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A PHYTOCHEMICAL INVESTIGATION OF *HOMALIUM CEYLANICUM*

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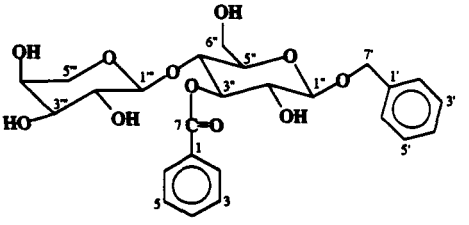
ABSTRACT.—Vacciniin [**4**] (6-*O*-benzoyl-D-glucopyranoside) and two new benzenoid glucosides, homaloside A [**1**] (1″-*O*-benzyl-3″-*O*-benzoyl-α-L-arabinopyranosyl(1‴→4″)-β-D-glucopyranoside) and homaloside D [**2**] [1-(1′-hydroxy-6′-oxocyclohex-2′-ene-carboxymethyl)-5-hydroxyphenyl-6″-*O*-benzoyl-β-D-glucopyranoside], were isolated from the *n*-BuOH fraction of *Homalium ceylanicum* (Flacourtiaceae). A novel cyclohexenone carboxylic acid ester, 1-hydroxy-6-oxocyclohex-2-enoic acid methyl ester [**3**], was also isolated from this fraction. The structures were elucidated by chemical and nmr (COLOC, FLOCK, and selective INEPT) techniques.

A limited number of compounds, polyamines (1), isocoumarins (2), and nickel complexes (3), have been reported from a few *Homalium* spp. The scant phytochemical information on members of this genus and the Flacourtiaceae in general (4–7) has prompted us to examine *Homalium ceylanicum* (Gardn.) Benth. Previously, we reported the isolation and structures of some phenolic, ionyl, and iridoid glucosides from the *n*-



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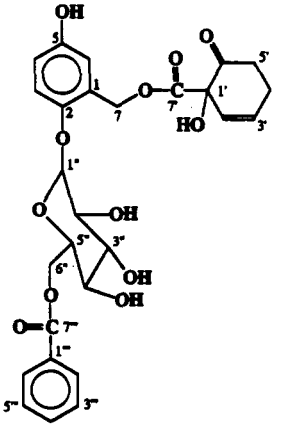

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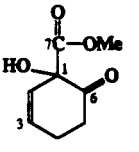

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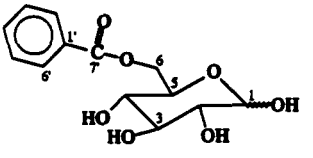

4

BuOH fraction (8). In this report, we describe the structural elucidation of two novel benzenoid glucosides **1** and **2**, a novel cyclohexenone carboxylic acid ester **3**, and vacciniin [**4**] which was reported, without ^{13}C-nmr data, as a major constituent of cranberry juice (9).

RESULTS AND DISCUSSION

Four compounds **1–4** were isolated from the *n*-BuOH soluble fraction. Compound **1**, which has been named homaloside A, was obtained as a white powder. It has been assigned a molecular formula of $C_{25}H_{30}O_{11}$. This has been confirmed by its hrfabms having an $[M+]^+$ ion at *m/z* 507.1866 (calcd 507.1868). Its uv spectrum (λ max 229 nm) was suggestive of a simple benzenoid compound. The presence of D-glucopyranosyl and L-arabinopyranosyl units in **1** was determined by comparing its ^{13}C-nmr spectrum with published spectra of the two sugars (11–13). The assignment of the β configuration to D-glucose and the α-configuration to L-arabinose at the anomeric carbons was based on the C-1″ and C-1‴ chemical shift values at 103.23 ppm and 106.55 ppm, respectively (Table 1). These assignments were supported by the chemical shifts and large coupling constants of the anomeric protons (4.57 ppm, $J=8.06$ Hz for β-D-glucose and 4.40 ppm, $J=6.7$ Hz for α-L-arabinose) (Table 2). The presence of the arabinopyranosyl moiety was confirmed further by its H-3‴ nmr signal. In the ^{1}H-nmr spectrum of **1** in pyridine-d_5, the broad signal due to H-4‴ and H-3‴ (4.03 ppm) was partly resolved by the partial relaxation method using the standard inversion recovery pulse sequence. The H-3‴ peak was centered at 4.04 ppm with the expected splitting pattern, dd, $J_{3''',4'''}=3.45$ Hz and $J_{3''',2'''}=6.95$ Hz. The eims of **1** had fragments at *m/z* 105 and 77 for a

