

## Long-Chain Fatty Acid Esters of Some Norditerpenoid Alkaloids

Yili Bai, Haridutt K. Desai, and S. William Pelletier

*J. Nat. Prod.*, **1994**, 57 (7), 963-970 • DOI:  
10.1021/np50109a013 • 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/np50109a013> 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

## LONG-CHAIN FATTY ACID ESTERS OF SOME NORDITERPENOID ALKALOIDS

YILI BAI, HARIDUTT K. DESAI, and S. WILLIAM PELLETIER\*

*Institute for Natural Products Research and Department of Chemistry,  
The University of Georgia, Athens, Georgia 30602-2556*

**ABSTRACT.**—Several C-8 long-chain fatty acid esters of aconitine-type norditerpenoid alkaloids namely, aconitine, delphinine, delphisine, falconerine-8-acetate, mesaconitine, and pseudoaconitine bearing a C-8 acetyl group, have been prepared. Preparation was achieved by heating the alkaloids with the neat fatty acid under vacuum. All the compounds have been fully characterized by physical and spectroscopic data. Identification and characterization of reaction byproducts are also included.

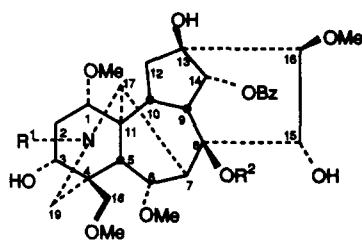
The medicinal use of *Aconitum* and *Delphinium* species spans many centuries. *Aconitum* preparations have been used as cardiotonics, febrifuges, sedatives, and anodynes (1,2). *Delphinium* extracts have been employed in analgesic balms and also as sedatives, emetics, and anthelmintics (1,2).

*Aconitum* tuber is an important ingredient of Chinese medicinal preparations used as analgesics, cardiotonics, diuretics, and stimulants (3). Kitagawa and co-workers (3) have studied the constituents of the unprocessed and processed Chinese crude drug "Chuanwu" (identified as *Aconitum chammichaeli*) and reported isolating a mixture of C-8 long-chain fatty acid esters of aconitine, mesaconitine, hyaconitine, and 3-deoxyaconitine, which they named "lipo-aconitines." During the course of our pharmacological studies of diterpenoid alkaloids and their derivatives (4–6) we have prepared a number of C-8 fatty acid esters of aconitine, mesaconitine, delphinine, delphisine, pseudoaconitine, and falconerine. We report here the preparation and characterization of seventeen C-8 long-chain fatty acid esters. Several byproducts produced under the reaction conditions have been isolated and identified through their spectroscopic data. The specific rotations, ir, ms,  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr spectra for all the compounds are presented.

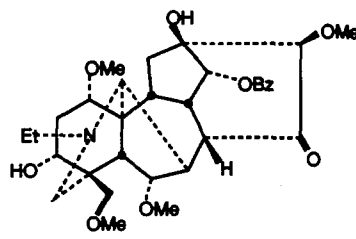
### RESULTS AND DISCUSSION

Attempted preparation of a series of C-8 long-chain fatty acid esters of norditerpenoid alkaloids using the procedure reported by Kitagawa (3) gave low yields of the desired products. After a detailed study of various reaction conditions, the amount of pyridine turned out to be the key factor, i.e., addition of a small amount of pyridine was essential, but with increasing amount of pyridine, the yield of the desired product decreased. An alternative vacuum procedure (see Experimental) was developed for this purpose which gave us consistent results. Some byproducts were formed but the major compounds isolated were the required esters (40–50% yield). The purity of the products was determined by checking their tlc in various solvent systems and their  $^{13}\text{C}$ -nmr spectra.

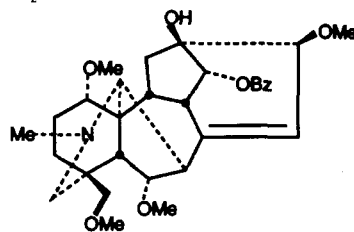
Five C-8 long-chain fatty acid esters of aconitine were prepared initially: 14-benzoylaconine-8-linoleate [**1**], 14-benzoylaconine-8-linolenate [**2**], 14-benzoylaconine-8-oleate [**3**], 14-benzoylaconine-8-palmitate [**4**], and 14-benzoylaconine-8-stearate [**5**]. The yields of compounds **1–5** were in the range of 40–50%, but all were accompanied by a byproduct, the known pyroaconitine [**6**] (30–35%) (7). Compounds **1–6** were fully characterized spectroscopically. The  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr chemical shifts of these compounds are based on the revised unambiguous assignments of aconitine (8,9) (see Table 1 for  $^{13}\text{C}$ -nmr shifts). The  $^{13}\text{C}$ -nmr chemical shift assignments for the fatty acid carbons



