

STUDIES ON BUTACEAE : PART IV<sup>1</sup> - CONVERSION OF ATALANTIN TO  
A RARE SPIROTETRAORTRITERPENOID

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**Abstract** - Boron trifluoride etherate treatment of atalantin, the tetraortriterpenoid constituent of *Atalantia wightii* Tan (Butaceae), afforded an interesting rearranged spiro-product, the structure of which was confirmed from spectral data.

Atalantin (1)<sup>2</sup>, a major constituent of *Atalantia wightii* Tan (Butaceae), afforded an interesting system for study. The tetrahydrofuran ring and the  $\alpha, \beta$ -unsaturated ester substituent at C<sub>10</sub> were suitably placed to allow the construction of the rare spiro-ring system of the type present in ichangin (2)<sup>3</sup>.

Atalantin (1) on treatment with boron trifluoride etherate in dry methylene chloride at 0-5°C under a nitrogen atmosphere for 1 h afforded the light yellow crystalline product (3) (Chart 1). The infrared spectrum of (3) showed the presence of a hydroxyl group (3420 cm<sup>-1</sup>), a six membered ketone (1710 cm<sup>-1</sup>), two  $\delta$ -lactones, one of which is  $\alpha, \beta$ -unsaturated (1745, 1725 cm<sup>-1</sup>), a double bond (1615 cm<sup>-1</sup>) and a furan moiety (875 cm<sup>-1</sup>). The 400 MHz <sup>1</sup>H-NMR spectrum of (3) in CDCl<sub>3</sub> showed the signals for C<sub>1</sub>-H and C<sub>2</sub>-H at  $\delta$  6.63 (1H, dd, J = 10.0 and 3.0 Hz) and  $\delta$  6.18 (1H, d, J = 10.0 Hz) respectively. The C<sub>19</sub>-methylene protons resonated at  $\delta$  4.42 (1H, d, J = 13.0 Hz) and  $\delta$  4.74 (1H, dd, J = 13.0 and 3.0 Hz). Compound (3) showed the absence of a carbomethoxy group and the C<sub>5</sub>-H which were present in atalantin (1). Signals for the other protons in (3) were almost similar with those in (1). This clearly indicated that rings B, C, D and the furan substituent at C<sub>17</sub> of (1) were unaffected during the reaction. An interesting rearrangement had occurred involving the  $\alpha, \beta$ -unsaturated methyl ester at C<sub>10</sub> and the tetrahydrofuran moiety resulting in the formation of an  $\alpha, \beta$ -unsaturated  $\delta$ -lactone and the generation of the 4,5-double bond.

The structure (3) was unambiguously settled from a detailed study of its <sup>13</sup>C-NMR data (Table 1). Atalantin (1) and atalantolide (4)<sup>2</sup> were chosen as model systems.

The spectrum of (3) showed the signals for 26 carbons. The differences between compounds (1) and (3) were the absence of the carbomethoxy group and the tetrahydrofuran moiety in the latter which were present in atalantin (1). The C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> in (3) appeared at 153.1, 120.4 and 162.3 ppm respectively confirming the presence of an  $\alpha,\beta$ -unsaturated  $\delta$ -lactone. The signals for C<sub>4</sub> and C<sub>5</sub> were observed at 84.4 and 64.5 ppm in (1) while in the rearranged product (3) they resonated at 158.4 and 130.2 ppm respectively thereby establishing the formation of the isopropylidene substituent at C<sub>5</sub>. These data were in good agreement with those reported for atalantolide (4)<sup>2</sup>.

This rearrangement appears to have been brought about by the generation of an electrophilic species with the coordination of the tetrahydrofuran oxygen with the electron-deficient boron in boron trifluoride. This resulted in the oxygen-C<sub>4</sub> bond cleavage with generation of the isopropylidene system at C<sub>5</sub>. Cyclisation involving the  $\alpha,\beta$ -unsaturated ester and the generated hydroxyl resulted in the formation of the  $\alpha,\beta$ -unsaturated  $\delta$ -lactone system.

