

X-Ray Crystal Structure of Angulatusine A, a New Sesquiterpene Alkaloid from *Celastrus angulatus*

Da-Gang Wu, Chun-Quan Cheng, and Ji-Kai Liu

J. Nat. Prod., **1992**, 55 (7), 982-985 • DOI:

10.1021/np50085a025 • Publication Date (Web): 01 July 2004

Downloaded from <http://pubs.acs.org> on April 4, 2009

More About This Article

The permalink <http://dx.doi.org/10.1021/np50085a025> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



ACS Publications
High quality. High impact.

Journal of Natural Products is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

X-RAY CRYSTAL STRUCTURE OF ANGULATUSINE A, A NEW
SESQUITERPENE ALKALOID FROM *CELASTRUS ANGULATUS*

DA-GANG WU, CHUN-QUAN CHENG,

Department of Phytochemistry, Kunming Institute of Botany, Academia Sinica, Kunming, People's Republic of China

and JI-KAI LIU*

Department of Chemistry, Zhongshan University, Guangzhou, People's Republic of China

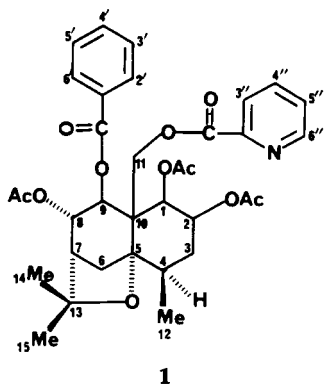
ABSTRACT.—A new sesquiterpene alkaloid, angulatusine A [1], has been isolated from the seeds of *Celastrus angulatus* (Celastraceae). The structure was determined using physical and spectral techniques and X-ray crystallography.

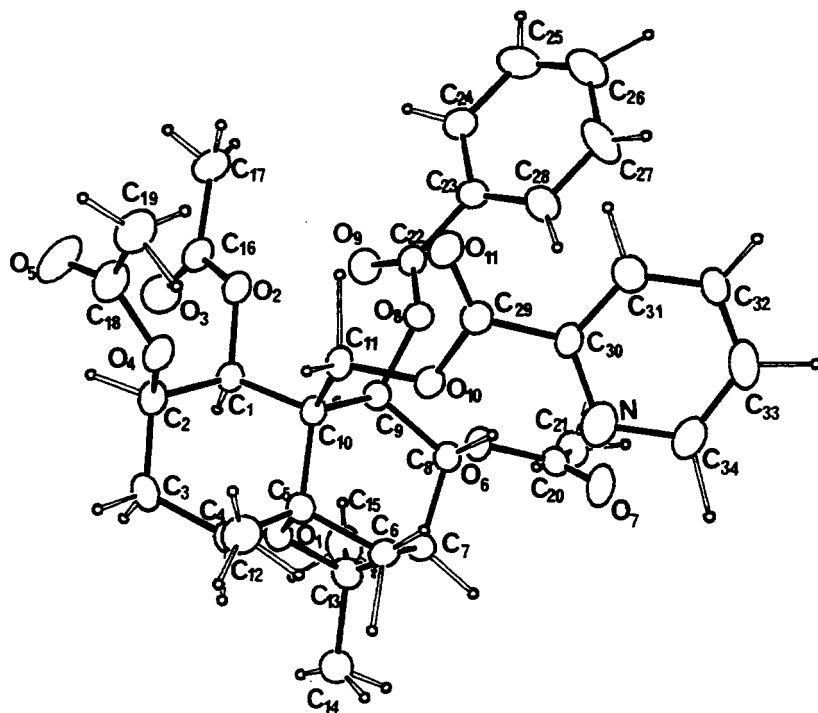
Polyester sesquiterpene alkaloids are frequently found in the Celastraceae (1). In our previous investigations of the root bark of *Celastrus angulatus* Maxim., a total of seven new sesquiterpene alkaloids were isolated which showed antifeedant action to several insects (2,3). The oil of the seeds of *C. angulatus* also had marked insect antifeedant effects to yellow melon beetle and imported cabbageworm larvae (4). We have now isolated from the seed oil a new sesquiterpene alkaloid that is identified as angulatusine A [1]. Insect antifeedant testing for angulatusine A is in progress.