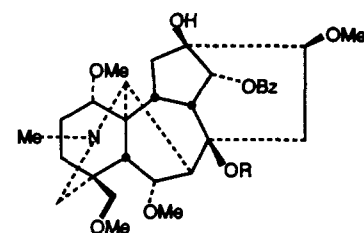
- 1  $R^1 = Et, R^2 = CO(CH_2)_7, CH = CHCH_2CH = CH(CH_2)_4, Me$   
 2  $R^1 = Et, R^2 = CO(CH_2)_7, CH = CHCH_2CH = CHCH_2CH = CHCH_2Me$   
 3  $R^1 = Et, R^2 = CO(CH_2)_7, CH = CH(CH_2)_7, Me$   
 4  $R^1 = Et, R^2 = CO(CH_2)_4, Me$   
 5  $R^1 = Et, R^2 = CO(CH_2)_{16}, Me$   
 19  $R^1 = Me, R^2 = CO(CH_2)_{14}, Me$



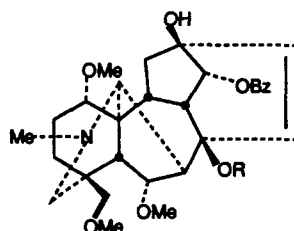
6



13



- 7  $R = CO(CH_2)_7, CH = CHCH_2CH = CH(CH_2)_4, Me$   
 8  $R = CO(CH_2)_7, CH = CHCH_2CH = CHCH_2CH = CHCH_2Me$   
 9  $R = CO(CH_2)_7, CH = CH(CH_2)_7, Me$   
 10  $R = CO(CH_2)_{14}, Me$   
 11  $R = CO(CH_2)_{16}, Me$   
 12  $R = COCH_2Me$

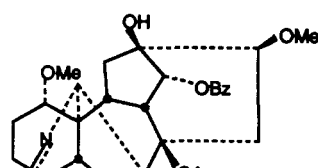
14  $R = CO(CH_2)_{14}, Me$ TABLE 1.  $^{13}C$ -Nmr Chemical Shifts and Assignments for Compounds 1-6, 16-18, and 20.

Carbon	Compound									
	1	2	3	4	5	6	16	17	18	20
1	82.3 d	82.2 d	82.3 d	82.3 d	82.4 d	83.5 d	77.5 d	77.9 d	82.8 d	82.1 d
2	33.5 t	33.4 t	33.4 t	33.4 t	33.5 t	34.0 t	28.8 t	27.6 t	33.1 t	33.2 t
3	71.5 d	71.4 d	71.5 d	71.3 d	71.6 d	71.8 d	35.3 t	35.4 t	71.8 d	71.6 d
4	43.0 s	42.9 s	43.0 s	42.9 s	43.1 s	43.6 s	38.8 s	39.2 s	43.0 s	43.0 s
5	46.4 d	46.3 d	46.3 d	46.3 d	46.4 d	48.4 d	48.7 d	49.6 d	46.4 d	48.6 d
6	83.4 d	83.3 d	83.4 d	83.3 d	83.4 d	84.0 d	83.4 d	82.3 d	83.5 d	83.0 d
7	44.6 d	44.5 d	44.6 d	44.5 d	44.6 d	41.6 d	49.3 d	45.8 d	48.6 d	47.4 d
8	91.7 s	91.6 s	91.6 s	91.6 s	91.7 s	49.3 d	85.2 s	83.8 s	85.5 s	85.2 s
9	44.2 d	44.1 d	44.2 d	44.1 d	44.2 d	38.6 d	44.3 d	44.2 d	44.9 d	44.6 d
10	40.9 d	40.8 d	40.9 d	40.8 d	41.0 d	44.7 d	43.8 d	43.8 d	43.5 d	40.8 d
11	50.0 s	49.9 s	50.0 s	49.9 s	50.1 s	51.1 s	49.3 s	48.4 s	50.5 s	50.2 s
12	35.7 t	35.6 t	35.6 t	35.6 t	35.7 t	32.8 t	29.2 t	29.1 t	28.1 t	34.9 t
13	74.0 s	73.9 s	74.0 s	73.9 s	74.0 s	77.3 s	38.3 d	35.7 d	39.4 d	74.6 s
14	78.9 d	78.8 d	78.9 d	78.8 d	78.9 d	78.4 d	74.9 d	74.2 d	75.3 d	78.5 d
15	78.9 d	78.8 d	78.9 d	78.8 d	78.9 d	211.7 s	37.7 t	125.9 d	38.4 t	39.9 t
16	90.0 d	89.9 d	89.9 d	89.9 d	90.0 d	86.0 d	82.9 d	133.3 d	82.3 d	83.6 d
17	61.0 d	60.9 d	61.2 d	60.9 d	61.3 d	61.6 d	60.4 d	61.8 d	61.2 d	61.5 d
18	76.6 t	76.6 t	76.6 t	76.4 t	76.8 t	76.7 t	79.9 t	80.3 t	77.2 t	76.9 t
19	46.9 t	46.9 t	46.9 t	46.9 t	47.0 t	47.2 t	54.1 t	54.2 t	48.5 t	46.8 t
NCH <sub>3</sub>	48.9 t	48.8 t	48.8 t	48.8 t	48.9 t	49.0 t	48.4 t	48.7 t	47.6 t	48.6 t
CH <sub>3</sub>	13.3 q	13.2 q	13.3 q	13.3 q	13.3 q	13.3 q	13.3 q	13.4 q	13.2 q	13.2 q
1-Ome	55.9 q	55.8 q	55.9 q	55.8 q	55.9 q	56.1 q	—	—	55.9 q	55.9 q
6-Ome	58.1 q	58.0 q	58.1 q	58.0 q	58.2 q	57.8 q	58.2 q	57.7 q	57.9 q	57.9 q
16-Ome	61.2 q	61.1 q	60.9 q	61.6 q	61.0 q	62.3 q	56.5 q	—	56.6 q	58.7 q
18-Ome	59.0 q	59.0 q	59.0 q	59.0 q	59.1 q	59.2 q	59.0 q	59.2 q	59.0 q	59.0 q

