Azadirachtin Derivatives from Seed Kernels of *Azadirachta excelsa*

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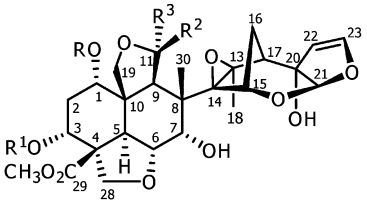
Three new azadirachtin derivatives, named azadirachtins O−Q (**1**−**3**), along with the known azadirachtin B (**4**), azadirachtin L (**5**), azadirachtin M (**6**) 11α-azadirachtin H (**7**), 11*β*-azadirachtin H (**8**), and azadirachtol (**9**) were isolated from seed kernels of *Azadirachta excelsa*. Their structures were established by spectroscopic techniques, and the structure of **3** was confirmed by X-ray analysis. Compounds **1**−**7** and **9** exhibited toxicity to the diamondback moth (*Plutella xylostella*) with an LD_{50} of 0.75−1.92 *μ*g/g body weight, in 92 h.

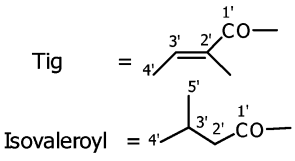
The genus *Azadirachta* (Meliaceae), which occurs in the tropics, contains only three species, *Azadirachta indica* A. Juss, *A. siamensis* Valeton, and *A. excelsa* (Jack) Jacobs. Thailand seems to be the only country in which all three species exist. The Indian neem tree (*A. indica*) grows mainly in the coastal area, and Thai neem (*A. siamensis*) grows widely in all parts of Thailand.[1] *A. excelsa* is found in the southern part of Thailand, and its local name is "Tiam" or "Sadao chang".[1] The Indian neem tree has been investigated intensively worldwide during the last three decades. More than 200 compounds have been isolated from various parts of this tree, and one-third of these are tetranortriterpenoids (limonoids). The active limonoid principle, azadirachtin A, has been known since 1968,[2] but its correct structure was reported nearly 20 years later.[3,4] The other structurally related compounds azadirachtins B−G,[5−8] azadirachtins H and I,[9,10] azadirachtins J and K,[11,12] and azadirachtin N[13] have also been found in *A. indica*. The investigation of *A. siamensis* led to the isolation of azadirachtin M,[14] while *A. excelsa* yielded azadirachtin L,[15,16] azadirachtin M,[17] and nimbolides.[18] In Thailand, farmers use the seed kernel extract of *A. excelsa* as a natural insecticide to protect cabbage and other related brassicae vegetables from insects, especially the diamondback moth.

We report herein the isolation, characterization, and bioactivity of three new azadirachtin derivatives, azadirachtins O−Q (**1**−**3**), together with six known compounds, azadirachtin B (**4**), azadirachtin L (**5**), azadirachtin M (**6**) 11α-azadirachtin H (**7**), 11*β*-azadirachtin H (**8**), and azadirachtol (**9**), from the seed kernels of *A. excelsa*. This is the first report of compounds **4**, **7**, **8**, and **9** from *A. excelsa*.

Results and Discussion

The structures of the isolated compounds were established by mass spectrometry and other spectroscopic means. X-ray crystallographic analysis confirmed the structure of compound **3**. The six known azadirachtins were identified by comparing their spectroscopic data with those reported as azadirachtin B (**4**),[6] azadirachtin L (**5**),[16] azadirachtin M (**6**),[14] 11α-azadirachtin H (**7**),[9,19] 11*β*-azadirachtin H (**8**),[9,19] and azadirachtol (**9**).[20]





	R	R^1	R^2	R^3
1	isovaleroyl	Ac	H	CO_2CH_3
2	Isovaleroyl	Ac	H	OH
3	Ac	Ac	H	CO_2CH_3
4	H	Tig	H	CO_2CH_3
5	Tig	Ac	H	OAc
6	Tig	Ac	H	CO_2CH_3
7	Tig	Ac	H	OH
8	Tig	Ac	OH	H
9	H	H	H	CO_2CH_3
Azadirachtin A	Tig	Ac	OH	CO_2CH_3

