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AN IRIDOID GLUCOSIDE FROM *NYCTANTHES ARBORTRISTIS**

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Key Word Index—*Nyctanthes arbortristis*; Verbenaceae; iridoid glucosides; arbortristoside A; 6β-hydroxyloganin.

Abstract—A new iridoid glycoside along with the known compounds, nyctanthic acid, oleanolic acid, friedelin, β-sitosterol glucoside, 6β-hydroxyloganin and arbortristoside A have been isolated from *Nyctanthes arbortristis* and characterized by spectral and chemical means.

INTRODUCTION

Nyctanthes arbortristis (Hindi-Harsingar) is used in the Ayurvedic system of medicine for the treatment of various diseases, such as fever, rheumatism and intestinal worm infections. A decoction of the leaves is recommended as a specific treatment for obstinate sciatica [1, 2]. The powdered seeds are used to cure scurfy infections of the scalp. The inflorescence and young fruits powdered in water is used for relieving cough by tribal people of central India. Bark of the plant mixed with that of *Terminalia arjuna* is rubbed on the body to cure internal injuries and to repair broken bones [3].

A 50% ethanolic extract of the aerial parts of the plant exhibited encouraging antileishmanial activity of the order of 85.89% at a dose level of 1 g/kg/day × 5 on the 28th day post-treatment against hamsters infected with *Amastigotes* parasites (Guru, P. Y., personal communication). The ethanolic extract of the leaves of the plant showed significant amoebicidal activity in rats (Prasad, B. N. K., personal communication).

Earlier workers have reported the isolation of crocin 1, 2 and 3 from corolla tubes [4], nyctanthic acid, β-sitosterol, oleanolic acid, friedlin, lupeol, astragalin and nictoflorin from leaves [5, 6] and nyctanthoside [7], arbortristosides A and B and polysaccharides from seed kernels [8, 9] of *N. arbortristis*.

RESULTS AND DISCUSSION

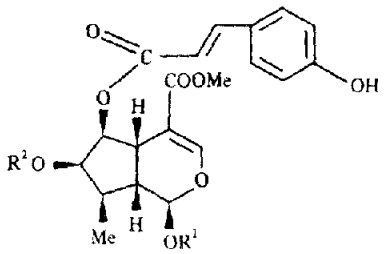
The *n*-butanol soluble fraction of the seeds of *N. arbortristis* after column chromatography resulted in the isolation of a new iridoid glucoside (**1**), arbortristoside A (**2**) and 6β-hydroxyloganin (**3**).

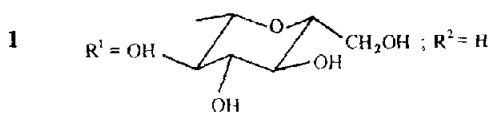
Compound **1** was obtained as a white amorphous powder, $C_{26}H_{32}O_{13}$, mp 200–202°, $[\alpha]_D$ −78° (MeOH). The characteristic bands in the IR spectrum showed the presence of an α,β-unsaturated carbonyl (1710), C=C (1650), aromatic (1620–1455) and hydroxyl (3400) cm^{-1} functions in the molecule. In addition to the UV absorption maxima at 229 nm, typical of an iridoid enol ether system conjugated with a C-4 carbonyl group, the UV spectrum showed peaks at 301 (sh) and 312 nm indicating the presence of a *p*-substituted aromatic ring [10, 11]. The EI mass spectrum of **1** exhibited typical features expected from the fragmentation pattern of a C_{10}-iridoid glucoside [12, 13], with peaks at *m/z* 226, 198, 178, 164, 161, 143 and 139. The ^{1}H NMR spectrum (DMSO-d_6) displayed singlets at δ7.40 and 3.75 unambiguously assigned to H-3 and a methoxy group, thereby suggesting the presence of a conjugated 4-carbomethoxy enol ether system of an iridoid. The occurrence of signals at δ6.36 and 7.56 due to a simple AB system (J_{AB} = 16 Hz) for *trans*-olefinic protons, an A_2B_2 system at δ6.75 and 7.51 ($J_{A_2B_2}$ = 10 Hz) and a broad singlet at δ9.98 indicated the presence of a *p*-hydroxycinnamoyl group in compound **1**.