TABLE 1. ^{13}C-nmr Spectra of Homaloside A [**1**].[a]

Group	Carbon	δ (ppm) in CD_3OD	δ (ppm) in pyridine-d_5
Benzoyl	C-1	132.13	131.49
	C-2	130.72	129.70
	C-3	129.10–129.29	127.60–128.30
	C-4	133.83	132.35
	C-5	129.10–129.29	127.60–128.307
	C-6	130.72	129.70
	C-7	167.90	166.12
Benzyl	C-1′	138.89	138.00
	C-2′	129.15	
	C-3′	129.10–129.29	
	C-4′	128.72	127.60–128.30
	C-5′	129.10–129.29	
	C-6′	129.15	
	C-7′	72.05	70.65
β-D-Glucosyl	C-1″	103.23	102.98
	C-2″	73.63	72.90
	C-3″	78.03	77.43
	C-4″	79.41	78.46
	C-5″	74.32	76.23
	C-6″	61.92	60.99
α-L-Arabinosyl	C-1‴	106.55	106.30
	C-2‴	72.79	72.43
	C-3‴	76.59	74.12
	C-4‴	69.70	68.88
	C-5‴	67.20	66.74

[a]Spectra were measured at 75 MHz or 90 MHz at ambient temperature. Chemical shifts were referenced on the solvent peaks, $\delta_{MeOH}=49$ ppm and $\delta_{pyridine}=135.5$ ppm.

TABLE 2. ^{1}H-nmr Spectra of Homaloside A [**1**].[a]

Group	Proton	δ (ppm) in CD_3OD	δ (ppm) in pyridine-d_5
Benzoyl	H-2	8.07, d, J = 8.3 Hz	8.27, d, J = 7.2 Hz
	H-3	7.47, m	
	H-4	7.58, dd, J = 6.8, 7.3 Hz	7.32–7.52, m
	H-5	7.47, m	
	H-6	8.07, d, J = 8.3 Hz	8.27, d, J = 7.2 Hz
Benzyl	H-2′	7.47, m	7.51, br
	H-3′		
	H-4′	7.27–7.36, m	7.32–7.52, m
	H-5′		
	H-6′	7.47, m	7.51, br
	H_a-7′	4.70, d, J = 11.80 Hz	4.82, d, J = 11.88 Hz
	H_b-7′	4.57, d, J = 11.73 Hz	5.13, d, J = 11.88 Hz
β-D-Glucosyl	H-1″	4.57, d, J = 8.06 Hz	4.98, d, J = 7.56 Hz
	H-2″	3.57–3.64, m	4.26, dd, J = 8.46, 8.46 Hz
	H-3″	5.35, dd, J = 9.35, 9.36 Hz	6.15, dd, J = 9.36, 9.36 Hz
	H-4″	3.93, dd, J = 9.55, 9.50 Hz	4.66–4.69, br
	H-5″	3.57–3.64, m	3.84, d, J = 9 Hz
	H_a-6″	3.98, br s	4.68–4.69, br
	H_b-6″		4.45–4.78, d, J = 11.88 Hz
α-L-Arabinosyl	H-1‴	4.40, d, J = 6.7 Hz	4.91, d, J = 7.2 Hz
	H-2‴	3.35–3.40, m	4.33, dd, J = 7.56, 7.56 Hz
	H-3‴		4.02–4.04, br d
	H-4‴	3.48–3.51, m	
	H_a-5‴	3.04, br s	3.33, d, J = 12.24 Hz
	H_b-5‴		3.59, d, J = 12.24 Hz

[a]Spectra were measured at 300 MHz or 360 MHz at room temperature. $\delta_{TMS} = 0$ ppm.

benzoyl group and a tropylium ion at *m/z* 91 from a benzyl group. The low resolution fabms also showed sequential losses of a benzyloxy and an arabinosyl fragment, giving *m/z* 399 $[M - C_7H_7O]^+$ (60.6%), 375 $[M - C_5H_9O_4 + 2H]^+$(100%), and 357 $[M - C_5H_9O_5]^+$ (75.4%). An ion at *m/z* 259 in the cims of **1** acetate indicated a terminal arabinosyl group.