Angulatusine A [1] has been obtained as colorless prisms, mp 227–230°, molecular formula $C_{34}H_{39}NO_{11}$. The ir spectrum showed an ester band but no alcohol band. The ms contained fragmentation ions attributable to picolinate or nicotinate (m/z 124 and 106), benzoate (m/z 105), and acetate (m/z 43)

groups. This was confirmed from the 1H -nmr spectrum of 1, which contained signals at δ 8.86 (1H, dd, $J = 1.7, 1.1$ Hz, picolinoyl H-6''), 8.54 (1H, dd, $J = 4.8, 1.7$ Hz, picolinoyl H-5''), 7.85 (2H, m, benzoyl H-2', -6'), 7.50 (2H, m, picolinoyl H-4'', benzoyl H-4'), and 7.30 (3H, m, picolinoyl H-3'', benzoyl H-3', -5'). The 1H -nmr spectrum of 1 contained signals assignable to protons on the carbon atoms carrying four secondary ester groups, i.e., δ 6.06 (1H, d, $J = 9.7$ Hz, H-9), 5.78 (1H, dd, $J = 9.7, 3.4$ Hz, H-8), 5.59 (1H, d, $J = 3.4$ Hz, H-1), and 5.46 (1H, dd, $J = 6.5, 3.4$ Hz, H-2), and one primary ester group, i.e., δ 5.35 and 4.83 (2H, ABq, $J = 13.2$ Hz, H-11). The 1H -nmr spectrum of 1 also showed signals corresponding to the protons of three acetate methyls as singlets at δ 2.10, 1.87, and 1.58, and three methyls at δ 1.60 (s), 1.35 (d, $J = 8.5$ Hz), and 1.23 (s). The ^{13}C -nmr spectrum also indicated the presence of five acyl groups (170.42, 169.75, 169.63, 165.51, 165.35) and three quaternary carbons (87.68, 82.04, 50.58).

From the above data it was supposed that angulatusine A possessed a structure related to a dihydro- β -agarofuran. Using single crystal X-ray diffraction, the complete structure of angulatusine A [1] was determined (Figure 1). Angulatusine A [1] contains a picolinoyl group which is found for the first time in sesquiterpene alkaloids belonging to the



FIGURE 1. Crystal structure of **1**.

Celastraceae. Usually, the basic group found in these alkaloids is nicotinoyl.

The atomic coordinates and their equivalent isotropic thermal parameters are given in Table 1.

The six-membered ring A of **1** has a chair conformation and is fused in the trans configuration with ring B, which takes a twisted chair form with C-5, C-7, C-8, and C-10 approximately in a plane. The five-membered ring C is nearly perpendicular to ring B. The average C-C distance in rings A, B, and C is 1.538 Å, and the average bond angle C-C-C in rings A, B, and C is 109.4°.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The mp was uncorrected. The ir spectrum was obtained with a Perkin Elmer 577 spectrophotometer. The uv spectrum was determined on a UV-210A spectrophotometer. ¹H- and ¹³C-nmr spectra were recorded with a Bruker AM-500 spectrometer in CDCl₃ using TMS as internal standard. The eims was obtained on a Varian MAT 711 spectrometer.

PLANT MATERIAL.—Seeds of *C. angulatus* were collected in October 1988 in the suburb of Kunming. A voucher specimen is preserved at the Kunming Institute of Botany.

ISOLATION OF ANGULATUSINE A [1].—Dried and powdered seeds (1 kg) were extracted three times with petroleum ether (bp 60–90) at room temperature for a week. The extract was concentrated to 1 liter and extracted with MeOH-H₂O (10:0.5) (3 × 400 ml). The aqueous layer was subsequently concentrated in vacuo to give a residue (83 g). The residue was chromatographed on a Si gel column eluted with petroleum ether-EtOAc (8:2, 7:3, 6:4). After rechromatography and repeated preparative tlc [Si gel, petroleum ether-EtOAc (7:3)], compound **1** was obtained.