Since the ^{1}H NMR of its hexaacetate derivative (**1a**) (Ac_2O/pyridine), showed a phenolic acetate peak at δ2.34 it was evident that the *p*-substituent in the aromatic nucleus was a hydroxyl group. A doublet at δ0.94 (*J* = 6 Hz) correlated well with the placement of a methyl group at C-8. The existence of H-7 as a triplet at δ4.06 (*J* = 4 Hz) and H-6 as a multiplet at δ4.98 was in accordance with the placement of a hydroxyl group at C-7 and a *p*-coumaroyl group at C-6 [10, 11]. Of the remaining signals, doublets at δ4.42 (*J* = 9 Hz) and 4.94 (*J* = 7.5 Hz) were assigned to CH_2OH and to the anomeric proton of the β-D-glucopyranosyl moiety, respectively, and for other sugar protons there was a complex absorption in the region δ3.5–4.5. The presence of a β-glucoside was confirmed by the ^{13}C NMR (SFORD) spectrum which showed characteristic resonances at δ100.21 (*d*, C-1′), 74.72 (*d*, C-2′), 78.04 (*d*, C-3′), 71.64 (*d*, C-4′), 77.64 (*d*, C-5′), 62.83 (*t*, C-6′). It is clear from both the constancy of the signals for glucose that compound **1** has a β-D-configuration at C-1′.

Mannich hydrolysis of **1** afforded glucose and an aglucone (**1b**). The ^{1}H NMR of **1b** showed that it retained the *p*-coumaroyl moiety. It also showed a pair of doublets at δ6.82 and 7.35 (*J* = 10 Hz), assigned to an A_2B_2 system of aromatic protons of a *p*-coumaroyl group and two *trans*-olefinic protons resonated at δ6.27 and 7.82 (*d*, *J* = 16 Hz). Alkaline hydrolysis (MeOH–KOH) of **1** afforded *p*-hydroxycinnamic acid and another compound which on subsequent methylation with diazomethane yielded a methyl ester which proved to be identical with another iridoid glycoside (**3**) isolated from the same plant and characterized as 6β-hydroxyloganin [14]. Furthermore structure **1** was confirmed by the ^{13}C NMR [SFORD] spectrum (Table 1).

*C.D.R.I. communication number 4110.





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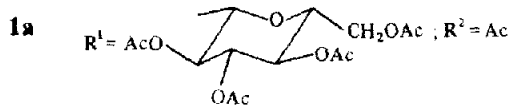
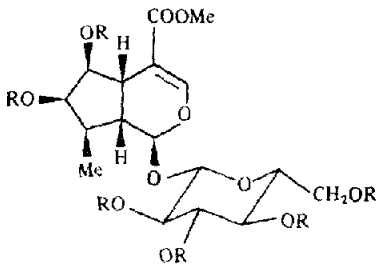


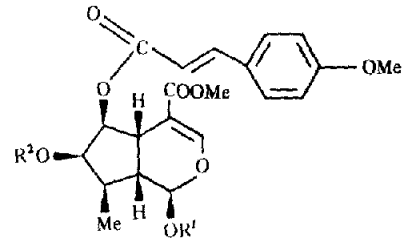
1a

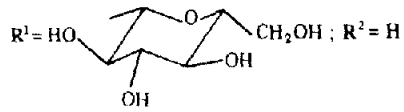
1b $R^1 = H$; $R^2 = H$



3 R = H

3a R = Ac





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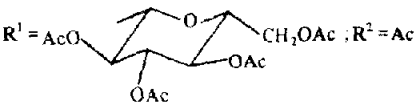

2a

2b $R^1 = H$; $R^2 = H$

Compound **2**, $C_{27}H_{34}O_{13}$, mp 220–222° (ethanol), $[\alpha]_D$ −92.5° (MeOH) was found to be identical to arbortristoside A, on the basis of its spectroscopic data. [IR: ν_{max}^{KBr} 3400 (OH), 1710 (>C=O), 1650 (C=C); EI mass spectrum *m/z* 226, 198, 178, 161, 139; UV: λ_{max}^{MeOH} 227 [C-(4)COOMe], 300 (sh), 308 nm.] The ^{1}H NMR (DMSO-d_6) spectrum contained signals at δ5.27 (*d*, J = 6 Hz), 7.40 (*s*), 4.13 (*t*, J = 4 Hz), 4.98 (*m*) for H-1, H-3, H-7 and H-6. A singlet at δ3.75 for a methoxy group with a pair of doublet centred at δ6.94 and 7.68 (J = 9 Hz each) assigned to the A_2B_2 system of aromatic protons and another pair of doublet for two *trans*-olefinic proton resonances at δ6.74 and 7.62 (J = 16 Hz) confirmed the presence of a *p*-methoxy cinnamoyl group in **2**. Compound **2** was found to be the *p*-methoxycinnamoyl derivative of **1**, as the methyl ester of **1** obtained by methylation (CH_2N_2) was identical with **2** (co-TLC, spectral data).