Attachment of the benzoate at C-3‴ was evident from the ^{1}H-^{1}H COSY and FLOCK experiments, both conducted in pyridine-d_5, and the selective INEPT spectrum, obtained in CD_3OD. Following irradiation of H-3″ (5.35 ppm) in the selective INEPT experiment, the carbonyl carbon signal at 167.90 ppm was enhanced. In the ^{1}H-^{1}H COSY spectrum, H-3″ was found to cause a cross peak with H-2″ (4.26 ppm), which in turn was coupled to the anomeric proton (4.98 ppm). These results were strengthened by the coupling of H-3″ to C-7 in the FLOCK spectrum (Figure 1). The point of linkage of arabinose to glucose was deduced by the coupling of H-1‴ to C-4″ in the COLOC spectrum of **1**. Similarly, H-1‴ had a long-range scalar coupling to H-4″ in the ^{1}H-^{1}H COSY spectrum and caused a cross peak with the same proton in the ^{1}H-^{1}H NOESY spectrum. In another selective INEPT experiment, irradiation of H-7′ led to the enhancement of C-1″. A cross peak was also observed between C-1″ and H-7′ in the FLOCK (Figure 1) and COLOC spectra. The benzyl group was deduced to be located at C-1″. The complete assignments of the other signals were made possible through the use of ^{1}H-^{13}C HETCOR, ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, COLOC, FLOCK, and selective INEPT spectroscopic methods. The results are summarized in Tables 1 and 2. Accordingly, **1** has been established as 1″-*O*-benzyl-3″-*O*-benzoyl-α-L-arabinosyl(1‴→4″)-β-D-glucopyranoside.

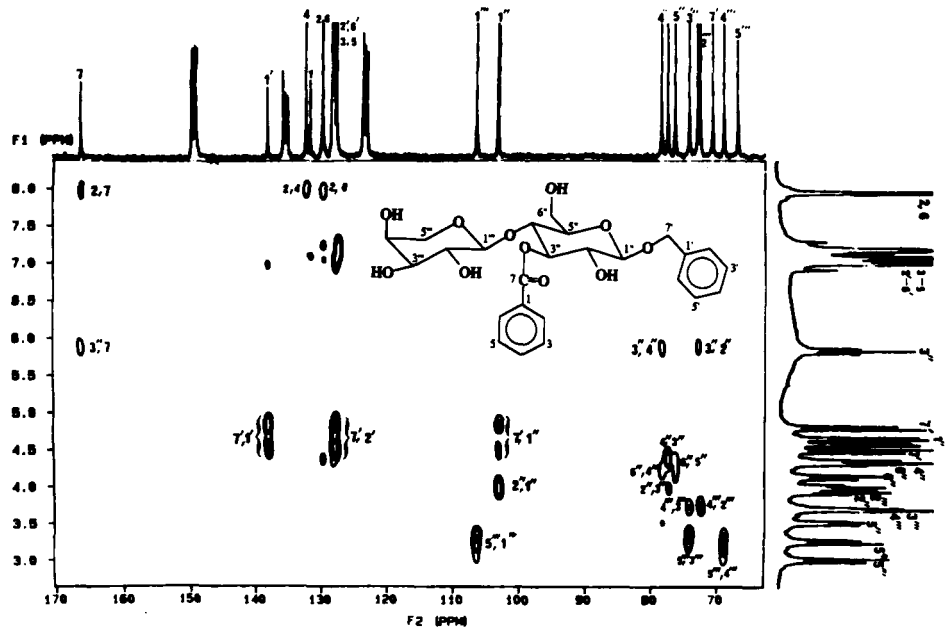

FIGURE 1. *FLOCK spectrum of homaloside A [1] in pyridine-d_5. Numbers in Cartesian coordinates denote long range proton/carbon (H,C) coupling as discussed in the text.*

Compound **2** was obtained as an amorphous brown solid and named homaloside D. It had a protonated molecular ion $[M+1]^+$ at *m/z* 545.1655 ($C_{27}H_{29}O_{12}$, calcd 545.1659). A cluster of ir peaks were observed between 1656–1720 cm^{-1}, corresponding to carbonyl functions. Other bands were observed at 3400 (OH), 2926, 2855 (C-H, aliphatic), 1459 (C=C, Ar), 1281, and 1069 (C-O-C) cm^{-1}. The uv spectrum showed bands at 206, 227, and 283 nm, which shifted to 212, 228, and 295 nm with the addition of a few drops of methanolic KOH. The bathochromic effect was abolished after neutralization of the base with HCl.