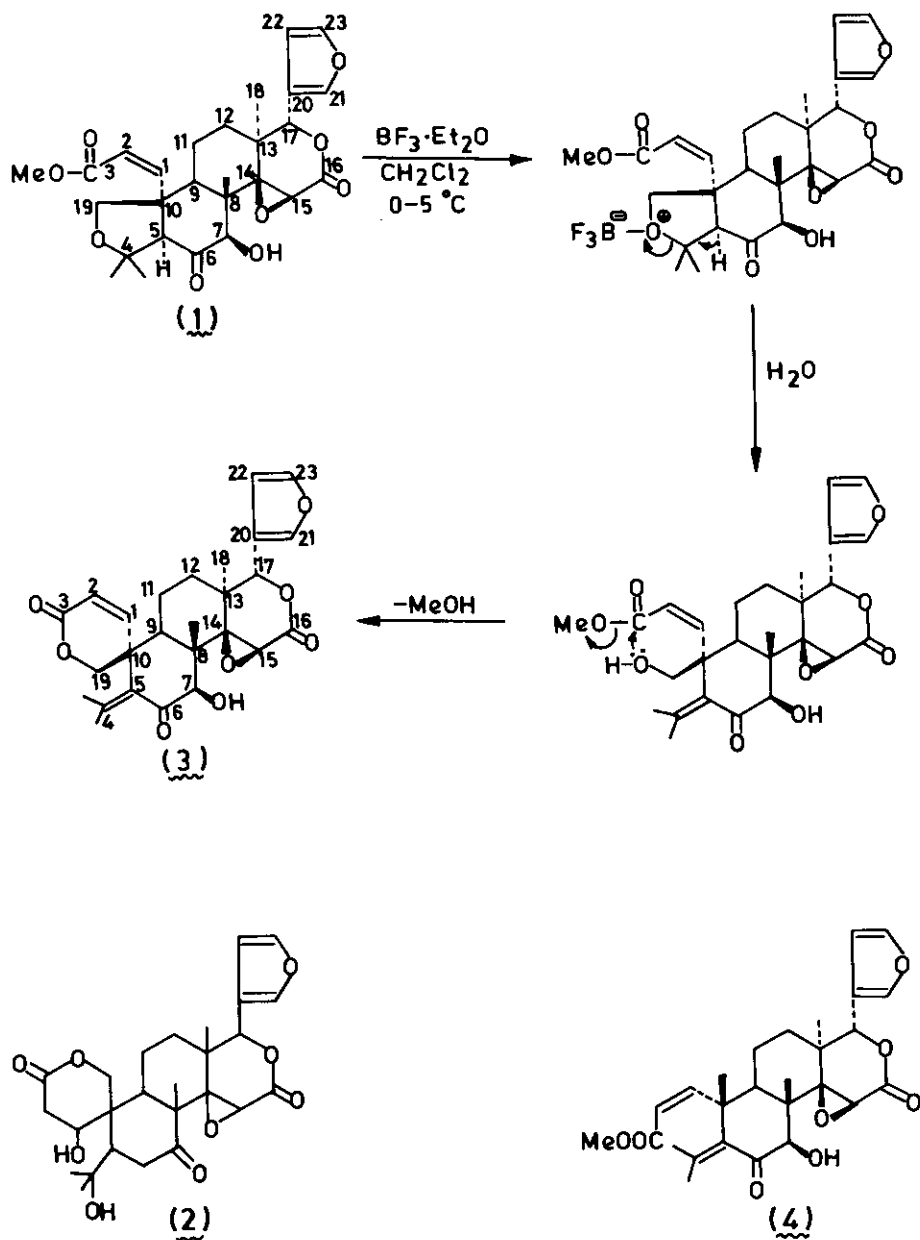
Table 1 20 MHz <sup>13</sup>C-NMR signals of (3) in CDCl<sub>3</sub>

Carbon Number	Chemical Shift (in ppm)	Carbon Number	Chemical Shift (in ppm)
1	153.1	14	66.9
2	120.4	15	51.5
3	162.3	16	167.0
4	158.4	17	78.0
5	130.2	18	20.8
6	199.4	19	71.0
7	81.2	20	120.0
8	44.9	21	140.9
9	41.4	22	109.7
10	44.6	23	143.0
11	18.6	30	12.8
12	32.1	C <sub>4</sub> -methyls	26.1, 27.1
13	37.5		

#### EXPERIMENTAL

Melting points were recorded on Kofler block apparatus and are uncorrected. The UV spectra (in 95% aldehyde free ethanol) were recorded on a Varian 634 spectro-

CHART 1



photometer, the IR spectra (KBr) on a Perkin-Elmer 782 spectrophotometer, the 400 MHz  $^1\text{H}$ -NMR spectra (in  $\text{CDCl}_3$  using tetramethylsilane as the internal standard) on a Bruker WH-400 spectrometer, the  $^{13}\text{C}$ -NMR spectrum (in  $\text{CDCl}_3$ ) on a Varian CFI-20 spectrometer and the mass spectrum on a 70 e.v. - Hitachi RMU 6L mass spectrograph.