Compound **1** was obtained as a white amorphous powder, and it was assigned the molecular formula $C_{35}H_{46}O_{15}$ from the HRESITOFMS *m/z* 729.2789 $[M + Na]^+$. The IR spectrum showed absorption bands of hydroxyl (3439 cm^{-1}) and ester carbonyl (1734 cm^{-1}) groups. The ^1H and ^{13}C NMR data of **1** (Table 1) were similar to those reported for azadirachtin M (3-acetalazadirachtol),[14] except for the absence of the tigloyl moiety at C-1, which was replaced by the isovaleroyl group from the resonances at δ_H/δ_C 2.18 (m, H_2-2′)/43.3, 2.08 (m, H-3′)/24.9, 0.94 (d, J = 6.3 Hz, H-4′)/22.6, and 0.92 (d, J = 6.3 Hz, H-5′)/22.5 and the ester carbonyl at δ 171.9 (C-1′). The COSY correlations of H-2′ to H-3′, and H-3′ to H-4′ and H-5′, together with the HMBC correlations of H-2′ to C-1′, C-4′, and C-5′; H-3′ to C-1′, C-4′, and C-5′; and H-4′ and H-5′ to C-2′ and C-3′, supported the presence of this group. In addition, correlation of H-1 to C-1′ in the HMBC spectrum revealed that the isovaleroyl group was attached to C-1. The ^1H NMR of spectrum of **1**

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Table 1. ^{1}H and ^{13}C NMR Data (δ, ppm) of **1**−**3** ($CDCl_3$, 400 MHz)[a]

	1		**2**		**3**	
position	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	4.54 brs[b]	70.3 d[c]	4.65 brs	73.1 d	4.50 brs[b]	70.7 d
2a,b	2.29 brt (2.6)	30.3 t	2.42 brs	30.6 t	2.32 dt (15.3, 2.6), 2.23 dt (15.3, 2.6)	29.9 t
3	5.46 t (2.6)	67.0 d	5.47 t (2.4)	67.2 d	5.46 t (2.6)	67.0 d
4		52.4 s		52.3 s		52.4 s
5	3.19 brd (12.5)	37.0 d	3.28 d (12.4)	36.9 d	3.22 d (12.4)	36.7 d
6	4.46 dd (12.5, 2.6)	73.7 d	4.46 dd (12.4, 2.2)	74.1 d	4.48 dd (12.4, 2.6)	73.8 d
7	4.75 d (2.6)	73.2[a] d	4.65 s	72.4 s	4.76 d (2.6)	73.2 s
8		44.0 s		42.9 s		44.4 s
9	3.27 s	44.6 d	2.74 s	48.4 d	3.28 s	44.0 d
10		48.9 s		47.4 s		49.0 s
11	4.54 s[b]	79.4 d	5.42 s	101.0 d	4.50 s[b]	79.4 d
12		172.4 s				172.4 s
13		66.5 s		66.6 s		66.4 s
14		69.3 s		69.8 s		69.2 s
15	4.58 d (3.0)	76.0 d	4.61 d (3.1)	76.1 d	4.56 d (3.1)	76.0 d
16a	1.67 ddd (12.8, 5.1, 4.2)	25.2 t	1.71 ddd (12.8, 5.3, 4.7)	25.4 t	1.67 ddd (13.0, 5.0, 4.2)	25.2 t
16b	1.28 d (12.8)		1.29 d (12.8)		1.28 d (13.0)	
17	2.39 d (5.1)	48.5 d	2.42 d (5.3)	48.5 d	2.38 d (5.0)	48.5 d
18	2.13 s	18.2 q	2.05 s	18.9 q	2.13 s	18.0 q
19a	3.62 d (9.7)	70.0 t	3.76 d (9.8)	70.4 t	3.60 d (9.7)	70.0 t
19b	3.82 d (9.7)		3.83 d (9.8)		3.85 d (9.7)	
20		83.7 q		83.5 q		83.7 q
21	5.68 s	108.8 d	5.71 s	108.7 d	5.69 s	108.8 d
22	5.05 d (2.8)	107.5 d	5.08 d (2.2)	107.5 d	5.04 d (2.8)	107.5 d
23	6.44 d (2.8)	147.0 d	6.47 d (2.2)	147.1 d	6.43 d (2.8)	147.0 d
28a	4.07 d (8.9)	73.2[a] t	4.10 d (8.8)	73.1 t	4.06 d (9.0)	73.1 t
28b	3.64 d (8.9)		3.71 d (8.8)		3.70 d (9.0)	
29		173.2 s		173.4 s		173.2 s
30	1.39 s	21.1 q[d]	1.35 s	21.1 q[d]	1.39 s	21.2 q
OH-7	2.79 brs		2.56 brs		2.76 brs	
OH-11			4.90 brs			
OH-20	2.98 brs		2.97 brs		3.01 brs	
CH$_3$COO-1					2.00 s	21.0 q
CH$_3$*C*OO-1						169.8 s
CH$_3$COO-3	2.05 s	21.1 q[d]	2.10 s	21.1 q[d]	2.05 s	21.1 q
CH$_3$*C*OO-3		169.8 s		169.8 s		169.7 s
O*CH*$_3$-12	3.66 s	52.8 q			3.66 s	52.8 q[d]
O*CH*$_3$-29	3.76 s	52.8 q	3.82 s	52.7 q	3.76 s	52.8 q[d]
isovaleroyl						
1′		171.9 s		172.0 s		
2′	2.18 m	43.3 t	2.14 m	43.5 t		
3′	2.08 m	24.9 d	2.10 m	24.8 d		
4′	0.94 d (6.3)	22.6 q	0.97 d (6.3)	22.5 q		
5′	0.92 d (6.3)	22.5 q	0.95 d (6.3)	22.4 q		