TABLE 1. Continued.

Carbon	Compound									
	1	2	3	4	5	6	16	17	18	20
(arom)C=O ...	166.0 s	165.9 s	166.0 s	165.9 s	166.0 s	166.0 s	—	—	165.8 s	165.8 s
1'	129.8 s	129.6 s	129.6 s	129.6 s	129.7 s	129.3 s	—	—	122.8 s	122.5 s
2'	129.7 d	129.6 d	129.6 d	129.6 d	129.7 d	129.6 d	—	—	112.0 d	111.8 d
3'	128.6 d	128.5 d	128.6 d	128.5 d	128.6 d	128.6 d	—	—	148.6 s	148.5 s
4'	133.2 d	133.2 d	133.2 d	133.2 d	133.3 d	133.6 d	—	—	152.9 s	152.9 s
5'	128.6 d	128.5 d	128.6 d	128.5 d	128.6 d	128.6 d	—	—	110.2 d	110.2 d
6'	129.7 d	129.6 d	129.6 d	129.6 d	129.7 d	129.6 d	—	—	123.6 d	123.6 d
3'-OMe	—	—	—	—	—	—	—	—	55.6 q	55.7 q
4'-OMe	—	—	—	—	—	—	—	—	55.8 q	55.7 q
(8-)1"	175.1 s	175.0 s	175.1 s	175.1 s	175.2 s	—	172.3 s	172.2 s	172.5 s	172.6 s
2"	34.7 t	34.6 t	34.7 t	34.6 t	34.8 t	—	34.4 t	35.0 t	34.8 t	34.7 t
3"	24.1 t	24.0 t	24.1 t	24.1 t	24.2 t	—	24.7 t	24.6 t	24.2 t	24.1 t
4"	28.8 t	28.7 t	28.8 t	28.7 t	28.9 t	—	28.9 t	29.1 t	29.1 t	29.0 t
5"	29.0 t	28.9 t	28.9 t	28.9 t	29.0 t	—	29.0 t	29.3 t	29.2 t	29.1 t
6"	29.0 t	28.9 t	28.9 t	29.2 t	29.4 t	—	29.2 t	29.6 t	29.3 t	29.2 t
7"	29.3 t	29.4 t	29.3 t	29.6 t	29.7 t	—	29.2 t	29.6 t	29.4 t	29.3 t
8"	27.1 t	27.1 t	27.1 t	29.6 t	29.7 t	—	27.1 t	27.2 t	29.6 t	29.6 t
9"	129.9 d	130.1 d	129.6 d	29.6 t	29.7 t	—	130.0 d	130.0 d	29.6 t	29.6 t
10"	128.1 d	128.1 d	130.0 d	29.6 t	29.7 t	—	128.1 d	128.1 d	29.6 t	29.6 t
11"	25.6 t	25.4 t	27.1 t	29.6 t	29.7 t	—	25.5 t	25.6 t	29.6 t	29.6 t
12"	127.8 d	126.9 d	29.6 t	29.6 t	29.7 t	—	127.8 d	127.9 d	29.6 t	29.6 t
13"	130.2 d	128.2 d	29.5 t	29.6 t	29.7 t	—	130.2 d	130.2 d	29.6 t	29.6 t
14"	27.1 t	24.0 t	29.6 t	31.8 t	29.7 t	—	27.1 t	27.2 t	31.8 t	31.8 t
15"	29.5 t	127.7 d	29.5 t	22.6 t	29.7 t	—	29.6 t	31.5 t	22.6 t	22.6 t
16"	31.5 t	131.8 d	31.8 t	14.0 q	31.9 t	—	31.4 t	31.8 t	14.1 q	14.1 q
17"	22.5 t	20.4 t	22.6 t	—	22.7 t	—	22.5 t	22.6 t	—	—
18"	14.1 q	14.2 q	14.1 q	—	14.1 q	—	14.0 q	14.1 q	—	—
1-OAc	—	—	—	—	—	—	170.3, 21.3	170.5, 21.1	—	—
14-OAc	—	—	—	—	—	—	170.7, 22.0	170.9, 22.0	—	—

