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## A REINVESTIGATION OF THE STRUCTURES OF ARBORTRISTOSIDES A AND B FROM NYCTANTHES ARBOR-TRISTIS<sup>1</sup>

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**ABSTRACT.**—The structures of arbortristosides A and B have been reinvestigated by proton decoupling experiments and 2D correlated nmr spectroscopy. The aryl ester groups in both arbortristosides A and B have been found to be at position 7, not at 6 as reported earlier.

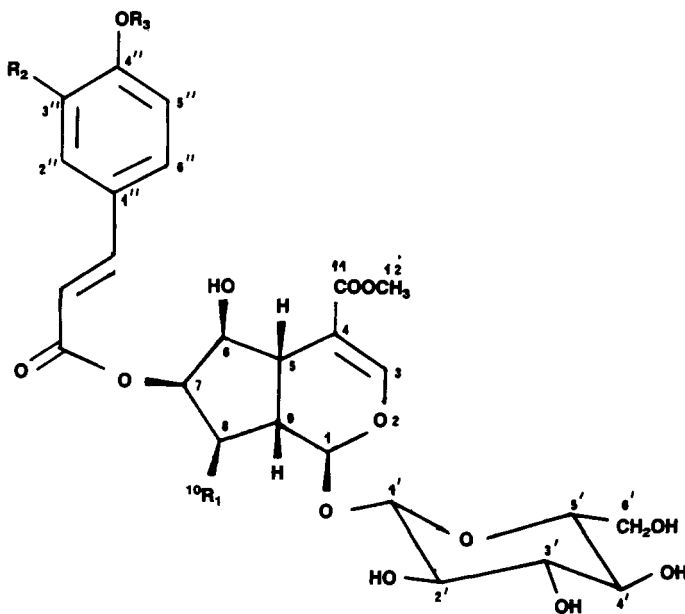
Chemical investigation of the seeds of *Nyctanthes arbor-tristis* L. (Oleaceae) in our laboratory resulted in the isolation of two new iridoid glucosides, arbortristosides A and B (1). In order to confirm the position of the *p*-methoxycinnamoyl ester group in arbortristoside A and the caffeoyl ester group in arbortristoside B, we took their <sup>1</sup>H-nmr spectra at 300.13 MHz and their 2D COSY spectra. The <sup>1</sup>H-nmr signals were better resolved than the previous <sup>1</sup>H-nmr spectra at 90 MHz. Earlier the aryl ester groups were placed at position 6 and the free OH was placed at position 7 in both arbortristosides A and B. In order to confirm their positions, extensive homodecoupling experiments were carried out with arbortristoside A and arbortristoside B octaacetate.

In the <sup>1</sup>H-nmr spectrum of arbortristoside A, the triplets at  $\delta$  4.07 and 5.16 ppm could be assigned to the protons attached to the carbons bearing the OH group and *p*-methoxycinnamoyl ester group, respectively. Irradiation of the methyl doublet at 1.03 ppm caused a sharpening of the multiplet at 2.2 (2H, m, H-8,-9). When the multiplet at 2.2 ppm was irradiated, the doublets at 5.3 (H-1) and 1.03 (H-10) collapsed to singlets and the triplets at 5.16 and 3.0 (H-5) collapsed to doublets. Irradiation

of the triplet at 3.0 ppm caused a sharpening of the signals at 2.2 and 4.07 ppm. Irradiation of the triplet at 4.07 ppm resulted in the triplets at 3.0 and 5.16 ppm collapsing to doublets. When the triplet at 5.16 ppm was irradiated, the triplet at 4.07 collapsed to a doublet and there was a sharpening of the multiplet at 2.2 but the triplet at 3.0 ppm was unaffected. This clearly shows that the *p*-methoxycinnamoyl ester group in arbortristoside A is at position 7. Had the aryl ester group been at 6, the triplet at 3.0 (H-5) would have collapsed to a doublet. When the doublet at 5.3 ppm was irradiated, the multiplet at 2.2 was greatly affected. The proton-decoupled spectrum of arbortristoside A pentaacetate gave additional support for the structure **1** for arbortristoside A. When the double doublet at 3.04 ppm (H-5) was irradiated, the triplet at 5.27 (acetate methine proton) in the <sup>1</sup>H-nmr spectrum of the pentaacetate collapsed to a doublet as expected.

