

CAESALPIN F: A NEW FURANODITERPENE FROM *CAESALPINIA BONDUCELLA*

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Seed kernels of grey and yellow nicker, *Caesalpinia bonducella* L. (Caesalpiniaaceae), are used extensively in Jamaican folk medicine. Chemical examination of the defatted kernel has led to the isolation of a group of furanoditerpenes— α -, β -, δ -, and ϵ -caesalpins. The structures of these have been established (1,2), and the absolute configuration of ϵ -caesalpin has been determined by X-ray studies on a suitable derivative (1). A tentative structure has been put forward for a related compound, χ -caesalpin, isolated from the bark of *Caesalpinia pulcherrima* Swartz (3). In this communication we describe the isolation and characterization of a new furanoditerpene, caesalpin F (2), from the seeds of *C. bonducella*.

RESULTS AND DISCUSSION

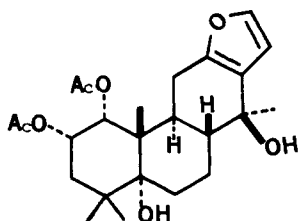
Extraction of the seeds of grey nicker by the published method (4,5) gave caesalpin F, $C_{26}H_{36}O_9$, mp 236.5–237.5°, as the only crystalline compound. We propose the structure 2 for caesalpin F on the basis of the following evidence.

The ir spectrum had hydroxy and ace-

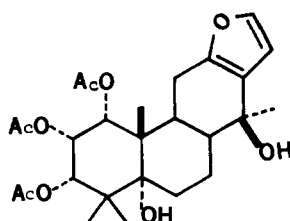
tate absorptions at 3400 and 1730 cm^{-1} , respectively. In the 1H -nmr spectrum, there were absorptions for a 2,3-disubstituted furan ring (δ 7.20 and 6.37, both doublets, $J=2$ Hz), three acetates [2.10 (two) and 1.97], and four tertiary C-methyls [1.33, 1.25 (two), and 1.13]. There were three hydrogens at the base of the acetates (5.48, t, $J=4$ Hz; 5.21, d, $J=4$ Hz; 5.15, d, $J=4$ Hz) and a signal at 3.33 (2H) which disappeared on shaking with D_2O .

On attempted sublimation, caesalpin F gave the olefin (3), λ max (EtOH) 238 nm (3.91) in which one tertiary methyl had disappeared (1H nmr) and two olefin singlets ($C=CH_2$) were present. The presence of the conjugated vinylfuran confirmed the relationship between the 2,3-disubstituted furan and the CH_3-C-OH group.

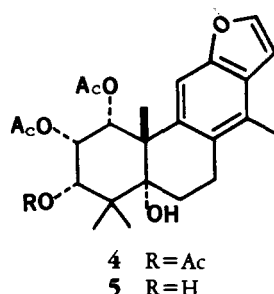
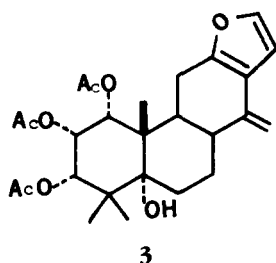
Treatment of caesalpin F with H_2SO_4 in dioxane at room temperature led to the formation of the benzofuran triacetate (4). In the 1H -nmr spectrum of 4 the signal (δ 6.01) for the C-1 proton at the base of acetate is shifted (0.86 ppm) downfield relative to its position in caesalpin F. A similar downfield shift



1



2



has been observed in ϵ -caesalpin (**1**) on the introduction of the aromatic ring (1). This suggests that the A/B ring fusion and the configuration of the C-1 acetate are identical in the two compounds. Further, in a *cis*-A/B-fused system, it would be expected that one of the C-4 methyls would experience a diamagnetic shift as it moved into the shielding zone of the aromatic ring (6,7). This was not observed.

Base hydrolysis of the triacetate **4** followed by acetylation with Ac_2O /pyridine under standard conditions gave the diacetate **5**. The location and configuration of the acetate groups in caesalpin F follow from the coupling constants of the protons on carbons bearing the acetates.

Inspection of Table 1 shows that in all the compounds mentioned these protons are mutually coupled with a coupling constant indicating that they are all *cis* to one another. In addition, decoupling experiments on the diacetate **5** showed that the triplet at δ 5.67 was mutually coupled to the doublet at δ 3.67 and the low field doublet at δ 6.03. This con-

firmed the relationship of the acetates and the hydroxy to be that found in **5**. The absolute configuration written into **2** is based on a presumed relationship with ϵ -caesalpin.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps are uncorrected. Uv and ir spectra were recorded on a Unicam model SP 800 and a Perkin-Elmer model 21 spectrophotometer, respectively. ^1H -nmr spectra were obtained on a JEOL JNM-PMX 60 MHz instrument and are for CDCl_3 solutions. Silica gel for tlc was Merck PF₂₅₄₊₃₆₆.

PLANT MATERIAL.—Seeds were collected from plants in the parish of St. Thomas in eastern Jamaica. A voucher specimen (No. 9712) is deposited in the herbarium at University of the West Indies, Mona.

