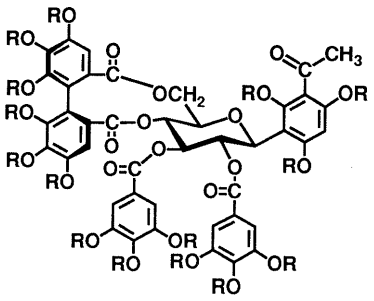
17



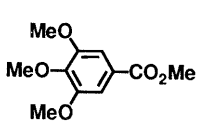
R
18 : H
19 : G



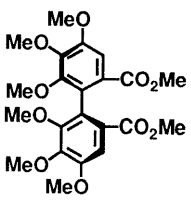
| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ |
|---|---|---|---|---|---|
| 20 : | H | H | H | H | H |
| 20a: | Me | H | H | H | H |
| 21 : | H | G | H | H | H |
| 22 : | H | H | H | H | G |
| 23 : | H | G | G | H | H |
| 24 : | H | G | H | H | G |
| 25 : | H | G | G | H | G |
| 26 : | H | G | G | G | G |



R
27 : H
27a: Me



27b



27c

at $\delta$ 13.02 (s), as well as a long-range coupling between the olefinic proton signal at $\delta$ 6.18 (d, $J=0.7$ Hz) and the methyl proton signal at $\delta$ 2.34 (3H, d, $J=7.0$ Hz), also supported the structure. The location of the *C*-glucosyl moiety was determined by examination of $^{1}H$–$^{13}C$ long-range shift-correlation spectroscopy ($^{1}H$–$^{13}C$ long-range COSY) spectrum ($J=8$ Hz) of **18** (Fig. 1). In this spectrum, a long-range coupling was observed between the lowfield hydroxyl proton ($\delta$ 13.02) and a hydroxy-bearing aromatic carbon ($\delta$ 160.4), the latter being thus assignable to C-5. Next, a similar correlation was observed between this C-5 signal and the aromatic proton signal at $\delta$ 6.24. These observations clearly indicated that the aromatic proton signal at $\delta$ 6.24 was assignable to the C-6 proton of the chromone skeleton. Thus, the location of the *C*-glycosyl moiety was concluded to be at the C-8 position, and compound **18** was shown to be 2-methyl-5,7-dihydroxychromone 8-*C*-$\beta$-D-glucopyranoside.

The $^{1}H$-NMR spectrum of **19** was closely correlated with that of **18**, except for the appearance of a two-proton galloyl singlet at $\delta$ 7.13 and the lowfield shift of the glucose C-6 proton signal [$\delta$ 4.56 (2H, br s)]. The structure of **19** was confirmed by tannase hydrolysis, which yielded **18** and gallic acid, thus establishing **19** to be 2-methyl-5,7-dihydroxychromone 8-*C*-$\beta$-D-(6′-*O*-galloyl)glucopyranoside.

Compound **20** showed, in the $^{13}C$-NMR spectrum (Table I), signals due to a phloroglucinol-type aromatic ring and an acetyl group, along with signals attributable to a *C*-glycosidically linked hexose residue. The $^{1}H$-NMR spectrum exhibited a one-proton aromatic singlet at $\delta$ 6.00 characteristic of a phloroglucinol ring proton. These observations suggested that **20** is a 2,4,6-trihydroxyacetophenone *C*-glycoside, and this was consistent with the negative ion FAB-MS data, which showed the $[M-H]^-$

TABLE I. $^{13}C$-NMR Spectral Data for Compounds **20**—**27** ($\delta$ Values)[a]

