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A FERULIC ACID ESTER OF SUCROSE AND OTHER CONSTITUENTS OF *BHESA PANICULATA*

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Key Word Index—*Bhesa paniculata*; Celastraceae; wood; β-(3,6-di-*O*-feruloyl)-fructofuranosyl-α-(2,3,4,6-tetra-*O*-acetyl)-glucopyranoside; glycerol 1-9′,12′-octadecadienoate; β-sitosterol; (±)-pinoresinol; 4-hydroxy-3-methoxybenzoic acid; anofinic acid; 2-(1′methylethenyl)-benzofuran-5-carboxylic acid.

Abstract—A novel derivative of sucrose, β-(3,6-di-*O*-feruloyl)-fructofuranosyl-α-(2,3,4,6-tetra-*O*-acetyl)-glucopyranoside, was isolated from the wood of *Bhesa paniculata*. Its structure was determined by a combination of 2D ^1H–^1H and ^1H–^{13}C correlation NMR spectroscopy. The known compounds, glycerol 1-9′,12′-octadecadienoate, β-sitosterol, (±)-pinoresinol, methyl 3,4-dihydroxybenzoate, 4-hydroxy-3-methoxybenzoic acid, anofinic acid and 2-(1′-methylethenyl)-benzofuran-5-carboxylic acid were also isolated.

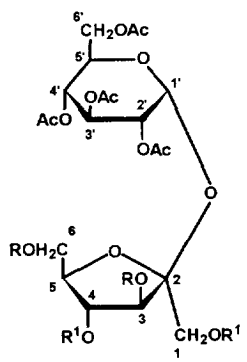
INTRODUCTION

Bhesa is a small genus of trees which is distributed throughout the Indomalesian and Pacific regions. Apart from one report of the alkaloidal constituents of the bark of *B. archeboldiana* [1], the chemistry of this genus appears to have been neglected.

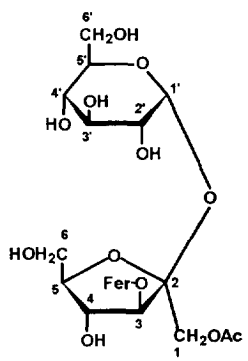
RESULTS AND DISCUSSION

Column chromatographic and HPLC fractionation of an extract of *B. paniculata* afforded a non-crystalline substance (**1**). Its IR and UV spectra (see Experimental) contained bands characteristic of hydroxyl, ester and aromatic groups. The ^1H and ^{13}C NMR spectra of the compound (Table 1) revealed the presence of two trisubstituted benzene rings, two *trans*-disubstituted double bonds, two methoxyl groups, six ester carbonyls and four acetate methyl groups, as well as the oxygenated carbon atoms belonging to a disaccharide residue. The non-sugar signals were readily assigned to four acetate groups and two ferulate groups by comparison of their NMR chemical shifts with those of the known compound β-D-(1-*O*-acetyl-3-*O*-feruloyl)-fructofuranosyl-α-D-glucopyranoside (**2**) [2].

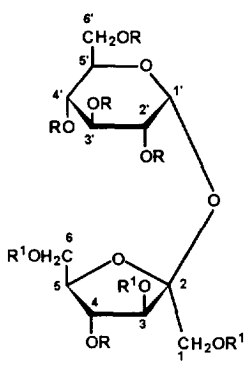
Analysis of the sugar proton resonances by ^1H–^1H COSY spectroscopy revealed that they belong to a β-fructofuranosyl-α-glucopyranoside moiety with *O*-acyl groups at positions 3, 6, 2′, 3′, 4′ and 6′. The corresponding sugar ring protons showed the expected deshielding relative to those of sucrose. Thus, the chemical shifts of the protons of the glucopyranosyl unit are the same as



(**1**) R = feruloyl, R^1 = H
(**5**) R = *O*-acetylferuloyl, R^1 = Ac



(**2**) Fer = feruloyl



(**3**) R = Ac, R^1 = *O*-acetyl-*p*-coumaroyl
(**4**) R = H, R^1 = *p*-coumaroyl