[a] Figures in parentheses are coupling constants in Hz. [b] Overlapping with other protons. [c] Multipicities were determined by analyses of the DEPT spectra. [d] Overlapping with other carbons.

indicated the presence of six oxymethine protons (H-1, H-3, H-6, H-7, H-11, and H-15), two oxymethylenes (H_2-19 and H_2-28), two methylenes (H_2-2 and H_2-16), and two methines (H-5 and H-9) together with resonances of a furan moiety at δ 5.05 and 6.44 (d, J = 2.8 Hz, both H-22 and H-23, respectively) and 5.68 (s, H-21), consistent with the basic skeleton of tetranortriterpenoid type.[3−15] The complete interpretation of these NMR data was established by DEPT, COSY, HMQC, HMBC, and NOESY experiments.

The relative configuration of **1** was assigned from the coupling constants together with the NOESY correlations of these protons (Figure 1). The small values of the coupling constants (2.6 Hz) observed between H-3 and H-2 revealed that H-3 was equatorial. The correlation between H-1 and H-19 in the NOESY spectrum confirmed the β-orientation of H-1. The 1,2-diaxial coupling between H-5 and H-6 (12.5 Hz), together with the coupling constant (2.6 Hz) between H-6 and H-7, revealed the α-orientation of the hydroxyl group at C-7. The intensive cross-peak of H-11 to H-7 and H-30 indicated that the methoxycarbonyl group at C-11 was in the α-orientation. The remaining correlations of protons corresponded to those of the azadirachtin analogues.[3−15] On the basis of the above, the structure of

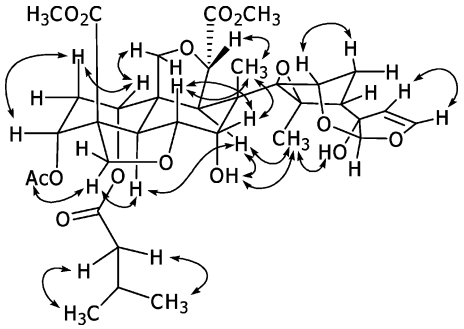

Figure 1. Selected NOESY correlations of **1**.

