thoxatin do not differ significantly.

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Registry No. **1**, 27318-90-7; **1** (acetone adduct), 85554-17-2; **1**OH$^-$, 85554-21-8; **2**, 82701-91-5; **2** (acetone adduct), 85554-15-0; **2**OH$^-$, 85554-16-1; **3**, 84-12-8; **3** (acetone adduct), 85554-18-3; **3**OH$^-$, 85554-22-9; **5**, 85554-20-7; 5-amino-6-hydroxy-4,7-phenanthroline hydrochloride, 85554-19-4; 1,10-phenanthroline-5,6-diol hydrochloride, 85565-50-0; 1,7-phenanthroline-5,6-diol hydrochloride, 85565-51-1; 4,7-phenanthroline-5,6-diol hydrochloride, 85565-52-2; acetone, 67-64-1; 1-(4-methylphenyl)ethanol, 536-50-5; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 84-58-2; 1-(4-nitrophenyl)ethanol, 6531-13-1; cyclohexylamine, 108-91-8; glycine, 56-40-6; morpholine, 110-91-8; *N*,*N*-dimethylbenzylamine, 103-83-3; hydrazine, 302-01-2.

Structure of Caesalpinine A: A Novel Spermidine Alkaloid from *Caesalpinia digyna* Rottl.

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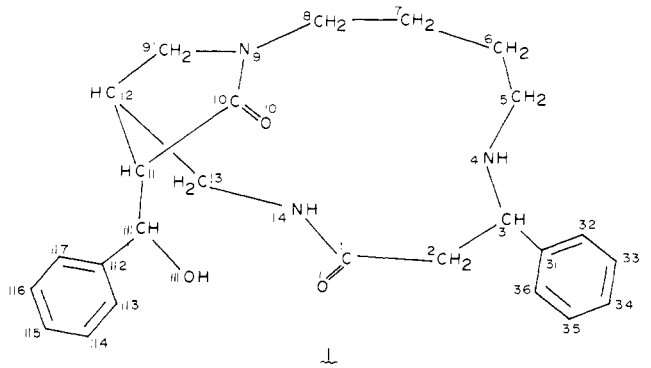
Abstract: The structure and stereochemistry of caesalpinine A (**1**), a novel macrocyclic spermidine alkaloid isolated from *Caesalpinia digyna* Rottl., have been determined by means of single-crystal X-ray analysis. The high-resolution mass and NMR spectra could satisfactorily be interpreted on the basis of the X-ray structure. The compound, $C_{25}H_{31}N_3O_3$, is orthorhombic, with space group $P2_12_12_1$ and unit-cell dimensions a = 24.017 (6) Å, b = 19.346 (2) Å, c = 9.578 (2) Å, V = 4450.3 Å^3, and Z = 8. The crystal structure was solved by direct methods and refined by least-squares methods including anisotropic (for non-hydrogen atoms) and isotropic (for hydrogen atoms) thermal parameters to a final R value of 4.5%. Caesalpinine A possesses a 13-membered lactam ring fused to a five-membered lactam ring. It also contains two monosubstituted benzene rings.

Caesalpinia digyna Rottl. (Leguminosae) is a prickly scandent shrub growing in eastern India, Burma, and Ceylon. It has the reputation for use in phthisis, scrofula, and diabetes.[2] Previous chemical investigations of the plant had disclosed the presence of bergenin[3,4] and gallic acid.[5] The present paper is concerned with the isolation and structure elucidation of caesalpinine A (**1**), a novel spermidine alkaloid having a new skeleton.

Results and Discussion

Caesalpinine A (**1**; mp 240–242 °C, $[\alpha]_D$ +16.6° ($CHCl_3$))



was isolated from the chloroform extract of the leaves of the plant by acid extraction followed by column chromatography and preparative TLC. High-resolution mass spectral and elemental analyses revealed the molecular formula $C_{25}H_{31}O_3N_3$ for **1**. Its UV spectrum showed absorptions at 222 nm (ϵ 17 762) and 258, 265, and 275 nm (ϵ 3921, 4383, and 4152 respectively). The IR spectrum showed strong bands at 3400, 3270 (OH and NH), 1650, 1550 (amide), 775, and 710 cm^{-1} (aromatic). The ^{1}H NMR spectrum contained signals for two monosubstituted benzene rings, methylene and methine groups, and a carbinyl proton. The presence of a secondary hydroxyl group and a secondary amine group was established by preparation of its diacetate (M$^+$ 505, accurate mass 505.2611, $C_{29}H_{35}N_3O_5$). Moreover, the hydroxyl group could be smoothly oxidized with Jones' reagent to a ketone as was evident from the CD curve. However, the mass spectrum

Table I. ^{13}C Chemical Shifts of **1** (Me_4Si = 0)[a]

δ	multiplicity	tentative assignment
22.3	t	C6[a]
28.6	t	C7[a]
31.6	d	C12
40.2	t	C2[b]
42.1	t	C5[b]
42.9	t	C8[b]
43.0	t	C13[b]
49.0	d	C11
51.0	t	C91
59.5	d	C3
71.3	d	C111
126.0	d	C32 + C36[c]
127.4	d	C34[d]
127.6	d	C113 + C117[c]
128.1	d	C115[d]
128.4	d	C114 + C116[e]
128.6	d	C33 + C35[e]
141.0	s	C31[f]
142.3	s	C112[f]
171.9	s	C1
176.2	s	C10

[a] Key: a-f may be reversed.