CHARACTERIZATION OF 1.—Crystallized from Me₂CO in colorless prisms: mp 227–230°; uv (EtOH) λ max 225.5 nm (log ε 4.2457); ir (KBr) ν max 1745, 1725, 1600, 1590, 1282, 1238, 745, 718 cm⁻¹; eims *m/z* (%) [M]⁺ 637 (14), 595 (14), 578 (77), 577 (100), 516 (79), 221 (38), 137 (37), 124 (81), 106 (64), 105 (78), 43 (66); ¹H nmr (CDCl₃) δ 8.86 (1H, dd, *J* = 1.7, 1.1 Hz, H-6''), 8.54 (1H, dd, *J* = 4.8, 1.7 Hz, H-5''), 7.85 (2H, m, H-2', -6'), 7.50 (2H, m, H-4', -4''), 7.30 (3H, m, H-3', -5', H-3''), 6.06 (1H, d, *J* = 9.7 Hz, H-9), 5.78 (1H, dd, *J* = 9.7, 3.4 Hz, H-8), 5.59 (1H, d, *J* = 3.4

TABLE 1. Positional Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B (Å ²)
O-1	0.2718 (2)	0.6185 (2)	0.2212 (2)	4.17 (7)
O-2	0.4423 (2)	0.4200 (2)	0.1340 (2)	3.83 (7)
O-3	0.4513 (4)	0.4893 (3)	0.0068 (2)	6.3 (1)
O-4	0.5575 (2)	0.4883 (2)	0.2636 (2)	4.42 (7)
O-5	0.6701 (3)	0.4696 (4)	0.1613 (3)	8.4 (1)
O-6	0.0750 (2)	0.4449 (2)	0.1785 (2)	3.98 (7)
O-7	-0.0341 (3)	0.4043 (3)	0.2771 (3)	6.08 (9)
O-8	0.2479 (2)	0.3481 (2)	0.1899 (2)	3.44 (6)
O-9	0.2549 (3)	0.3539 (2)	0.0445 (2)	4.84 (8)
O-10	0.3002 (2)	0.3706 (2)	0.3597 (2)	3.80 (6)
O-11	0.3774 (3)	0.2433 (2)	0.3637 (3)	5.77 (9)
N	0.1496 (4)	0.3108 (4)	0.4589 (3)	6.7 (1)
C-1	0.4126 (3)	0.4987 (3)	0.1763 (3)	3.51 (9)
C-2	0.5026 (4)	0.5461 (3)	0.2084 (3)	4.2 (1)
C-3	0.4756 (4)	0.6265 (4)	0.2587 (4)	5.1 (1)
C-4	0.3957 (4)	0.6141 (3)	0.3280 (4)	4.7 (1)
C-5	0.3097 (4)	0.5637 (3)	0.2899 (3)	3.78 (9)
C-6	0.2236 (4)	0.5532 (3)	0.3518 (3)	4.0 (1)
C-7	0.1405 (4)	0.5475 (3)	0.2865 (3)	3.9 (1)
C-8	0.1480 (3)	0.4579 (3)	0.2449 (3)	3.49 (9)
C-9	0.2441 (3)	0.4417 (3)	0.1990 (3)	3.32 (8)
C-10	0.3361 (3)	0.4759 (3)	0.2458 (3)	3.25 (8)
C-11	0.3778 (3)	0.4056 (3)	0.3058 (3)	3.57 (9)
C-12	0.4375 (4)	0.5816 (4)	0.4137 (4)	5.7 (1)
C-13	0.1661 (4)	0.6237 (3)	0.2267 (4)	4.8 (1)
C-14	0.1277 (5)	0.6223 (4)	0.1346 (4)	6.4 (1)
C-15	0.1376 (5)	0.7099 (4)	0.2692 (5)	6.7 (2)
C-16	0.4602 (4)	0.4245 (4)	0.0477 (3)	4.7 (1)
C-17	0.4889 (5)	0.3385 (4)	0.0155 (4)	6.2 (1)
C-18	0.6367 (4)	0.4509 (4)	0.2297 (4)	5.7 (1)
C-19	0.6740 (5)	0.3820 (5)	0.2886 (5)	7.3 (2)
C-20	-0.0138 (4)	0.4190 (3)	0.2034 (4)	4.3 (1)
C-21	-0.0811 (4)	0.4139 (4)	0.1282 (4)	5.2 (1)
C-22	0.2448 (3)	0.3129 (3)	0.1091 (3)	3.63 (9)
C-23	0.2267 (4)	0.2188 (3)	0.1151 (3)	3.81 (9)
C-24	0.2470 (4)	0.1688 (4)	0.0425 (4)	5.2 (1)
C-25	0.2259 (5)	0.0814 (4)	0.0457 (5)	6.7 (2)
C-26	0.1844 (6)	0.0437 (4)	0.1140 (5)	6.9 (2)
C-27	0.1627 (6)	0.0952 (4)	0.1866 (4)	7.2 (2)
C-28	0.1857 (5)	0.1824 (4)	0.1868 (4)	5.2 (1)
C-29	0.3080 (3)	0.2867 (3)	0.3810 (3)	3.70 (9)
C-30	0.2215 (3)	0.2554 (3)	0.4268 (3)	3.54 (9)
C-31	0.2089 (5)	0.1666 (4)	0.4390 (4)	5.4 (1)
C-32	0.1330 (4)	0.1324 (3)	0.4756 (4)	5.2 (1)
C-33	0.0671 (5)	0.1829 (4)	0.5056 (4)	6.2 (1)
C-34	0.0694 (4)	0.2734 (4)	0.5009 (4)	5.6 (1)