are based on the published values for these acids (10). The same series of esters of delphinine were prepared: 14-benzoyldelphinine-8-linoleate [7], 14-benzoyldelphinine-8-linolenate [8], 14-benzoyldelphinine-8-oleate [9], 14-benzoyldelphinine-8-palmitate [10], 14-benzoyldelphinine-8-stearate [11], and 14-benzoyldelphinine-8-propio-



15

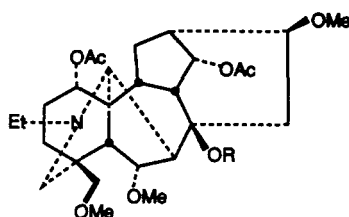
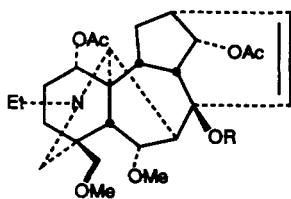
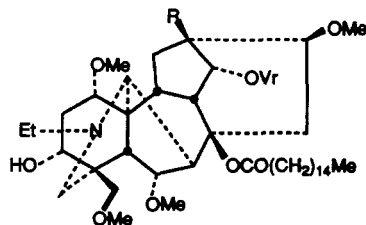
16 R=CO(CH<sub>2</sub>)<sub>7</sub>CH=CHCH<sub>2</sub>CH=CH(CH<sub>2</sub>)<sub>4</sub>Me17 R=CO(CH<sub>2</sub>)<sub>7</sub>CH=CHCH<sub>2</sub>CH=CH(CH<sub>2</sub>)<sub>4</sub>Me18 R=H  
20 R=OH

TABLE 2.  $^{13}\text{C}$ -Nmr Chemical Shifts and Assignments for Compounds 7-15 and 19.