The ^{1}H-nmr and ^{13}C-nmr spectra consisted of a familiar pattern of peaks attributable to benzoyl (7.46–8.01; 167.71, 129.89–134.34 ppm), gentisyl alcohol (5.25, 6.55–7.03; 64.35, 116.46–154.03 ppm) and glucosyl (3.47–4.76; 65.26–77.93, 104.14 ppm) groups. Additional peaks were found around 5.6–6.2 and 2.4–2.9 ppm. The ^{13}C-nmr spectrum also indicated a keto (207.34 ppm) and two ester functions (167.71, 171.34 ppm). Glucose was substituted at the anomeric and sixth carbons as revealed by their chemical shift values at 104.14 and 65.26 ppm, respectively. The remaining seven carbons to be assigned had a partial molecular formula of $C_7H_7O_3$ and consisted of two carbonyls (171.34, 207.34 ppm), two methylenes (27.17, 36.74 ppm), a vinylic unit (129.17, 133.30 ppm) and a quarternary carbinol carbon showing a very small peak at 79.16 ppm. The eims showed a peak at *m/z* 267 for the benzoylglucosyl oxonium ion $[C_6H_5CO{\cdot}C_6H_{10}O_5]$. Secondary ions arising from the disintegration of the oxonium and benzoyl ions were also observed at *m/z* 231 $[C_6H_5CO{\cdot}C_6H_{10}O_5 - 2H_2O]^+$, 105 [benzoyl ion]$^+$, and 77 [phenyl ion]$^+$ amu. Two significant ions at *m/z* 389 and 407 in the cims and positive ion fabms represented the gentisyl alcohol, glucosyl, and benzoyl groups intact as a unit with a partial formula $[C_7H_5O{\cdot}C_6H_{10}O_5{\cdot}C_7H_7O_3+H]^+$ (*m/z* 407) and $[C_7H_5O{\cdot}C_6H_{10}O_5{\cdot}C_7H_6O_2]^+$ (*m/z* 389). The eims of acetylated homaloside D had a peak at *m/z* 574 for $[C_{20}H_{18}O_9Ac_4]^+$ derived from acetylation of the $[C_7H_5O{\cdot}C_6H_{10}O_5{\cdot}C_7H_7O_3]^+$unit in **2**. There was an

intense benzoyltriacetylated glucosyl oxonium ion at *m/z* 393, which supported the substitution of the glucose moiety at C-6‴ (14). In the negative ion fabms a peak was observed at *m/z* 139 for the unassigned carbons ($[C_7H_7O_3]^+$, MW = 139). This peak indicated $[C_7H_7O_3]^+$ to be a single unit. It underwent facile elimination upon impact in the ms probe and fragments further by elimination of H_2O, CO, CHO to produce the following: $[C_7H_5O_2]^+$ (*m/z* 121, 100%), $[C_6H_8O_2]^+$ (*m/z* 112, 25%), and $[C_6H_7O_2]^+$ (*m/z* 111, 69%). The fragment $[C_7H_7O_3]^+$ contained at least four degrees of unsaturation, of which two were accounted for by the two carbonyl carbons, the third by the double bond, and the fourth by a ring. From spin decoupling and ^1H-^1H-COSY experiments, the methylene protons were found to be coupled to each other and to only one of the vinylic protons. These results enabled the partial arrangement -CH=CH-CH_2CH_2- to be proposed.

