

ARBORSIDE D, A MINOR IRIDOID GLUCOSIDE FROM *NYCTANTHES ARBOR-TRISTIS*¹

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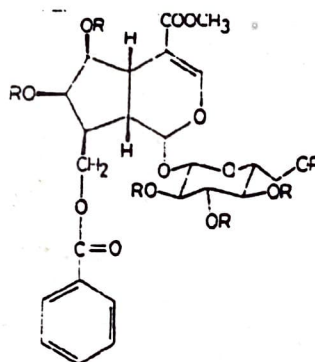
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ABSTRACT.—Re-examination of the leaves of *Nyctanthes arbor-tristis* led to the isolation and identification of a new minor iridoid glucoside, arborside D [1], as its acetyl derivative, together with the previously reported arborside C. The structure of the new compound was determined using spectral methods.

Nyctanthes arbor-tristis L. (Nyctanthaceae) (1), a large shrub cultivated as a garden plant throughout India, is also found growing wild in the forests of Madhya Pradesh and in sub-Himalayan regions. The leaves of the plant are used extensively in Ayurvedic medicine for the treatment of sciatica, chronic fever, rheumatism, and intestinal worms, and are also employed for laxative, cholagogue, diuretic, diaphoretic, expectorant, and antiamebic purposes (2–4). Earlier phytochemical studies on this plant have resulted in the isolation of a number of iridoid glycosides, arbortristiosides A–E (5–7) and arborsides A–C (8), of which arbortristiosides A and C exhibited antileishmanial (9), antiviral (7), immunostimulant, antifungal, and hepatoprotective (7) activities. The isolation and identification of a new minor iridoid glucoside is discussed in this communication.

In a continuation of our studies on the *Nyctanthes arbor-tristis* leaves, we have isolated a new iridoid glucoside, arborside D [1] along with the previously isolated arborsides A–C (8). The complete characterization of 1 is based on the spectral data of its acetylated derivative [2].

The molecular formula of arborside D hexaacetate [2] was established as



1 R=H
2 R=Ac

$C_{36}H_{46}O_{19}$ by fabms (m/z 778 M^+). It showed a typical uv absorption at λ_{max} 228 and 272 nm, corresponding to a C-4 methoxy carbonyl and a benzoyl group (10) and ir bands for an ester carbonyl group (1740), enolic bonds (1630), an acetyl carbonyl group (1210 cm^{-1}) and an aromatic ring ($1360, 1030\text{ cm}^{-1}$). The complete 1H - and ^{13}C -nmr assignment of the compound was accomplished by using 2D COSY (11), DEPT (12), and low-power selective 1H decoupled ^{13}C -nmr experiments. Table 1 shows the 1H - and ^{13}C -nmr chemical shifts and 1H - 1H coupling constants of 2. The coupling pattern was resolved by 2D nmr, with connectivities as shown in Figure 1.

The position of the benzoyl moiety was confirmed by carrying out a low-power selective proton ^{13}C -nmr experiment. On selectively decoupling the methylene protons centered at δ 4.32 (H-

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TABLE 1. ^{13}C - and ^1H -Nmr Chemical Shifts for 2.^a

Position	δ_{C}	δ_{H}
1	94.46	5.36, br s
1'	96.00	4.74, d (8.0)
2	—	—
2'	70.56	4.87, t (9.0)
3	151.64	7.23, s
3'	72.07	5.12, t (12.0)
4	108.74	—
4'	68.07	4.99, t (12.0)
5	39.35	2.97, dd (13.0, 3.0)
5'	72.37	3.60, m
6	76.36	5.38, br s
6'	61.59	4.18, dd (13.0, 4.2)
7	76.63	5.32, m
8	35.25	2.53, t (8.0)
9	41.88	2.71, t (2.8)
10	63.85	4.32, dd, 2H (9.0)
12	51.00	3.62, s
C=O(Acetyl)	171.0–169.0	—
Me(Acetyl)	20.0–21.0	—
1''	133.3	—
2'' and 6''	129.5	7.96, d (8.0)
3'' and 5''	128.4	7.38–7.43, m
4''	130.0	7.56, s
-CO-OCH ₃	166.4	—
-CO-Ph	166.0	—

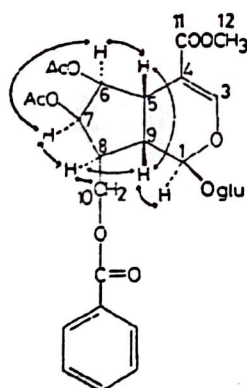
^aCoupling constants (*J*) are given in Hz in parentheses.