(1) (a) Indian Institute of Chemical Biology; (b) Freie Universität Berlin.
(2) "The Wealth of India, Raw Materials"; CSIR, Delhi, 1950; Vol. II, 4.
(3) Chaudhury, G. R.; Sharma, V. N.; Dhar, M. L. *J. Sci. Ind. Res. Sect. B* **1954**, *13*, 147.
(4) Chaudhury, G. R. *J. Sci. Ind. Res. Sect. B* **1957**, *16*, 511.
(5) Biswas, H. G. *Sci. Cult.* **1943**, *9*, 89.

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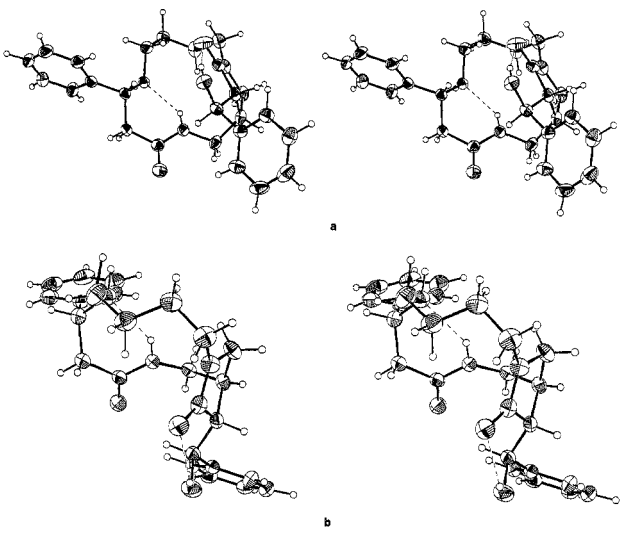


Figure 1. ORTEP stereoviews of the two independent molecules of caesalpinine A. The thermal ellipsoids are plotted at a 30% probability level: (a) molecule 1; (b) molecule 2.

of the ketone showed the molecular ion at m/z 435, indicating concomitant introduction of an oxygen atom presumably with the transformation of the secondary amine group to a >N–OH group (IR and MS).

The nature of the 25 carbon atoms was revealed from ^{13}C NMR studies, which showed that caesalpinine A has 10 aromatic = CH—, 2 aromatic quaternary carbons, 2 carbonyls, 1 >CHOH, 7 methylenes, and 2 methines. The ^{13}C NMR data are shown in Table I. Assignments of the ^{13}C signals are made on the basis of the chemical shifts and off-resonance studies.[6]

The foregoing results indicated that caesalpinine A might be a macrocyclic spermidine alkaloid involving 1 mol of spermidine and 2 mol of cinnamic acid. However, hydrolysis (acidic or alkaline) of caesalpinine A did not yield either cinnamic acid or spermidine.

The detailed structure and stereochemistry of caesalpinine A were established unambiguously by single-crystal X-ray diffraction. The X-ray investigations demonstrated the presence of two independent molecules linked by a hydrogen bond in the asymmetric unit. The conformation of the two molecules are shown in Figure 1.[7] In both molecules intramolecular hydrogen bonds N14–H14···N4 and O111–H111···O10 were observed. However, it is clear from Figure 1 the macrocycles C1···N14 have some conformational differences, and this is shown by the comparison of the ring torsion angles (Table II). If the macrocycle is subdivided into two halves, one consisting of the sequence C1–C8, the second one of the atoms C8–N14, the main differences are present in the first half. For example, along the bonds C3–N4 and N4–C5 trans arrangements are found in molecule 1, which is not true for molecule 2. However, in the second half, where the macrocycle is attached to the five-membered ring, only minor conformational differences are observed.

The five-membered ring N9–C10–C11–C12–C91 tends to have an envelope form in both molecules, which is indicated by the almost zero torsion angle C91–N9–C10–C11 and the Cremer–Pople[8,9] puckering parameters. They were calculated as q_2 = 0.276 (5) [0.308 (5)], φ_2 = 284 (1) [282 (1)] (the values for molecule 2 are given in square brackets; estimated standard deviations were calculated after Norrestam[10]). The Cremer–Pople parameters

Table II. Selected Torsion Angles for Caesalpinine A (deg, Estimated Standard Deviations in Parentheses)

sequence	mol 1	mol 2
O1-C1-C2-C3	142.1 (5)	−132.3 (5)
O1-C1-N14-C13	3.7 (7)	8.6 (7)
C1-C2-C3-N4	68.0 (5)	−66.6 (6)
C2-C3-N4-C5	−172.8 (4)	−80.4 (6)
C3-N4-C5-C6	−176.4 (4)	113.0 (6)
N4-C5-C6-C7	−60.4 (6)	70.6 (7)
C5-C6-C7-C8	−58.3 (7)	−158.4 (5)
C6-C7-C8-N9	98.9 (6)	73.0 (6)
C7-C8-N9-C10	−116.5 (5)	−112.1 (6)
C7-C8-N9-C91	76.6 (6)	75.1 (6)
C8-N9-C10-C11	−166.1 (4)	−170.2 (5)
N9-C10-C11-C12	−18.2 (5)	−21.2 (5)
C10-C11-C12-C91	26.3 (4)	29.8 (4)
C11-C12-C91-N9	−25.5 (4)	−28.2 (5)
C12-C91-N9-C10	15.8 (5)	16.6 (6)
C91-N9-C10-C11	1.6 (5)	3.1 (5)
C10-C11-C111-O111	−41.1 (5)	−58.6 (5)
C11-C111-C112-C113	73.0 (5)	−122.3 (4)
C10-C11-C12-C13	−95.5 (5)	−92.6 (4)
C11-C12-C13-N14	52.0 (6)	60.7 (5)
C12-C13-N14-C1	−138.7 (4)	−129.1 (4)
C13-N14-C1-C2	−176.8 (4)	−172.9 (4)
N14-C1-C2-C3	−37.4 (6)	49.1 (6)
C2-C3-C31-C32	118.0 (5)	−86.3 (6)

