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# Novel Antiinsectan Oxalicine Alkaloids from Two Undescribed Fungicolous *Penicillium* spp.

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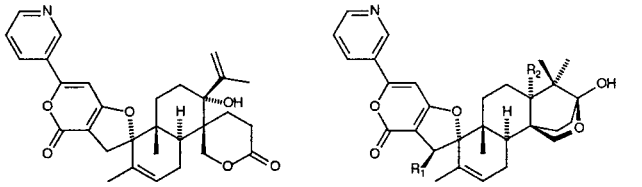
## ABSTRACT



**1** **2**: $R_1$ = H, $R_2$ = OH **3**: $R_1$ = OH, $R_2$ = H

**15-Deoxyoxalicine B (1) and decaturins A (2) and B (3) have been isolated from *Penicillium decaturense* and *Penicillium thiersii*, two previously undescribed species obtained as colonists of wood-decay fungi. The structures were determined by 2D NMR experiments and/or single-crystal X-ray diffraction analysis. These compounds are members of a rare structural class, and decaturins A and B feature a new polycyclic ring system. Decaturin B (3) exhibited potent antiinsectan activity against the fall armyworm (*Spodoptera frugiperda*).**

Our ongoing studies of mycoparasitic and fungicolous fungal isolates as sources of bioactive natural products[1−6] have recently led to the identification of a large group of previously undescribed *Penicillium* spp. Chemical investigations of some of these isolates are beginning to afford new bioactive secondary metabolites. In this paper, we describe the isolation and structure determination of three new antiinsectan alkaloids (15-deoxyoxalicine B, **1**; decaturin A, **2**; and decaturin B, **3**) that we have obtained from two new species, *Penicillium decaturense*[7] and *Penicillium thiersii*.[8]

Bioassay-guided fractionation of the antiinsectan EtOAc extract from *P. decaturense* cultures on Sephadex LH-20, followed by purification using reversed-phase HPLC, afforded compounds **1**[9] and **2**.[10] HRESIMS, $^{13}$C NMR, and HMQC data for **1** revealed that it has the molecular formula $C_{30}H_{33}NO_6$ (15 unsaturations) and contains one exchangeable proton. The $^{1}$H and $^{13}$C NMR data (Table 1) indicated the presence of a 3-substituted pyridine moiety, two trisubstituted olefins, a terminal olefin, an isolated oxymethylene unit, two carboxyl groups, an isolated methylene unit attached to an olefin or a carbonyl, and three methyl groups. Analysis of these data suggested that compound **1** is closely related to the known compounds oxalicines A (**4**)[11] and B (**5**).[12] These compounds (**4** and **5**) were originally isolated from *P. oxalicum*, but only oxalicine A (**4**) has been previously reported in the primary literature. The NMR data for

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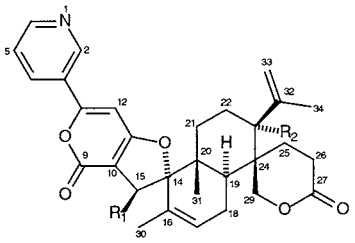
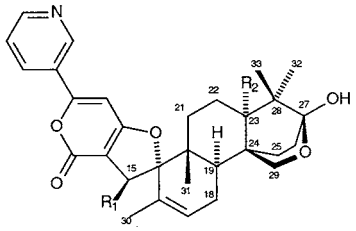


**1**: $R_1$ = H, $R_2$ = OH

**4**: $R_1$ = OH, $R_2$ = H

**5**: $R_1$ = OH, $R_2$ = OH



**2**: $R_1$ = H, $R_2$ = OH

**3**: $R_1$ = OH, $R_2$ = H

compound **1** were similar to the partial set of data reported for oxalicine A,[11] except that an oxygenated methine and an allylic methine present in oxalicine A were replaced by an oxygenated quaternary carbon ($\delta_c$ 76.3) and an isolated methylene group ($\delta_H$ 2.97, d, 16 Hz; 3.10, d, 16 Hz) in **1**. These differences implied that the C-15 hydroxyl group in oxalicine A is absent, while a new hydroxyl group is present at C-23 in compound **1**. Analysis of COSY and HMBC data (Table 2) confirmed the structure as shown in **1**. Given the similarity to the two previously reported oxalicines, the name 15-deoxyoxalicine B is proposed for **1**.