Table 1. ^{1}H (300 MHz, $CDCl_3$) and ^{13}C NMR spectral data of compounds **1** and **2** (*J* in parentheses)

	1		**2**	
Position	δ_H	δ_C	δ_H	δ_C
1	3.73 *d* (12.3) 3.60 *d* (12.3)	63.6	4.25 *d* (12.0)	63.6
2	—	104.8	—	104.1
3	5.33 *d* (7.6)	79.2	5.62 *d* (6.2)	76.2
4	4.43 *t* (7.6)	73.7	5.53 *t* (6.2)	75.2
5	4.20 *dt* (5.1, 7.6)	81.1	4.38 *dt* (4.9, 6.2)	79.2
6	4.50 *br d* (5.1)	64.2	4.55 *dd* (4.9, 11.8) 4.45 *dd* (6.2, 11.8)	64.2
1′	5.68 *d* (3.8)	89.1	5.70 *d* (3.6)	90.2
2′	4.92 *dd* (3.8, 9.8)	70.1	4.93 *dd* (3.6. 10.0)	70.1
3′	5.45 *dd* (9.8, 10.5)	69.9	5.45 *t* (10.0)	69.6
4′	4.95 *dd* (10.3, 10.5)	68.2	5.03 *t* (10.0)	68.3
5′	4.30 *ddd* (2.9, 4.7, 10.3)	68.6	4.30 *ddd* (2.2, 4.4, 10.0)	68.5
6′	4.13 *m*	62.2	4.17 *br d* (12.3) 4.22 *dd* (4.4, 12.3)	61.9
1″	—	126.5	—	133.2[a]
2″	7.03 *d* (1.8)[a]	113.5	7.27 *d* (1.3)[a]	111.5[b]
3″	—	146.8[a]	—	151.5[c]
4″		148.2[b]		141.9[d]
5″	6.90 *d* (8.4)	109.8[c]	7.07 *d* (8.2)	123.3[e]
6″	7.14 *dd* (1.8, 8.4)[b]	123.7	7.14 *dd* (1.3, 8.2)[b]	121.9[f]
7″	7.70 *d* (15.9)[c]	146.8	7.73 *d* (15.8)[c]	146.4[g]
8″	6.41 *d* (15.9)[d]	114.7	6.50 *d* (15.8)	117.4[h]
9″	—	167.9	—	166.3[i]
1‴		126.7		133.0[a]
2‴	7.06 *d* (1.8)[a]	114.4	7.13 *br s*[a]	111.4[b]
3‴	—	146.8[a]	—	151.5[c]
4‴	—	148.6[b]	—	141.7[d]
5‴	6.90 *d* (8.4)	109.5[c]	7.06 *d* (8.2)	123.3[e]
6‴	7.10 *dd* (1.8, 8.4)[b]	123.3	7.18 *dd* (1.3, 8.2)[b]	121.4[f]
7‴	7.65 *d* (15.9)[c]	146.0	7.70 *d* (15.8)[c]	145.2[g]
8‴	6.32 *d* (15.9)[d]	114.4	6.44 *d* (15.8)[d]	116.5[h]
9‴		167.4	—	165.4[i]
3″-OMe	3.94 *s*[e]	56.00	3.91 *s*[e]	56.0[j]
3‴-OMe	3.92 *s*[e]	55.95	3.68 *s*[e]	55.96[j]

Acetates: (**1**) δ_H 1.60 *s*, 1.96 *s*, 2.01 *s*, 2.03 *s*; δ_C 20.6 *q*, 20.6 *q*, 20.6 *q*, 20.3 *q*, 169.6 *q*, 169.7 *q*, 170.1 *q*, 170.8 *q*. (**2**) δ_H 1.84 *s*, 1.96 *s*, 2.06 *s*, 2.10 *s*, 2.12 *s*, 2.14 *s*, 2.32 *s*, 2.32 *s*; δ_C 20.4 *q*, 20.6 *q*, 20.6 *q*, 20.6 *q*, 20.6 *q*, 20.6 *q*, 20.8 *q*, 168.7 *s*, 169.6 *s*, 169.6 *s*, 169.8 *s*, 170.1 *s*, 171.4 *s*, 171.7 *s*.