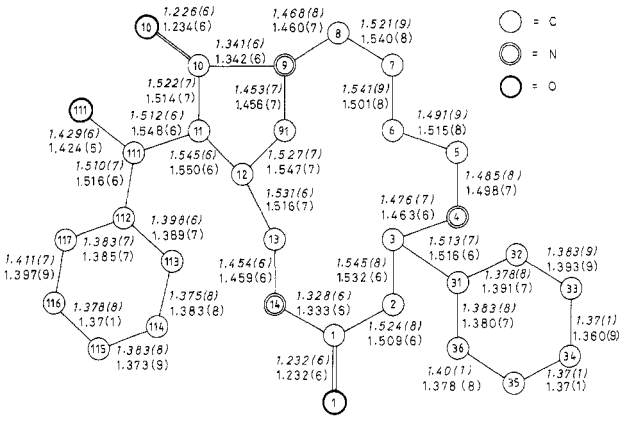


Figure 2. Atom numbering scheme and bond lengths (angstroms, estimated standard deviations in parentheses) for molecule 1 (lower values) and molecule 2 (upper values) of caesalpinine A.

describe the out of plane displacement of ring atoms by a puckering amplitude q and a phase angle φ. The latter adopts characteristic values for the envelope and the twist form. The nearest φ values are 270° for a pure twist form and 288° for a pure envelope form. So the observed φ values indicate the presence of an envelope conformation with a tendency toward a twist form. C12 is the out-of-plane atom. The deviations from the least-squares planes through N9, C10, C11, C91 are 0.44 and 0.49 Å for molecules 1 and 2, respectively. Atom numbering scheme and bond lengths are given in Figure 2. The atoms of the two independent molecules are numbered in the same way except that for molecule 2 primed atomic numbers are used. Bond distances and valence angles are quite normal and require no special comments.

The structures of the characteristic mass spectral fragments of **1** may reasonably be assigned as shown in Scheme I, based on the high-resolution mass spectral values (Table III).

The structure of caesalpinine A is a novel one, whose biogenetic pathway of formation may be envisaged as outlined in Scheme II. Besides one molecule of cinnamic acid, a molecule each of benzoylacetic acid and an appropriately substituted spermidine rather than spermidine itself appear to be involved. Elimination of the spermidine substituent (possibly involving the aziridinium ion) is followed by an attack from the carbanion derived from benzoylacetic acid with the formation of a new C–C bond that is hitherto unknown in spermidine alkaloids. The other reactions involved in the biogenesis are of well-established nature, namely,

(6) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972. Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1978.

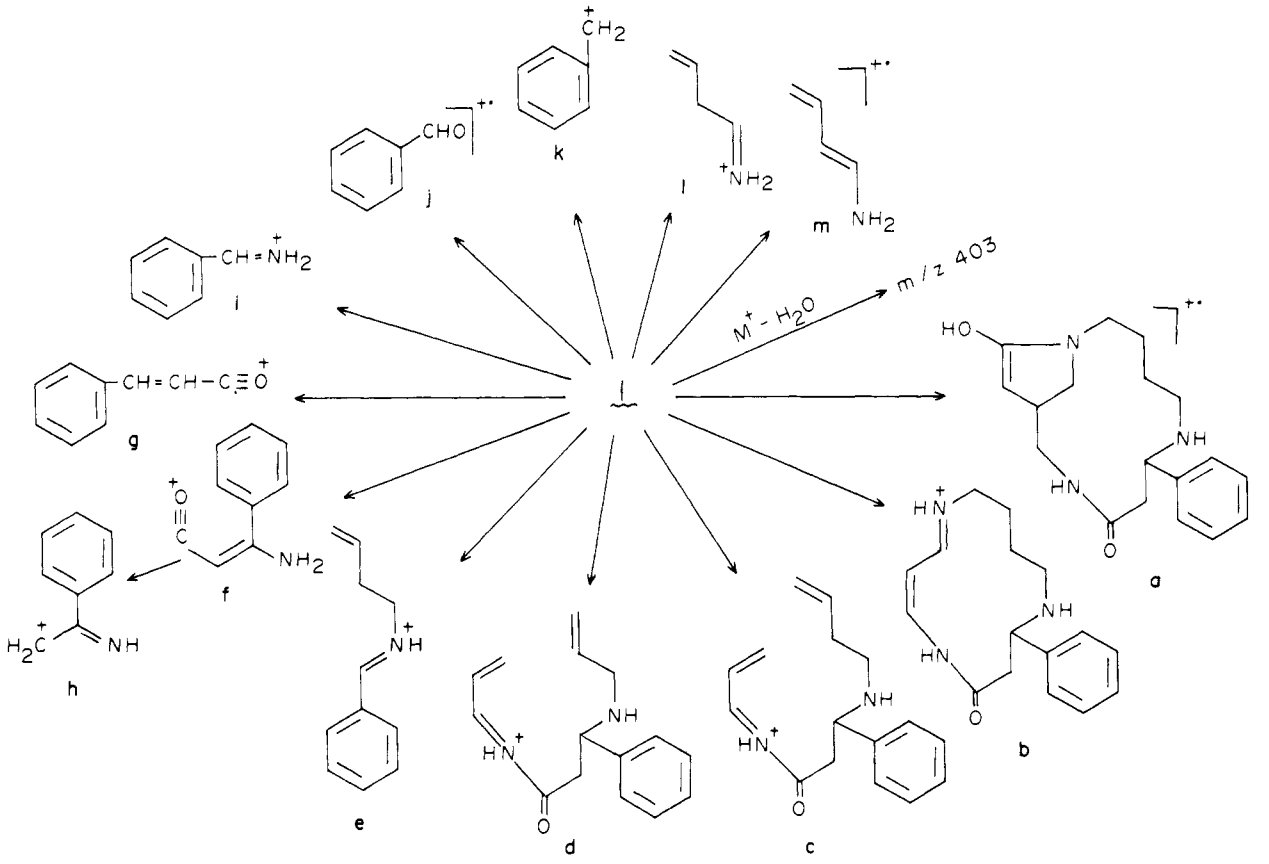
(7) Johnson, C. K. ORTEP, Report ORNL-3794 (2nd revision), Oak Ridge National Laboratory: TN, 1970.