The complete structure of the fragment $[C_7H_7O_3]^+$ was solved from selective INEPT, HETCOR, and COLOC spectra. From the HETCOR spectrum, ^1H peaks at 2.46 (H-4′), 2.85 (H-5′), 5.73 (H-2′), and 6.10 (H-3′) ppm were assigned to C-4′ (27.17), C-5′ (36.74), C-3′ (133.30), and C-2′ (129.17) in that order. When H-3′ was irradiated in the selective INEPT experiment, C-1′, C-5′, C-4′, and C-2′ were enhanced. In the COLOC spectrum, H-3′ also caused a cross peak with C-1′ (Figure 2). Irradiation of H-5′, H-4′, and H-2′ produced the following groups of enhancements: (C-5′, C-4′, C-3′, C-6′), (C-6′, C-3′, C-2′), and (C-4′, C-3′, C-2′), respectively. The enhancement of C-5′ following irradiation of H-5′ could be explained by the overlapping of H-4′ and H-5′ protons. Based on these data the structure of the $[C_7H_7O_4]^+$ fragment was deduced as 1′-hydroxy-6′-oxocyclohex-2′-enoate. The assembly of the various subunits of **2** was solved also by selective INEPT and COLOC spectroscopy. It was observed from the selective INEPT experiment that C-2 and C-7′ were enhanced when H-7 was irradiated. C-2 and C-7″ were also enhanced when the anomeric proton and H-6″ were pulsed, in that order. It appeared from these results that the cy-

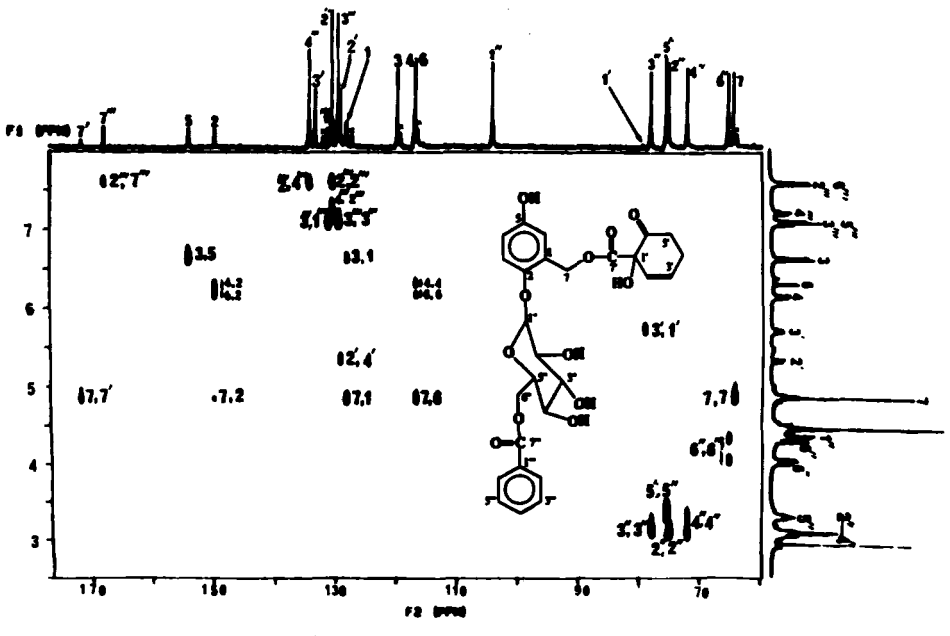

FIGURE 2. COLOC spectrum of homaloside D [**2**] in CD_3OD. Numbers in Cartesian coordinates denote long-range and one-bond proton/carbon (H,C) correlation as discussed in the text. Impurity peaks are denoted by an "x" in the 1D ^{13}C-nmr plot.

clohexenyl and glucopyranosyl groups were connected to the aglycone (gentisyl alcohol) at C-7 and C-2, respectively. The benzoyl group was confirmed to be located at C-6‴. The assignment of the remaining protons and carbons was accomplished with the COLOC spectrum (Figure 2). The structure of **2** was solved as 1-(1′-hydroxy-6′-oxocyclohex-2′-ene-carboxymethyl)-5-hydroxyphenyl-6″-*O*-benzoyl-β-D-glucopyranoside.