Compound **3**, $C_{17}H_{26}O_{11}$, mp 221–223° was obtained as white needles (EtOH–H_2O). Its IR (1705 and 1650 cm^{-1}) and UV spectrum (235 nm) were characteristic of carbomethoxy enol ether system, which was confirmed by the presence of an olefinic signal at δ7.54 (*s*, H-3) and a methoxy signal at δ3.82 in its ^{1}H NMR (DMSO-d_6) spectrum. The ^{13}C NMR spectrum displayed signals for 17 carbon atoms and correlated well with that of 6β-hydroxyloganin [14].

Structures **1**–**3** were also unambiguously assigned by their ^{13}C NMR (SFORD and DEPT) data (Table 1). The chemical shifts were assigned on the basis of structurally similar compounds [15, 16].

EXPERIMENTAL

General. Mps uncorr. EIMS: 70 eV. ^{1}H NMR: 80, 90 and 400 MHz; ^{13}C NMR: 100 MHz. TMS int. std. CC: silica gel

Table 1. ^{13}C NMR data of **1**, **1a**, **2**, **2a** and **3** (100 MHz)

C	**1** (CD_3OD)	**1a** ($CDCl_3$)	**2** (CD_3OD)	**2a** ($CDCl_3$)	**3** (DMSO-d_6)
1	97.80 *d*	94.40	97.42	94.32	95.42
3	154.00 *d*	150.64	154.49	150.56	151.38
4	110.52 *s*	110.39	109.85	110.35	109.33
5	39.67 *d*	36.15	39.23	36.10	37.57
6	78.36 *d*	77.00	76.86	77.25	77.12
7	79.04 *d*	72.37	70.74	72.26	72.58
8	37.45 *d*	35.51	36.88	35.42	36.60
9	46.07 *d*	44.91	41.94	44.84	44.04
10	14.87 *q*	13.19	14.36	13.12	13.96
11	170.13 *s*	170.32	169.73	170.25	167.34
12	52.01 *q*	51.30	51.94	51.22	50.92
1′	100.21 *d*	96.00	99.33	95.91	98.50
2′	74.72 *d*	70.72	73.73	70.63	73.03
3′	78.04 *d*	72.54	77.06	72.45	77.74
4′	71.64 *d*	68.42	70.74	68.32	70.04
5′	77.64 *d*	74.96	77.84	74.61	76.63
6′	62.83 *t*	61.71	62.20	61.71	61.08
1″	127.33 *s*	129.22	127.64	128.19	—
2″	131.13 *d*	131.97	130.25	129.72	—
3″	116.85 *d*	122.09	114.81	114.33	—
4″	161.16 *s*	152.35	162.09	161.54	—
5″	116.85 *d*	122.09	113.89	114.33	—
6″	131.13 *d*	131.97	129.27	129.72	—
α	115.30 *d*	117.64	115.60	114.88	—
β	146.66 *d*	144.18	145.57	144.89	—
CO	168.99 *s*	168.79	168.01	168.87	—
–OMe	—	—	55.63 *q*	55.25	—
6 × CO	—	165.86 *s*	—	166.23	—
	—	166.38 *s*	—	166.33	—
	—	168.94 *s*	—	169.17	—
	—	169.23 *s*	—	169.46	—
	—	169.52 *s*	—	169.85	—
	—	169.92 *s*	—	—	—
6 × –OCO–	—	20.02 *q*	—	19.95	—
Me	—	20.40 *q*	—	20.34	—
	—	20.45 *q*	—	20.48	—
	—	20.59 *q*	—	20.54	—
	—	20.95 *q*	—	—	—

60–120. TLC and prep-TLC: silica gel 60, spots and bands were detected by I_2 vapour and spraying reagents for iridoids: (i) 1% ceric sulphate in 1 M H_2SO_4 (ii) vanillin (3%) and H_2SO_4 (1%) in 100 ml EtOH followed by heating at 100–110° for 5–10 min.