| | **20** | **21** | **22** | **23** | **24** | **25** | **26** | **27** |
|---|---|---|---|---|---|---|---|---|
| Aglycone | | | | | | | | |
| C-1,3 | 103.8<br>105.4 | 102.5<br>105.2 | 103.4<br>105.3 | 102.1<br>105.1 | 102.2<br>105.2 | 101.9<br>105.1 | 101.8<br>105.1 | 102.1<br>105.0 |
| C-5 | 95.9 | 95.8 | 95.8 | 95.8 | 95.8 | 95.6 | 95.7 | 95.2 |
| C-2,4,6 | 163.7<br>164.1<br>164.3 | 163.9 (2C)<br>164.2 | 163.7<br>164.0<br>164.3 | 163.9 (3C) | 163.9 (3C) | 163.9<br>164.0<br>164.7 | 163.7<br>164.1<br>165.1 | 163.3 (2C)<br>164.4 |
| $CH_3$ | 32.9 | 32.8 | 32.9 | 32.8 | 32.8 | 32.8 | 32.9 | 32.8 |
| CO | 204.2 | 203.9 | 204.6 | 204.0 | 204.1 | 204.2 | 204.1 | 204.0 |
| Glucose | | | | | | | | |
| C-1 | 75.6 | 73.7 | 75.6 | 73.5 | 73.7[b] | 73.4 | 73.4 | 73.6 |
| C-2 | 70.5 | 70.9 | 70.8 | 69.1 | 71.1 | 69.5 | 69.9 | 70.8[b] |
| C-3 | 79.1 | 77.2 | 78.7[b] | 78.1 | 76.9 | 77.9 | 75.5 | 76.2 |
| C-4 | 73.2 | 73.7 | 73.0 | 71.4 | 73.8[b] | 71.3 | 71.1 | 71.1[b] |
| C-5 | 81.7 | 82.1 | 79.0[b] | 82.1 | 79.4 | 79.4 | 77.4 | 77.1 |
| C-6 | 61.5 | 61.6 | 64.4 | 61.5 | 64.1 | 64.1 | 63.5 | 63.9 |
| Galloyl | | | | | | | | |
| C-1 | — | 121.6 | 120.9 | 120.9<br>121.3 | 121.2<br>121.5 | 120.7<br>121.1 (2C) | 120.3<br>120.6<br>120.8<br>121.2 | 120.7<br>121.0 |
| C-2,6 | — | 110.0 (2C) | 109.9 (2C) | 110.0 (4C) | 109.9 (2C)<br>110.4 (2C) | 110.0 (6C) | 110.0 (8C) | 109.9 (2C)<br>110.1 (2C) |
| C-3,5 | — | 145.7 (2C) | 145.9 (2C) | 145.6 (2C)<br>145.8 (2C) | 145.7 (2C)<br>146.1 (2C) | 145.5 (2C)<br>145.8 (2C)<br>146.0 (2C) | 145.8 (2C)<br>146.0 (6C) | 145.2 (2C)<br>145.7 (2C) |
| C-4 | — | 138.5 | 139.1 | 138.8 (2C) | 138.7<br>139.1 | 138.9 (2C)<br>139.1 | 138.9<br>139.1 (2C)<br>139.4 | 138.8<br>139.0 |
| –COO– | — | 166.0 | 167.5 | 165.7<br>166.8 | 166.2<br>167.1 | 165.9<br>166.9<br>167.2 | 165.6<br>166.1<br>166.4<br>166.8 | 165.6<br>166.8 |
| Hexahydroxydiphenoyl | | | | | | | | |
| C-1,1′ | — | — | — | — | — | — | — | 115.8 (2C) |
| C-2,2′ | — | — | — | — | — | — | — | 126.0<br>126.5 |
| C-3,3′ | — | — | — | — | — | — | — | 107.9<br>108.1 |
| C-4,4′,6,6′ | — | — | — | — | — | — | — | 144.3<br>145.2<br>145.7 (2C) |
| C-5,5′ | — | — | — | — | — | — | — | 136.4<br>136.5 |
| –COO– | — | — | — | — | — | — | — | 167.9<br>168.4 |

a) Measured in acetone-$d_6$ + $D_2O$. b) Assignments may be interchanged in each column.

peak at *m/z* 329. Further structural confirmation was obtained by methylation of **20** with ethereal diazomethane, which afforded the trimethyl ether (**20a**) [FAB-MS *m/z*: 373 $(M+H)^+$].

The *C*-glycosidically linked hexose residue was considered to be glucose from the fact that the chemical shifts of the sugar carbon signals were in good agreement with those of 2,4,6,3′,4′-pentahydroxybenzophenone 3-*C*-glucoside [$\delta$ 76.0 (C-1), 70.4 (C-2), 78.9 (C-3), 73.5 (C-4), 81.6 (C-5) and 61.5 (C-6)].[18] Furthermore, to confirm the structure, an attempt was made to prepare **20** by coupling of D-glucose and 2,4,6-trihydroxyacetophenone. Among various conditions tested,[19] heating in phosphate buffer (pH 7.3) afforded the desired product, the $[\alpha]_D$ and the $^1$H-NMR spectrum of which were identical with those of **20**. On the basis of these chemical and spectroscopic findings, the structure of **20** was unequivocally established to be 2,4,6-trihydroxyacetophenone 3-*C*-$\beta$-D-glucopyranoside.