[a–j]Identically labelled resonances within a column are interchangeable.

those in hydropiperoside octaacetate (**3**) [3]. Similarly, the chemical shifts of the ring protons of the fructofuranosyl unit correspond well with the shifts of the same protons in hydropiperoside (**4**) [3]. The greater shielding experienced by H_2-1 of **1** indicated that this position is not acylated.

Examination of the heteronuclear multiple bond correlation spectrum [4] indicated that, as expected, the two most shielded carbonyl signals belong to the ferulate groups; thus, in each α,β-unsaturated ester system, a correlation is observed between the β-olefinic proton and the carbonyl carbon. Further correlations appear between these carbonyl carbons and H-3 and H_2-6 of the fructofuranose moiety, indicating that these positions bear the ferulate esters. The acetate groups must, therefore, be attached to the C-2′, C-3′, C-4′ and C-6′ oxygens of the glucopyranosyl ring. The observation of correlations between H-2′, H-3′, H-4′ and H_2-6′ and the remaining carbonyl carbons provides further evidence for this. The compound is, therefore, β-(3,6-di-*O*-feruloyl)-fructofuranosyl-α-(2′,3′,4′,6′-tetra-*O*-acetyl)-glucopyranoside (**1**). The absolute configuration of **1** was not determined but it is assumed that the sugars have the D-configuration.

Acetylation of **1** afforded the octaacetate (**5**), which showed the expected changes in the ^{1}H and ^{13}C NMR spectra. The ^{13}C chemical shifts of the sugar moiety are in excellent agreement with those previously determined for sucrose octaacetate by 2D ^{1}H–^{13}C shifts correlation spectroscopy [5].

Esters of sucrose with cinnamic acid derivatives (*p*-coumaric, ferulic and sinapic acids) have previously been reported from *Polygala chamaebuxus* [2], *Polygonum*

hydropiper [3], *Raphanus sativus* [6] and *Lilium speciosum* [7, 8].

In addition to **1**, six other compounds were isolated. These are glycerol 1-9′,12′-octadecadienoate [9], β-sitosterol, (±)-pinoresinol (identified as the acetate [10]), and the benzoic acid derivatives, vanillic (4-hydroxy-3-methoxybenzoic) acid [11], anofinic acid (2,2-dimethylbenzopyran-5-carboxylic acid) [12] and 2-(1′-methylethenyl)-benzofuran-5-carboxylic acid [12]. These substances were identified by comparison of their spectroscopic properties with the corresponding literature values.

EXPERIMENTAL

Branches of *B. paniculata* (Arn.) were collected in the Singapore Botanical Gardens. The dried and ground wood (11 kg) was extracted with hot MeOH. The resulting soln was concd and partitioned between EtOAc and H_2O. A portion (54 g) of the EtOAc soluble material (164 g) was chromatographed over a column of silica gel using increasing proportions of EtOAc in hexane. Three frs (I–III) were collected. Fr. I was recrystallized from MeOH to give β-sitosterol (identified by comparison with an authentic sample, TLC, ^{1}H NMR).

Fr. II was further fractionated over Sephadex LH-20 (50% MeOH–$CHCl_3$). Fr. IIA was purified by HPLC (silica, 10 μ, 8 × 250 mm, 1 and 0.2% MeOH–$CHCl_3$) to give glycerol 1-9′,12′-octadecadienoate (162 mg). Fr. IIB was purified by flash CC ($CHCl_3$) followed by HPLC (C18, 10 μ, 8 × 250 mm, 37% MeOH–H_2O) to give (±)-pinoresinol (9 mg). Fr. IIC was subjected to HPLC (silica, 10 μ, 8 × 250 mm, 18% EtOAc–hexane) to afford a mixt. of two compounds which were sepd by flash CC (25% EtOAc–hexane), yielding 2-(1′methylethenyl)-benzofuran-5-carboxylic acid (4 mg) and anofinic acid (2 mg). Fr. IID was chromatographed over TSK gel (MeOH) and subjected to HPLC (silica, 10 μ, 8 × 250 mm, 20% EtOAc–hexane) to give 4-hydroxy-3-methoxybenzoic acid (3 mg).