(8) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

(9) Jeffrey, G. A.; Yates, J. H. *Carbohydr. Res.* **1979**, *74*, 319.

(10) Norrestam, R. *Acta Crystallogr. Sect. A* **1981**, *A37*, 764.

Scheme I



Scheme II

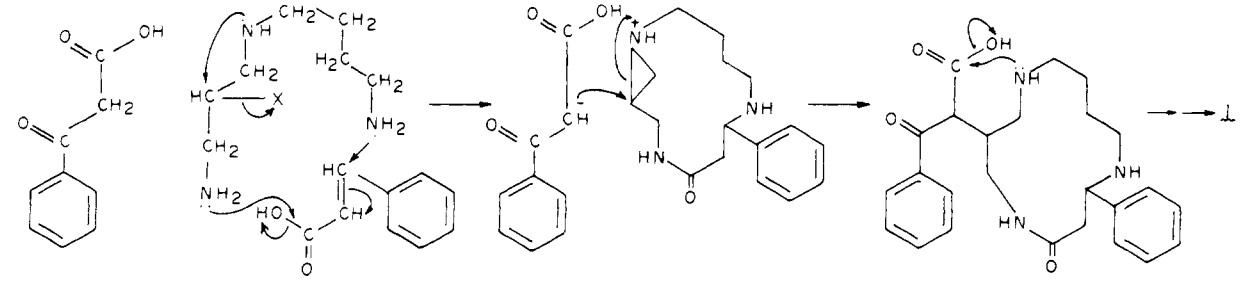


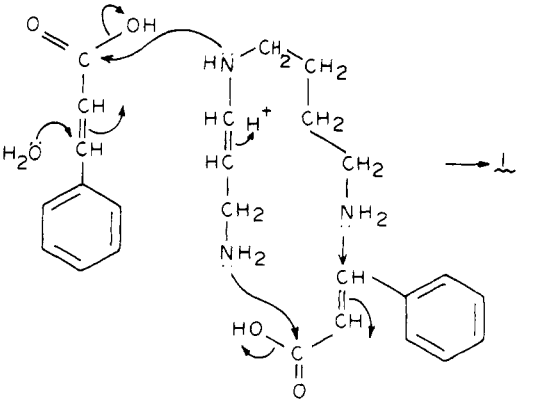
Table III. Most Characteristic Mass Spectral Ions (Experimental High-Resolution Values) of Caesalpinine A

ion[a]	accurate mass	empirical formula	% of base peak
M^+	421.2407	$C_{25}H_{31}N_3O_3$	39.6
$M^+ - H_2O$	403.2245	$C_{25}H_{29}N_3O_2$	17.0
a	315.1950	$C_{18}H_{25}N_3O_2$	10.7
b	272.1755	$C_{16}H_{22}N_3O$	12.5
c	257.1613	$C_{16}H_{21}N_2O$	24.8
d	243.1507	$C_{15}H_{19}N_2O$	47.8
e	160.1131	$C_{11}H_{14}N$	53.3
f	146.0619	C_9H_8NO	51.9
g	131.0499	C_9H_7O	31.2
h	118.0658	C_8H_8N	32.3
i	106.0654	C_7H_8N	100.0
j	106.0408	C_7H_6O	25.7
k	91.0549	C_7H_7	65.8
l	70.0666	C_4H_8N	80.7
m	69.0591	C_4H_7N	76.3

[a] See Scheme I.

Michael addition, carbonyl reduction, and amide formation. Although the carbonyl reduction step (and possibly even the cyclization to the γ-lactam) necessarily follows the C–C bond formation, the generation of the other C–N bonds may either precede or succeed the above step.

Scheme III



An alternative proposition envisages participation of two cinnamic acid moieties along with a dehydrospermidine. Periphylline, a dehydrospermidine alkaloid, has, in fact, already been reported from a plant source.[11] The C–C bond is then supposed to arise via protonation of the spermidine as proposed in Scheme III and

(11) Hocquemiller, R.; Leboeuf, M.; Das, B. C.; Husson, H. P.; Potier, P.; Cave, A. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1974**, *278*, 525.

