

Alkaloids from *Celastrus angulatus*

Y. Q. Tu, G. S. Huang, Y. X. Ma, X. L. Wu, and Q. B. Song

J. Nat. Prod., **1992**, 55 (9), 1320-1322 • DOI:
10.1021/np50087a024 • 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/np50087a024> 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

ALKALOIDS FROM *CELASTRUS ANGULATUS*

Y.Q. TU,* G.S. HUANG, Y.X. MA, X.L. WU, and Q.B. SONG

Department of Chemistry, Lanzhou University, Lanzhou, Gansu Province, People's Republic of China

ABSTRACT.—Four new β -dihydroagarofuran alkaloids were isolated from the seed oil of *Celastrus angulatus*. Their structures have been elucidated on the basis of spectrometry.

Celastrus angulatus Max. (Celastraceae) is widely distributed in China and has long been used in China as a natural insecticide to protect plants from insect damage (1). A previous study of the chemical constituents dealt with the isolation from the root bark of antifeedants, which belonged to the β -dihydroagarofuran polyol ester group (2). Recent investigations have shown that the seed oil also contains this kind of compound, and in this paper we report the structure elucidation of four major new alkaloids. The compounds of the β -dihydroagarofuran type were described by Wagner *et al.* as early as 1975 (3).

RESULTS AND DISCUSSION

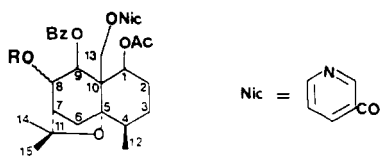
The pulverized seed of *C. angulatus* was extracted with petroleum ether to give seed oil, which was re-extracted with MeOH to obtain the crude sesquiterpene mixture. This was chromatographed on a Si gel column and then on a reversed-phase column to yield successively compounds 1–4.

Compound 1 analyzed for $C_{30}H_{35}NO_8$ by hrms. The mass spectrum exhibited peaks corresponding to acetyl (m/z 43,

40%), benzoyl (m/z 105, 100%), and nicotinoyl (m/z , 106, 75%) functions. Furthermore, the 1H -nmr and ^{13}C -nmr spectral data indicated the presence of one acetate ester, one benzoate ester, one nicotinate ester, and a 1,8,9,13-tetra-substituted β -dihydroagarofuran skeleton (4). In addition, the molecular composition suggested the presence of one free hydroxy group. Generally, H-1 in this class of compounds has an axial configuration (5). The coupling constant ($J_{8,9} = 9.2$ Hz) between H-8 and H-9 suggested that both H-8 and H-9 had axial stereochemistry. The ester distribution was determined on the basis of the 1H - ^{13}C long-range correlation (COLOC) spectrum (6), which indicated that the esters at C-1, C-9, and C-13 were acetate, benzoate, and nicotinate, respectively, and that the free hydroxy group was thus located at C-8. Therefore, the structure of 1 was elucidated as 1 β -acetoxy-9 β -benzoyloxy-8 α -hydroxy-13-nicotinoyloxy- β -dihydroagarofuran.

Compound 2 analyzed for $C_{35}H_{43}NO_9$ by hrms. The spectral data suggested the presence of one acetate ester, one benzoate ester, one α -methylbutanoate ester, one nicotinate ester, and the 1,8,9,13-tetrasubstituted β -dihydroagarofuran skeleton. The COLOC spectrum suggested the esters at C-1, C-9, and C-13 were acetate, benzoate, and nicotinate, respectively. Therefore, the remaining α -methylbutanoate ester was located at C-8, and the structure of 2 was elucidated as 1 β -acetoxy-9 β -benzoyloxy-8 α (α -methylbutanoyloxy)-13-nicotinoyloxy- β -dihydroagarofuran.

Compound 3 analyzed for $C_{34}H_{41}NO_9$ by hrms. The spectral data suggested the



- 1 R = α -OH
- 2 R = α -COCH(CH₂CH₃)CH₃
- 3 R = α -COCH(CH₃)CH₃
- 4 R = β -Bz

TABLE 1. ^1H -nmr Spectral Data of **1-4** (400 MHz, CDCl_3 , TMS).^a

Proton	Compound			
	1	2	3	4
H-1	5.34 dd (3.6, 12)	5.40 dd (4, 12)	5.40 dd (4, 11.8)	5.48 dd (4, 12)
H-4	1.37–2.53 m	1.38–2.64 m	1.42–2.65 m	1.46–2.72 m
H-8	4.22 dd (4.4, 9.2)	5.63 dd (3.3, 9.8)	5.64 dd (3.4, 9.8)	5.72 dd (3.7, 5.2)
H-9	5.81 d (9.2)	6.05 d (9.8)	6.04 d (9.8)	5.81 d (5.2)
H-12	1.08 d (7.7)	1.12 d (7.8)	1.13 d (8)	1.20 d (8)
H-13	4.73, 5.10 ABq (13)	4.91 brs	4.92 brs	5.08, 5.37 ABq (13)
H-14	1.56 s	1.54 s	1.57 s	1.59 s
H-15	1.15 s	1.19 s	1.17 s	1.24 s

^aCoupling constants are in parentheses.

presence of one acetate ester, one benzoate ester, one isobutanoate ester, one nicotinate ester, and the 1,8,9,13-tetra-substituted β -dihydroagarofuran skeleton. By a careful comparison of **3** with **2**, it could be established that these two compounds possessed very similar ^1H -nmr (Table 1) and ^{13}C -nmr (Table 2) data, which indicated the esters at C-1, C-9, and C-13 in **3** were the same as those of **2**, and the ester at C-8 was isobutanoate. Thus, the structure assigned to **3** is 1 β -acetoxy-9 β -benzoyloxy-8 α -isobutanoyloxy-13-nicotinoyloxy- β -dihydroagarofuran.