#### Isolation of Atalantin (1)

The air dried and finally milled whole plant of Atalantia Wrightii Tan (10 kg) were exhaustively extracted with petrol (60-80°C) in a Soxhlet apparatus for 72 h. The extract was concentrated and chromatographed over silica gel, the column being eluted with solvents of increasing polarity. The benzene - ethyl acetate (4:1) eluate afforded atalantin (1) which was crystallised from benzene-ethyl acetate (1:1), mp 184-185°C, yield 10 g (0.1%)  $\lambda_{\text{max}}^{\text{D}}(\text{KBr})$ : 3420, 1740, 1705, 1615, 1580, 1520, 1200, 875  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$ : 6.62 (1H, d,  $J = 12.0$  Hz,  $\text{C}_1\text{-H}$ ), 5.90 (1H, d,  $J = 12.0$  Hz,  $\text{C}_2\text{-H}$ ), 3.11 (1H, br.s,  $\text{C}_5\text{-H}$ ), 4.77 (1H, br.s.,  $\text{C}_7\text{-H}$ ), 4.44 (1H, s,  $\text{C}_{15}\text{-H}$ ), 5.53 (1H, s,  $\text{C}_{17}\text{-H}$ ), 3.79 (1H, d,  $J = 9.5$  Hz,  $\text{C}_{19}\text{-H}$ ), 4.17 (1H, d,  $J = 9.5$  Hz,  $\text{C}_{19}\text{-H}$ ), 7.41 (1H, m,  $\text{C}_{21}\text{-H}$ ), 6.36 (1H, m,  $\text{C}_{22}\text{-H}$ ), 7.44 (1H, m,  $\text{C}_{23}\text{-H}$ ), 3.69 ( $-\text{COOCH}_3$ ), 1.36, 1.30, 1.24, 0.89 ( $4\times\text{CH}_3$ ).

#### Reaction of Atalantin (1) with Boron Trifluoride Etherate

To a well-stirred solution of atalantin (50 mg) in dry methylene chloride (10 ml) at 0-5°C was added dropwise a solution of boron trifluoride etherate (0.4 ml) in methylene chloride (5 ml) for 1 h under a nitrogen atmosphere. The reaction mixture was then diluted with water (50 ml) and extracted with methylene chloride (3x50 ml). The methylene chloride solution was washed with 2% aqueous sodium bicarbonate (3x30 ml), water (3x50 ml) and dried. The solution was concentrated and subjected to chromatographic resolution over silica gel. Compound (3) was eluted with benzene - ethyl acetate (4:1) and crystallised as a light yellow solid from benzene - ethyl acetate (1:1) (Found: C, 66.81; H, 5.60%. Calculated for  $\text{C}_{26}\text{H}_{28}\text{O}_8$ : C, 66.60; H, 5.98%), mp 223-224°C, yield 28 mg (60%);  $\lambda_{\text{max}}(\text{EtOH})$ : 213 and 249 nm ( $\log \epsilon = 4.83$  and 4.55 respectively),  $\lambda_{\text{max}}(\text{EtOH}+\text{NaOH})$ : 223 and 353 nm ( $\log \epsilon = 4.61$  and 3.89 respectively);  $\delta(\text{CDCl}_3)$ : 6.63 (1H, dd,  $J = 10.0$  and 3.0 Hz,  $\text{C}_1\text{-H}$ ), 6.18 (1H, d,  $J = 10.0$  Hz,  $\text{C}_2\text{-H}$ ), 4.21 (1H, d,  $J = 3.0$  Hz,  $\text{C}_7\text{-OH}$ ), 4.32 (1H, d,  $J = 3.0$  Hz,  $\text{C}_7\text{-H}$ ), 2.24 (1H, d,  $J = 12.0$  Hz,  $\text{C}_9\text{-H}$ ), 1.39 (1H, m,  $\text{C}_{11}\text{-H}$ ), 1.89 (1H, m,  $\text{C}_{12}\text{-H}$ ), 4.26 (1H, s,  $\text{C}_{15}\text{-H}$ ), 5.51 (1H, s,  $\text{C}_{17}\text{-H}$ ), 4.42 (1H, d,  $J = 13.0$  Hz,  $\text{C}_{19}\text{-H}$ ), 4.74 (1H, dd,  $J = 13.0$  and 3.0 Hz,  $\text{C}_{19}\text{-H}$ ),

7.41 (1H, m, C<sub>21</sub>-H), 6.35 (1H, m, C<sub>22</sub>-H), 7.39 (1H, m, C<sub>23</sub>-H), 2.10, 2.08, 1.28 and 0.79 (4 x CH<sub>3</sub>); m/z : 468 (M<sup>+</sup>), 440, 425, 373, 345 (100%), 329.

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