Compound **3** was easily identified by comparing its nmr spectra with those of **2**. Except for the MeO signal at 3.80 ppm and 53.45 ppm in the ^{1}H-nmr and ^{13}C-nmr spectra, respectively, of **3**, there was a striking resemblance in these nmr spectra with those of the 1′-hydroxy-6′-oxocyclohex-2′-ene-carboxyl moiety $[C_7H_7O_3]^+$ in **2**. The cims of **3** gave an $[M+1]^+$ peak at *m/z* 171.06 (98.1%) and an hreims $[M]^+$ ion at *m/z* 170.0576, which agreed with the formula $C_8H_{10}O_4$. The fragmentation pattern of **3** was also identical with that of the $C_7H_7O_3$ fragment in **2** (vide supra). The nmr peak assignments for **3** are presented in Tables 3 and 4. The low yield of **3** made it difficult to determine its absolute stereochemistry.

Compound **4** exhibited a ^{13}C-nmr spectrum suggestive of a simple benezenoid glucoside. This was confirmed by the eims of **4** with fragments at *m/z* 105 [benzoyl ion]$^+$ and *m/z* 77 [phenyl ion]$^+$. A protonated parent ion $[M+1]^+$ at *m/z* 285 in the fabms was in agreement with the formula $C_{13}H_{17}O_7$. The cims of peracetylated **4** had an $[M+1]^+$ ion at *m/z* 453.28 (0.10%) (rel. int.) indicating that **4** gained four acetyl groups. There was a prominent characteristic ion at *m/z* 393 (100%) representing the 6-*O*-benzoylglucopyranosyloxonium ion. This fragment is diagnostic for 6-*O*-benzoyl-substituted hexapyranosides as seen previously in **2**. Both the α and β epimers of **4** existed in a 1:1 ratio as determined by the ratio of the intensities of the anomeric proton

TABLE 3. ^{1}H-nmr Spectra of **2** and **4** in CD_3OD and **3** in $CDCl_3$[a].

Group	Proton	Compound			
		2	**3**	**4A**[b]	**4B**[b]
Gentisyl alcohol	H-3	7.03, d, J = 8.8	—	—	
	H-4	6.55, dd, J = 3, 8.8	—	—	
	H-6	6.71, d, J = 2.8	—	—	
	H-7	5.25, s	—	—	
Cyclohexenyl	H-2′	5.73, d, J = 11.5	5.77–5.81 dd, J = 1.6, 10	—	
	H-3′	6.10, m	6.10–6.15, m	—	
	H-4′	2.36–2.6, m	2.64–2.71, m	—	
	H-5′	2.77–2.90, m	2.64–2.71, m	—	
		2.54–2.67, m	2.96–3.02, m	—	
β-D-Glucosyl	H-1″	4.76, d, J = 7.3	—	5.11, d, J = 3.60	4.53, d, J = 7.92
	H-2″	3.47–3.5, m	—	3.37–3.46, m	3.18, dd, J = 8.27, 8.28
	H-3″	3.71, m	—	3.72 dd, J = 9.20, 9.18	3.37–3.46, m
	H-4″	3.47–3.5, m	—	3.37–3.46, m	3.37–3.46, m
	H-5″	—	—	4.08–4.12, m	3.59–3.64, m
	H_a-6″	4.44, dd, J = 2.1, 1.0	—	4.59, dd, J = 1.62, 11.88	4.65, dd, J = 1.62, 11.52
	H_b-6″	4.72, dd, J = 7.4, 1.0	—	4.41–4.78, m	
Benzoyl	H-2‴, -6‴	8.01, dd, J = 1.4, 7.8	—	8.04, d, J = 7.56	
	H-3‴, -5‴	7.49, dd, J = 7.4, 7.8	—	7.47, dd, J = 7.47, 7.47	
	H-4‴	7.62, dd, J = 7.4, 7.4	—	7.60, dd, J = 7.20, 7.20	
OMe	—	—	3.80, s	—	

[a]Spectra were measured at 300 MHz or 360 MHz at room temperature. δ_{TMS} = 0 ppm. Coupling constants (J) are in Hz.
[b]A and B represent the α and β isomers of **4**, respectively.

TABLE 4. ^{13}C-nmr Spectra of **2** and **4** in CD_3OD and **3** in $CDCl_3$[a].