1 was established as 1-isovaleroyl-3-acetylazadirachtol, which has been named azadirachtin O. This is the first azadirachtin containing an isovaleroyl moiety.

Compound **2** was obtained as a white amorphous powder and was assigned the molecular formula $C_{33}H_{44}O_{14}$ from the HRESITOFMS m/z 687.2632 $[M + Na]^+$. The IR spectrum showed characteristic absorption bands of hydroxyl (3449 cm^{-1}) and ester carbonyl (1745 and 1728 cm^{-1}) groups. Analysis of the ^{1}H and ^{13}C NMR spectra of **2**

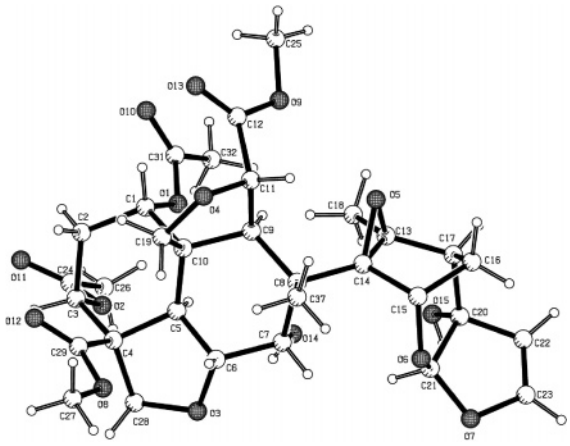

Figure 2. Perspective drawing of the crystal structure of **3**.

indicated that its structure was related to **1**, with obvious differences being a lack of the methoxycarbonyl group at C-11 when compared with **1**. The signals at δ_H/δ_C 5.42 (s)/101.0 corresponded to the hemiacetal carbon of C-11, which is comparable to those of 11α-hydroxyazadirachtin H.[9] The complete ^{1}H and ^{13}C NMR spectral data assignments of **2** were established from the DEPT, COSY, HMQC, HMBC, and NOESY experiments (Table 1).

The relative configuration of **2** was identical to that of **1**, on the basis of the same characteristic NOESY correlations and coupling constants of those protons, as well as the same specific optical rotation value (see Experimental Section). Thus, **2** was assigned as an 1-isovaleroyl-11α-hydroxyazadirachtin H and has been named azadirachtin P.

Compound **3** was obtained as colorless prisms and was assigned the molecular formula $C_{32}H_{40}O_{15}$ from the HRESITOFMS *m/z* 687.2268 $[M + Na]^+$. The IR spectrum showed characteristic absorption bands of hydroxyl (3375 cm^{-1}) and ester carbonyl (1740 cm^{-1}) groups. The ^{1}H and ^{13}C NMR spectra of **3** displayed characteristic resonances and coupling patterns similar to those of azadirachtin **1**. The only significant difference was the absence of the isovaleroyl moiety at C-1, which was replaced by an acetoxy group (δ_H/δ_C at 2.0 (s)/21.0, δ_C at 169.8). The HMBC spectrum exhibited correlations of H-1 to the carbonyl signal at δ 169.8, confirming the connection of the acetate unit at C-1. The complete ^{1}H and ^{13}C NMR spectral data assignments of **3** were established from the DEPT, COSY, HMQC, HMBC, and NOESY experiments (Table 1). Finally, X-ray crystallographic analysis was performed to confirm the structure and configuration of **3** (Figure 2). Thus, **3** was defined as 1,3-diacetylazadirachtol and named azadirachtin Q.

Compounds **1**−**7** and **9** were evaluated for their activity against the diamondback moth, *Plutella xylostella*. The activity of **8** could not be tested because of sample limitation. Their LD_{50} values are given in Table 2. The toxicities of two new azadirachtins, **1** and **2**, and the known **7** were significantly stronger than those of azadirachtin A after 96 h exposure. Azadirachtin **2** was found to be the most active principle after 24, 48, and 72 h exposure followed by **1**, which gave equal toxicity to **2** after 72 h exposure. These observations suggest that the presence of an isovaleroyl unit at C-1 increases activity. In addition, **7**, with a tigloyl unit at C-1, was the most active after 96 h exposure, suggesting that the hydroxyl group at C-11 can play some role in accumulative toxicity with longer time exposure. Among these, **5** was the least active principle, which could be a result of the acetate group at C-11.