The relative stereochemistry of **1** was determined by analysis of $^1$H NMR *J* values and NOESY data. The signal for $H_3$-31 showed NOESY correlations to $H_2$-15 and $H_2$-29. These data required $CH_3$-31 and $CH_2$-29 to have a cis-1,3-diaxial relationship with respect to the cyclohexane ring and revealed that $CH_3$-31 and $CH_2$-15 occupy the same face of the cyclohexene ring. A NOESY correlation of methine proton H-19 with H-25a and a trans-diaxial (11 Hz) coupling with the pseudoaxial proton on C-18 indicated that H-19 adopts an axial orientation. These data require a trans ring fusion of the cyclohexane and cyclohexene rings. NOESY correlations of $H_3$-34 with both H-26a and H-29b require that the isopropenyl group adopt an equatorial orientation. Thus, the relative stereochemistry of 15-deoxyoxalicine B was assigned as shown in **1** and is consistent with the relevant features of the stereochemistry originally assigned for oxalicine A (**4**) by X-ray crystallography.[11]

HRESIMS analysis of decaturin A (**2**) indicated that it has the molecular formula $C_{30}H_{35}NO_6$ (14 unsaturations), differing from 15-deoxyoxalicine B (**1**) by the addition of two hydrogen atoms. The $^1$H and $^{13}$C NMR spectra of compound **2** were similar to those of **1**, except that the signals for the propenyl group and the lactone carbonyl of **1** were replaced by two nonvinylic methyl singlets, along with additional aliphatic and doubly oxygenated quaternary carbons ($\delta_C$ 46.3, 98.1).

The differences between structures **1** and **2** were established by analysis of HMBC and COSY data. The signals for $CH_3$-32 and $CH_3$-33 each showed reciprocal HMBC correlations, as well as correlations with quaternary carbon C-28, oxygenated quaternary carbon C-23, and doubly oxygenated quaternary carbon C-27. HMBC correlations of isolated oxygenated methylene protons $H_2$-29 with C-23, C-27, and quaternary carbon C-24 permitted extension of this substructure to form a tetrahydropyran ring. A significant four-bond $^1$H−$^1$H coupling was observed between H-29b and one of the C-25 protons in **2** (and in **3**) that was not observed for **1**, suggesting additional rigidity in the ring system. The

(7) This culture was determined by Dr. S. W. Peterson of the USDA National Center for Agricultural Utilization Research (NCAUR) in Peoria, IL, to be a previously undescribed species and was assigned the name *Penicillium decaturense* (MYC 505 = NRRL 28152). Subcultures have been deposited in the Agricultural Research Service (ARS) collection at the NCAUR. The strain of *P. decaturense* was originally isolated from an overwintered resupinate basidioma of an unidentified polypore that had formed on a dead hardwood log at Ramsey Lake State Park, Decatur, IL, by Dr. H. D. Thiers on August 12, 1996. The culture was grown by solid-substrate fermentation on rice (carried out in eight 500-mL Erlenmeyer flasks, each containing 50 g of rice). The fermented material was extracted with EtOAc. The EtOAc extract (458 mg) was solvent-partitioned between $CH_3CN$ (60 mL) and hexane (3 × 20 mL). The $CH_3CN$ fraction (340 mg) was separated using column chromatography over a prepacked Sephadex LH-20 column (30 g). Eleven fractions were collected by eluting with a standard step gradient (from 20% hexane in $CH_2Cl_2$ to 20% acetone in $CH_2Cl_2$ to 40% acetone in $CH_2Cl_2$ to 60% acetone in $CH_2Cl_2$ to 80% acetone in $CH_2Cl_2$ to 100% acetone to 100% MeOH). Fraction 2 (46 mg; eluted with 20% hexane in $CH_2Cl_2$) was further purified using reversed phase HPLC (Alltech HS Hyperprep 100 BDS $C_{18}$ column, 8-$\mu$m particles, 1 × 25 cm; flow rate 1.8 mL/min; gradient from 10 to 54% $CH_3CN$ in $H_2O$ over 10 min, then from 54 to 64% $CH_3CN$ in $H_2O$ over 10 min, then from 54 to 64% $CH_3CN$ in $H_2O$ over 30 min, and finally a gradient from 64 to 100% $CH_3CN$ in $H_2O$ over 4 min; monitored by UV absorption at 215 nm) to yield decaturin A (**2**; 3 mg, $t_R$ 16 min) and 15-deoxyoxalicine B (**1**; 5 mg, $t_R$ 22 min).

