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The X-Ray Analysis of Caesalpin J from Sappan Lignum

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The chemical structure of caesalpin J (**1**) isolated from Sappan Lignum, the dried heartwood of *Caesalpinia sappan* L., was established by an X-ray crystallographic study of its triacetate.

Keywords——Sappan Lignum; *Caesalpinia sappan*; Leguminosae; caesalpin J; brazilin; X-ray analysis; oxidative coupling

Sappan Lignum, the dried heartwood of *Caesalpinia sappan* L. (Leguminosae), has long been used as an oriental crude drug,[1] for example, as an anti-inflammatory agent. In the course of a systematic screening for antihypercholesteremic activity, the methanolic extractive of this plant was shown to have a significant effect.[2] From this extractive, we obtained seventeen aromatic compounds together with brazilin[3] and sappanchalcone,[4] and we reported the chemical characterization of nine compounds, **1**—**6**,[5] **7**, **8**,[6] and caesalpin P (**10**),[7] among them. Furthermore, we reported the plane structure of one additional compound, named caesalpin J (**1**),[7] on the basis of its infrared (IR), proton (^{1}H) and carbon-13 (^{13}C)nuclear magnetic resonance (NMR) spectra. Caesalpin J (**1**) was of interest because it is a novel substance having a new framework, probably biosynthetically derived from a 3-benzyl-

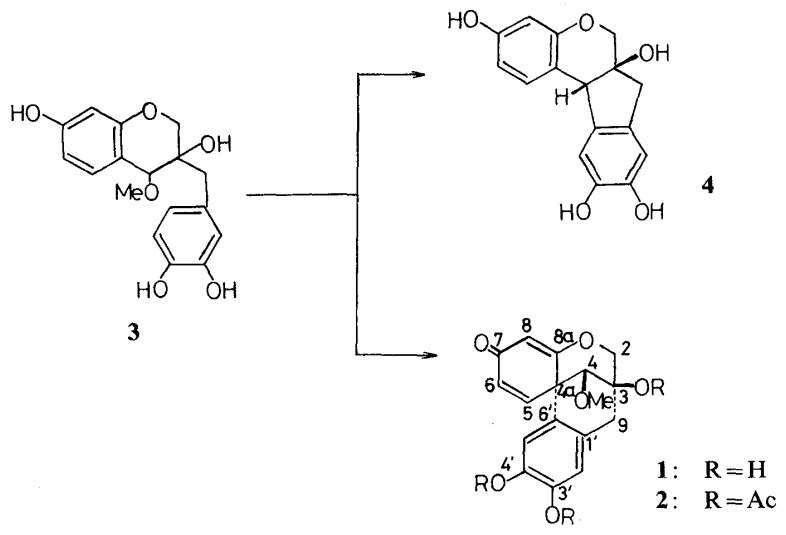

Chart 1

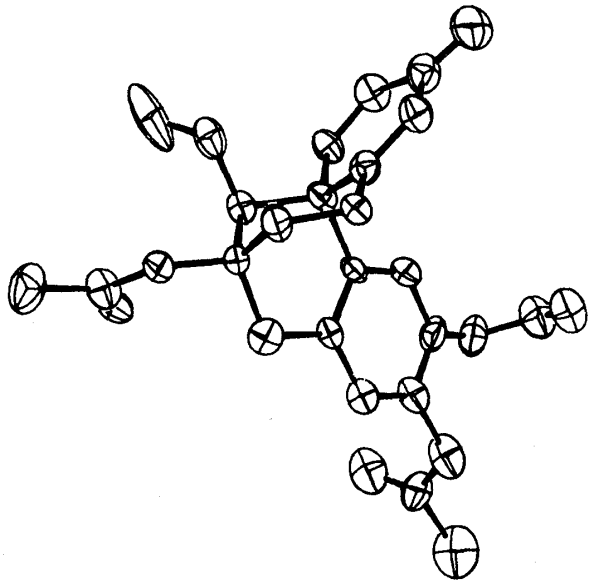

Fig. 1. The Molecular Structure of Caesalpin J Triacetate (**2**)