Carbon	Compound									
	7	8	9	10	11	12	13	14	15	19
1	84.9 d	84.8 d	84.9 d	84.9 d	84.9 d	84.9 d	86.1 d	85.1 d	82.1 d	82.4 d
2	26.4 t	26.2 t	26.4 t	26.4 t	26.4 t	26.3 t	25.2 t	26.3 t	22.5 t	34.0 t
3	34.7 t	34.6 t	34.7 t	34.7 t	34.7 t	34.6 t	35.2 t	34.8 t	27.9 t	71.2 d
4	39.5 s	39.3 s	39.4 s	39.4 s	39.4 s	39.2 s	40.0 s	39.5 s	46.5 s	43.4 s
5	48.4 d	48.2 d	48.4 d	48.4 d	48.4 d	48.4 d	48.4 d	48.7 d	45.7 d	46.3 d
6	83.0 d	82.8 d	83.0 d	83.0 d	83.0 d	82.9 d	83.5 d	82.2 d	83.6 d	83.2 d
7	48.1 d	48.0 d	48.1 d	48.1 d	48.1 d	48.0 d	50.3 d	44.6 d	53.7 d	43.6 d
8	85.3 s	85.1 s	85.3 s	85.2 s	85.2 s	85.2 s	146.8 s	83.4 s	84.3 s	91.5 s
9	45.1 d	44.9 d	45.1 d	45.1 d	45.1 d	45.0 d	47.5 d	44.2 d	42.9 d	44.3 d
10	41.1 d	40.9 d	41.1 d	41.1 d	41.1 d	41.0 d	46.5 d	42.2 d	40.2 d	40.9 d
11	50.3 s	50.2 s	50.3 s	50.3 s	50.3 s	50.2 s	51.8 s	50.1 s	51.6 s	50.0 s
12	35.4 t	35.3 t	35.4 t	35.4 t	35.4 t	35.4 t	38.2 t	38.9 t	35.9 t	35.7 t
13	74.8 s	74.7 s	74.8 s	74.8 s	74.8 s	74.7 s	77.5 s	76.2 s	74.7 s	74.0 s
14	78.8 d	78.7 d	78.8 d	78.8 d	78.8 d	78.7 d	79.1 d	78.2 d	78.9 d	78.9 d
15	39.3 t	39.1 t	39.3 t	39.3 t	39.3 t	39.3 t	116.2 d	125.7 d	38.7 t	78.9 d
16	83.6 d	83.5 d	83.6 d	83.6 d	83.6 d	83.5 d	83.5 d	137.0 d	83.0 d	90.0 d
17	63.4 d	63.3 d	63.4 d	63.4 d	63.4 d	63.3 d	78.6 d	64.3 d	61.2 d	62.2 d
18	80.2 t	80.0 t	80.2 t	80.2 t	80.2 t	80.1 t	80.3 t	80.4 t	77.9 t	76.3 t
19	56.1 t	55.9 t	56.0 t	56.1 t	56.0 t	56.0 t	56.5 t	56.1 t	166.0 d	49.4 t
NCH <sub>3</sub>	42.5 q	42.4 q	42.5 q	42.5 q	42.5 q	42.4 q	42.8 q	42.5 q	—	42.4 q
1-OMe	58.8 q	58.7 q	58.8 q	58.8 q	58.8 q	58.7 q	56.8 q	57.5 q	56.1 q	56.4 q
6-OMe	58.0 q	57.8 q	57.9 q	58.0 q	58.0 q	57.8 q	58.2 q	56.5 q	57.2 q	58.1 q
16-OMe	56.6 q	56.4 q	56.6 q	56.7 q	56.6 q	56.5 q	57.2 q	—	58.8 q	61.2 q
18-OMe	59.1 q	58.9 q	59.1 q	59.1 q	59.1 q	59.0 q	59.3 q	59.2 q	59.0 q	59.1 q
14-aromatic										
C=O	166.3 s	166.2 s	166.3 s	166.3 s	166.3 s	166.2 s	168.2 s	166.8 s	165.9 s	166.0 s
1'	129.7 s	130.1 s	129.9 s	130.2 s	129.9 s	130.2 s	130.1 s	130.0 s	129.7 s	129.7 s
2'	129.7 d	129.6 d	129.7 d	129.7 d	129.7 d	129.6 d	130.0 d	129.7 d	129.3 d	129.7 d
3'	128.5 d	128.4 d	128.5 d	128.5 d	128.5 d	128.4 d	128.2 d	128.4 d	128.4 d	128.6 d
4'	133.1 d	132.9 d	133.1 d	133.1 d	133.1 d	133.0 d	132.9 d	133.2 d	132.7 d	133.3 d
5'	128.5 d	128.4 d	128.5 d	128.5 d	128.5 d	128.4 d	128.2 d	128.4 d	128.4 d	128.6 d
6'	129.7 d	129.6 d	129.7 d	129.7 d	129.7 d	129.6 d	130.0 d	129.7 d	129.3 d	129.7 d
8-fatty acid										
1"	172.6 s	172.5 s	172.6 s	172.6 s	172.6 s	173.1 s	—	172.4 s	169.5 s	175.2 s
2"	34.7 t	34.5 t	34.7 t	34.7 t	34.7 t	27.9 t	—	35.0 t	21.4 q	34.7 t
3"	24.1 t	24.0 t	24.1 t	24.1 t	24.1 t	8.3 q	—	24.2 t	—	24.1 t
4"	28.9 t	28.8 t	29.0 t	28.9 t	28.9 t	—	—	28.9 t	—	28.9 t
5"	29.1 t	28.9 t	29.0 t	29.1 t	29.1 t	—	—	29.1 t	—	29.0 t
6"	29.1 t	28.9 t	29.0 t	29.4 t	29.4 t	—	—	29.4 t	—	29.3 t
7"	29.3 t	29.4 t	29.3 t	29.4 t	29.4 t	—	—	29.4 t	—	29.3 t
8"	27.2 t	27.1 t	27.2 t	29.7 t	29.7 t	—	—	29.7 t	—	29.7 t
9"	130.0 d	130.1 d	129.7 d	29.7 t	29.7 t	—	—	29.7 t	—	29.7 t
10"	128.1 d	128.2 d	130.0 d	29.7 t	29.7 t	—	—	29.7 t	—	29.7 t
11"	25.6 t	25.4 t	27.2 t	29.7 t	29.7 t	—	—	29.7 t	—	29.7 t
12"	127.8 d	126.9 d	29.8 t	29.7 t	29.7 t	—	—	29.7 t	—	29.7 t
13"	130.2 d	128.2 d	29.3 t	29.7 t	29.7 t	—	—	29.7 t	—	29.7 t
14"	27.2 t	25.4 t	29.8 t	31.9 t	29.7 t	—	—	31.9 t	—	31.9 t
15"	29.6 t	127.6 d	29.5 t	22.7 t	29.7 t	—	—	22.7 t	—	22.7 t
16"	31.5 t	131.8 d	31.9 t	14.1 q	31.9 t	—	—	14.1 q	—	14.1 q
17"	22.6 t	20.4 t	22.7 t	—	22.7 t	—	—	—	—	—
18"	14.1 q	14.2 q	14.1 q	—	14.1 q	—	—	—	—	—

