

**Caesalpinin, a Rearranged Cassane Furanoditerpene of *Caesalpinia bonducella*****Sonia R. Peter, Winston F. Tinto\***Laboratory of Bioorganic Chemistry, Department of Biological and Chemical Sciences,  
University of the West Indies, Cave Hill Campus, Barbados**Stewart McLean, William F. Reynolds,\* Li-Lin Tay**

Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 1A1, Canada

**Abstract:** A new rearranged cassane furanoditerpene, caesalpinin (**1**), was isolated from the roots of *Caesalpinia bonducella*. The structure and relative stereochemistry was determined by 2D NMR spectroscopy. This represents the first report of a rearranged cassane diterpene.

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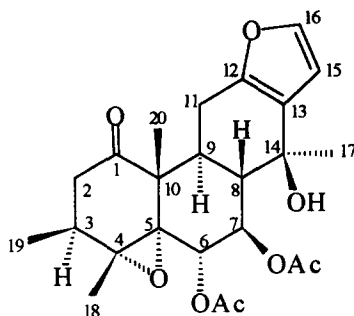
*Caesalpinia bonducella* Flem. (Caesalpinaceae) is widely distributed throughout the tropical and subtropical regions and is used in different systems of traditional medicine for the treatment of a variety of diseases, including hypertension and malaria.<sup>1-3</sup> The seeds of the plant have been the subject of several chemical investigations, in which a number of cassane furanoditerpenes have been isolated.<sup>1,3-12</sup> We have investigated the roots of *C. bonducella* collected in Barbados, and report here, the isolation and structure elucidation of a new rearranged cassane furanoditerpene, designated caesalpinin (**1**). The complete proton and carbon assignments as well as the relative stereochemistry of **1** were determined by 2D NMR spectroscopy, using the COSY, HMQC, HMBC and NOESY experiments.

Caesalpinin **1**,<sup>13</sup> was isolated as white crystals, mp 108-109°C, and had the molecular formula, C<sub>24</sub>H<sub>30</sub>O<sub>8</sub>. The IR spectrum exhibited absorptions due to hydroxy (3595 cm<sup>-1</sup>), ester (1741 cm<sup>-1</sup>) and ketone (1710 cm<sup>-1</sup>) functionalities. The <sup>1</sup>H NMR spectrum of **1** had signals due to three tertiary methyls at δ 1.53 (6H) and δ 1.50 and a secondary methyl at δ 1.10 (d, *J* = 7.0 Hz), while two acetate methyl groups had signals at δ 2.02 and δ 2.05. Two oxymethine protons had resonances at δ 5.72 (d, *J* = 8.5 Hz) and δ 5.54 (t, *J* = 8.5 Hz) and were assigned to H-6 and H-7, respectively, on the basis of a COSY experiment. In the low field region of the spectrum, the two protons of a 1,2-disubstituted furan had resonances at δ 7.23 (d, *J* = 2.4 Hz, H-α) and δ 6.37 (d, *J* = 2.4 Hz, H-β).

**Table 1.** NMR Characteristics of Caesalpinin (1) in CDCl<sub>3</sub>.<sup>a</sup>

Position	$\delta_C$	$\delta_H$ ( $J_{HH'}/\text{Hz}$ )	HMBC	NOESY
1	208.46	----		
2 $\alpha$	40.94	2.04 (d, 12.5)	C-1, C-4	H-2 $\beta$ , H-18, H-19
2 $\beta$		2.72 (dd, 12.5, 8.5)	C-3, C-19	H-2 $\alpha$ , H-3, H-20
3	35.92	2.34 (dq, 8.0, 6.8)	C-1, C-19	H-2 $\beta$ , H-18, H-20
4	66.32	----		
5	71.00	----		
6	68.62	5.72 (d, 9.6)	C-1', C-7	H-7, H-8, H-20
7	71.70	5.54 (dd, 10.4, 9.6)	C-1'', C-6, C-8, C-14	H-6, H-9, H-17
8	48.84	2.28 (dd, 12.0, 10.4)	C-7, C-9, C-14, C-17	H-20
9	36.12	2.47 (ddd, 12.0, 10.6, 4.0)	C-10, C-12, C-13, C-14, C-20	H-8, H-17
10	50.33	----		
11 $\alpha$	24.78	2.89 (dd, 14.6, 4.0)	C-8, C-12, C-13	H-11 $\beta$
11 $\beta$		2.45 (dd, 14.6, 10.6)	C-9, C-10, C-12, C-13	H-11 $\alpha$ , H-20
12	148.19	----		
13	124.46	----		
14	72.54	----		
15	107.15	6.37 (d, 2.2)	C-12, C-13, C-16	H-16, H-17
16	141.81	7.23 (d, 2.2)	C-12, C-13, C-15	H-15
17	24.88	1.53 (s)	C-8, C-13, C-14	H-7, H-9, H-15
18	18.24	1.50 (s)	C-4, C-5	H-2 $\alpha$ , H-3, H-19, H-20
19	16.61	1.10 (d, 6.8)	C-2, C-3, C-4	H-2 $\alpha/\beta$ , H-3, H-18
20	18.24	1.53 (s)	C-1, C-5, C-9, C-10	H-6, H-9, H-11
1'	170.27	----		
2'	21.28	2.02 (s)	C-1'	H-18, H-19
1''	169.81	----		
2''	21.14	2.05 (s)	C-1''	

<sup>a</sup>Chemical shifts were measured at 125 MHz for <sup>13</sup>C and 500 MHz for <sup>1</sup>H with TMS as internal standard.