Group	Carbon	Compound			
		2	**3**	**4A**[b]	**4B**[b]
Gentisyl alcohol	C-1	128.09	—	—	
	C-2	149.65	—	—	
	C-3	119.77	—	—	
	C-4	116.46	—	—	
	C-5	154.03	—	—	
	C-6	116.88	—	—	
	C-7	64.35	—	—	
Cyclohexenyl	C-1′	79.16	77.94	—	
	C-2′	129.17	127.47	—	
	C-3′	133.30	131.88	—	
	C-4′	27.17	26.83	—	
	C-5′	36.74	35.09	—	
	C-6′	207.34	205.42	—	
	C-7′	171.34	170.30	—	
β-D-Glucosyl	C-1″	104.14	—	94.05	98.30
	C-2″	74.96	—	73.84	76.25
	C-3″	77.93	—	74.82	77.93
	C-4″	71.96	—	71.80[c]	72.08[c]
	C-5″	75.42	—	70.83	75.47
	C-6″	65.26	—	65.38[d]	65.47[d]
Benzoyl	C-1‴	131.18	—	131.38	
	C-2‴, -6‴	130.59	—	130.58	
	C-3‴, -5‴	129.89	—	129.53	
	C-4‴	134.34	—	134.27	
	C-7‴	167.71	—	167.95	
OMe	—	—	53.45	—	

[a]Spectra were acquired at 75 MHz or 90 MHz at room temperature. Chemical shifts were referenced on solvent peaks, $\delta_{MeOH} = 49.00$ ppm, $\delta_{CHCl_3} = 77$ ppm.

[b]**4A** and **4B** represent the α and β isomers of **4** respectively.

[c,d]Chemical shifts may be interchanged.

peaks. The complete ^{1}H and ^{13}C assignments of **4** were made through the use of ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, and ^{1}H-^{13}C HETCOR spectroscopies. The results are shown in Tables 3 and 4; **4** is vacciniin, a known compound (9).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were determined with a Kofler hot stage apparatus and are not corrected. Uv spectra were obtained with a Beckman DU-7 spectrophotometer. Eims were measured with a Varian MAT 112S double focusing spectrometer at 70 eV. Cims and fabms were recorded with Finnigan MAT 4510 and MAT 90 instruments, respectively. Reagent gas for cims was CH_4. Polarimetry was conducted using a Perkin-Elmer polarimeter model 241. ^{1}H-, ^{13}C-, and 2D nmr spectra were recorded with a Varian XL-300 or Nicolet NT-360 spectrometers. All 2D experiments were performed employing the standard pulse sequences. Selective INEPT experiments were carried out using the routine pulse sequences with a Nicolet NT-360 instrument. Countercurrent chromatography was performed using an Ito multilayer coil separator-extractor model #1. Conventional cc was carried out using Merck Si gel 60, 70–230 mesh. Tlc was performed with Merck Kieselgel 60 F_{254} coated Al_2O_3 aluminum plates, 0.2 mm thick. All solvents used for chromatography were redistilled before use. Acetylating reagents, pyridine and Ac_2O, were obtained from Fisher Scientific Co., Fairlawn, New Jersey. Ac_2O was used as purchased. Pyridine was dried over KOH pellets.

PLANT COLLECTION.—The twigs and stems of *H. ceylanicum* were collected at Mae Sa, Thailand, in February of 1990. Voucher specimens were identified by one of us (T.S.) and have been deposited in the Forest Herbarium of the Royal Forestry Department, Bangkok, Thailand.

EXTRACTION AND ISOLATION.—Ground twigs and stems of *H. ceylanicum* (14 kg) were extracted three times with $CHCl_3$ (30 liters × 3). The solvent was evaporated in vacuo at about 40° to give 107 g of residue. The dried marc was exhaustively extracted with MeOH, and the solvent removed as described above. The dried MeOH extract was partitioned in succession between H_2O and Et_2O, EtOAc, and *n*-BuOH and yielded 255.25 g, 19.18 g, 65.25 g, and 50 g of the respective extracts. Si gel cc of the *n*-BuOH extract gave six major fractions. The column was eluted initially with $CHCl_3$, then with increasing amounts of MeOH in $CHCl_3$. Fractions were collected in 500-ml portions and pooled according to their tlc profile in $CHCl_3$-MeOH-H_2O (7:2:1) (organic phase).