Fr. III was chromatographed over Sephadex LH-20 (50% MeOH–$CHCl_3$). Further purification by VLC (MeOH–$CHCl_3$ gradient) and HPLC (C18, 10 μ, 8 × 250 mm, 55% MeOH–H_2O) gave β-(3,6-di-*O*-feruloyl)-fructofuranosyl-α-(2′,3′,4′,6′-tetra-*O*-acetyl)-glucopyranoside (40 mg).

Glycerol 1-9′,12′-octadecadienoate [10]. Oil. HRMS *m/z* 354.2762 ($C_{21}H_{38}O_4$ requires *m/z* 354.2770). $[\alpha]_D$ + 0.3 (MeOH; *c* 4.7). IR ν_{max}^{neat} cm^{-1}: 3410 (*br*, OH), 2920–2850 (alkyl group), 1724 (ester C=O), 1635 (w, olefin), EIMS 70 eV, *m/z* (rel. int.): 354 $[M]^+$ (2), 299 (4), 280 (7), 262 $[C_{18}H_{30}O]^+$ (39), 256 (6), 239 (22), 149 (10), 134 (16), 123 (14), 112 (14), 110 (22), 95 (60), 91 $[C_3H_7O_3]^+$ (15), 85 (11), 67 (100), 55 (81). ^{1}H NMR (300 MHz): δ 5.36 (4H, *m*, H-9′, H-10′, H-12′ and H-13′), 4.16 (1H, *d*, *J* = 2.1 Hz, H-1a), 4.14 (1H, *d*, *J* = 2.7 Hz, H-1b), 3.92 (1H, *br dd*, *J* = 3.8 and 5.5 Hz, H-2), 3.69 (1H, *dd*, *J* = 3.8 and 11.5 Hz, H-3a), 3.58 (1H, *dd*, *J* = 6.0 and 11.5 Hz, H-3b), 2.77 (2H, *t*, *J* = 5.7 Hz, H_2-11′), 2.35 (2H, *t*, *J* = 7.6 Hz, H_2-2′), 2.04 (4H, *m*, H_2-8′ and H_2-14′), 1.62 (2H, *m*, H_2-3′), 1.30 (14H, *m*, H_2-4′, H_2-5′, H_2-6′, H_2-7′, H_2-15′, H_2-16′ and H_2-17′), 0.89 (3H, *t*, *J* = 6.8 Hz), H_3-18′). ^{13}C NMR (22.5 MHz): δ 174.1 (*s*, C=O), 130.1, 129.9, 128.0 and 127.9 (each *d*, C-9′, C-10′, C-12′ and C-13′), 70.2 (*d*, C-2) 65.0 and 63.4 (each *t*, C-1 and C-3), 38.1, 31.4, 29.5, 29.3, 29.0, 29.0, 29.0, 27.1, 25.6, 24.8 and 22.5 (each *t*, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′, C-8′, C-11′, C-14′, C-15′, C-16′, C-17′), 14.0 (*q*, C-18′).