Compound **4** analyzed for $\text{C}_{37}\text{H}_{39}\text{NO}_9$ by hrms. The spectral data pointed to the presence of one acetate ester, two benzoate esters, one nicotinate ester, and the 1,8,9,13-tetra-substituted β -dihydroagarofuran skeleton. The qualitative nOe difference experiment suggested H-8 had equatorial and H-9 axial stereochemistry. The COLOC spectrum indicated that the acetate ester was located at C-1, the two benzoate esters at C-8 and C-9, and the nicotinate at C-9. Hence the structure of **4** was elucidated as 1 β -acetoxy-8 β ,9 β -dibenzoyloxy-13-nicotinoyloxy- β -dihydroagarofuran.

TABLE 2. ^{13}C -nmr Chemical Shifts of **1-4** (100 MHz, CDCl_3 , TMS).^a

Carbon	Compound			
	1	2	3	4
C-1 ^b	75.5	74.9	75.1	71.3
C-2	22.9	22.7	22.8	23.6
C-3	26.5	26.4	26.5	27.2
C-4	39.7	39.7	39.7	39.9
C-5	88.6	88.0	88.1	88.3
C-6	36.5	36.4	36.5	32.0
C-7	49.4	47.2	47.3	47.8
C-8 ^b	78.5	75.8	76.1	74.4
C-9 ^b	80.0	78.2	78.3	78.9
C-10	50.1	50.0	50.1	50.1
C-11	81.9	81.6	81.7	81.0
C-12	16.9	17.0	17.0	17.0
C-13	62.9	62.9	63.0	62.9
C-14	24.7	24.4	24.5	22.9
C-15	31.0	30.6	30.7	29.8

^aAssignments of ^{13}C -nmr chemical shifts were made with the aid of DEPT spectra.

^bData in the same column may be exchangeable.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—¹H-nmr, ¹³C-nmr DEPT, nOe difference, and COLOC spectra were obtained on a Bruker AM-400 nmr spectrometer. Eims were obtained on a VG ZAB-HS instrument operating at 70 eV ionizing energy. Rotation data were recorded on a J-20C instrument. Plant material was collected from Guizhou Province, China. Voucher specimens were deposited at the Biology Department, Lanzhou University.

COMPOUND 1.—Compound 1 was obtained as an amorphous white powder: $[\alpha]^{23}_D +47.6^\circ$ ($c=0.500$, CHCl₃); eims m/z (rel. int.) [M]⁺ 537 (15), 477 (5), 415 (57), 387 (12), 372 (5), 355 (6), 327 (6), 312 (8), 163 (15), 137 (64), 124 (88), 106 (75), [PhCO]⁺ 105 (100), 77 (41), 43 (40); hrms m/z 537.2361 (calcd for C₃₈H₃₅NO₈, 537.2353); ¹H nmr see Table 1; ¹³C nmr see Table 2.

COMPOUND 2.—Compound 2 was obtained as an amorphous white powder: $[\alpha]^{23}_D +44.4^\circ$ ($c=0.495$, CHCl₃); eims m/z (rel. int.) [M + H]⁺ 622 (30), 576 (60), 561 (8), 537 (9), 501 (15), 464 (11), 356 (12), 239 (21), [PhCO]⁺ 105 (100), 77 (53), 43 (41); hrms m/z 622.3018 (calcd for C₃₅H₄₄NO₉, 622.3004); ¹H nmr see Table 1; ¹³C nmr see Table 2.

Compound 3.—Compound 3 was obtained as an amorphous white powder: $[\alpha]^{23}_D +49.9^\circ$ ($c=0.505$, CHCl₃); eims m/z (rel. int.) [M]⁺ 607 (55), 547 (5), 537 (11), 536 (5), 487 (37), 414

(5), 356 (13), 137 (29), 124 (35), 106 (31), [PhCO]⁺ 105 (100), 78 (11), 77 (21), 71 (25), 43 (53); hrms m/z 607.2795 (calcd for C₃₄H₄₁NO₉, 607.2770); ¹H nmr see Table 2; ¹³C nmr see Table 2.

COMPOUND 4.—Compound 4 was obtained as an amorphous white powder: $[\alpha]^{23}_D -102^\circ$ ($c=0.530$, CHCl₃); hrms m/z (rel. int.) [M + H]⁺ 642 (22), 521 (20), 520 (8), 461 (2), 137 (30), 124 (18), [PhCO]⁺ 105 (100), 77 (27); hrms m/z 642.2715 (calcd for C₃₇H₄₀NO₉, 642.2692); ¹H nmr see Table 1; ¹³C nmr see Table 2.

LITERATURE CITED

1. M. Jacobson, "Insecticides from Plants, A Review of the Literature, 1941-1953," Agricultural Handbook No. 154, USDA, U.S. Government Printing Office, Washington, DC, 1958, p. 44.
2. N. Wakabayashi, W.J. Wu, R.M. Waters, R.E. Redfern, G.D. Mills Jr., A.B. DeMilo, W.R. Lusby, and D. Andrzejewski, *J. Nat. Prod.*, **51**, 537 (1988).
3. H. Wagner, E. Heckel, and J. Sonnenbichler, *Tetrahedron*, **31**, 1949 (1975).
4. H.J. Den Hertog Jr., D. Kruk, D.D. Nanavati, and Sukh Dev, *Tetrahedron Lett.*, 2219 (1974).
5. R. Bruning and H. Wagner, *Phytochemistry*, **17**, 1821 (1978).
6. H. Sang, H.Q. Wang, Y.Q. Tu, and Y.Z. Chen, *Magn. Reson. Chem.*, **29**, 650 (1991).

Received 10 February 1992