Compounds **21**—**26** showed dark blue colorations with the ferric chloride reagent, suggesting the presence of galloyl group(s) in each molecule. The $^{13}$C-NMR spectra (Table I) of these compounds indicated the occurrence of a *C*-glucosyl 2,4,6-trihydroxyacetophenone (**20**) moiety as a common structural framework. Hydrolysis of each compound with tannase yielded gallic acid and **20**. The number(s) of the galloyl group(s) in each molecule was confirmed by their negative ion FAB-MS and also by the observation of characteristic two-proton singlet(s) around $\delta$ 7.0 in the $^1$H-NMR spectrum (Table II). The location(s) of the galloyl group(s) was determined by comparison of the $^1$H-NMR chemical shifts of the glucose proton signals with those of **20**. For example, the $^1$H-NMR spectra of **25** exhibited lowfield shifts of the glucose C-2, C-3 and C-6 proton signals, which indicated that galloyl groups were located at these positions. On the basis of spectral examination analogous to that described for **25**, compounds **21**—**26** were characterized as 2′-*O*- (**21**), 6′-*O*- (**22**), 2′,3′-di-*O*- (**23**), 2′,6′-di-*O*- (**24**), 2′,3′,6′-tri-*O*- (**25**) and 2′,3′,4′,6′-tetra-*O*- (**26**) galloyl esters of **20**.

Compound **27** gave, with the sodium nitrite–acetic acid reagent,[20] a reddish brown coloration which is characteristic of ellagitannins. The $^{13}$C-NMR spectrum of **27** is closely related to that of **26**. In particular, the chemical shifts of the signals arising from the 2,4,6-trihydroxyacetophenone framework were almost identical with those of **26**. The lowfield shifts of all the sugar signals in the $^1$H-NMR spectrum (Table II) suggested that the hydroxyl groups in the glucosyl moiety are completely acylated. The presence of two galloyl and one hexahydroxydiphenoyl ester group was readily deduced from the $^1$H- and $^{13}$C-NMR spectra (Table I).

Methylation of **27** with dimethyl sulfate and anhydrous potassium carbonate in dry acetone gave the pentadecamethyl ether (**27a**), which showed the $[M+H]^+$ peak at *m/z* 1147 in the FAB-MS. Subsequent alkaline methanolysis of **27a** with methanolic sodium methoxide yielded methyl 3,4,5-trimethoxybenzoate (**27b**), dimethyl 4,4′,5,5′,6,6′-hexamethoxydiphenate (**27c**) and **20a**. The production of **20a** confirmed the presence of the trihydroxyacetophenone *C*-glucoside core in **27**, while the specific optical rotation [$-28.0°$ ($CHCl_3$)] of **27c** indicated the chirality of the biphenyl bond to be in the *S*-series.[21]

In the $^1$H-NMR spectrum of **27**, a large coupling constant ($J=10$ Hz) of the glucose ring proton signals indicated that the glucopyranose ring adopts the $^4C_1$ conformation. This fact, coupled with the observation of a fairly lowfield shift [$\delta$ 5.39 (dd, $J=6$, 13 Hz)] of one of the glucose C-6 methylene signals, which is consistent with those observed in tannins having a hexahydroxydiphenoyl group at the glucose C-4 and C-6 positions[11] [*e.g.*, eugeniin (**10**)], im-

TABLE II. $^1$H-NMR Spectral Data for Compounds **20**—**27** ($\delta$ Values)[a]