Plant material. Twigs of *N. arbortristis* L. were collected from Lucknow (Uttar Pradesh) in January, 1985. A voucher specimen (1176 CDRI) is deposited in the Herbarium of Medicinal Plants of the Central Drug Research Institute, Lucknow.

Isolation of iridoids. Seeds of *N. arbortristis* (7 kg) were exhaustively extracted with 50% EtOH (5 × 1.5 l.) at room temp. The combined extract were evapd *in vacuo* below 45° to give a residue (850 g). The concd EtOH extract (400 g) on subsequent fractionation with hexane, $CHCl_3$ and *n*-BuOH gave hexane (10 g), $CHCl_3$ (60 g) and *n*-BuOH (140 g) sol fractions.

The concd *n*-BuOH ext (70 g) was chromatographed on a silica gel (1.5 kg) column and eluted with EtOAc and EtOAc (satd with H_2O)–MeOH of increasing MeOH content; this afforded fraction A (8 g) and fraction B (4.6 g), respectively. Fraction A was rechromatographed on silica gel (250 g) and eluted with $CHCl_3$–MeOH, when 7% MeOH–$CHCl_3$ gave compound **2** (4 g) as white needles, mp 220–222° (EtOH) and 10% MeOH–$CHCl_3$ gave compound **1** (0.965 g) as a white amorphous powder from $CHCl_3$–MeOH, mp 200–202°. Fraction B was also chromatographed on silica gel (100 g) using EtOAc–MeOH when 2% MeOH–EtOAc yielded compound **3** (90 mg) which was further purified by prep. TLC (EtOAc–MeOH–H_2O; 14:3:3). It was recrystallized from EtOH–H_2O as colourless needles, mp 221–223°.

Compound **1**. $[\alpha]_D^{28}$ −78.0° (MeOH; *c* 1.0): UV λ_{max}^{MeOH} nm: 229 (O–C=C–CO_2Me), 301 (sh), 312 (*p*-substituted benzene ring); IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 2970, 1710 (conjugated carbonyl) 1650 (C=C), 1620, 1530, 1450 (aromatic), 1300, 1220, 1190, 1090, 890, 855, 790; FD-MS: *m/z* 553 $[M+H]^+$, 552 $[M]^+$; EI-MS 70 eV, *m/z* 390 $[M]^+$ $[(M-\text{glucose})]^+$, 389, 372, 344, 244, 226, 198, 195, 164, 161, 148, 139; ^{1}H NMR (400 MHz) see Table 2; ^{13}C NMR (100 MHz) see Table 1.

Acetylation of **1**. **1** (100 mg) was acetylated with Ac_2O–pyridine (0.25 ml each) at room temp. and kept for 14 hr. The reaction mixt after usual work-up and recrystallization from EtOH afforded a hexaacetate (**1a**, 40 mg) as colourless needles,

Table 2. ^{1}H NMR Spectral data of compounds **1**, **1a**, **1b**, (400 MHz)

H	**1** (DMSO-d_6)	**1a** ($CDCl_3$)	**1b** ($CDCl_3$)
1	5.32 *d*, J = 6 Hz	5.35 *m*	5.42 *t*, J = 5.5 Hz
3	7.40 *s*	7.47 *s*	7.41 *s*
5	3.09 *m*	3.04 *dd*, J = 1.5 and 8 Hz	3.07 *dd*, J = 1.5 and 8 Hz
6	4.98 *m*	5.35 *m*	4.96 *dd*, J = 2.5 and 5 Hz
7	4.06 *br t*, J = 4 Hz	—	4.54 *t*, J = 6 Hz
8	2.01 *m*	2.50 *m*	2.16 *m*
9	2.14 *m*	2.59 *t*, J = 11 Hz	2.16 *m*
10	0.94 *d*, J = 8 Hz	1.1 *d*, J = 7.27 Hz	1.13 *d*, J = 7 Hz
12	3.61 *s*	3.68 *s*	3.76 *s*
α	6.36 *d*, J = 16 Hz	6.42 *d*, J = 16 Hz	6.27 *d*, J = 16 Hz
β	7.56 *d*, J = 16 Hz	7.68 *d*, J = 16 Hz	7.60 *d*, J = 16 Hz
3″ and 5″	6.75 *d*, J = 10 Hz	7.14 *d*, J = 10 Hz	6.82 *d*, J = 10 Hz
2″ and 6″	7.51 *d*, J = 10 Hz	7.58 *d*, J = 10 Hz	7.35 *d*, J = 10 Hz
OH	9.98 *br s*	—	9.95 *br s*
H-1′	4.94 *d*, J = 7.5 Hz	5.29 *m*	—
$-CH_2OH$	4.42 *d*, J = 9 Hz	4.32 *m*	—
remaining sugar protons	3.5–4.5 *m*		
6 × OAc	—	1.92, 2.02, 2.06	—
group protons	—	2.1 *s*	—
Phenolic –OAc protons	—	2.34 *s*	—
> CHOAc of glucose	—	4.85, 5.0, 5.12 *m*	—