Compound **3** was obtained partially pure from fraction A by Si gel cc in $CHCl_3$. It was further purified by preparative tlc in the same solvent. Homaloside A was purified by cc of fraction B (2.5 g) on a Si gel column which was eluted with $CHCl_3$-MeOH-H_2O (7:2:1) (lower phase). Homaloside A separated as a white precipitate, and it was crystallized from this solvent system. Fraction C (6 g) was separated by countercurrent distribution using an Ito multilayer separator-extractor to give compounds **2** and **4** in semi-pure form. The solvent system consisted of EtOAc-MeOH-H_2O (10:1:5), with the upper layer serving as the mobile phase. Compounds **2** and **4** were purified further by preparative tlc. Multiple developments of the preparative tlc plates was performed with the EtOAc-MeOH-H_2O (10:1:5) solvent system (upper phase). Homaloside D [**2**] was obtained as an amorphous solid and vacciniin [**4**] as a syrup.

Homaloside A (1"-O-benzyl-3"-O-benzoyl-α-L-arabinopyranosyl(1"↦4")-β-D-glucopyranoside) [**1**].—White powder (290 mg): mp 181–183°; $[\alpha]_D$ −12.11 (*c* = 0.19, MeOH); uv λ max (MeOH) (log ε) 209 (4.01), 216 (3.96) sh, 229 (4.06) nm; ir ν max (KBr) 3400, 2929, 2879, 1717, 1602, 1452, 1279, 1047, 712 cm^{-1}; hrfabms *m/z* $[M+1]^+$ 507.1866 (calcd 507.1868 for $C_{25}H_{31}O_{11}$); eims *m/z* (rel. int.) 399.16 (2.5), 357.17 (3.4), 295.08 (18.1), 267.07 (24.1), 237.10 (13.4), 105 (100), 90.96 (18.9), 77 (17.6); ^1H nmr see Table 2; ^{13}C nmr see Table 1.

Homaloside D [1-(1'-hydroxy-6-oxocyclohex-2'-ene-carboxymethyl)-5-hydroxyphenyl-6"-O-benzoyl-β-D-glucopyranoside] [**2**].—Amorphous brown solid (220 mg): $[\alpha]_D$ −89.39 (*c* = 0.33, MeOH); uv λ max (MeOH) (log ε) 206 (4.15), 227 (4.16), 283 (3.53) nm, red shift λ max 210, 229, 302 nm; ir ν max 3400, 2926, 1459, 1069; hrfabms *m/z* $[M+1]^+$ 545.1655 (calcd 545.1659 for $C_{27}H_{29}O_{12}$); negative ion fabms *m/z* (rel. int.) $[M-1]^+$ 543 (69.2), 527 (46.6), 139 (50.2), 121 (100), 111 (69.5); cims 389.8 (2.4), 371.3 (1.6), 267.2 (14.8), 231.2 (3.1), 140.2 (26.7), 123 (100), 114 (49.4), 105 (59.6), 96 (73.7); ^1H nmr see Table 3; ^{13}C nmr see Table 4.

1-Hydroxy-6-oxocyclohex-2-enoic acid methyl ester [**3**].—Syrup (13 mg): hreims *m/z* $[M]^+$ 170.0576 (calcd 170.0579 for $C_8H_{10}O_4$); cims *m/z* $[M+1]^+$ 171.06 (98.1), 153.45 (100), 139.03 (36.7), 121.34 (13.7), 111.09 (59.5); ^1H nmr see Table 3; ^{13}C nmr see Table 4.

Vacciniin (6-O-benzoyl-D-glucopyranoside) [**4**].—Syrup (15 mg): $[\alpha]_D$ +3.3 (*c* = 0.52, MeOH); uv λ max (MeOH) (log ε) 203 (4.18), 229 (4.34), 272 (3.35), 2.79 (3.29) nm; fabms *m/z* (rel. int.) $[M+1]^+$ 285 (22.77) (calcd 285.27 for $C_{13}H_{17}O_7$), 267 (68.32), 249 (11.62), 105 (100); cims (acetylated product) *m/z* (rel. int.) $[M+1]^+$ 453.280.10), 393.31 (100); ^1H nmr see Table 3; ^{13}C nmr see Table 4.

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