Recently, Rathore *et al.* (2) have reported arbortristoside A, 6 $\beta$ -hydroxyloganin, and a new iridoid glucoside from the 50% EtOH extract of the seeds of *N. arbor-tristis*. The new iridoid is reported to contain a *p*-hydroxycinnamoyl group at position 6 instead of the *p*-methoxycinnamoyl group in arbortristoside A, and it has been converted to arbortristoside A by methylation with CH<sub>2</sub>N<sub>2</sub>/Et<sub>2</sub>O. As the structure of arbor-

<sup>1</sup>CSDMRIA Communication No. 280.



- 1  $R_1=R_3=Me$ ,  $R_2=H$   
 2  $R_1=CH_2OH$ ,  $R_2=OH$ ,  $R_3=H$

tristoside A is now proved beyond any doubt, it follows that the groups at 6 and 7 have to be interchanged in the new iridoid as in arbortristoside A [1].

In the  $^1H$ -nmr (300.13 MHz) spectrum of arbortristoside B, H-1 appears as a doublet at 5.25 ppm ( $J=5.3$  Hz), and the proton attached to the carbon carrying the caffeoyl group comes as a multiplet centered at 5.25 ppm. In the 2D COSY-90 spectrum of arbortristoside B, the signal at 5.25 is correlated to the multiplet at 2.25 ppm (H-8,-9), which strongly suggests that the caffeoyl group is at position 7 and not at 6 as reported earlier. This was confirmed by homodecoupling experiments on arbortristoside B octaacetate. In the  $^1H$ -nmr spectrum of arbortristoside B octaacetate, the triplet at 4.07 ppm in arbortristoside B disappeared; instead there appeared a triplet at 5.43 ppm ( $J=3.7$  Hz) which could be ascribed to the proton attached to the carbon carrying the acetoxy group.

The multiplet at 5.38 ppm (as in arbortristoside B) resonating for two protons was assigned for H-1 (d,  $J=2.4$

Hz) and for the proton on the carbon carrying the aryl ester group in arbortristoside B octaacetate.

Irradiation of the multiplet at 2.53 ppm (H-8) resulted in the multiplet at 5.38 collapsing to a doublet (merged with H-1 doublet), thereby showing the presence of the aryl ester group at position 7. The doublet at 4.29 (H<sub>2</sub>-10) and the doublet of a triplet at 2.68 ppm (H-9) also collapsed to a singlet and a double doublet, respectively. When the signal at 2.68 ppm was irradiated, the double doublet at 3.06 (H-5) collapsed to a doublet and the doublet at 5.38 (H-1) collapsed to a singlet. Irradiation of the signal at 3.06 ppm caused the collapse of the triplet at 5.43 (acetate methine proton) to a doublet, which clearly shows that the acetoxy group is at position 6. Hence, in arbortristoside B, the free OH is at C-6, the caffeoyl ester group is at C-7, and 2 is its revised structure.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.— $^1H$ -nmr spectra were recorded on a Bruker spectrometer at 300.13 MHz. Chemical shifts are

presented in  $\delta$  values relative to TMS.  $^{13}\text{C}$  nmr was run at 75.5 MHz. Standard procedures were used for nmr experiments.

**PLANT MATERIAL.**—The seeds of *N. arbor-tristis* were collected from Jaipur, India in February 1984 and identified by the botanist of Regional Research Institute, Jaipur. A voucher specimen No. 701 is deposited in the CSMDRIA Herbarium.

**ISOLATION.**—Arbortristoides A and B were isolated from the alcohol and hot MeOH extracts, respectively, of the seeds of *N. arbor-tristis* as in our earlier publication (1).