mp 76–78°, $C_{38}H_{44}O_{19}$; IR ν_{max}^{KBr} cm^{-1}: 2970, 1760, 1725, 1650, 1620, 1515, 1440, 1380, 1220, 1170, 1090, 1040, 960, 920; FD-MS: *m/z* 805 $[M+H]^+$, 331 (acetylated glucose fragment); ^{1}H NMR (400 MHz) and ^{13}C NMR, (100 MHz) see Tables 1 and 2.

Mannich hydrolysis of **1**. **1** (100 mg) dissolved in Me_2CO (15 ml) was treated with conc HCl (0.15 ml) and kept at room temp. After 3 weeks the reaction mixt was extd with EtOAc × 4 and H_2O. The organic layer was washed × 3 with H_2O, dried (Na_2SO_4), concd and purified by prep. TLC ($CHCl_3$–MeOH; 19:1) to obtain the aglycone (**1b**) as a viscous mass (15 mg), $C_{20}H_{22}O_8$; UV λ_{max}^{MeOH} nm: 228, 305 (sh), 312; IR ν_{max}^{KBr} cm^{-1}: 3400, 2970, 1720, 1710, 1645, 1615, 1530, 1460, 1400, 1230, 1180, 770; EI-MS: *m/z* 390 $[M]^+$ 389 $[M-H]^+$, 385, 369, 355, 226, 185, 160, 147; ^{1}H NMR see Table 2. The aq layer was neutralized with Amberlite IR 410 CO_3^{2-} resin and subjected to PC with authentic sugar samples in *n*-BuOH–HOAc–H_2O; (4:1:5); glucose was identified as the sugar present in compound **1**.

Alkaline hydrolysis of **1**. **1** (100 mg) was dissolved in 10 ml of 2% KOH in MeOH and refluxed. After 2 hr the reaction mixt was concd, neutralized with dil HCl and immediately extracted with 2 × 10 ml EtOAc and 2 × 15 ml *n*-BuOH, successively. The EtOAc layers were combined, dried (Na_2SO_4) and concd under red. pres. The mixt. was examined by TLC and the product isolated by prep. TLC in hexane–EtOAc (7:3, with 3 drops HOAc). The chromatographic behaviour and ^{1}H NMR spectrum of the major product was identical to that of *p*-hydroxycinnamic acid (**4**), mp 210–212° (EtOH).

The *n*-BuOH extract on concn *in vacuo* was dissolved in MeOH and treated with CH_2N_2 at 0° for 14–16 hr. The reaction product after removal of solvent was purified by prep. TLC ($CHCl_3$–MeOH, 3:1, with a trace of HOAc) and recrystallized from EtOH as white needles of **3** (14 mg); mp 221–223°, $C_{17}H_{26}O_{11}$; UV λ_{max}^{MeOH} nm: 235; IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 2990, 1705, 1650, 1300, 1210, 1190, 1090, 890 and 760; FD-MS: *m/z* 406 $[M]^+$; ^{1}H NMR (400 MHz, DMSO-d_6): δ1.21 (3H, *d*, J = 7 Hz, Me), 1.96 (1H, *m*, H-8), 2.24 (1H, *m*, H-9), 2.75 (1H, *m*, H-5), 3.85 (3H, *s*, COOMe), 3.98 (2H, *br t*, J = 5 Hz, H-6 and H-7), 3.5–4.5 (*m*, sugar H), 4.65 (2H, *d*, J = 6.5 Hz, $-CH_2OH$), 5.42 (1H, *d*, J = 4.5 Hz, H-1), 7.50 (1H, *s*, H-3).