Hz, H-1), 5.46 (1H, dd, $J = 6.5, 3.4$ Hz, H-2), 5.35 (1H, d, $J = 13.2$ Hz, H_a-11), 4.83 (1H, d, $J = 13.2$ Hz, H_b-11), 2.68 (1H, dd, $J = 13.0, 0.6$ Hz, H-6), 2.43 (2H, m, H-7, -3), 2.10 and 1.87 (3H for each, s, 2Me-OAc), 1.96 (1H, m, H-4), 1.77 (1H, ddd, $J = 15.2, 2.9, 1.3$ Hz, H-3), 1.60 and 1.23 (3H for each, s, 2Me-14, -15), 1.58 (3H, s, Me-OAc), 1.35 (3H, d, $J = 8.5$ Hz,

Me-12); ¹³C nmr (CDCl₃) 75.35^a (CH, C-1), 69.15^a (CH, C-2), 31.00 (CH₂, C-3), 39.14 (CH, C-4), 87.68 (C, C-5), 36.36 (CH₂, C-6), 47.22 (CH, C-7), 76.75^a (CH, C-8), 76.29^a (CH, C-9), 50.58 (C, C-10), 63.34 (CH₂, C-11), 18.60 (Me, C-12), 82.04 (C, C-13), 24.43 (Me, C-14), 30.62 (Me, C-15), 170.42, 169.75, 169.63, 165.51, 165.35 (5C, carbonyl), aroma-

tic C 133.18 (CH), 129.57 (C), 129.40 (CH), 128.56 (CH), 153.75 (CH), 150.96 (CH), 137.15 (CH), 125.75 (C), 123.73 (CH). Chemical shifts denoted by the superscript letter a can be interchanged.

DETERMINATION OF THE CRYSTAL STRUCTURE OF [1]¹.—Crystal data: orthorhombic, space group $P2_12_12_1$, $a = 10.479(1)$, $b = 12.438(1)$, $c = 27.195(3)$ Å, $V = 3544.5(5)$ Å³, $Z = 4$, $D_c = 1.259$ g·cm⁻³, $\lambda = 1.5411$ Å (Cu K α), $\mu_{K\alpha} = 7.746$ cm⁻¹, $F(000) = 712$, room temperature, $R = 0.050$, $R_w = 0.051$, 2749 observed reflections ($I > 3.0\sigma_I$). The data were collected on a ENRAF-NONIUS CAD 4 four circle diffractometer. All calculations were performed on a PDP-11 computer using SDP software (Non-

ius, 1982). A single crystal of **1** was obtained by recrystallization from Me₂CO.

LITERATURE CITED

1. R. Brening and H. Wagner, *Phytochemistry*, **17**, 1821 (1978).
2. J.K. Liu, Z.J. Jia, D.G. Wu, J. Zhou, and Q.G. Wang, *Phytochemistry*, **29**, 2503 (1990).
3. J.K. Liu, X.W. Han, Z.J. Jia, Y. Ju, and H.Q. Wang, *Phytochemistry*, **30**, 3437 (1991).
4. Z.G. Ke, L.M. Lu, and Y.S. Nan, *Acta Phytophylacica Sin.*, **12**, 283 (1985).

Received 22 November 1991

¹Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.