| | **20** | **21** | **22** | **23** | **24** | **25** | **26** | **27** |
|---|---|---|---|---|---|---|---|---|
| Aglycone | | | | | | | | |
| H-5 | 6.00 (s) | 5.90 (s) | 5.92 (s) | 5.89 (s) | 5.84 (s) | 5.93 (s) | 5.96 (s) | 6.01 (s) |
| $CH_3$ | 2.60 (s) | 2.51 (s) | 2.58 (s) | 2.54 (s) | 2.49 (s) | 2.51 (s) | 2.53 (s) | 2.55 (s) |
| Glucose | | | | | | | | |
| H-1 | 4.89 (d, $J=10$) | 5.15 (d, $J=10$) | 5.01 (d, $J=9$) | 5.32 (d, $J=10$) | 5.25 (d, $J=10$) | 5.37 (d, $J=10$) | 5.49 (d, $J=10$) | 5.32 (d, $J=10$) |
| H-2 | 3.47—3.89 (m) | 5.43 (t, $J=10$) | 3.64—3.80 (m) | 5.52 (t, $J=10$) | 5.46 (t, $J=10$) | 5.58 (t, $J=10$) | 5.88 (t, $J=10$) | 5.66 (t, $J=10$) |
| H-3 | 3.47—3.89 (m) | 3.50—3.90 (m) | 3.64—3.80 (m) | 5.69 (t, $J=10$) | 3.91 (m) | 5.87 (t, $J=10$) | 6.09 (t, $J=10$) | 6.27 (t, $J=10$) |
| H-4 | 3.47—3.89 (m) | 3.50—3.90 (m) | 3.64—3.80 (m) | 4.11 (t, $J=10$) | 3.91 (m) | 4.12 (m) | 5.71 (t, $J=10$) | 5.32 (t, $J=10$) |
| H-5 | 3.47—3.89 (m) | 3.50—3.90 (m) | 3.64—3.80 (m) | 3.72—3.95 (m) | 3.91 (m) | 4.12 (m) | 4.30—4.64 (m) | 4.30 (dd, $J=6$, 10) |
| H-6 | 3.47—3.89 (m) | 3.50—3.90 (m) | 4.55 (2H, m) | 3.72—3.95 (m) | 4.62 (2H, br s) | 4.64 (2H, br s) | 4.30—4.64 (m) | 3.87 (d, $J=13$) |
| | — | — | — | — | — | — | — | 5.39 (dd, $J=6$, 13) |
| Galloyl | — | 7.01 (2H, s) | 7.15 (2H, s) | 6.90 (2H, s) | 7.02 (2H, s) | 6.92 (2H, s) | 6.93 (2H, s) | 6.92 (2H, s) |
| | — | — | — | 7.03 (2H, s) | 7.18 (2H, s) | 7.05 (2H, s) | 6.95 (2H, s) | 6.97 (2H, s) |
| | — | — | — | — | — | 7.19 (2H, s) | 7.18 (2H, s) | — |
| | — | — | — | — | — | — | 7.19 (2H, s) | — |
| Hexahydroxydiphenoyl | | | | | | | | |
| | — | — | — | — | — | — | — | 6.51 (1H, s) |
| | — | — | — | — | — | — | — | 6.66 (1H, s) |

a) Measured in acetone-$d_6$ + $D_2O$. $J$ = values are expressed in Hz.

plied the location of the hexahydroxydiphenoyl group at the C-4 and C-6 positions. Consequently, **27** was concluded to be 2,4,6-trihydroxyacetophenone 3-*C*-*β*-D-[2′,3′-di-*O*-galloyl-4′,6′-*O*-(*S*)-hexahydroxydiphenoyl)-glucopyranoside.

Although a number of *C*-glycosidic ellagitannins having an open-chain form of the glucose moiety, *e.g.*, casuariin (**13**), have been isolated from the plants of Myrtaceae,[2b] Fagaceae,[13,22] Casuarinaceae,[8,13] Stachyuraceae,[8,13] Punicaceae,[13,23] Betulaceae,[13,24] *etc.*, only two, stenophynins A and B,[25] having a pyranose form have previously been found. Compound **27** is hence the third example of an ellagitannin having a *C*-glucopyranoside core. As for the gallotannins based on a *C*-glucopyranoside core, the galloyl esters of benzophenone *C*-glucopyranosides and bergenin were previously isolated from *Mangifera indica*[18] and from *Mallotus japonicus*,[26] respectively.

## Experimental

The instruments and chromatographic conditions used throughout this work were essentially the same as described in the preceding paper.[1]