FIGURE 1. Correlations of 2 based on 2D COSY studies.

10), the signal of the C-10 carbon at δ 63.18 collapsed into a singlet. Moreover, the signal of the benzoyl carbonyl at δ 169 and that at δ 35.2 (C-8) also collapsed, confirming the position of the benzoyl moiety.

In conclusion, the structure of arborside D [1] was assigned as 10-benzoylnyctanthoside.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps are reported uncorrected. Eims spectra were recorded at 70 eV, and fabms were taken on a JEOL 5 102 DA 6000 instrument. Uv spectra were obtained on a Perkin-Elmer Lambda-15 spectrophotometer. ^1H -nmr spectra were taken at 100.13 MHz with TMS as an internal standard. Cc was performed over Si gel 60–120, (Sisco), tlc and prep. tlc over Si gel 660 (Sisco, spots and bands visualized by I_2 vapor). Visualization reagents for the iridoid were (a) 1% ceric sulphate in 2 N H_2SO_4 and (b) vanillin and H_2SO_4 (1%) in 100 ml EtOH, followed by heating at 100–110° for 5–10 min.

PLANT MATERIAL.—As described previously (8).

EXTRACTION AND ISOLATION.—Preliminary work-up as described previously (8). Continued elution of the column with $\text{C}_6\text{H}_6/\text{EtOAc}$ yielded fractions containing arborside D [1] in a mixture with arborsides A and B. The mixture was acetylated with Ac_2O /pyridine at room temperature. The acetylated product on the usual workup and separation by prep. tlc (C_6H_6 - Me_2CO (9:1), triple run) afforded pure compounds arborsides A, B, and D in the form of their acetyl derivatives.

Arborside D hexa acetate [2].—Colorless needles (60 mg), mp 144° (EtOAc/C₆H₁₄), $[\alpha]_D^{25} -53.57^\circ$ ($c=1.0$, MeOH); uv λ max (MeOH) 272 (ϵ 2334), 228 (ϵ 24,312) nm; ir ν max (KBr) 2960, 1740, 1630, 1330, 1360, 1210, 1030 cm^{-1} ; fabms m/z M^+ 778, 759, 741, 683, 431, 399, 371, 357, 331, 307, 289, 271, 207, 189, 169, 136, 127, 105, 89, 77; ^1H - (400 MHz) and ^{13}C -nmr data, see Table 1; *anal.*, calcd for C₃₆H₄₂O₉, C 54.99, H 5.55; found C 55.6, H 5.4.

LITERATURE CITED

1. R.S. Thakur, H.S. Puri, and A. Hussein, "Major Medicinal Plants of India," CIMAP, Lucknow, 1989.
2. R.N. Chopra, S.L. Nayar, and I.C. Chopra, "Glossary of Indian Medicinal Plants," CSIR, New Delhi, 1956, p. 177.
3. "Medicinal Plants of India," ICMR Publication, New Delhi, India, 1987, p. 343.
4. V.C. Chitravanshi, A.P. Singh, S. Ghosal, B.N.K. Prasad, V. Srivastava, and J.S. Tandon, *Int. J. Pharmacog.*, **30**, 71 (1992).
5. K.K. Purshothaman, V. Mathuram, and A. Sarda, *Phytochemistry*, **24**, 773 (1985).
6. A. Rathore, R.K. Juneja, and J.S. Tandon, *Phytochemistry*, **28**, 1913 (1989).
7. A. Rathore, V. Srivastava, K.C. Srivastava, and J.S. Tandon, *Phytochemistry*, **29**, 1917 (1989).
8. V. Srivastava, A. Rathore, S.M. Ali, and J.S. Tandon, *J. Nat. Prod.*, **53**, 303 (1990).
9. J.S. Tandon, V. Srivastava, and P.Y. Guru, *J. Nat. Prod.*, **54**, 1102 (1991).
10. J.N. Bobbitt and K.P. Segebarth, in: "Cyclopentanoid Terpene Derivatives." Ed. by W.I. Taylor and A.R. Battersby, Marcel Dekker, New York, 1969, pp. 112–113.
11. W.P. Aue, E. Bartholdi, and R.R. Ernst, *J. Chem. Phys.*, **64**, 2229 (1976).
12. M.R. Bendall, D.M. Doddrell, D.T. Pegg, and W.E. Hull, *J. Magn. Reson.*, **44**, 236 (1981).

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