Table IV. Final Atomic Parameters and Standard Deviations (in Parentheses) for Non-Hydrogen Atoms in Caesalpinine A

mol 1					mol 2				
atom	x	y	z	U_{eq} or U, Å^2 × 100	atom	x	y	z	U_{eq} or U, Å^2 × 100
C1	0.8580 (2)	0.2808 (2)	−0.1234 (5)	4.9 (1)					
O1	0.8729 (2)	0.2792 (2)	−0.2464 (4)	7.1 (1)	C1′	0.8107 (2)	0.8368 (2)	0.7556 (6)	5.3 (1)
C2	0.8630 (2)	0.2176 (2)	−0.0320 (5)	4.6 (1)	O1′	0.7741 (1)	0.8235 (2)	0.6695 (5)	7.3 (1)
C3	0.8802 (2)	0.2293 (2)	0.1203 (5)	4.2 (1)	C2′	0.7956 (2)	0.8589 (3)	0.9037 (7)	6.3 (2)
N4	0.8352 (2)	0.2652 (2)	0.1938 (4)	4.4 (1)	C3′	0.8258 (2)	0.9231 (3)	0.9622 (6)	5.9 (2)
C5	0.8525 (3)	0.2860 (3)	0.3382 (5)	6.3 (2)	N4′	0.8858 (2)	0.9093 (3)	0.9807 (5)	6.1 (1)
C6	0.8045 (3)	0.3191 (3)	0.4164 (6)	6.6 (2)	C5′	0.9004 (3)	0.8708 (4)	1.1097 (7)	8.1 (2)
C7	0.7812 (2)	0.3835 (3)	0.3517 (6)	6.5 (2)	C6′	0.9225 (3)	0.8003 (3)	1.0804 (7)	7.4 (2)
C8	0.8213 (2)	0.4446 (3)	0.3289 (6)	6.1 (2)	C7′	0.9811 (2)	0.8012 (3)	1.0147 (6)	6.8 (2)
N9	0.8420 (2)	0.4488 (2)	0.1858 (4)	5.3 (1)	C8′	0.9932 (3)	0.7342 (3)	0.9371 (7)	7.3 (2)
C10	0.8957 (2)	0.4418 (2)	0.1493 (5)	4.8 (1)	N9′	0.9619 (2)	0.7297 (2)	0.8057 (4)	5.5 (1)
O10	0.9330 (1)	0.4216 (2)	0.2279 (4)	7.1 (1)	C10′	0.9207 (2)	0.6846 (2)	0.7815 (5)	5.1 (1)
C11	0.9032 (2)	0.4665 (2)	0.0005 (5)	4.5 (1)	O10′	0.8992 (2)	0.6456 (2)	0.8668 (4)	6.5 (1)
C12	0.8432 (2)	0.4659 (2)	−0.0588 (5)	4.7 (1)	C11′	0.9064 (2)	0.6882 (2)	0.6269 (5)	4.5 (1)
C13	0.8269 (2)	0.4014 (3)	−0.1387 (6)	5.3 (2)	C12′	0.9291 (2)	0.7597 (2)	0.5834 (5)	4.6 (1)
N14	0.8372 (2)	0.3372 (2)	−0.0629 (4)	4.5 (1)	C13′	0.8872 (2)	0.8193 (2)	0.5909 (5)	4.7 (1)
C31	0.8977 (2)	0.1622 (2)	0.1891 (5)	4.8 (1)	N14′	0.8648 (2)	0.8319 (2)	0.7297 (4)	4.9 (1)
C32	0.9514 (2)	0.1529 (3)	0.2398 (5)	5.7 (2)	C31′	0.8157 (2)	0.9864 (2)	0.8730 (6)	5.8 (2)
C33	0.9661 (3)	0.0907 (3)	0.3032 (6)	7.2 (2)	C32′	0.8476 (3)	1.0025 (3)	0.7579 (7)	6.8 (2)
C34	0.9287 (3)	0.0383 (3)	0.3155 (6)	7.1 (2)	C33′	0.8373 (3)	1.0612 (3)	0.6794 (8)	8.0 (2)
C35	0.8757 (3)	0.0472 (3)	0.2658 (7)	7.2 (2)	C34′	0.7948 (3)	1.1055 (3)	0.7143 (9)	8.5 (3)
C36	0.8603 (2)	0.1084 (3)	0.2029 (6)	6.1 (2)	C35′	0.7622 (3)	1.0898 (3)	0.828 (1)	9.0 (3)
C91	0.8072 (2)	0.4755 (3)	0.0738 (6)	5.7 (2)	C36′	0.7724 (2)	1.0303 (3)	0.9069 (8)	7.3 (2)
C111	0.9489 (2)	0.4283 (2)	−0.0833 (5)	4.3 (1)	C91′	0.9779 (2)	0.7697 (3)	0.6837 (6)	6.1 (2)
O111	0.9966 (1)	0.4166 (2)	0.0017 (4)	5.4 (1)	C111′	0.8473 (2)	0.6678 (2)	0.5915 (5)	4.9 (1)
C112	0.9678 (2)	0.4699 (2)	−0.2089 (5)	4.6 (1)	O111′	0.8370 (2)	0.5987 (2)	0.6376 (5)	6.7 (1)
C113	1.0008 (2)	0.5281 (3)	−0.1897 (6)	5.4 (2)	C112′	0.8368 (2)	0.6693 (2)	0.4360 (5)	4.6 (1)
C114	1.0202 (2)	0.5653 (3)	−0.3030 (6)	6.4 (2)	C113′	0.7946 (2)	0.7107 (3)	0.3804 (6)	5.2 (1)
C115	1.0075 (3)	0.5450 (4)	−0.4367 (7)	7.4 (2)	C114′	0.7858 (2)	0.7131 (3)	0.2387 (6)	6.1 (2)
C116	0.9744 (3)	0.4881 (4)	−0.4574 (6)	7.6 (2)	C115′	0.8193 (2)	0.6763 (3)	0.1476 (6)	5.7 (2)
C117	0.9543 (2)	0.4503 (3)	−0.3438 (5)	6.0 (2)	C116′	0.8615 (2)	0.6359 (3)	0.2006 (6)	5.9 (2)
					C117′	0.8701 (2)	0.6317 (3)	0.3460 (5)	5.4 (2)