**ARBORTRISTOSIDE A [1].**—Colorless solid; mp 226–228°; 2D COSY enabled the assignment of all the sugar protons.  $^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ , 300.13 MHz) 1.03 (3H, d,  $J=6$  Hz, H-10), 2.2 (2H, m, H-8,-9), 3.0 (1H, t,  $J=6$  Hz, H-5), 3.15 (1H, dd,  $J=6.2, 6.3$  Hz, H-2'), 3.15 (1H, dd,  $J=6.3, 9.3$  Hz, H-3'), 3.2 (1H, t,  $J=9.3$  Hz, H-4'), 3.3 (1H, dd,  $J=3.3, 9$  Hz, H-5'), 3.65 (1H, dd,  $J=3.3, 9.3$  Hz, H-6'), 3.85 (1H, d,  $J=9.3$  Hz, H-6'), 3.68 (3H, s, H-12), 3.77 (3H, s, OMe), 4.07 (1H, t,  $J=4.5$  Hz, H-6), 4.6 (1H, d,  $J=6.2$  Hz, H-1'), 5.16 (1H, t,  $J=4.5$  Hz, H-7), 5.3 (1H, d,  $J=3$  Hz, H-1), 6.41 (1H, AB q,  $J=15.1$  Hz, H- $\alpha$ ), 6.9 (2H, d,  $J=6.3$  Hz, H-3'', -5''), 7.46 (1H, s, H-3), 7.52 (2H, d,  $J=6.3$  Hz, H-2'', -6''), 7.7 (1H, AB q,  $J=15.1$  Hz, H- $\beta$ );  $^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ , 75.5 MHz) 170.6 (C-11), 169.4 (C=O), 163.7 (C-4''), 154.7 (C-3), 148.9 (C- $\beta$ ), 131.5 (C-2'', -6''), 128.9 (C-1''), 116.6 (C- $\alpha$ ), 116.0 (C-3'', -5''), 110.9 (C-4), 100.6 (C-1'), 98.2 (C-1), 79.4 (C-6), 78.9 (C-3'), 78.5 (C-5'), 78.2 (C-7), 75.2 (C-2'), 72.1 (C-4'), 63.3 (C-6'), 56.4 (OMe), 52.6 (C-12), 46.5 (C-9), 40.1 (C-5), 37.9 (C-8), 15.5 (C-10).

**ARBORTRISTOSIDE A PENTAACETATE.**—Arbortristoides A pentaacetate was prepared as given previously (1): colorless solid; mp 85–87°; 2D COSY enabled the assignment of all the protons.  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 300.13 MHz)  $\delta$  1.08 (3H, d,  $J=6.8$  Hz, H-10), 1.91, 2.01, 2.11 (s, 3  $\times$  OAc), 2.04 (s, 2  $\times$  OAc), 2.15 (1H, m, H-8), 2.58 (1H, dt,  $J=2.2, 9.0, 9.0$  Hz, H-9), 3.04 (1H, dd,  $J=3.7, 9.0$  Hz, H-5), 3.68 (3H, s, H-12), 3.77 (1H, ddd, H-5'), 3.85 (3H, s, OMe), 4.15 (1H, dd,  $J=1.8, 12.2$  Hz, H-6'), 4.33 (1H, dd,  $J=4.5, 12.4$  Hz, H-6'), 4.86 (1H, d,  $J=8.1$  Hz, H-1'), 5.0 (1H, dd,  $J=8.1, 9.5$  Hz, H-2'), 5.11 (1H, t,  $J=9.5$  Hz, H-4'), 5.23 (1H, t,  $J=9.5$  Hz, H-3'), 5.27 (1H, t, H-6), 5.33 (1H, d,  $J=2.3$  Hz, H-1), 5.35 (1H, t,  $J=5$  Hz, H-7), 6.31 (1H, d,  $J=16.0$  Hz, H- $\alpha$ ), 6.92 (2H, d,  $J=8.7$  Hz, H-3'', -5''), 7.38 (1H, s, H-3), 7.51 (2H, d,  $J=8.7$  Hz, H-2'', -6''), 7.64 (1H, d,  $J=16.0$  Hz, H- $\beta$ );  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 75.5 MHz) 170.3, 169.9, 169.5, 169.2, 168.9

(5  $\times$  OCOMe), 166.3 (C-11), 166.2 (C=O), 161.4 (C-4''), 150.5 (C-3), 144.9 (C- $\beta$ ), 129.7 (C-2'', -6''), 126.8 (C-1''), 114.7 (C- $\alpha$ ), 114.2 (C-3'', -5''), 110.2 (C-4), 95.7 (C-1'), 94.1 (C-1), 77.1 (C-6), 74.6 (C-7), 72.3 (C-3'), 72.1 (C-5'), 70.4 (C-2'), 68.1 (C-4'), 61.6 (C-6'), 55.2 (OMe), 51.2 (C-12), 44.7 (C-9), 36.0 (C-5), 35.3 (C-8), 13.0 (C-10), 20.5, 19.9 (2  $\times$  OCOCH<sub>3</sub>), 20.5 (3  $\times$  OCOCH<sub>3</sub>). The  $^{13}\text{C}$  assignments were all substantiated by the C-H correlation experiment.