(8) The culture of *P. thiersii* was originally isolated from an old stroma of *Hypoxylon* sp. found at New Glaurus Woods State Park, near New Glaurus, WI, by Dr. H. D. Thiers on August 21, 1996. This isolate was determined to be a new species and was assigned the name *P. thiersii* (MYC 500 = NRRL 28147) by Dr. S. W. Peterson. The crude EtOAc extract obtained from solid-substrate fermentation cultures (3.6 g; derived from eight 500-mL Erlenmeyer flasks, each containing 50 g of rice) was partitioned between $CH_3CN$ and hexane. The $CH_3CN$-soluble portion (2.3 g) was subjected to Sephadex LH-20 column chromatography using the hexane−$CH_2Cl_2$−acetone solvent gradient as described above to yield eleven fractions. The eleventh fraction (83 mg) was subjected to HPLC (same column as above; flow rate 2.0 mL/min; gradient from 50 to 70% $CH_3CN$ in $H_2O$ over 20 min) to yield decaturin B (**3**; 6.5 mg, $t_R$ 10.8 min).

(9) Data for 15-deoxyoxalicine B (**1**): colorless crystals from $CH_3CN$/$H_2O$; mp 165−167 °C; $[\alpha]_D$ + 34 (*c* 1.0 mg/mL, $CH_2Cl_2$); UV (MeOH) $\lambda_{max}$ 205 ($\epsilon$ 16 000), 235 (14 000), 335 nm (5600); IR ($CH_2Cl_2$) $\gamma_{max}$ 3463, 2959, 2935, 2846, 2349, 2323, 1726, 1633, 1567 cm$^{-1}$; $^1$H and $^{13}$C NMR data, see Table 1; HMBC and NOESY data, see Table 2; EIMS (70 eV) obsd *m/z* 503 ($M^+$, rel int. 5), 406 (12), 267 (15), 202 (54), 157 (20), 148 (41), 119 (24), 106 (48), 97 (40), 69 (100), 55 (85); HRESIMS (4000v; PEG.; MeOH/$H_2O$/1% formic acid) obsd $(M + H)^+$ at *m/z* 504.2393, calcd for $C_{30}H_{34}NO_6$ 504.2386.

(10) Data for decaturin A (**2**): colorless crystals from $CH_3CN/H_2O$; mp 160−162 °C; $[\alpha]_D$ +32 (*c* 0.5 mg/mL, $CH_2Cl_2$); UV (MeOH) $\lambda_{max}$ 205 ($\epsilon$ 16 000), 235 (16 000), 335 nm (5800); IR ($CH_2Cl_2$) $\gamma_{max}$ 3423, 2919, 2853, 1706, 1627 cm$^{-1}$; $^1$H and $^{13}$C NMR data, see Table 1; HMBC and NOESY data, see Table 2; EIMS (70 eV) obsd *m/z* 505 ($M^+$, rel int 17), 487 (28), 475 (35), 299 (20), 255 (25), 202 (85), 148 (75), 106 (82), 43 (100); HRESIMS obsd $(M + H)^+$ at *m/z* 506.2547, calcd for $C_{30}H_{36}NO_6$ 506.2543.