subsequent attack by the cinnamoyl bond with concomitant hydroxylation.

Experimental Section

Melting points are uncorrected. UV spectra were recorded on a Specord UV–vis instrument. IR spectra were taken on a Perkin-Elmer Infracord Model 177. CD spectra were taken in a JASCO Model 20A automatic recording spectropolarimeter. ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ solution on a JEOL-FX-100 spectrometer at 100 and 25.15 MHz, respectively, with Me_4Si as internal reference. Mass spectra were obtained on Hitachi RMU-6L and MS-50 mass spectrometers at an ionizing potential of 70 eV.

Isolation of Caesalpinine A (1). The air-dried leaves of *C. digyna* Rottl. (1 Kg) were powdered and then extracted with petroleum ether followed by chloroform in a Soxhlet extractor for 20 and 25 h, respectively. The chloroform extract was concentrated to 300 mL and extracted with 5% HCl (3 × 100 mL). The combined acid extract was cooled at 4 °C and basified with ammonia (35%). The precipitate thus formed was again extracted with chloroform (4 × 50 mL) and dried. The crude alkaloid mixture (300 mg) contained three alkaloids as revealed by TLC on silica gel G (solvent system benzene–ethyl acetate–diethylamine, 7:2:1; developed by Dragendorff's reagent[12,13]) and designated as caesalpinine A, B, and C according to the increasing order of their polarities. The alkaloid mixture was partially purified by chromatography over a column of silica gel (20 g) with petroleum ether, petroleum ether–benzene mixture (1:1), benzene, benzene–chloroform mixture (1:1), chloroform, and chloroform–methanol mixture (98:2) and (95:5) as successive eluents. The chloroform–methanol (98:2) eluate (152.2 mg) contained the three alkaloids as revealed by TLC. This was subjected to preparative TLC on silica gel G. Thus caesalpinine A could be separated, but caesalpinine B and C still remained as a mixture whose separation and purification are in progress. Caesalpinine A crystallized from ethyl acetate as colorless prismatic crystals; mp 240–242 °C; $[\alpha]_D$ +16.6° (*c*, 0.42, $CHCl_3$); UV (EtOH), 222 nm (ϵ 17 762) and 258, 265, and 275 nm (ϵ, 3921, 4383, and 4152, respectively); CD (MeOH) $[\theta]_{224}$ +15 577 ($\Delta\epsilon$ 4.7); IR (Nujol) 3400, 3270 (OH and NH), 1650, 1550 (amide), 1275, 1205, 1020, 940, 920, 775, 710 cm^{-1}; ^{1}H NMR δ 2.56 (d, C2–H_2, *J* = 7 Hz), 3.84 (d, C3–H, *J* = 7 Hz), 5.04 (d, C111–H, *J* = 12 Hz); MS, *m/z* (relative intensity) 421 (39.6; M^+), 403 (17; $M^+ - H_2O$), 335 (22.2), 315 (10.7), 272 (12.5), 271 (10.2), 270 (31.4), 257 (24.8), 244 (20.0), 243 (47.8), 203 (22.6), 176 (15.6), 160 (53.3), 159 (25.5), 158 (15.1), 153 (15.5), 146 (51.9), 144 (14.8), 138 (23.7), 132 (22.0), 131 (31.2), 130 (16.1), 129 (17.9), 128 (11.8), 125 (19.1), 120 (27.5), 119 (26.0), 118 (32.3), 106 (100.0), 104 (44.7), 91 (65.8), 79 (29.5), 77 (54.6), 70 (80.7), 69 (76.3). Anal. Calcd for $C_{25}H_{31}N_3O_3$: C, 71.23; H, 7.41; N, 9.97. Found: C 71.18; H, 7.38; N, 9.89.

Acetate of 1. A solution of **1** (10 mg) in 1 mL of pyridine and 2 mL of acetic anhydride was kept for 2 h on a steam bath. Standard workup yielded the diacetate (amorphous): $[\alpha]_D$ +18° (*c*, 0.85, $CHCl_3$); IR (Nujol) 3200–3500 (br), 1735, 1235, 1680, 1635, 1500, 1550, 1025, 975, 970, 710 cm^{-1}; ^{1}H NMR δ 6.32 (C111–H, *J* = 12 Hz), 2.61 (d, C2–H_2, *J* = 7 Hz), 3.86 (d, C3–H, *J* = 7 Hz); MS, *m/z* (relative intensity) 505 (1.1; M^+), 463 (3.8; $M^+ - C_2H_2O$), 445 (22.5; $M^+ - CH_3COOH$), 403 (37.9; $M^+ - CH_3COOH - C_2H_2O$), 402 (100), 312 (20.7), 205 (10.2), 131 (40.8), 112 (12.1), 91 (12.8), 70 (19.1), 43 (13.5). Anal. Calcd for $C_{29}H_{35}O_5N_3$: C, 68.89; H, 6.98; N, 8.31. Found: C, 68.81; H, 6.93; N, 8.25.

