# CAESALPININ B, A REARRANGED CASSANE FURANODITERPENE OF *CAESALPINIA BONDUC*

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**Abstract**-A new rearranged cassane furanoditerpene, caesalpinin B, was isolated from the roots of *Caesalpinia bonduc*, collected in Barbados, West Indies. The structure was established on the basis of spectroscopic data, including 2D NMR spectroscopy.

*Caesalpinia bonduc* (L.) Roxb. (Fabaceae) is widely distributed throughout the tropics and subtropics and has been used for the treatment of hypertension, malaria, dysentery and as an emetic.[1-3] This plant has been the subject of several phytochemical investigations wherein a number of cassane furanoditerpenes have been isolated.[3-15] In a previous chemical investigation of *C. bonduc*, we reported the isolation of a new rearranged cassane furanoditerpene, caesalpinin (**1**), this being the first report of a 19(4→3)-*abeo*-cassane diterpene.[15] We have further investigated root extracts of *C. bonduc* collected in Barbados, West Indies, and report here the isolation and characterisation of a new 5(4→3)-*abeo*-cassane furanoditerpene, caesalpinin B (**2**). The structure of **2** was established by 2D NMR spectroscopy using $^1$H-$^1$H COSY, HMQC and HMBC experiments.

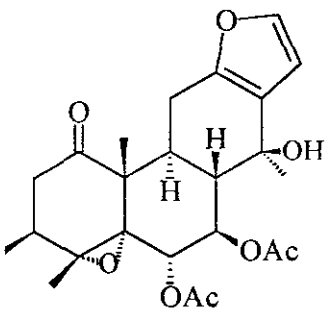
The ethanolic extract of the roots of *C. bonduc* was partitioned between methanol/water and hexane, followed by dichloromethane. The residue obtained on evaporation of the dichloromethane was separated by flash chromatography on silica gel followed by preparative TLC to give caesalpinin B.

Caesalpinin B (**2**), was isolated as a white solid, mp 163-165°C, $[\alpha]_D$ +7.2°. The molecular formula, $C_{24}H_{32}O_8$, was established by high resolution MS. The IR spectrum had absorptions due to hydroxyl (3428 cm$^{-1}$), ester (1735 cm$^{-1}$) and furan (757 cm$^{-1}$) functionalities, respectively. The $^1$H-NMR spectrum had resonances at δ 6.39 (1H, d, $J$ = 1.9 Hz, H-15) and δ 7.25 (1H, d, $J$ = 1.9 Hz, H-16) due to the presence of a 1,2-disubstituted furan moiety. This was supported by an ultraviolet absorption maximum at 216 nm. The $^1$H-NMR spectrum

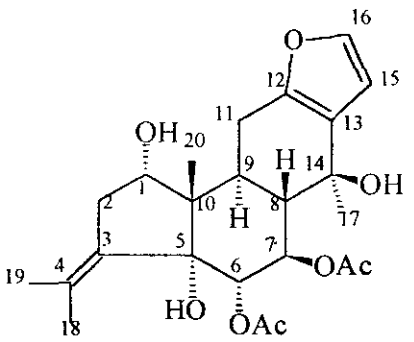
Table 1. $^{13}C$-, $^{1}H$- NMR and HMBC Spectral Data for Caesalpinin B (**2**)[a]

| position | $\delta_C$ | $\delta_H$ | HMBC |
|---|---|---|---|
| 1 | 70.9 | 3.89 (m) | |
| 2 | 39.1 | 2.53 (br d, 19.1) | |
| | | 2.20 (br d, 19.1) | C-1, C-3 |
| 3 | 127.7 | --- | |
| 4 | 127.7 | --- | |
| 5 | 76.6 | --- | |
| 6 | 76.0 | 5.38 (d, 8.3) | 6-$CH_3CO$, C-7 |
| 7 | 74.2 | 5.63 (dd, 10.2, 8.3) | |
| 8 | 48.1 | 2.30 (dd, 11.9, 10.2) | |
| 9 | 33.2 | 2.95 (ddd, 11.9, 11.2, 5.6) | |
| 10 | 43.3 | --- | |
| 11 | 23.2 | 2.80 (dd, 15.6, 5.6) | C-8, C-12, C-13 |
| | | 2.48 (dd, 15.6, 11.2) | C-9, C-12, C-13 |
| 12 | 148.4 | --- | |
| 13 | 125.6 | --- | |
| 14 | 72.9 | --- | |
| 15 | 107.5 | 6.39 (d, 1.9) | C-12, C-13, C-16 |
| 16 | 141.9 | 7.25 (d, 1.9) | |
| 17 | 24.8 | 1.56 (s) | C-8, C-13, C-14 |
| 18 | 20.5 | 1.68 (br s) | C-3, C-4 |
| 19 | 14.7 | 1.74 (br s) | C-3, C-4 |
| 20 | 15.8 | 1.04 (s) | C-1, C-5, C-9, C-10 |
| 1-OH | --- | 3.02 (d, 6.4) | |
| 5-OH | --- | 3.44 (br s) | |
| 6-OAc | 170.9 | --- | |
| | 21.8 | 2.10 (s) | 6-$CH_3CO$ |
| 7-OAc | 171.1 | --- | |
| | 21.7 | 1.99 (s) | 7-$CH_3CO$ |

[a]Multiplicity and coupling constants (in Hz) are in parenthesis.