**Extraction and Isolation** The dried leaves (4.0 kg) of *S. aromaticum* collected in Indonesia were extracted with 70% aqueous acetone at room temperature. The acetone was removed by evaporation under reduced pressure (*ca.* 40 °C), and the resulting precipitates, consisting mainly of chlorophylls, were removed by filtration. The filtrate was further concentrated and applied to a column of Sephadex LH-20. Elution with $H_2O$ containing increasing amounts of MeOH and finally with a mixture of $H_2O$ and acetone gave six fractions; I (*ca.* 150 g), II (45 g), III (150 g), IV (252 g), V (71 g) and VI (83 g). Fraction I, consisting mainly of sugars, was almost negative to the ferric chloride reagent and was not examined further. Fraction II was chromatographed over MCI-gel CHP 20P with $H_2O$–MeOH and then over Sephadex LH-20 with $H_2O$–MeOH to afford compounds **18** (263 mg) and **20** (236 mg). Fraction III was repeatedly chromatographed over MCI-gel CHP 20P, Cosmosil 75$C_{18}$-OPN and Toyopearl HW-40F with $H_2O$–MeOH and Avicel cellulose with 2% acetic acid to give compound **21** (379 mg), gallic acid 3-*O*-*β*-D-(6′-*O*-galloyl)-glucoside (**2**) (10 mg), 4-hydroxy-3-methoxyphenol 1-*O*-*β*-D-(6′-*O*-galloyl)-glucoside (**3**) (160 mg), 2,3-di-*O*-galloylglucose (**4**) (858 mg), strictinin (**7**) (400 mg), gemin D (**8**) (4.7 g), casuariin (**13**) (39 mg) and pterocarinin A (**14**) (86 mg). Fraction IV was separated into two fractions (IV-1 and IV-2) by MCI-gel CHP 20P chromatography with $H_2O$–MeOH. Chromatography of fraction IV-1 over Sephadex LH-20 with $H_2O$–MeOH and then Cosmosil 75$C_{18}$-OPN with $H_2O$–MeOH furnished 1-desgalloyleugeniin (**9**) (48.7 g). Repeated chromatography of fraction IV-2 on Cosmosil 75$C_{18}$-OPN, MCI-gel CHP 20P, Bondapak $C_{18}$/Porasil B and Toyopearl HW-40F with $H_2O$–MeOH and Sephadex LH-20 with EtOH yielded valoneic acid bislactone (**1**) (720 mg) and compounds **17** (860 mg), **19** (59 mg), **22** (205 mg), **23** (1.13 g), **24** (741 mg) and **25** (1.22 g). Fraction V was rechromatographed on MCI-gel CHP 20P, Toyopearl HW-40F and Cosmosil 75$C_{18}$-OPN with $H_2O$–MeOH and Sephadex LH-20 with EtOH to furnish 1,2,3,6-tetra-*O*-galloyl-*β*-D-glucose (**5**) (199 mg), 1,2,3,4,6-penta-*O*-galloyl-*β*-D-glucose (**6**) (135 mg), eugeniin (**10**) (35.8 g) and compounds **26** (2.97 g) and **27** (633 mg). On similar chromatographies, fraction VI gave 1(*β*)-*O*-galloylpedunculagin (**11**) (458 mg) and rugosins A (**12**) (65 mg), E (**15**) (3.9 g) and D (**16**) (7.7 g). The known compounds **1**—**16** were identified by direct comparisons of the $^1$H-NMR data and $[\alpha]_D$ with those of authentic samples.

**General Procedures for Enzymatic Hydrolysis** A solution of a sample (10—200 mg) in $H_2O$ (2—8 ml) was treated with tannase at room temperature for 10 h. The reaction mixture was directly applied to a column of MCI-gel CHP 20P. Elution with $H_2O$ containing increasing proportions of MeOH furnished gallic acid, which was identified by co-TLC with an authentic sample [solvent, benzene–ethyl formate–formic acid (5 : 4 : 1)], and a hydrolysate.

**Eugenol 4-*O*-*β*-D-(6′-*O*-Galloyl)glucoside (17)** Colorless needles ($H_2O$), mp 207—208 °C, $[\alpha]_D^{25}$ −30.3° (*c*=0.9, acetone). *Anal.* Calcd for $C_{23}H_{26}O_{11}$: C, 57.74; H, 5.48. Found: C, 57.45; H, 5.39. Negative ion FAB-MS *m/z*: 477 $[M-H]^-$. $^1$H-NMR (acetone-$d_6$ + $D_2O$, 100 MHz) *δ*: 3.29 (2H, d, *J*=7 Hz, H-7), 3.48—3.64 (3H, m, H-2′,3′,4′), 3.81 (3H, s, $OCH_3$), 3.89 (1H, m, H-5′), 4.36 (1H, dd, *J*=6, 12 Hz, H-6′), 4.64 (1H, dd, *J*=2, 12 Hz, H-6′), 4.93 (1H, br d, *J*=8 Hz, H-1′), 5.01 (1H, br d, *J*=10 Hz, H-9), 5.04 (1H, br d, *J*=17 Hz, H-9), 5.94 (1H, m, H-8), 6.69 (1H, dd, *J*=2, 8 Hz, H-6), 6.82 (1H, d, *J*=2 Hz, H-2), 7.12 (1H, d, *J*=8 Hz, H-5), 7.17 (2H, s, galloyl-H). $^{13}$C-NMR (acetone-$d_6$ + $D_2O$, 25.05 MHz) *δ*: 40.2 (C-7), 56.3 ($OCH_3$), 64.5 (C-6′), 71.2, (C-4′), 74.4, 75.0, 77.4 (C-2′, 3′, 5′), 102.3 (C-1′), 109.9 (galloyl-2,6), 113.7 (C-2), 115.8 (C-9), 117.4 (C-5), 121.5 (galloyl-1), 121.8 ((C-6), 135.5 (C-1), 138.6 (C-8), 138.8 (galloyl-4), 145.8 (C-4), 146.0 (galloyl-3, 5), 149.9 (C-3), 166.9 (COO).