(±)-Pinoresinol. Solid (9 mg), mp 155–156° [lit. [13] 158°]. HRMS *m/z* 358.1411 ($C_{20}H_{22}O_6$ requires *m/z* 358.1416). $[\alpha]_D$ 0.0 (*c* 0.8). UV λ_{max}^{EtOH} nm (log ε): 208 (3.74), 232 (3.54), 280 (3.16). IR ν_{max} cm^{-1}: 3540 (OH), 3000, 2920, 1599, 1510, 1458, 1421, 1364. EIMS 70 eV, *m/z* (rel. int.): 358 $[M]^+$ (26), 327 (8), 205 (18), 196 (8), 179 (6), 163 (34), 151 (100), 150 (29), 137 (53), 131 (39), 124 (16). ^{1}H NMR (300 MHz): δ 6.90 (1H, *d*, J_{meta} = 1.8 Hz, H-2′), 6.89 (1H, *d*, J_{AB} = 8.1 Hz, H-5′), 6.81 (1H, *dd*, J_{meta} = 1.8 and J_{AB} = 8.1 Hz, H-6′), 4.74 (1H, *d*, *J* = 4.3 Hz, H-2), 4.25 (1H, *dd*, *J* = 6.9 and 9.1 Hz, H-8_a), 3.87 (1H, *dd*, *J* = 3.7 and 9.1 Hz, H-8_b), 3.91 (3H, *s*, OMe-3′), 3.10 (1H, *m*, H-1). ^{13}C NMR (75 MHz): δ 146.7 (*s*, C-3′), 145.3 (*s*, C-4′), 132.6 (*s*, C-1′), 114.3 (*d*, C-6′), 119.0 (*d*, C-5′), 108.6 (*d*, C-2′), 85.9 (*d*, C-2), 71.6 (*t*, C-8), 54.2 (*d*, C-1).

Acetylation of pinoresinol. (±)-Pinoresinol (3 mg) was acetylated (Ac_2O–pyridine) to give pinoresinol diacetate (2 mg). HRMS *m/z* 442.1633 ($C_{24}H_{26}O_8$ requires *m/z* 442.1628).UV λ_{max}^{EtOH} nm (log ε): 206 (3.92), 218 (3.71), 274 (3.18). IR ν_{max} cm^{-1}: 3010, 1752 (MeCO), 1591, 1504, 1451, 1405, 1366. EIMS 70 eV, *m/z* (rel. int.): 442 $[M]^+$ (9), 400 (61), 358 (12), 327 (10), 234 (12), 205 (19), 179 (15), 163 (45), 151 (100), 137 (59), 131 (32), 124 (9). ^{1}H NMR (300 MHz): δ 7.0 (1H, *d*, J_{AB} = 8.2 Hz, H-5′), 6.99 (1H, *br d*, H-2′), 6.88 (1H, *dd*, J_{meta} = 1.7 and J_{AB} = 8.1 Hz, H-6′), 4.80 (1H, *d*, *J* = 4.0 Hz, H-2), 4.28 (1H, *dd*, *J* = 6.8 and 9.1 Hz, H-8a), 3.93 (1H, *dd*, *J* = 3.5 and 9.3 Hz, H-8b), 3.85 (3H, *s*, OMe-3′), 3.10 (1H, *m*, H-1), 2.31 (3H, *s*, MeCO).

2-(1′-Methylethenyl)-benzofuran-5-carboxylic acid. Gum. HRMS *m/z* 202.0631 ($C_{12}H_{10}O_3$ requires *m/z* 202.0628). UV λ_{max}^{MeOH} nm (log ε): 234 (4.25), 276 (4.05), 282 (4.07), 294 (3.91), 308 (3.65). IR ν_{max} cm^{-1}: 3500–2600 (br, OH), 1708 (C=O), 1620, 1589 (aromatic rings). EIMS 70 eV, *m/z* (rel. int.): 202 $[M]^+$ (100), 189 (19), 187 (14), 185 (26), 157 (14), 128 (5), 115 (6), 77 (7), 69 (9). ^{1}H NMR (500 MHz, Me_2CO-d_6): δ 8.32 (1H, *d*, J_{meta} = 1.3 Hz, H-4), 8.03 (1H, *dd*, J_{meta} = 1.3 Hz and J_{AB} = 8.6 Hz, H-6), 7.58 (1H, *d*, J_{AB} = 8.6 Hz, H-7), 6.98 (1H, *s*, H-3), 5.81 (1H, *br s*, H-9a), 5.22 (1H, *br s*, H-9b), 2.16 (3H, *s*, H_3-10). ^{13}C NMR (125 MHz, Me_2CO-d_6) δ 168.1 (*s*, C=O), 159.4 (*s*, C-7a), 158.5 (*s*, C-2), 134.1 (*s*, C-8), 130.4 (*s*, C-3a), 127.9 (*d*, C-6), 127.1 (*s*, C-5), 124.8 (*d*, C-4), 114.7 (*t*, C-9), 111.9 (*d*, C-7), 104.7 (*d*, C-3), 19.7 (*q*, C-10).