1



2

also had resonances for two acetoxy methyls at δ 1.99 and δ 2.10, two olefinic methyls at δ 1.68 and δ 1.74 and two tertiary methyl singlets at δ 1.04 and δ 1.56. In addition, there were three oxymethine resonances at δ 3.89 (m), δ 5.38 (d, $J$ = 8.3 Hz, H-6) and δ 5.63 (dd, $J$ = 10.2, 8.3 Hz, H-7). The latter two oxymethines were associated with the acetoxy groups and were attached to C-6 (δ 76.0) and C-7 (δ 74.2) on the basis of $^1$H-$^1$H COSY, HMQC and HMBC experiments. The third oxymethine proton was assigned to C-1 since the C-20 methyl group at δ 1.04 showed HMBC correlations to the C-1 carbon at δ 70.9 as well as C-5 (δ 76.6), C-9 (δ 33.2) and C-10 (δ 43.3). On the other hand, the C-17 methyl group had HMBC correlations to C-8 (δ 48.1), C-13 (δ 125.6) and C-14 (δ 72.9). In the $^1$H-$^1$H COSY spectrum, H-1 had cross peaks with methylene protons at δ 2.53 and δ 2.20; these protons showed direct connectivity to C-2 (δ 39.1) in the HMQC spectrum. The methylene group at C-2 also had $^1$H-$^1$H COSY cross peaks with the C-18 and C-19 methyl protons at δ 1.68 and δ 1.74, respectively, while these methyl protons had cross peaks with each other, establishing their geminal disposition. Further, the C-18 protons showed HMBC correlations to C-3 and C-4, while the C-19 protons had HMBC correlations to C-3 and C-4. The NMR data, which are summarized in Table 1, led to structure (**2**) for caesalpinin B. The stereochemistry at C-1, C-6 and C-7 followed from their coupling constants. Caesalpinin B (**2**) represents only the second example of a cassane furanoditerpene with a rearranged skeleton.[15]

## EXPERIMENTAL

The IR spectrum was obtained on a Perkin-Elmer 1725X FT-IR spectrophotometer. The UV spectrum was recorded on a Hewlett-Packard 8452A spectrophotometer in MeOH solutions. The optical rotation was measured on a Perkin-Elmer 341 polarimeter in $CHCl_3$ solutions. All NMR spectra were obtained on a Varian Unity 500 MHz spectrometer in $CDCl_3$ solutions using TMS as an internal standard. MS spectra were recorded on a VG 70-25S mass spectrometer operating at 70 eV.

**Plant material** The roots of *C. bonduc* were collected in February, 1997 along the east coast road, St. Andrew, Barbados. The plant was identified by Dr. Sean Carrington, Department of Biological and Chemical Sciences, University of the West Indies, where a voucher specimen has been deposited.

**Extraction and Isolation** The dried, ground roots (500 g), were extracted with ethanol (2500 mL) for 24 h at 26°C and the solvent evaporated to give a dark brown solid (26 g). The solid was dissolved in 90% MeOH/$H_2O$ (100 mL) and extracted with hexane (300 mL). The aqueous MeOH layer was diluted with water (50 mL) and extracted with $CH_2Cl_2$ (300 mL) to yield a brown extract (9.4 g) on evaporation of the solvent. The $CH_2Cl_2$ extract was flash chomatographed on silica gel using hexane/acetone (4:1) as eluent followed by preparative TLC using the same solvent mixture, gave caesalpinin B (2.1 mg).

**Caesalpinin B (2)**: White solid, mp 218-220°; $[\alpha]_D$ +7.2° ($c$ = 0.11, $CHCl_3$); IR $\nu_{max}$ (film) 3428, 1735, 757 $cm^{-1}$; UV $\lambda_{max}$ (MeOH) nm (log $\epsilon$) 216 (3.76); EIMS *m/z* (rel. int.): 448 ($M^+$, 3 ), 335 (41), 313 (59), 187 (76), 149 (79), 123 (100), 109 (85); HRMS: [$M^+$] 448.2107 ($C_{24}H_{32}O_8$ requires 448.2097).

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