onate [12]. Three byproducts were formed under the reaction conditions and were isolated from these reactions: pyrodelphinine [13], 16-demethoxy-15,16-didehydro-14-benzoyldelphonine-8-palmitate [14] (in the case of reaction with palmitic acid), and *N*-demethyl-*N*,19-didehydrodelphinine [15]. The preparation of long-chain fatty acid esters of delphisine was difficult because of the facile epimerization of the C-1- $\alpha$ -hydroxyl group (12). The reaction of 1-acetyldelphisine with linoleic acid furnished 1-acetyl-8-deacetyldelphisine-8-linoleate [16] along with a byproduct, 1-acetyl-8-deacetyl-16-demethoxy-15,16-didehydrodelphisine-8-linoleate [17]. Palmitic esters of three more alkaloids were prepared: falconerine-8-palmitate [18], 14-benzoylmesaconine-8-palmitate [19], and 8-deacetylpsuedaconitine-8-palmitate [20]. The  $^{13}\text{C}$ -nmr data of

these compounds are listed in Tables 1 and 2. Ms, ir, optical rotations, and  $^1\text{H}$ -nmr data are given in the Experimental. The biological activities of the compounds reported in this work will be published elsewhere.

## EXPERIMENTAL

**GENERAL EXPERIMENTAL PROCEDURES.**—Optical rotations were measured in  $\text{CHCl}_3$  in a Perkin-Elmer model 141 polarimeter. Ir spectra were taken on a Perkin-Elmer model 1420 spectrophotometer in Nujol.  $^1\text{H}$ -,  $^{13}\text{C}$ - (including DEPT), and 2D nmr spectra were recorded in  $\text{CDCl}_3$ , on Bruker AC-250 and AC-300 instruments equipped with the standard Bruker software. Ms were recorded on a Finnigan Quadrupole 4023 instrument at 70 eV. Isolation of the reaction products was carried out through separation on an  $\text{Al}_2\text{O}_3$  rotor (1 mm, EM-1104) of a Chromatotron (13).

**GENERAL PROCEDURE FOR PREPARATION OF LONG-CHAIN FATTY ACID ESTERS.**—The norditerpenoid alkaloid and the long-chain fatty acid (in excess) were mixed and placed into a small sublimation apparatus, and then heated in an oil bath ( $110^\circ$ ) for 3 h. A vacuum was applied during heating (0.1–0.5 mm/Hg). The reaction mixture was then dissolved in  $\text{CHCl}_3$  and the solution was passed through a basic  $\text{Al}_2\text{O}_3$  (activity III) column followed by separation on a Chromatotron rotor using a gradient of hexane and EtOH.

**14-BENZOYLACONINE-8-LINOLEATE [1].**—Aconitine (100 mg, 0.15 mmol) and oleic acid (200 mg, 0.71 mmol) were thoroughly mixed and the mixture was heated for 3 h. The workup and fractionation of the reaction mixture (as described above) gave **1** as an oil ( $\text{C}_{50}\text{H}_{77}\text{NO}_{11}$ , 53 mg, 39.9%) [ $\alpha$ ] $^{30\text{D}}$  + 7.1 $^\circ$  ( $c=0.77$ ); ir  $\nu$  max 3495, 1729, 1714, and 1280  $\text{cm}^{-1}$ ; eims  $m/z$  554 [ $\text{M}-\text{R}^3-\text{OH}-\text{OMe}$ ] $^+$  (32), 444 (2), 266 (11), and 105 (100);  $^1\text{H}$  nmr  $\delta$  0.88 (3H, t,  $J=7.0$  Hz, H-18 $''$ ), 1.08 (3H, t,  $J=7.2$  Hz, N- $\text{CH}_2\text{CH}_3$ ), 3.15 (3H, s, OMe-6), 3.25 (3H, s, OMe-1), 3.29 (3H, s, OMe-18), 3.33 (1H, d,  $J=5.4$  Hz, H-16 $\alpha$ ), 3.45 and 3.60 (1H each, d,  $J=9.0$  Hz, H-18), 3.75 (3H, s, OMe-16), 3.95 (1H, s, OH-13), 4.02 (1H, d,  $J=6.3$  Hz, H-6 $\beta$ ), 4.42 (1H, dd,  $J=5.3$  and 2.6 Hz, H-15 $\beta$ ), 4.48 (1H, d,  $J=2.6$  Hz, OH-15), 4.85 (1H, d,  $J=4.8$  Hz, H-14 $\beta$ ), 5.35 (4H, m, H-9 $''$ , 10 $''$ , 12 $''$ , and 13 $''$ ), 7.43 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.56 (1H, t,  $J=7.2$  Hz, H-4'), and 8.02 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}\text{C}$ -nmr data, see Table 1.