TABLE I. Atomic Positional Parameters ($\times 10^4$) of Caesalpin J Triacetate (**2**) and Equivalent Isotropic Parameters with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}
O(2)	1480 (3)	7692 (6)	1410 (4)	3.02 (12)
O(3)	−816 (3)	7158 (7)	2258 (4)	3.15 (13)
O(4)	−297 (3)	10607 (7)	1633 (4)	3.51 (14)
O(7)	2988 (4)	12985 (8)	747 (5)	5.77 (20)
O(3′)	4141 (3)	6580 (8)	7279 (4)	4.19 (15)
O(4′)	4526 (3)	10047 (8)	6717 (4)	4.52 (16)
AcO(3)	−1055 (3)	8274 (7)	4120 (4)	3.89 (15)
AcO(3′)	3451 (4)	7725 (9)	8758 (5)	5.64 (18)
AcO(4′)	5460 (4)	9314 (12)	5459 (7)	8.25 (27)
C(2)	453 (5)	7182 (11)	1308 (6)	3.48 (21)
C(3)	233 (4)	7745 (10)	2596 (6)	2.47 (17)
C(4)	344 (4)	9746 (10)	2760 (6)	2.49 (17)
C(4a)	1448 (5)	10193 (9)	2865 (6)	2.53 (18)
C(5)	1594 (5)	12141 (9)	2972 (6)	2.91 (19)
C(6)	2063 (5)	13045 (10)	2261 (7)	3.56 (22)
C(7)	2464 (5)	12163 (11)	1273 (6)	3.57 (21)
C(8)	2217 (5)	10293 (11)	1000 (6)	3.54 (21)
C(8a)	1706 (4)	9448 (10)	1674 (6)	2.61 (18)
C(9)	864 (5)	6781 (10)	3842 (6)	3.01 (19)
C(1′)	1879 (4)	7616 (9)	4496 (6)	2.28 (17)
C(2′)	2552 (5)	6749 (10)	5562 (6)	2.99 (19)
C(3′)	3447 (5)	7508 (10)	6240 (6)	3.05 (19)
C(4′)	3689 (5)	9155 (11)	5884 (6)	3.44 (21)
C(5′)	3060 (5)	10000 (10)	4795 (6)	2.90 (19)
C(6′)	2150 (4)	9260 (9)	4107 (6)	2.42 (18)
Me(4)	−1035 (7)	11722 (16)	1836 (9)	7.74 (39)
AcC(3)(1)	−1376 (5)	7557 (11)	3077 (6)	3.30 (20)
AcC(3)(2)	−2418 (5)	6863 (14)	2457 (7)	5.11 (27)
AcC(3′)(1)	4061 (5)	6775 (11)	8535 (7)	3.87 (22)
AcC(3′)(2)	4828 (7)	5658 (15)	9484 (8)	6.32 (31)
AcC(4′)(1)	5333 (6)	10153 (14)	6319 (7)	4.93 (26)
AcC(4′)(2)	6042 (6)	11537 (13)	7133 (8)	5.08 (27)

4-methoxychroman compound (**3**).[5] Now, we have verified the correctness of the proposed structure and determined the stereo-configurations at C-3 and -4 by X-ray crystallographic analysis. A crystal suitable for X-ray analysis was obtained from the triacetyl derivative (**2**).