Table 2. Toxicity of Azadirachtin Derivatives **1**−**7** and **9** to Diamondback Moth (*Plutella xylostella)*

	LD_{50} (μg/g body weight of larvae)			
compound	24 h	48 h	72 h	96 h
azadirachtin O (**1**)	3.92	1.92	1.19	0.79
azadirachtin P (**2**)	2.19	1.73	1.19	0.79
azadirachtin Q (**3**)	5.95	1.89	1.40	1.10
azadirachtin B (**4**)	4.85	2.26	1.56	1.06
azadirachtin L (**5**)	10.27	7.89	5.39	1.92
azadirachtin M (**6**)	8.46	4.84	4.23	1.30
11α-azadirachtin H (**7**)	5.75	4.20	1.38	0.75
azadirachtol (**9**)	4.88	3.28	2.35	1.78
azdirachtin A	7.04	4.12	1.28	0.87

However, all tested azadirachtins showed potential toxicity after 96 h exposure, with LD_{50} values of 0.75−1.92 μg/g body weight of larvae.

Experimental Section

General Experimental Procedures. Melting points (uncorrected) were determined using a Gallenkamp melting point apparatus. Optical rotations were obtained using a JASCO DIP-1000 digital polarimeter. UV spectra were measured on an Agilent 8453 UV−visible spectrophotometer. IR spectra were carried out on a Perkin-Elmer Spectrum One spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Varian Mercury Plus 400 spectrometer, using residual $CHCl_3$ as an internal standard. HRESITOFMS were obtained using a Micromass LCT mass spectrometer, and the lock mass calibration was applied for the determination of accurate masses. EIMS were measured on a Finnigan Mat INCOS 50 mass spectrometer. Column chromatography and preparative TLC were carried out on silica gel 60 (230−400 mesh) and PF_{254}, respectively. HPLC grade solvents were used for separation by preparative HPLC.

Plant Material. Seeds of *A. excelsa* were collected in Songkhla Province, Thailand, in June 1999, and the plant was identified by Prof. Pranom Chantaranothai, Department of Biology, Khon Kaen University. A voucher specimen (S. Kanokmedhakul 5) was deposited at the herbarium of the Department of Biology, Faculty of Science, Khon Kaen University, Khon Kaen, Thailand.

Extraction and Isolation. Fresh seed kernels of *A. excelsa* (2.6 kg) were ground and extracted successively with hexane (4 L × 3) and MeOH (4 L × 2) at room temperature. The filtered samples were combined and the solvents evaporated in vacuo to yield crude hexane (261 g) and MeOH extracts. The MeOH extract was partitioned between hexane−H_2O, and then EtOAc−H_2O, to give P−hexane (4.6 g) and P−EtOAc extracts (30 g), respectively. The P−EtOAc extract (30 g) was subjected to silica gel (200 g) flash column chromatography and eluted with increasing concentrations of EtOAc in hexane followed by MeOH in EtOAc. Each fraction (100 mL) was monitored by TLC; fractions with similar TLC were combined into seven fractions (F_1−F_7). Fraction F_5 (16.9 g) was rechromatographed on silica gel (300 g) column chromatography, eluted with EtOAc−hexane (50:50) and increasing polarity of the solvents, to yield 10 subfractions designated as $F_{5.1}$−$F_{5.10}$. Subfraction $F_{5.3}$ was further chromatographed by silica gel column chromatography, eluted with an isocratic system of EtOAc−hexane (50:50), to obtain two subfractions ($F_{5.3.1}$ and $F_{5.3.2}$). Subfraction $F_{5.3.2}$ was further purified by preparative TLC developed with MeOH−CH_2Cl_2 (4:96) to afford a white amorphous powder of **4** (320.5 mg, R_f 0.41). Fraction $F_{5.4}$ was rechromatographed by silica gel column chromatography with an isocratic elution of EtOAc−hexane (50:50) to give three subfractions ($F_{5.4.1}$−$F_{5.4.3}$). Subfraction $F_{5.4.2}$ was further purified by preparative TLC elution with MeOH−CH_2Cl_2 (4:96) (developed × 2) to yield **1** (32.6 mg, R_f 0.32). Fraction $F_{5.5}$ was chromatographed by silica gel column chromatography, eluted with EtOAc−hexane (65:35) and increasing polarity of solvents, to yield three subfractions ($F_{5.5.1}$−$F_{5.5.3}$). Subraction $F_{5.5.1}$