**14-BENZOYLACONINE-8-LINOLENATE [2].**—Aconitine (100 mg, 0.15 mmol) and linolenic acid (200 mg, 0.72 mmol) were mixed thoroughly. The reaction and workup were carried out as per the general procedure to give **2** ( $\text{C}_{50}\text{H}_{73}\text{NO}_{11}$ , 60 mg, 44.9%) as an oil, [ $\alpha$ ] $^{30\text{D}}$  + 0.14 $^\circ$  ( $c=0.47$ ); ir  $\nu$  max 3480, 1731, and 1711  $\text{cm}^{-1}$ ; eims  $m/z$  554 [ $\text{M}-\text{R}^3-\text{OH}-\text{OMe}$ ] $^+$  (65), 536 (8), and 105 (100);  $^1\text{H}$  nmr  $\delta$  0.97 (3H, t,  $J=7.2$  Hz, H-18 $''$ ), 1.09 (3H, t,  $J=7.2$  Hz, N- $\text{CH}_2\text{CH}_3$ ), 3.15 (3H, s, OMe-6), 3.26 (3H, s, OMe-1), 3.29 (3H, s, OMe-18), 3.34 (1H, d,  $J=5.0$  Hz, H-16 $\alpha$ ), 3.45 and 3.60 (each 1H, d,  $J=8.8$  Hz, H-18), 3.76 (3H, s, OMe-16), 3.95 (1H, s, OH-13), 4.03 (1H, d,  $J=6.5$  Hz, H-6 $\beta$ ), 4.43 (1H, dd,  $J=5.2$  and 2.5 Hz, H-15 $\beta$ ), 4.48 (1H, d,  $J=2.5$  Hz, OH-15), 4.85 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 5.36 (6H, m, H-9 $''$ , 10 $''$ , 12 $''$ , 13 $''$ , 15 $''$ , and 16 $''$ ), 7.44 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.56 (1H, t,  $J=7.2$  Hz, H-4'), and 8.03 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}\text{C}$ -nmr data, see Table 1.

**14-BENZOYLACONINE-8-OLEATE [3].**—Aconitine (100 mg, 0.15 mmol) and oleic acid (200 mg, 0.71 mmol) were thoroughly mixed. The reaction and workup were carried out as per the general procedure to give compound **3** ( $\text{C}_{50}\text{H}_{77}\text{NO}_{11}$ , 52 mg, 38.7%) as an oil, [ $\alpha$ ] $^{30\text{D}}$  + 2.29 $^\circ$  ( $c=0.26$ ); ir  $\nu$  max 3495, 1729, 1712, 1280, 1100, and 710  $\text{cm}^{-1}$ ; eims  $m/z$  554 [ $\text{M}-\text{R}^3-\text{OH}-\text{OMe}$ ] $^+$  (27), 264 (3), and 105 (93);  $^1\text{H}$  nmr  $\delta$  0.87 (3H, t,  $J=7.0$  Hz, H-18 $''$ ), 1.09 (3H, t,  $J=7.2$  Hz, N- $\text{CH}_2\text{CH}_3$ ), 3.15 (3H, s, OMe-6), 3.25 (3H, s, OMe-1), 3.29 (3H, s, OMe-18), 3.34 (1H, d,  $J=5.0$  Hz, H-16 $\alpha$ ), 3.45 and 3.60 (1H each, d,  $J=8.9$  Hz, H-18), 3.75 (3H, s, OMe-16), 3.95 (1H, s, OH-13), 4.02 (1H, d,  $J=6.9$  Hz, H-6 $\beta$ ), 4.44 (1H, dd,  $J=5.3$  and 2.8 Hz, H-15 $\beta$ ), 4.48 (1H, d,  $J=2.7$  Hz, OH-15), 4.85 (1H, d,  $J=4.9$  Hz, H-14 $\beta$ ), 5.34 (2H, m, H-9 $''$  and 10 $''$ ), 7.44 (2H, t,  $J=7.3$  Hz, H-3', 5'), 7.56 (1H, t,  $J=7.4$  Hz, H-4'), and 8.02 (2H, d,  $J=7.3$  Hz, H-2', 6'); for  $^{13}\text{C}$ -nmr data, see Table 1.

**14-BENZOYLACONINE-8-PALMITATE [4].**—Aconitine (200 mg, 0.31 mmol) and palmitic acid (400 mg, 1.56 mmol) were mixed thoroughly. The reaction and workup were carried out as mentioned in the general procedure to give **4** ( $\text{C}_{48}\text{H}_{73}\text{NO}_{11}$ , 110 mg, 42.2%) as thick oil, [ $\alpha$ ] $^{30\text{D}}$  + 5.30 $^\circ$  ( $c=0.34$ ); ir  $\nu$  max 3495, 1730, 1713, 1278, and 1096  $\text{cm}^{-1}$ ; eims  $m/z$  554 [ $\text{M}-\text{R}^3-\text{OH}-\text{OMe}$ ] $^+$  (14), 257 (6), 213 (6), 105 (22), and 43 (100);  $^1\text{H}$  nmr  $\delta$  0.86 (3H, t,  $J=7.1$  Hz, H-16 $''$ ), 1.08 (3H, t,  $J=7.2$  Hz, N- $\text{CH}_2\text{CH}_3$ ), 3.14 (3H, s, OMe-6), 3.24 (3H, s, OMe-1), 3.28 (3H, s, OMe-18), 3.33 (1H, d,  $J=5.5$  Hz, H-16 $\alpha$ ), 3.44 and 3.60 (each 1H, d,  $J=8.9$  Hz, H-18), 3.74 (3H, s, OMe-16), 3.95 (1H, s, OH-13), 4.01 (1H, d,  $J=6.7$  Hz, H-6 $\beta$ ), 4.42 (1H, dd,  $J=5.3$  and 2.8 Hz, H-15 $\beta$ ), 4.48 (1H, d,  $J=2.7$  Hz, OH-15), 4.84 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 7.43 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.55 (1H, t,  $J=7.2$  Hz, H-4'), and 8.01 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}\text{C}$ -nmr data, see Table 1.