Compound **2**. $[\alpha]_D^{28}$ −92.5° (MeOH; *c* 1.0); UV λ_{max}^{MeOH} nm: 227, 300 (sh), 308; IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 1710, 1650, 1620, 1520, 1455, 1300, 1290, 1260, 1200, 1160, 1090, 1030, 975, 960, 880, 845, 810, 790, 635; FD-MS: *m/z* 565 $[M-H]^+$; ^{1}H NMR (400 MHz, DMSO-d_6): δ0.94 (3H, *d*, J = 6 Hz, Me), 2.04 (1H, *m*, H-8), 214 (1H, *m*, H-9), 3.10 (1H, *m*, H-5), 3.60 (3H, *s*, COOMe), 3.75 (3H, *s*, OMe), 4.13 (1H, *t*, J = 4 Hz, H-7), 4.42 (2H, *d*, J = 9 Hz, $-CH_2OH$), 4.95 (1H, *d*, J = 7 Hz, H-1′), 4.98 (1H, *m*, H-6), 4.5–5.0 (*m*, sugar protons), 5.27 (1H, *d*, J = 6 Hz H-1), 6.45 (1H, *d*, J = 16 Hz, H-α), 6.94 (2H, *d*, J = 10 Hz, H-3″ and H-5″), 7.40 (1H, *s*, H-3), 7.62 (1H, *d*, J = 16 Hz, H-β), 7.68 (2H, *d*, J = 10 Hz, H-2″ and H-6″). ^{13}C NMR (100 MHz) see Table 1.

Arbortristoside A pentaacetate (**2a**). Acetylation of **2** was carried out using a standard procedure, mp 85° (EtOH) (lit. 85–87°), $C_{37}H_{44}O_{18}$; ^{1}H NMR (400 MHz, $CDCl_3$): δ1.90, 2.00, 2.02, 2.09 (15H, *s*, 5 × OAc), 4.23 (2H, *m*, $-CH_2OAc$), 5.35 (1H, *m*, H-1′); ^{13}C NMR (100 MHz) see Table 1.

Mannich hydrolysis of **2** afforded the aglucone **2b** in small yield and glucose as the sugar moiety identified by PC. ^{1}H NMR (400 MHz, $CDCl_3$): 1.17 (3H, *d*, J = 6.5 Hz, −Me), 2.10 (1H, *m*, H-8), 2.16 (1H, *m*, H-9), 3.08 (1H, *dd*, J = 2, 8 Hz, H-5), 3.76 (3H, *s*, COOMe), 3.83 (3H, *s*, OMe), 4.20 (1H, *d*, J = 4.5 Hz, H-7), 4.96 (1H, *dd*, J = 2, 4 Hz, H-6), 5.42 (1H, *t*, J = 5.5 Hz, H-1), 6.37 (1H, *d*, J = 16 Hz, H-α), 6.87 (2H, *d*, J = 10 Hz, H-3″ and H-5″), 7.37 (2H, *d*, J = 10 Hz, H-2″ and H-6″), 7.43 (1H, *s*, H-3), 7.57 (1H, *d*, J = 16 Hz, H-β).

Alkaline hydrolysis of **2**. Methanolic KOH yielded *p*-methoxycinnamic acid, identified by co-TLC, mmp and superimposable IR with an authentic sample and another compound which on methylation with CH_2N_2 resulted in the formation of 6β-hydroxy loganin.

Compound **3**. Prep. TLC (EtOAc–MeOH–H_2O; 14:3:3) of a portion of fraction B yielded **3** (R_f 0.5), recrystallized as colourless needles (20 mg) from EtOH–H_2O, mp 221–223° (lit. [8] 220–222°), $C_{17}H_{26}O_{11}$.

Conversion of **1** *to arbortristoside A.* To a soln of **1** (50 mg) in MeOH was added a small excess of CH_2N_2–Et_2O and the reaction mixt. kept overnight. Solvent was evapd *in vacuo* and the product purified by prep. TLC ($CHCl_3$–MeOH; 43:7) to give the Me ester of **1** (23 mg) as a white amorphous powder, which on recrystallization from EtOH was identified as arbortristoside A (co-TLC, mp, superimposable IR).

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