**2-Methyl-5,7-dihydroxychromone 8-*C*-*β*-D-Glucoside (18)** Colorless needles ($H_2O$), mp 183—184 °C, $[\alpha]_D^{21}$ +74.2° (*c*=0.7, pyridine). *Anal.* Calcd for $C_{16}C_{18}O_9 \cdot 1/2H_2O$: C, 52.89; H, 5.27. Found: C, 52.80; H, 5.24. Negative ion FAB-MS *m/z*: 353 $[M-H]^-$. UV $\lambda_{max}^{MeOH}$ nm (log *ε*): 294 (3.89), 256 (4.43), 249 (4.41). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log *ε*): 308 (3.98), 265 (4.44). $^1$H-NMR (DMSO-$d_6$, 100 MHz) *δ*: 2.34 (3H, d, *J*=0.7 Hz, $CH_3$), 3.18—3.88 (m, sugar-H), 4.47 (1H, br s, OH), 4.63 (1H, d, *J*=10 Hz, H-1′), 4.90 (2H, br s, OH), 6.18 (1H, d, *J*=0.7 Hz, H-3), 6.24 (1H, s, H-6), 13.02 (1H, s, OH). $^{13}$C-NMR (DMSO-$d_6$, 25.05 MHz) *δ*: 19.7 ($CH_3$), 61.3 (C-6′), 70.4, 70.8 (C-2′, 4′), 73.1 (C-1′), 78.5 (C-3′), 81.2 (C-5′), 98.4 (C-6), 103.5 (C-4a), 104.4 (C-8), 107.5 (C-3), 156.2 (C-8a), 160.4 (C-5), 162.6 (C-7), 167.3 (C-2), 182.0 (C-4).

**2-Methyl-5,7-dihydroxychromone 8-*C*-*β*-D-(6′-*O*-Galloyl)glucoside (19)** A white amorphous powder, $[\alpha]_D^{28}$ −54.9° (*c*=1.0, MeOH). *Anal.* Calcd for $C_{23}H_{22}O_{13} \cdot 1/2H_2O$: C, 53.70; H, 4.50. Found: C, 53.99; H, 4.74. Negative ion FAB-MS *m/z*: 505 $[M-H]^-$. $^1$H-NMR (acetone-$d_6$ + $D_2O$, 100 MHz) *δ*: 2.37 (3H, d, *J*=0.7 Hz, $CH_3$), 3.44—4.03 (m, H-2′, 3′, 4′, 5′), 4.56 (2H, br s, H-6′), 5.09 (1H, d, *J*=10 Hz, H-1′), 6.08 (1H, d, *J*=0.7 Hz, H-3), 6.22 (1H, s, H-6), 7.13 (2H, s, galloyl-H). $^{13}$C-NMR (DMSO-$d_6$, 25.05 MHz) *δ*: 19.7 ($CH_3$), 63.8 (C-6′), 70.0, 70.7 (C-2′, 4′), 73.3 (C-1′), 78.1, 78.3 (C-3′, 5′), 98.3 (C-6), 103.5 (C-4a), 104.0 (C-8), 107.5 (C-3), 108.5 (galloyl-2, 6), 119.4 (galloyl-1), 138.3 (galloyl-4), 145.5 (galloyl-3, 5), 156.3 (C-8a), 160.5 (C-5), 162.6 (C-7), 165.8 (COO), 167.2 (C-2), 181.9 (C-4). Tannase hydrolysis of **19** (12 mg) gave gallic acid and **18** (3 mg).