(1)

The  $^{13}\text{C}$  NMR spectrum of **1** displayed resonances for all twenty-four carbon atoms. In particular, there were signals due to five carbons bearing oxygen at  $\delta$  72.54 (s),  $\delta$  71.70 (d),  $\delta$  71.00 (s),  $\delta$  68.62 (d) and  $\delta$  66.32 (s). An HMQC experiment<sup>14</sup> revealed that the carbons with resonances at  $\delta$  68.62 and  $\delta$  71.70 were directly attached to the oxymethine protons at  $\delta$  5.72 (H-6) and  $\delta$  5.54 (H-7), respectively. In the HMBC experiment,<sup>15</sup> H-6 showed long range correlations to an acetate carbonyl at  $\delta$  170.27 and to C-7, while H-7 showed long range correlations to the other acetate carbonyl at  $\delta$  169.81 as well as to C-6, C-8 and C-14. On the other hand, H<sub>3</sub>-18 showed long range correlations to the C-4 and C-5 epoxide carbons, while H<sub>3</sub>-19 showed correlations to C-2, C-3 and C-4. The COSY spectrum also revealed the spin system involving the C-19 methyl group and the C-2 and C-3 protons. The ketone was located at C-1 since H-2 $\alpha$ , H-3 and H<sub>3</sub>-20 all showed long range correlations to the ketone resonance at  $\delta$  208.46.

The stereochemistry of **1** was determined from a detailed analysis of a NOESY experiment (Table 1). In the NOESY spectrum, H-6 had cross-peaks with H-8 and H-20 showing that they were all on the same side and that they were  $\beta$ -oriented, while H-7 had cross-peaks with H-9 and H<sub>3</sub>-17 indicating that they were  $\alpha$ -oriented. Similarly, H<sub>3</sub>-18 had cross-peaks with H<sub>3</sub>-19 and H<sub>3</sub>-20. Polycyclic terpenoids in which one of the C-4 methyl groups has migrated to C-5 is quite common,<sup>16</sup> however, migration of a C-4 methyl to C-3 is quite rare. Caesalpinin **1** is the first example of a cassane diterpene in which one of the C-4 methyl groups has migrated.

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## REFERENCES AND NOTES

1. Carrington, S. *Wild Plants of Barbados*; Macmillan Press: London and Basingstoke (1993); p 37.
2. Adams, C. D. *Flowering Plants of Jamaica*; The University Press: Glasgow (1972); p 320.
3. Pascoe, K. O. Diterpenes from Jamaican Caesalpiniaceae and Euphorbiaceae. Ph.D. Thesis, University of the West Indies, Mona, Jamaica, 1980, pp 9-10.
4. Ali, M. E.; Khuda, M. Q. *Chem. Ind. (London)* **1960**, 463.
5. Khuda, M. Q.; Ali, M. E. *Pakistan J. Sci. Ind. Research* **1963**, 65.
6. Canonica, L.; Jommi, G.; Manitto, P.; Pagoni, U. M.; Pelizzoni, F. *Gazz. Chim. Ital.*, **1966**, 662.
7. Canonica, L.; Jommi, G.; Manitto, P.; Pagoni, U. M.; Pelizzoni, F. *Gazz. Chim. Ital.*, **1966**, 687.
8. Canonica, L.; Jommi, G.; Manitto, P.; Pagoni, U. M.; Pelizzoni, F. *Gazz. Chim. Ital.*, **1966**, 698.
9. Balmain, A.; Connolly, J. D.; Ferrari, M.; Ghisalberti, E. L.; Pagoni, U. M.; Pelizzoni, F. *Chem. Commun.*, **1970**, 1244.
10. Connolly, J. D.; Orsini, F.; Pelizzoni, F.; Ricca, G. *Magn. Reson. Chem.*, **1981**, 17, 163.
11. Balmain, A.; Bjåmer, K.; Connolly, J. D.; Ferguson, G. *Tetrahedron Lett.*, **1967**, 5027.
12. Pascoe, K. O.; Burke, B. A.; Chan, W. R. *J. Nat. Prod.*, **1986**, 49, 913.
13. Other physical data for caesalpinin (1).-  $[\alpha]_D^{+29.5^\circ}$  (c 1.23, CHCl<sub>3</sub>); IR  $\nu_{\max}$  (CHCl<sub>3</sub>) 3595, 1741, 1710 cm<sup>-1</sup>; UV  $\lambda_{\max}$  (MeOH) 214 nm (log  $\epsilon$  3.64); EIMS  $m/z$  [M]<sup>+</sup> 446 (17), 431 (13), 404 (7), 386 (10), 371 (99), 329 (46), 308 (49), 265 (43), 203 (35), 183 (65), 141 (66), 109 (100); HREIMS 446.1934 calcd for C<sub>24</sub>H<sub>30</sub>O<sub>8</sub> 446.1941.
14. Bax, A.; Subramanian, S. *Magn. Reson. Chem.*, **1986**, 67, 565.
15. Bax, A.; Summers, M. F. *J. Am. Chem. Soc.*, **1986**, 108, 2093.
16. Connolly, J. D.; Hill, R. A. *Dictionary of the Terpenoids*; Chapman and Hall: London (1991); Vol. 1.

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