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**Table 1.** $^1$H and $^{13}$C NMR Data for Compounds **1**−**3** in $CDCl_3$[a]

| | 15-deoxyoxalicine B (**1**) | | decaturin A (**2**) | | decaturin B (**3**) | |
|---|---|---|---|---|---|---|
| position | $\delta_C$[b] | $\delta_H$[c] (mult; *J*, Hz) | $\delta_C$[b] | $\delta_H$[c] (mult; *J*, Hz) | $\delta_C$[b] | $\delta_H$[c] (mult; *J*, Hz) |
| 2 | 146.9 | 9.00 (brs) | 146.9 | 9.00 (brs) | 147.1 | 9.01 (d, 1.5) |
| 3 | 127.4[d] | | 128.3[e] | | 127.4 | |
| 4 | 133.2 | 8.11 (dt; 8.1, 1.8) | 133.2 | 8.12 (dt; 8.1, 1.8) | 133.4 | 8.12 (dt; 8.1, 1.5) |
| 5 | 123.7 | 7.39 (dd; .1, 4.8) | 123.7 | 7.41 (dd; 8.1, 4.8) | 123.7 | 7.40 (dd; 8.4, 4.8) |
| 6 | 151.5 | 8.67 (brd; 4.8)[f] | 151.5 | 8.68 (brd; 4.8) | 151.9 | 8.69 (dd; 4.8, 1.5) |
| 7 | 160.7 | | 160.2 | | 161.8 | |
| 9 | 170.2 | | 170.2 | | 170.6 | |
| 10 | 101.9 | | 102.0 | | 105.8 | |
| 11 | 160.3 | | 160.8 | | 160.3 | |
| 12 | 93.7 | 6.63 (s) | 93.7 | 6.62 (s) | 93.9 | 6.65 (s) |
| 14 | 100.1 | | 100.2 | | 101.2 | |
| 15a | 28.4 | 2.97 (d; 16) | 28.3 | 2.95 (d; 16) | 74.2 | 5.46 (brs) |
| 15b | | 3.10 (d; 16) | | 3.08 (d; 16) | | |
| 16 | 131.7 | | 131.4 | | 130.7 | |
| 17 | 127.4[d] | 5.72 (brs) | 128.3[e] | 5.72 (brd; 6.0) | 130.9 | 5.77 (brd; 6.0) |
| 18a | 24.3 | 2.22 (m) | 23.1 | 1.88 (m) | 23.6 | 1.90 (m) |
| 18b | | 2.22 (m) | | 2.05 (m) | | 2.09 (dt; 18, 4.0) |
| 19 | 42.0 | 2.67 (dd; 11, 6.2) | 38.2 | 2.25 (dd; 13, 4.8) | 43.8 | 2.60 (brdd; 13, 4) |
| 20 | 40.3 | | 40.0 | | 40.8 | |
| 21eq | 24.8 | 1.52 (dt; 14, 3.7) | 25.0 | 1.29 (dt; 14, 4) | 30.4 | 1.49 (m) |
| 21ax | | 2.33 (m) | | 1.83 (td; 14, 4) | | 1.59 (m) |
| 22eq | 29.1 | 1.39 (dt; 13, 4) | 26.0 | 1.48 (dt; 15, 4) | 19.1 | 1.51 (m) |
| 22ax | | 2.05 (ddd; 13, 13, 4) | | 2.11 (ddd; 15, 14, 4) | | 1.73 (m) |
| 23 | 76.3 | | 75.0 | | 49.8 | 1.32 (brd; 13) |
| 24 | 44.1 | | 39.6 | | 35.4 | |
| 25a | 25.8 | 1.65 (m) | 28.7 | 1.73 (m) | 34.6 | 1.28 (m) |
| 25b | | 2.49 (ddd; 4, 14, 4.9) | | 1.93 (m) | | 2.17 (m) |
| 26a | 29.8 | 2.38 (m) | 29.4 | 1.66 (m) | | 29.5, 1.73 (dd; 13, 4.0) |
| 26b | | 2.43 (ddd; 14, 4.9, 3.8) | | 2.22 (m) | | 2.17 (m) |
| 27 | 173.3 | | 98.1 | | 98.0 | |
| 28 | | | 46.3 | | 40.2 | |
| 29a | 67.5 | 4.37 (d; 13) | 67.7 | 3.91 (d; 9.6) | 67.8 | 3.88 (dd; 9.6, 1.5) |
| 29b | | 4.43 (d; 13) | | 4.18 (dd; 9.6, 2.4) | | 4.25 (dd; 9.6, 2.4) |
| 30 | 18.4 | 1.70 (s) | 18.4 | 1.67(s) | 19.3 | 1.54 (s) |
| 31 | 15.9 | 0.92 (s) | 15.7 | 0.87(s) | 16.1 | 1.20 (s) |
| 32 | 150.5 | | 19.2 | 1.01(s) | 27.2 | 1.02 (s) |
| 33a[g] | 115.2 | 5.07 (s) | 20.6 | 1.09(s) | 18.2 | 0.97 (s) |
| 33b | | 5.17 (s) | | | | |
| 34 | 21.6 | 1.87 (s) | | | | |