**2,4,6-Trihydroxyacetophenone 3-*C*-*β*-D-Glucoside (20)** A white amorphous powder, $[\alpha]_D^{21}$ +49.3° (*c*=0.8, MeOH). *Anal.* Calcd for $C_{14}H_{18}O_9 \cdot 1/2H_2O$: C, 49.56; H, 5.64. Found: C, 49.49; H, 5.58. Negative ion FAB-MS *m/z*: 329 $[M-H]^-$. UV $\lambda_{max}^{MeOH}$ nm (log *ε*): 286 (4.28), 228 (4.30). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log *ε*): 307 (4.47), 237 (4.11), 222 (4.37).

**Methylation of 20** A solution of **20** (138 mg) in MeOH (5 ml) was treated with ethereal diazomethane. The mixture was concentrated and subjected to silica gel chromatography. Elution with benzene–EtOH (3 : 1) furnished 2,4,6-trimethoxyacetophenone 3-*C*-*β*-D-glucoside (**20a**) (43.5 mg) as a white amorphous powder, $[\alpha]_D^{16}$ +8.0° (*c*=0.7, MeOH). *Anal.* Calcd for $C_{17}H_{24}O_9 \cdot 1/2H_2O$: C, 53.54; H, 6.45. Found: C, 53.59; H, 6.82. FAB-MS *m/z*: 395 $[M+Na]^+$, 373 $[M+H]^+$. $^1$H-NMR (acetone-$d_6$, 100 MHz) *δ*: 2.38 (3H, s, $CH_3$), 3.74, 3.86, 3.87 (each 3H, s, $OCH_3$), 4.78 (1H, d, *J*=10 Hz, H-1′), 6.54 (1H, s, H-5).

**Preparation of 20** A mixture of 2,4,6-trihydroxyacetophenone (1.0 g) and D-glucose (1.0 g) in 0.2 M potassium phosphate buffer (pH 7.3) (150 ml) was heated at 80 °C for 4 h. The solution was acidified with 1 N HCl and directly subjected to MCI-gel CHP 20P chromatography with $H_2O$ containing increasing proportions of MeOH to yield **20** (270 mg), which was identified by comparison of the *Rf* value on TLC, $[\alpha]_D$ and the $^1$H- and $^{13}$C-NMR spectra with those of an authentic sample.

**2,4,6-Trihydroxyacetophenone 3-*C*-*β*-D-(2′-*O*-Galloyl)glucoside (21)** A white amorphous powder, $[\alpha]_D^{27}$ −98.6° (*c*=0.9, MeOH). *Anal.* Calcd for $C_{21}H_{22}O_{13} \cdot H_2O$: C, 50.41; H, 4.83. Found: C, 50.33; H, 4.70. Negative ion FAB-MS *m/z*: 481 $[M-H]^-$. Tannase hydrolysis of **21** (10 mg) afforded gallic acid and **20** (4 mg).

**2,4,6-Trihydroxyacetophenone 3-*C*-*β*-D-(6′-*O*-Galloyl)glucoside (22)** A white amorphous powder, $[\alpha]_D^{28}$ −49.0° (*c*=1.4, MeOH). *Anal.* Calcd for $C_{21}H_{22}O_{13}$: C, 52.29; H, 4.60. Found: C, 52.04; H, 4.79. Negative ion FAB-MS *m/z*: 481 $[M-H]^-$. Tannase hydrolysis of **22** (15 mg) yielded gallic acid and **20** (7 mg).

**2,4,6-Trihydroxyacetophenone 3-*C*-*β*-D-(2′,3′-Di-*O*-galloyl)glucoside (23)** A white amorphous powder, $[\alpha]_D^{28}$ +30.2° (*c*=1.7, MeOH). *Anal.* Calcd for $C_{28}H_{26}O_{17}$: C, 53.00; H, 4.13. Found: C, 52.74; H, 4.15. Negative ion FAB-MS *m/z*: 633 $[M-H]^-$. Tannase hydrolysis of **23** (50 mg) afforded gallic acid, **21** (5 mg) and **20** (7 mg).

**2,4,6-Trihydroxyacetophenone 3-*C*-*β*-D-(2′,6′-Di-*O*-galloyl)glucoside (24)** A white amorphous powder, $[\alpha]_D^{28}$ −140.4° (*c*=1.3, MeOH). *Anal.* Calcd for $C_{28}H_{26}O_{17} \cdot 1/2H_2O$: C, 52.26; H, 4.23. Found: C, 52.42; H, 4.31. Negative ion FAB-MS *m/z*: 633 $[M-H]^-$. Tannase hydrolysis of **24** (50 mg) afforded galic acid and **20** (9 mg).