was further purified by preparative TLC, eluting with MeOH−CH_2Cl_2 (6:94), to yield an additional amount of **1** (18.9 mg, R_f 0.62). Fraction $F_{5.5.2}$ was rechromatographed by silica gel column chromatography, eluted with EtOAc−hexane (70:30), to give four subfractions ($F_{5.5.2.1}$−$F_{5.5.2.4}$). Recrystallization of subfraction $F_{5.5.2.3}$ from EtOAc−hexane afforded **6** (235.7 mg). Subfraction $F_{5.5.2.4}$ was reseparated by silica gel column chromatography, eluted with an isocratic system of EtOAc−hexane (50:50), to obtain five subfractions ($F_{5.5.2.4.1}$−$F_{5.5.2.4.5}$). Subfraction $F_{5.5.2.4.4}$ was further purified by preparative HPLC on a RP18 column (HI-5C18-2990, ODS, 5 μm, 4.6 mm × 250 mm), using CH_3CN−H_2O (30:70) as eluent at a flow rate of 1.0 mL/min. The peak at 25.89 min gave an additional amount of **6** (44.3 mg), and the peak at 38.37 min gave **5** (20.6 mg). Subfraction $F_{5.5.2.4.5}$ was recrystallized from EtOAc−hexane to give an additional amount of **6** (187.8 mg). Subfraction $F_{5.5.3}$ was further purified by preparative TLC, eluted with MeOH−CH_2Cl_2 (6:74). The band at R_f 0.29 gave **2** (52.1 mg), and the band at R_f 0.44 gave an additional amount of **6** (183.3 mg). Fraction $F_{5.6}$ was further purified by preparative TLC, eluted with MeOH−CH_2Cl_2 (5:95) (developed × 2), to yield an additional amount of **6** (180.3 mg). Fraction $F_{5.7}$ was dissolved with EtOAc to give a solid, which further recrystallized from MeOH to yield colorless needles of **7** (159.1 mg). The residue was then separated by preparative TLC, eluting with MeOH−CH_2Cl_2 (6:94), to give **3** (40.8 mg, R_f 0.42), **8** (20.0 mg, R_f 0.48), and an additional portion of **7** (65.3 mg, R_f 0.43). Subfraction $F_{5.8}$ was chromatographed by silica gel column chromatography, eluted with a gradient system of EtOAc−hexane (70:30) and increasing polarity of the solvents, to give five subfractions ($F_{5.8.1}$−$F_{5.8.5}$). Subfraction $F_{5.8.3}$ was reseparated by preparative TLC, eluting with EtOAc−hexane−MeOH (60:34:6) (developed × 2), to yield colorless needles of **9** (102.0 mg, R_f 0.25).

Azadirachtin O (1): white amorphous powder, yield 0.002% w/w; R_f 0.52 (EtOAc); mp 254−256 °C; $[\alpha]^{26}_D$ −38.3° (*c* 0.32, $CHCl_3$); IR (KBr) ν_{max} 3439, 2950, 1734, 1618, 1434, 1375, 1251, 1219, 1076, 1041 cm^{-1}; ^1H and ^{13}C NMR, see Table 1; EIMS, *m/z* 706 $[M]^+$ (0.5), 688 $[M - H_2O]^+$ (4), 605 (14), 586 (12), 521 (16), 503 (9), 445 (8), 392 (14), 365 (16), 331 (44), 273 (93), 255 (57), 242 (42), 210 (39), 182 (42), 96 (100), 83 (36), 57 (27); HRESITOFMS *m/z* 729.2789 $[M + Na]^+$ (calcd for $C_{35}H_{46}O_{15}$ + Na, 729.2734).