Ketone of 1. To a solution of 10 mg of **1** in acetone (2 mL) was added Jones' reagent (prepared by dissolving chromium trioxide (2.6 g) in concentrated H_2SO_4 (2.3 mL) and adding water to 10 mL total volume) drop by drop at 0 °C while stirring until a permanent orange persisted. The stirring was continued for 15 min. Usual workup yielded the ketone, which crystallized from ethyl acetate in needles (6 mg): mp 220 °C; $[\alpha]_D$ +22° (*c*, 0.76, $CHCl_3$); CD (MeOH) $[\theta]_{243}$ −25 489 ($\Delta\epsilon$ 7.7), $[\theta]_{330}$ +4911 ($\Delta\epsilon$ 1.2); IR (Nujol) 3220–3450 (br), 1660, 1640, 1500, 1020, 970, 770, 710 cm^{-1}; MS, *m/z* (relative intensity) 435 (41, M^+), 419 (40; $M^+ - O$), 418 (100; $M^+ - OH$), 363 (23), 330 (59), 313 (18), 271 (32), 243 (14), 228 (20), 217 (18), 215 (16), 176 (64), 169 (32), 165 (68), 163 (70), 160 (65), 159 (41), 146 (95). Anal. Calcd for $C_{25}H_{29}O_3N_3$: C, 68.94; H, 6.71; N, 9.65. Found: C, 69.01; H, 6.75; N, 9.74.

Crystallization and Crystal Data. Colorless prismatic crystals of caesalpinine A were obtained from ethyl acetate. A specimen with approximate dimensions of 0.15 × 0.30 × 0.33 mm was selected for the X-ray measurements. Precise lattice constants and the intensity data of an octant (*h*, *k*, *l* all ≥ 0) were measured on a DEC PDP 15/40 controlled four-circle diffractometer with Ni-filtered Cu Kα radiation (λ 1.5418 Å). The lattice constants were refined from 15 high-order reflections. The reflection intensities were recorded by using the θ–2θ scan

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Table V. Valence Angles in Caesalpinine A (deg, Estimated Standard Deviations in Parentheses)

	mol 1	mol 2
O1-C1-C2	120.7 (4)	120.8 (4)
O1-C1-N14	123.1 (4)	123.9 (5)
C2-C1-N14	116.2 (4)	115.3 (4)
C1-C2-C3	117.0 (4)	116.8 (5)
C2-C3-N4	109.3 (3)	111.0 (4)
C2-C3-C31	111.2 (4)	111.8 (5)
N4-C3-C31	113.7 (4)	111.7 (4)
C3-N4-C5	111.6 (4)	114.9 (5)
N4-C5-C6	111.1 (5)	112.7 (5)
C5-C6-C7	115.5 (5)	113.1 (5)
C6-C7-C8	117.6 (5)	111.4 (5)
C7-C8-N9	112.9 (4)	111.8 (5)
C8-N9-C10	124.5 (4)	124.4 (3)
C8-N9-C91	121.0 (4)	121.6 (4)
C10-N9-C91	113.3 (4)	113.7 (4)
N9-C10-O10	124.8 (4)	126.6 (5)
N9-C10-C11	109.2 (4)	107.8 (4)
O10-C10-C11	125.9 (4)	125.6 (4)
C10-C11-C12	103.4 (4)	102.9 (4)
C10-C11-C111	115.0 (4)	114.7 (4)
C12-C11-C111	117.8 (4)	120.3 (4)
C11-C12-C13	115.5 (4)	115.5 (4)
C11-C12-C91	102.6 (4)	102.3 (4)
C13-C12-C91	111.7 (4)	112.3 (4)
C12-C13-N14	114.0 (4)	114.4 (4)
C1-N14-C13	122.9 (4)	123.0 (4)
C3-C31-C32	121.3 (4)	123.1 (5)
C3-C31-C36	120.5 (4)	119.1 (5)
C32-C31-C36	118.2 (4)	117.8 (5)
C31-C32-C33	120.0 (5)	121.4 (6)
C32-C33-C34	120.9 (6)	120.8 (7)
C33-C34-C35	119.4 (6)	118.5 (7)
C34-C35-C36	120.1 (6)	120.9 (6)
C31-C36-C35	121.0 (5)	120.6 (7)
N9-C91-C12	104.0 (4)	103.7 (4)
C11-C111-O111	110.5 (4)	109.7 (4)
C11-C111-C112	111.7 (4)	111.9 (4)
O111-C111-C112	107.3 (3)	107.1 (4)
C111-C112-C113	119.7 (4)	120.5 (4)
C111-C112-C117	121.7 (4)	120.5 (4)
C113-C112-C117	118.6 (5)	118.9 (4)
C112-C113-C114	120.7 (5)	120.5 (5)
C113-C114-C115	120.5 (6)	121.1 (5)
C114-C115-C116	119.6 (6)	119.1 (5)
C115-C116-C117	120.5 (6)	120.3 (5)
C112-C117-C116	120.2 (5)	120.0 (5)

technique. A variable scan range $\Delta\theta$ was used with $\Delta\theta = 0.50 + 0.46 \tan\theta$. Maximum and minimum scan speeds were 0.05 and 0.0167 deg/s. In each background counting rates were measured stationarily for half the time needed for the reflection scan.