**2,4,6-Trihydroxyacetophenone 3-*C*-*β*-D-(2′,3′,6′-Tri-*O*-galloyl)glucoside (25)** A white amorphous powder, $[\alpha]_D^{28}$ −13.0° (*c*=1.4, MeOH). *Anal.*

Calcd for $C_{35}H_{30}O_{21}$: C, 53.44; H, 3.84. Found: C, 53.17; H, 3.91. Negative ion FAB-MS *m/z*: 785 $[M-H]^-$. Tannase hydrolysis of **25** (100 mg) yielded gallic acid, **21** (11 mg) and **20** (5 mg).

**2,4,6-Trihydroxyacetophenone 3-*C*-*β*-D-(2′,3′,4′,6′-Tetra-*O*-galloyl)-glucoside (26)** A white amorphous powder, $[\alpha]_D^{21}$ −16.3° (*c*=1.0, MeOH). *Anal.* Calcd for $C_{42}H_{34}O_{25}\cdot 2H_2O$: C, 51.75; H, 3.93. Found: C, 51.93; H, 3.84. Negative ion FAB-MS *m/z*: 937 $[M-H]^-$. Tannase hydrolysis of **26** (200 mg) yielded gallic acid (48 mg), **21** (21 mg) and **20** (25 mg).

**2,4,6-Trihydroxyacetophenone 3-*C*-*β*-D-(2′,3′-Di-*O*-galloyl-4′,6′,-*O*-(*S*)-hexahydroxydiphenoyl)glucoside (27)** A tan amorphous powder, $[\alpha]_D^{21}$ 59.3° (*c*=1.0, MeOH). *Anal.* Calcd for $C_{42}H_{32}O_{25}\cdot 2H_2O$: C, 51.86; H, 3.73. Found: C, 51.86; H, 3.78. Negative ion FAB-MS *m/z*: 935 $[M-H]^-$.

**Methylation of 27** A mixture of **27** (200 mg), dimethyl sulfate (2 ml) and anhydrous potassium carbonate (2.0 g) in dry acetone (30 ml) was heated under reflux for 2 h with stirring. After removal of the inorganic salts by filtration, the filtrate was concentrated to a syrup, which was chromatographed over silica gel. Elution with benzene–acetone (9 : 1) gave the pentadecamethyl ether (**27a**) (192 mg) as a white amorphous powder, $[\alpha]_D^{21}$ +4.7° (*c*=1.0, acetone). *Anal.* Calcd for $C_{57}H_{62}O_{25}$: C, 59.68; H, 5.45. Found: C, 60.07; H, 5.45. FAB-MS *m/z*: 1147 $[M+H]^+$. $^1$H-NMR ($CDCl_3$, 100 MHz) *δ*: 2.32 (3H, s, $CH_3$), 3.68, 3.72, 3.74, 3.80, 3.81, 3.89, 3.91, 3.94, 4.03 (47H in total, $OCH_3$, H-5′, 6′), 5.06 (1H, d, *J*=10 Hz, H-1′), 5.28—5.49 (2H, m, H-4′, 6′), 5.72 (1H, t, *J*=10 Hz, H-2′), 6.28 (1H, s, H-5), 6.30 (1H, t, *J*=10 Hz, H-2′), 6.73, 6.80 (each 1H, s, aromatic H), 7.01, 7.19 (each 2H, s, aromatic H).

**Alkaline Methanolysis of 27a** A solution of **27a** (161 mg) in 2% methanolic sodium methoxide (5 ml) was left standing at room temperature for 20 h. The reaction mixture was neutralized with Amberlite IR-120B ($H^+$ form), and chromatographed over silica gel. Elution with benzene–acetone (48 : 2) furnished methyl 3,4,5-trimethoxybenzoate (**27b**) (59.1 mg), colorless needles, mp 81 °C, and dimethyl 4,4′,5,5′,6,6′-hexamethoxydiphenate (**27c**) (56.4 mg), a colorless syrup, $[\alpha]_D^{20}$ −28.0° (*c*=1.0, $CHCl_3$). Further elution with benzene–ethanol (3 : 1) afforded **20a** (47.0 mg), which was identified by comparison of the *Rf* value on TLC, $[\alpha]_D$ and the $^1$H-NMR data with those of an authentic sample.

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