**ARBORTRISTOSIDE B [2].**—Amorphous hygroscopic powder:  $^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ , 300.13 MHz)  $\delta$  2.25 (2H, m, H-8,-9), 2.95 (1H, t,  $J=7.3$  Hz, H-5), 3.1–3.8 (sugar protons), 3.68 (3H, s, H-12), 4.07 (1H, t,  $J=4.3$  Hz, H-6), 4.25, 4.40 (1H each, m, 2H-10), 4.6 (1H, d,  $J=7.8$  Hz, H-1'), 5.25 (1H, d,  $J=5.3$  Hz, H-1), 5.25 (1H, m, H-7), 6.25 (1H, d,  $J=15.9$  Hz, H- $\alpha$ ), 6.75 (1H, d,  $J=8.2$  Hz, H-5''), 6.9 (1H, dd,  $J=1.8, 8.2$  Hz, H-6''), 7.0 (1H, d,  $J=1.74$  Hz, H-2''), 7.45 (1H, s, H-3), 7.5 (1H, d,  $J=16.1$  Hz, H- $\beta$ );  $^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ , 75.5 MHz) 170.9 (C-11), 169.9 (C=O), 154.8 (C-3), 150.0 (C-4''), 147.5 (C- $\beta$ ), 147.2 (C-3''), 128.2 (C-1''), 123.5 (C-6''), 117.1 (C-2''), 115.7 (C-5''), C- $\alpha$ ), 110.8 (C-4), 100.9 (C-1'), 99.1 (C-1), 80.4 (C-6), 78.6 (C-3'), 78.3 (C-5'), 75.0 (C-2'), 73.4 (C-7), 71.7 (C-4'), 65.4 (C-10), 63.1 (C-6'), 52.6 (C-12), 43.5 (C-9), 42.1 (C-5), 39.5 (C-8).  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr values for arbortristoides B were not reported earlier.

**ARBORTRISTOSIDE B OCTAACETATE.**—Arbortristoides B octaacetate was prepared as in Purushothaman *et al.* (1): colorless solid; mp 156–158°;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 300.13 MHz)  $\delta$  1.91, 1.99, 2.03, 2.04, 2.06, 2.08, 2.3, 2.31 (s, 6  $\times$  OAc), 2.53 (1H, m, H-8), 2.68 (1H, dt,  $J=2.6, 8.5, 8.5$  Hz, H-9), 3.06 (1H, dd,  $J=2.9, 8.3$  Hz, H-5), 3.71 (3H, s, H-12), 4.12 (1H, dd,  $J=2.0, 12.5$  Hz, H-6'), 4.26 (1H, dd,  $J=4.2, 12.5$  Hz, H-6'), 4.29 (2H, d,  $J=7.1$  Hz, H-10), 4.84 (1H, d,  $J=8.1$  Hz, H-1'), 4.98 (1H, dd,  $J=8.2, 9.5$  Hz, H-2'), 5.08 (1H, t,  $J=9.6$  Hz, H-4'), 5.21 (1H, t,  $J=9.5$  Hz, H-3'), 5.38 (1H, d,  $J=2.4$  Hz, H-1), 5.38 (1H, m, H-7), 5.43 (1H, t,  $J=3.7$  Hz, H-6), 6.36 (1H, d,  $J=16.0$  Hz, H- $\alpha$ ), 7.22 (1H, d,  $J=1.6$  Hz, H-2''), 7.26 (1H, d,  $J=8.0$  Hz, H-5''), 7.40 (1H, dd,  $J=1.6, 7.5$  Hz, H-6''), 7.42 (1H, s, H-3), 7.64 (1H, d,  $J=16.0$  Hz, H- $\beta$ );  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 75.5 MHz) 170.4, 170.0, 169.8, 169.5, 169.3, 169.0, 167.9, 167.8 (8  $\times$  OCOCH<sub>3</sub>), 166.1 (C-11, C=O), 151.6 (C-3), 143.7 (C-4'', C- $\beta$ ), 142.5 (C-3''), 133.0 (C-1''), 126.4 (C-6''), 124.0 (C-2''), 122.9 (C-5''), 118.5 (C- $\alpha$ ), 108.8 (C-4), 96.0 (C-1'), 94.5 (C-1), 76.4 (C-6), 72.4 (C-7, C-3'), 72.0 (C-5'), 70.6 (C-2'), 68.2 (C-4'), 63.3 (C-10), 61.5 (C-6'), 51.5 (C-12), 41.6 (C-9), 39.4 (C-5), 35.3

(C-8), 20.7, 20.1 ( $2 \times \text{OCOCH}_3$ ), 20.5 ( $6 \times \text{OCOCH}_3$ ).

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