TABLE II. Bond Lengths (Å) of Caesalpin J Triacetate (**2**) with Estimated Standard Deviations in Parentheses

O(2)–C(2)	1.465 (10)	C(4a)–C(5)	1.493 (10)
O(2)–C(8a)	1.379 (9)	C(4a)–C(8a)	1.522 (10)
O(3)–C(3)	1.472 (9)	C(4a)–C(6′)	1.546 (10)
O(3)–AcC(3)(1)	1.371 (9)	C(5)–C(6)	1.332 (10)
O(4)–C(4)	1.411 (9)	C(6)–C(7)	1.489 (11)
O(4)–Me(4)	1.404 (13)	C(7)–C(8)	1.469 (12)
O(7)–C(7)	1.222 (10)	C(8)–C(8a)	1.321 (11)
O(3′)–C(3′)	1.409 (10)	C(1′)–C(2′)	1.390 (10)
O(3′)–AcC(3′)(1)	1.373 (10)	C(1′)–C(6′)	1.403 (10)
O(4′)–C(4′)	1.404 (10)	C(1′)–C(9)	1.516 (10)
O(4′)–AcC(4′)(1)	1.328 (12)	C(2′)–C(3′)	1.366 (11)
AcO(3)–AcC(3)(1)	1.185 (10)	C(3′)–C(4′)	1.378 (11)
AcO(3′)–AcC(3′)(1)	1.196 (11)	C(4′)–C(5′)	1.373 (11)
AcO(4′)–AcC(4′)(1)	1.166 (14)	C(5′)–C(6′)	1.378 (10)
C(2)–C(3)	1.545 (11)	AcC(3)(1)–AcC(3)(2)	1.500 (13)
C(3)–C(4)	1.531 (10)	AcC(3′)(1)–AcC(3′)(2)	1.488 (14)
C(3)–C(9)	1.526 (10)	AcC(4′)(1)–AcC(4′)(2)	1.518 (14)
C(5)–C(4a)	1.556 (10)		

TABLE III. Bond Angles (deg.) of Caesalpin J Triacetate (**2**) with Estimated Standard Deviations in Parentheses

C(2)–O(2)–C(8a)	115.5 (6)	O(2)–C(8a)–C(4a)	115.3 (6)
C(3)–O(3)–AcC(3)(1)	120.4 (6)	O(2)–C(8a)–C(8)	119.3 (7)
C(4)–O(4)–Me(4)	117.3 (7)	C(4a)–C(8a)–C(8)	124.9 (7)
C(3′)–O(3′)–AcC(3′)(1)	117.0 (6)	C(2′)–C(1′)–C(6′)	118.7 (7)
C(4′)–O(4′)–AcC(4′)(1)	117.5 (7)	C(2′)–C(1′)–C(9)	118.6 (6)
O(2)–C(2)–C(3)	108.8 (6)	C(6′)–C(1′)–C(9)	122.7 (6)
O(3)–C(3)–C(2)	99.2 (6)	C(1′)–C(2′)–C(3′)	120.6 (7)
O(3)–C(3)–C(4)	112.8 (6)	O(3′)–C(3′)–C(2′)	119.9 (7)
O(3)–C(3)–C(9)	109.5 (6)	O(3′)–C(3′)–C(4′)	119.8 (7)
C(2)–C(3)–C(4)	109.5 (6)	C(2′)–C(3′)–C(4′)	120.3 (7)
C(2)–C(3)–C(9)	113.9 (6)	O(4′)–C(4′)–C(3′)	119.7 (7)
C(4)–C(3)–C(9)	111.5 (6)	O(4′)–C(4′)–C(5′)	119.7 (7)
O(4)–C(4)–C(3)	110.4 (6)	C(3′)–C(4′)–C(5′)	120.2 (8)
O(4)–C(4)–C(4a)	108.7 (6)	C(4′)–C(5′)–C(6′)	120.1 (7)
C(3)–C(4)–C(4a)	106.8 (6)	C(4a)–C(6′)–C(1′)	119.8 (6)
C(4)–C(4a)–C(5)	109.4 (6)	C(4a)–C(6′)–C(5′)	120.2 (6)
C(4)–C(4a)–C(8a)	110.3 (6)	C(1′)–C(6′)–C(5′)	120.0 (7)
C(4)–C(4a)–C(6′)	108.7 (6)	C(3)–C(9)–C(1′)	113.9 (6)
C(5)–C(4a)–C(8a)	111.6 (6)	O(3)–AcC(3)(1)–AcO(3)	124.0 (7)
C(5)–C(4a)–C(6′)	110.7 (6)	O(3)–AcC(3)(1)–AcC(3)(2)	108.6 (7)
C(8a)–C(4a)–C(6′)	106.1 (6)	AcO(3)–AcC(3)(1)–AcC(3)(2)	127.3 (8)
C(4a)–C(5)–C(6)	123.3 (7)	O(3′)–AcC(3′)(1)–AcO(3′)	122.1 (8)
C(5)–C(6)–C(7)	121.5 (7)	O(3′)–AcC(3′)(1)–AcC(3′)(2)	109.3 (8)
O(7)–C(7)–C(6)	120.0 (7)	AcO(3′)–AcC(3′)(1)–AcC(3′)(2)	128.6 (9)
O(7)–C(7)–C(8)	123.0 (8)	O(4′)–AcC(4′)(1)–AcO(4′)	124.3 (10)
C(6)–C(7)–C(8)	117.1 (7)	O(4′)–AcC(4′)(1)–AcC(4′)(2)	109.7 (8)
C(7)–C(8)–C(8a)	119.9 (8)	AcO(4′)–AcC(4′)(1)–AcC(4′)(2)	126.0 (10)