A summary of crystallographic data is as follows: molecular formula $C_{25}H_{31}N_3O_3$, lattice constants $a = 24.017$ (6) Å, $b = 19.346$ (2) Å, $c = 9.578$ (2) Å, cell volume $V = 4450.3$ Å^3, $Z = 8$, space group orthorhombic $P2_12_12_1$, X-ray density $\rho_x = 1.250$ (Mg m^{-3}), linear absorption coefficient (Cu Kα) μ 6.75 cm^{-1}, total number of reflections ($\theta < 60°$) 3735, unobserved ($I < 2\sigma I$) 594.

Structure Determination. Phase determination was carried out successfully with direct methods (MULTAN).[14] The refinement with least-squares methods was executed with the corresponding programs of the X-RAY 76[15] program system. Scattering factors were taken from the corresponding standard routine of the X-RAY 76 system.[16,17] Because of the small linear absorption coefficient, an absorption correction was not applied. All hydrogen atoms were located from difference syntheses. During the refinement, which was made with anisotropic temperature factors for the non-hydrogen atoms and isotropic thermal parameters for the hydrogens, a weighting scheme was applied that made $w\Delta F$ independent of $|F|$. This was achieved by setting $w = xy$, with $x = 1$ for $\sin\theta > 0.7$, $x = \sin\theta/0.7$ otherwise, and $y = 1$ for $F_o < 14.0$, $y = 14.0/F_o$ if $F_o > 14.0$. Unobserved reflections were included in the refinement only if $|F_c| > |F_o|$. After convergence of all parameters a final R value of 4.5% ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 5.5\%$) was obtained. The maximum and average shift/error ratio at the end of the refinement were 2.1 and 0.35. A final electron density map showed all residual density below 0.2 e Å^{-3}. The final atomic coordinates are given in Table IV. Bond lengths (Figure 2) and angles (Table V) have standard deviations of 0.006–0.01 Å and 0.4–0.7°. Generally, the corresponding bond lengths and valence angle values for the two molecules agree within 3 times the standard deviation. However, a number of exceptions exist, mainly in the valence angles. Most of these discrepancies are in the range C1–C8 of the macrocycle, which as already discussed has different conformations for the two molecules.

Table VI. Hydrogen Bonding

X-H···Y	X-H, Å	X···Y, Å	H···Y, Å	sym op for
N14-H14···N4	0.84 (6)	2.826 (5)	2.13 (6)	x, y, z
O111-H111···O10	0.74 (8)	2.652 (5)	1.96 (8)	x, y, z
N14′-H14′···N4′	0.86 (6)	2.877 (6)	2.16 (6)	x, y, z
O111′-H1111′···O′	0.77 (7)	2.806 (6)	2.18 (6)	x, y, z
N4-H4···O1′	0.92 (4)	3.146 (5)	2.26 (4)	$3/2 - x, 1 - y, -1/2 + z$

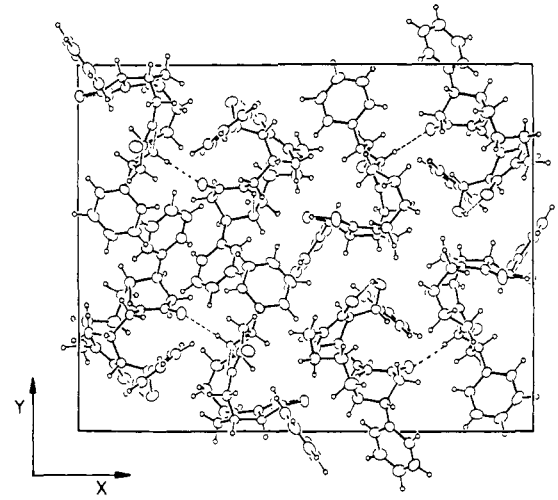

Figure 3. Unit cell of caesalpinine A projected on the xy plane. Hydrogen bonds are plotted by dashed lines.

Chemical investigations disclosed that among the 31 heavy atoms of one molecule 3 nitrogens and 3 oxygens are present. All these six positions could be assigned with certainty. The found molecular skeleton, the peak height, the refinement results for the isotropic temperature factors, and finally the distribution of the found hydrogen atoms gave altogether unambiguous evidence for the positions of the heteroatoms as displayed in Figure 2. Thus the chemical structure of caesalpinine A is **1**. The final valence angles and selected torsion angles are given in Tables V and II. Table VI, giving the data of the hydrogen bonds, shows that besides the two intramolecular hydrogen bonds only one weak intermolecular hydrogen bond N4–H4···O1′ exists, which connects the two independent molecules. Hydrogen bonds are shown by dashed lines in Figures 1 and 3.

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Registry No. 1, 85702-14-3; **1** diacetate, 85702-15-4; **1** ketone, 85702-16-5; caesalpinine B, 85702-47-2; caesalpinine C, 85702-48-3.

Supplementary Material Available: Listings of complete atomic parameters with the anisotropic temperature factors for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, final atomic parameters for hydrogen atoms, and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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