[a] Compounds **2** and **3** contain a ring system different from that in **1**, but a numbering scheme was chosen to retain most of the same numbers as in **1**; only atoms 28, 32, 33, and 34 are assigned differently. [b] 100 MHz. [c] 600 MHz. [d,e] These $^{13}$C NMR signals were fortuitously coincident. [f] The signals for H-2 and H-6 showed broadened lines in some NMR samples. [g] This entry refers to position 33 for compounds **2** and **3**.

signals for $H_2$-26 of the isolated C25−C26 ethylene unit correlated to C-24, C-25, C-27, and C-28, while methylene protons $H_2$-25 correlated to C-24. These data required the ethylene unit to form a bridge between C-24 and C-27, and additional HMBC correlations supported this assignment. Thus, the structure of this compound was determined as shown in **2**. Although it is structurally related to **1**, compound **2** could not be readily named as a derivative of oxalicine A or B, and was assigned the name decaturin A.

The relative stereochemistry of decaturin A (**2**) was elucidated by analysis of $^1$H NMR *J* values and NOESY data and by analogy to 15-deoxyoxalicine B (**1**). As was the case for **1**, a large NMR *J* value (13 Hz) between H-19 and pseudoaxial proton H-18, NOESY correlations of $H_3$-31 with $H_2$-15 and H-29b, and correlation of H-19 with H-25a led to recognition that H-19, $CH_3$-31, and $CH_2$-29 all adopt axial orientations with respect to the central cyclohexane ring and that $CH_3$-31 and $CH_2$-15 are cis to each other with respect to the cyclohexene ring. The signal for $H_3$-33 showed NOESY correlations with H-22ax and H-29b, while the signal for $H_3$-32 showed NOESY correlations with H-26b and H-22eq. These data require decaturin A to have the relative configuration shown in **2**.