EXTRACTION AND ISOLATION OF CAESALPIN F (2).—The milled seed kernel (1 kg) was defatted by percolation with petrol (5 liters) and, after drying, was further percolated with CHCl_3 (3 liters). Removal of the solvent gave a brown gum (21.5 g) that was dissolved in Et_2O (60 ml) and set aside overnight at 4° . A solid (200 mg) settled from which caesalpin F was obtained by plc (EtOAc -petroleum ether; 1:1). Recrystallization from EtOAc gave **2**, mp 236.5 - 237.5° ; uv λ max (EtOH) 233 nm (3.20); ir ν max (CHCl_3) 3400,

TABLE 1. Chemical Shifts (ppm) of H-1, H-2, and H-3 of Caesalpin F and Its Derivatives

Compound	H-1	H-2	H-3
Caesalpin F (2)	5.15, d $J=4$ Hz	5.48, t $J=4$ Hz	5.21, d $J=4$ Hz
Olefin (3)	5.15, d $J=3.5$ Hz	5.50, t $J=3.5$ Hz	5.23, d $J=3.5$ Hz
Benzofuran triacetate (4)	6.01, d $J=3.5$ Hz	5.70, t $J=3.5$ Hz	5.23, d $J=3.5$ Hz
Benzofuran diacetate (5)	6.03, d $J=3.5$ Hz	5.67, t $J=3.5$ Hz	3.67, d $J=3.5$ Hz

1730 cm^{-1} ; ^1H nmr δ 1.13 (s, 3H, CMe), 1.25 (s, 6H, 2×CMe), 1.33 (s, 3H, CMe), 1.97 (s, 3H, OAc), 2.10 (s, 6H, 2×OAc), 3.33 (s, 2H, 2×OH), 5.15 (d, 1H, $J=4$ Hz, CHOAc), 5.21 (d, 1H, $J=4$ Hz, CHOAc), 5.48 (t, 1H, $J=4$ Hz, CHOAc), 6.37 and 7.20 (each d, 1H, $J=2$ Hz, furan) (Found: C, 63.6; H, 7.5, $\text{C}_{26}\text{H}_{36}\text{O}_9$ requires C, 63.4; H, 7.4%).

PYROLYSIS OF 2.—Sublimation of caesalpin F from a block preheated to 240° gave as sublimate the olefin **3**, mp 234° (d); uv λ max (EtOH) 238 nm (3.91); ir ν max (CHCl_3) 3440, 1735 cm^{-1} ; ^1H nmr δ 1.14 (s, 3H, CMe), 1.28 (s, 6H, 2×CMe), 1.97 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.12 (s, 3H, OAc), 3.32 (bs, 1H, OH), 4.90 and 5.10 (each s, 1H, C=CH₂), 5.15 (d, 1H, $J=3.5$ Hz, CHOAc), 5.23 (d, 1H, $J=3.5$ Hz, CHOAc), 5.50 (t, 1H, $J=3.5$ Hz, CHOAc), 6.39 and 7.17 (each d, 1H, $J=2$ Hz, furan) (Found: C, 65.4; H, 7.5; O, 26.8, $\text{C}_{26}\text{H}_{34}\text{O}_8$ requires C, 65.8; H, 7.6; O, 26.8%).

BENZOFURAN TRIACETATE (4).—A dioxane solution of caesalpin F was treated with H_2SO_4 . After 4 h, caesalpin F was converted quantitatively to the benzofuran triacetate (**4**), which was recrystallized from MeOH as needles, mp 256–257°; uv λ max (EtOH) 251, 282, 292 nm (4.06, 3.40, and 3.43); ir ν max (CHCl_3) 3450, 1750, 1610, 1430 cm^{-1} ; ^1H nmr δ 1.23 (s, 3H, CMe), 1.30 (s, 3H, CMe), 1.50 (s, 3H, CMe), 1.92 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.37 (s, 3H, ArMe), 3.42 (s, 1H, OH), 5.23 (d, 1H, $J=3.5$ Hz, CHOAc), 5.70 (t, 1H, $J=3.5$ Hz, CHOAc), 6.01 (d, 1H, $J=3.5$ Hz, CHOAc), 6.67 and 7.43 (each d, 1H, $J=2$ Hz, furan), 7.00 (s, 1H, ArH) (Found: C, 65.8, H, 6.8; O, 27.4, $\text{C}_{26}\text{H}_{32}\text{O}_8$ requires C, 66.1, H, 6.8; O, 27.1%).

BENZOFURAN DIACETATE (5).—Hydrolysis of the benzofuran triacetate (**4**) ($\text{K}_2\text{CO}_3/\text{MeOH}$, 24 h) followed by acetylation of the product ($\text{Ac}_2\text{O}/\text{pyridine}$, 24 h) gave the diacetate **5**, which was purified by plc as an amorphous solid; uv λ max (EtOH) 252, 282, 293 nm (3.96, 3.38, and 3.36); ir ν max (CHCl_3) 3540, 1745, 1590, 1430 cm^{-1} ; ^1H nmr δ 1.23 (s, 3H, CMe), 1.40 (s, 3H, CMe), 1.52 (s, 3H, CMe), 1.92 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.40 (s, 3H, ArMe), 3.60 (s, 1H, OH), 3.67 (d, 1H, $J=3.5$ Hz, CHOAc), 5.67 (t, 1H, $J=3.5$ Hz, CHOAc), 6.03 (d, 1H, $J=3.5$ Hz, CHOAc), 6.70 and 7.41 (each d, 1H, $J=2$ Hz, furan), 7.03 (s, 1H, ArH); high resolution molecular weight determination. Found: 430.1976. $\text{C}_{24}\text{H}_{30}\text{O}_7$.

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