Anofinic acid. Gum. HRMS *m/z* 204.0774 ($C_{12}H_{12}O_3$ requires *m/z* 204.0784). UV λ_{max}^{MeOH} nm (log ε): 236 (4.07), 274 (3.13), 304 (2.94). IR ν_{max} cm^{-1}: 1685 (C=O). EIMS 70 eV, *m/z* (rel. int.): 204 $[M]^+$ (10), 189 (100), 144 (8), 115 (13), 69 (8). ^{1}H NMR (500 MHz): δ 7.78 (1H, *dd*, J_{meta} = 2.0 Hz and J_{AB} = 8.4 Hz, H-7), 7.65 (1H, *d*, J_{meta} = 2.0 Hz, H-5), 6.72 (1H, *d*, J_{AB} = 8.4 Hz, H-8), 6.28 (1H,

d, J = 9.9 Hz, H-4), 5.58 (1H, *d*, J = 9.9 Hz, H-3), 1.39 (6H, *s*, H_3-10 and H_3-11).

4-Hydroxy-3-methoxybenzoic acid. Gum. HRMS *m/z* 168.0415 ($C_8H_8O_4$, requires *m/z* 168.0421). UV λ_{max}^{EtOH} nm (log ε): 211 (4.18), 220 (4.21), 260 (4.07), 290 (3.77). IR ν_{max}^{KBr} cm^{-1}: 3700–2600 (br, OH), 1672 (acid C = O), 1598 (aromatic ring). EIMS 70 eV, *m/z* (rel. int.): 168 $[M]^+$ (100), 153 $[M - Me]^+$ (72), 125 $[M - Me - CO]^+$ (12), 97 (11), 79 (3). ^{1}H NMR (500 MHz, Me_2CO-d_6): δ7.59 (1H, *dd*, J_{meta} = 1.2 Hz and J_{AB} = 8.2 Hz, H-6), 7.57 (1H, *br s*, H-2), 6.90 (1H, *d*, J_{AB} = 8.2 Hz, H-5), 3.90 (3H, *s*, Me-3). ^{13}C NMR (125 MHz, Me_2CO-d_6): 167.6 (*s*, C = O), 152.0 (*s*, C-4), 148.0 (*s*, C-3), 124.8 (*d*, C-6), 123.0 (*s*, C-1), 115.5 (*d*, C-5), 113.5 (*d*, C-2), 56.3 (*q*, OMe-3).

β-(3,6-di-O-Feruloyl)-fructofuranosyl-α-(2′,3′,4′,6′-tetra-O-acetyl)-glucopyranoside (**1**). $[\alpha]_D^{25}$ + 62.1° (MeOH; *c* 0.5). UV λ_{max}^{MeOH} nm (log ε) 217 (4.6), 234 (4.5), 298 (4.6), 326 (4.7). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3527 (OH), 1749 (ester), 1720 (α,β-unsaturated ester), 1701 (α,β-unsaturated ester). ^{1}H and ^{13}C NMR: Table 1.

Acetylation of β-D-(3,6-*di*-O-*feruloyl*)-*fructofuranosyl*-α-D-(2′,3′,4′,6′-*tetra*-O-*acetyl*)-*glucopyranoside*. Compound **1** (5.6 mg) was treated with Ac_2O in pyridine (1:1) to afford the corresponding octaacetate (**2**). UV λ_{max}^{EtOH} nm (log ε): 214 (3.64), 226 (3.58), 232 (3.57), 282 (3.74), 312 (3.49). IR ν_{max}^{KBr} cm^{-1}: 1751 (C = O), 1588 (aromatic ring). ^{1}H and ^{13}C NMR: Table 1.

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