Azadirachtin P (2): white amorphous powder, yield 0.0016% w/w; R_f 0.42 (MeOH−CH_2Cl_2, 5:95); mp 235−236 °C; $[\alpha]^{26}_D$ −34.5° (*c* 0.42, $CHCl_3$); IR (KBr) ν_{max} 3449, 2959, 1745, 1728, 1618, 1435, 1375, 1296, 1248, 1042 cm^{-1}; ^1H and ^{13}C NMR, see Table 1; EIMS, *m/z* 664 $[M]^+$ (1), 647 (3), 563 (17), 549 (8), 423 (13), 368 (20), 313 (12), 233 (36), 183 (21), 151 (100), 123 (21), 111 (26), 95 (28), 67 (21); HRESITOFMS *m/z* 687.2632 $[M + Na]^+$ (calcd for $C_{33}H_{44}O_{14}$ + Na, 687.2629).

Azadirachtin Q (3): colorless prisms, yield 0.0015% w/w; R_f 0.48 (EtOAc); mp 218−219 °C; $[\alpha]^{26}_D$ −44.6° (*c* 0.67, $CHCl_3$); IR (KBr) ν_{max} 3375, 3092, 2950, 1740, 1612, 1375, 1263, 1251, 1202, 1043 cm^{-1}; ^1H and ^{13}C NMR, see Table 1; EIMS, *m/z* 664 $[M]^+$ (1), 605 $[M - OAc]^+$(3), 587 (7), 563 (16), 521 (11), 451 (19), 391 (12), 333 (33), 273 (48), 255 (36), 183 (36), 151 (51), 124 (36), 95 (100), 67 (15); HRESITOFMS *m/z* 687.2268 $[M + Na]^+$ (calcd for $C_{32}H_{40}O_{15}$ + Na, 687.2265).

Toxicity Assays. A toxicity assay against the diamondback moth (*Plutella xylostella*) was performed employing the modified method described by Robert and co-workers.[21] Second- or third-instar larvae were treated with 1 μL of acetone solution of each azadirachtin derivative. Dose mortality relationships were measured using triplicate assays with five doses (5, 10, 15, 20, and 25 μg/mL) and 10 larvae per dose. Each larva was placed on the cabbage disk (4 cm diameter cut from young shoot leaves), then each specific azadirachtin solution was dropped on the larvae. Individual cabbage disks from each treatment were placed in a Petri dish. Mortality was recorded every 24 h up to 96 h and compared to controls that were treated with acetone only. Lethal dose, LD_{50}, values were calculated according to the method of Heinrich and coworkers[22] (Table 2).

X-ray Crystal Structure Analysis of Azadirachtin Q (3). Crystal data for **3**: $C_{32}H_{40}O_{15}$, MW = 664.65, orthorhombic, space group $P2_12_12_1$, a = 7.5715(2) Å, b = 9.4360(3) Å, c = 43.9343(13) Å, V = 3138.9(2) $Å^3$, Z = 4, D_{calc} = 1.411 Mg/m^3. A total of 5150 unique reflections (4653 observed, $|F_o| > 4\sigma|F_o|$) were measured at room temperature from a 0.20 × 0.15 × 0.10 mm^3 colorless crystal using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker-Nonius kappaCCD diffractometer. The crystal structure was solved by direct methods using SIR-97, and then all atoms, except hydrogen atoms, were refined anisotropically on F^2 using SHELXL-97 to give a final R-factor of 0.0554 and R_w = 0.1580 (all data).

Crystallographic data of **3** have been deposited at the Cambridge Crystallographic Data Centre under the reference number CCDC 251069. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: X-ray crystallographic tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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