Chemical investigation of another new *Penicillium* species (*P. thiersii*)[6] led to the discovery of a third isomeric metabolite (decaturin B; **3**)[13] having NMR and MS data that were nearly identical to those of decaturin A. The major difference in the $^1$H NMR spectrum of **3** was that the signals for $H_2$-15 in the spectrum of decaturin A (**2**) were replaced by a broad oxymethine singlet at $\delta$ 5.46. These data suggested that **3** differs from **2** only in the position of the nonhemiacetal OH group, by analogy to the difference

**Table 2.** HMBC and NOESY Data[a] for 15-Deoxyoxalicine B (**1**) and Decaturin A (**2**) in $CDCl_3$.

| | 15-deoxyoxalicine B (**1**) | | decaturin A (**2**) | |
|---|---|---|---|---|
| pos. (H#) | HMBC(H→C) | NOESY | HMBC(H→C) | NOESY |
| 2 | | 12 | 3, 4, 6, 7 | 12 |
| 3 | | | | |
| 4 | 2, 6, 7 | 5, 12 | 2, 6, 7 | 5, 12 |
| 5 | | 4, 6 | 3, 6 | 4, 6 |
| 6 | | | 2, 4, 5 | 5 |
| 7 | | | | |
| 9 | | | | |
| 10 | | | | |
| 11 | | | | |
| 12 | 3, 7, 9, 10, 11 | 2, 4 | 3, 7, 9, 10 | |
| 14 | | | | 2, 4 |
| 15a | 9, 10, 16 | 30, 31 | 9, 10, 14, 16, 20 | 30, 31 |
| 15b | 9, 10, 14, 16, 20 | 22eq, 31 | 9, 10, 14, 16, 20 | 21eq, 31 |
| 16 | | | | |
| 17 | | 18, 19, 30 | 14, 17, 19, 30 | 18a,b, 30 |
| 18a | | | | 17, 22ax, 29a,b, 31 |
| 18b | | | | 17, 29a |
| 19 | 20, 21, 24, 31 | 17, 18, 25a | 14, 18, 24, 25, 29, 31 | 25a |
| 20 | | | | |
| 21eq | | 31, 34 | | 15a,b, 21ax, 22eq, 31 |
| 21ax | | | | 21eq |
| 22eq | | 15b, 22ax | 21, 23 | 21eq, 22ax, 33 |
| 22ax | | 22eq | 21 | 18a, 22eq, 29a, 31, 34 |
| 23 | | | | |
| 24 | | | | |
| 25a | | 18a,b, 19 | | 19 |
| 25b | 24 | 33b | 24 | 19 |
| 26a | | 34 | 24, 25, 27, 28 | 25a,b, 33 |
| 26b | 27 | 29a,b, 34 | 24, 25 | 25a,b, 33 |
| 27 | | | | |
| 28 | | | | |
| 29a | 23 | 18a,b, 26b, 29b, 31, 34 | 23, 24, 25, 27 | 18a,b, 29b |
| 29b | 23, 25, 27 | 26b, 29a, 31, 34 | 23, 25 | 22ax, 29a, 31, 32 |
| 30 | 14, 16, 17 | 15a, 17 | 14, 16, 17 | 15a, 17 |
| 31 | 14, 19, 20, 21 | 15a,b, 18a,b, 21eq, 29a,b | 14, 19, 20, 21 | 15a,b, 18a, 21eq, 22ax, 29b |
| 32 | | | 23, 27, 28, 33 | 22eq, 26b |
| 33a[b] | 23, 32, 34 | 34 | 23, 27, 28, 32 | 22ax, 29b |
| 33b | | 25b | | |
| 34 | 23, 32, 33 | 26a, 29b, 33a | | |

[a] Data were recorded at 600 MHz ($^1$H dimension). [b] Refers to $H_3$-33 for compound **2**.

between oxalicine A (**4**) and 15-deoxyoxalicine B (**1**). Ultimately, the structure of **3** was determined by single-crystal X-ray diffraction analysis.[14] Given its similarity to the structure of decaturin A (**2**), it was assigned the name decaturin B. The final X-ray crystallographic model of decaturin B (**3**) (Figure 1) revealed its structure and relative stereochemistry and indirectly supported the structural assignment of decaturin A.