The crystal data were as follows: $C_{23}H_{22}O_9$, $M_r=442.43$, size $0.2\times0.2\times0.3$ mm, monoclinic; space group $P2_1$, $Z=2$, cell dimensions $a=14.034$ (2), $b=7.592$ (1), $c=10.555$ (3) Å, $\beta=108.1$ (1)°, $V=1069.5$ (6) Å^3. In total, 1275 unique reflections were collected by the 2θ–ω scan method within $2\theta<120°$ on a Rigaku AFC-5 FOS four-circle diffractometer using graphite-monochromated Cu-K_α ($\lambda=1.5418$ Å) radiation. Twenty-eight atomic positions were revealed by the direct method (MULTAN)[8] and several cycles of isotropic least-squares refinement and subsequent Fourier synthesis gave those of the remaining non-hydrogen atoms. The structure was refined by the block-diagonal least-squares method (UNICS III)[9] to an R-value of 0.041 for the total reflections. An ORTEP[10] drawing of **2** (less hydrogen atoms) is shown in Fig. 1. This crystallographic analysis of **2** has proved the proposed structure for **1** to be correct, though the absolute configuration could not be determined. It should be noted that the molecule of **1** takes a spiroform at C-4a. In the preceding paper,[5] we reported the isolation of the 3-benzyl-4-methoxychroman derivative (**3**), which is considered an important intermediate on the biogenetic route to brazilin (**4**). Caesalpin J (**1**) may also be derived from compound **3** by oxidative coupling.

Experimental[11]

Caesalpin J Triacetate (2)——A solution of caesalpin J (**1**), 30 mg, in pyridine (1 ml) and Ac_2O (1 ml) was heated on a hot bath for 4 h. Usual work-up afforded the product, which was purified on a silica gel column with *n*-hexane–acetone=2:1 to give the acetate (**2**) (28 mg). Colorless prisms, mp 216—218 °C. MS (*m/z*): 442 (M^+), 400 (M^+-CH_2CO), 382, 358, 340, 316, 298, 129. ^{1}H-NMR ($CDCl_3$) δ: 2.10 (3H, s, aliph. OAc), 2.24 (6H, s, 2×phen. OAc), 3.54 (3H, s, OMe), 3.78 (2H, br s, 9-H_2), 4.30 (1H, s, 4-H), 4.28, 4.69 (each 1H, ABq, $J=11$ Hz, 2-H_2), 5.77 (1H, d, $J=2$ Hz, 8-H), 6.53 (1H, dd, $J=10$, 2 Hz, 6-H), 6.78 (1H, d, $J=10$ Hz, 5-H), 6.82, 7.02 (each 1H, s, 2′,5′-H).

Bond Lengths and Bond Angles Obtained from the Crystallograpic Analysis of Caesalpin J Triacetate (2)—— Tables II and III.

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