Compounds **1**−**3** are new members of a rare skeletal class, and the polycyclic ring system found in decaturins A and B (**2** and **3**) has not been previously described. Oxalicines A (**4**) and B (**5**) are the only close known analogues.[11,12] The

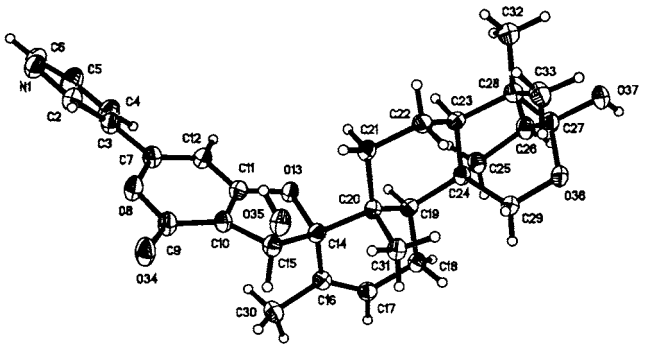


**Figure 1.** X-ray model of decaturin B (**3**).

oxalicines and the decaturins are biogenetically related to the pyripyropenes, which have been reported from *Aspergillus fumigatus* as highly potent inhibitors of acyl-CoA cholesterol acyltransterase (ACAT).[15]

Compounds **1**−**3** exhibited antiinsectan activity in dietary assays[16] against the fall armyworm (*Spodoptera frugiperda*). 15-Deoxyoxalicine B (**1**) caused 23% reduction in growth rate relative to controls (RGR) when tested at the 140 ppm dietary level, while decaturin A (**2**) showed 31% RGR at 100 ppm. Interestingly, despite the structural similarities, decaturin B (**3**) showed significantly more potent activity in this assay, causing 89% RGR at the 100 ppm dietary level.

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**Supporting Information Available:** $^1$H and $^{13}$C NMR spectra for 15-deoxyoxalicine B (**1**) and decaturin B (**3**) and X-ray crystallographic data for decaturin B (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Data for decaturin B (**3**): colorless crystals from $CH_2Cl_2$; mp 235−237 °C; $[\alpha]_D$ +124 (*c* 0.2, $CH_2Cl_2$); UV (MeOH) $\lambda_{max}$ 233 ($\epsilon$ 19 000), 270 ($\epsilon$ 7800), 317 ($\epsilon$ 5500); IR ($CH_2Cl_2$) $\gamma_{max}$ 3397, 2949, 2853, 1716, 1645, 1567 cm$^{-1}$; $^1$H and $^{13}$C NMR data, see Table 1; EIMS (70 eV) obsd *m*/*z* 505 ($M^+$, rel int 24), 487 (15), 472 (12), 322 (11), 304 (10), 216 (19), 202 (26), 173 (37), 148 (72), 106 (86); HRESIMS obsd $(M + H)^+$ at *m*/*z* 506.2554, calcd for $C_{30}H_{36}NO_6$, 506.2543.

(14) Data were collected using a colorless blade of **3** (0.57 × 0.14 × 0.05 mm) with a Nonius Kappa CCD diffractometer (Mo K$\alpha$ radiation, graphite monochromator) at 190 K (cold $N_2$ gas cooling). Standard CCD techniques were used, yielding 23945 data. Lorentz and polarization corrections were applied. A multiscan absorption correction was also applied. Equivalent data were averaged yielding 2358 unique data (R-int = 0.068, 1946 > 4$\sigma$(*F*)). Based on preliminary examination of the data, the space group *P*2(1) was assigned (no significant exceptions to the 0*k*0, *k* = odd; systematic absence was noted). Computer programs from the HKLint package were used for data reduction. The preliminary model of the structure was obtained using XS, a direct methods program. Least-squares refining of the model vs the data was accomplished with the XL computer program. Illustrations were drawn with the XP program, and tables were constructed with the XCIF program. All are in the SHELXTL v5.1 package. Thermal ellipsoids are drawn at the 35% level unless otherwise noted. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included with a riding model using default values. Crystallographic data for compound **3** have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 198186).

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