**14-BENZOYLACONINE-8-STEARATE [5].**—Aconitine (100 mg, 0.15 mmol) and stearic acid (200 mg, 0.7 mmol) were mixed thoroughly. The reaction and workup were carried out as mentioned in the general procedure to give **5** ( $C_{50}H_{79}NO_{11}$ , 55 mg, 40.8%) as an oil,  $[\alpha]^{24}_D + 6.75^\circ$  ( $c=0.28$ );  $\nu$  max 1730, 1712, and 1097  $cm^{-1}$ ; eims  $m/z$  554  $[M-R^3-OH-OMe]^+$  (3), 257 (6), 105 (39), and 44 (100);  $^1H$  nmr  $\delta$  0.88 (3H, t,  $J=7.0$  Hz, H-18"), 1.10 (3H, t,  $J=7.1$  Hz,  $N-CH_2CH_3$ ), 3.16 (3H, s, OMe-6), 3.27 (3H, s, OMe-1), 3.30 (3H, s, OMe-18), 3.35 (1H, d,  $J=5.3$  Hz, H-16 $\alpha$ ), 3.47 and 3.61 (each 1H, d,  $J=8.8$  Hz, H-18), 3.77 (3H, s, OMe-16), 3.96 (1H, s, OH-13), 4.03 (1H, d,  $J=6.9$  Hz, H-6 $\beta$ ), 4.44 (1H, dd,  $J=5.3$  and 2.6 Hz, H-15 $\beta$ ), 4.50 (1H, d,  $J=2.6$  Hz, OH-15), 4.87 (1H, d,  $J=4.9$  Hz, H-14 $\beta$ ), 7.45 (2H, t,  $J=7.3$  Hz, H-3', 5'), 7.57 (1H, t,  $J=7.1$  Hz, H-4'), and 8.03 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 1.

**PYROACONITINE [6].**—This compound was isolated from all the reactions of aconitine with fatty acids, as an amorphous solid ( $C_{32}H_{43}NO_9$ , 30–35%):  $[\alpha]^{22}_D - 82.41^\circ$  ( $c=0.59$ );  $\nu$  max 3400, 1720, 1710, 1271, and 1092  $cm^{-1}$ ; eims  $m/z$  554  $[M-31]^+$  (94), 536 (7), 455 (7), and 105 (100);  $^1H$  nmr  $\delta$  1.04 (3H, t,  $J=7.0$  Hz,  $N-CH_2CH_3$ ), 2.04 (1H, d,  $J=6.6$  Hz, H-5), 3.25 (6H, s, OMe-1 and -6), 3.30 (3H, s, OMe-18), 3.72 (2H, dd,  $J=16.5$  and 9.0 Hz, H-18), 3.81 (3H, s, OMe-16), 3.90 (1H, d,  $J=6.5$  Hz, H-6 $\beta$ ), 5.42 (1H, d,  $J=4.9$  Hz, H-14 $\beta$ ), 7.47 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.60 (1H, t,  $J=7.2$  Hz, H-4'), and 7.93 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 1.

**14-BENZOYLDELPHONINE-8-LINOLEATE [7].**—Delphinine (100 mg, 0.166 mmol) and linoleic acid (200 mg, 0.71 mmol) were mixed thoroughly. The usual reaction and workup yielded compound **7** ( $C_{49}H_{73}NO_9$ , 60 mg, 43.9%) as an oil,  $[\alpha]^{22}_D + 23.7^\circ$  ( $c=0.59$ );  $\nu$  max 3440, 1730, 1280, 1096, and 710  $cm^{-1}$ ; eims  $m/z$  789  $[M-31]^+$  (2), 539 (7), 524 (5), 508 (33), and 41 (100);  $^1H$  nmr  $\delta$  0.88 (3H, t,  $J=7.2$  Hz, H-18"), 2.32 (3H, s,  $N-CH_3$ ), 3.15 (3H, s, OMe-6), 3.27 (6H, s, OMe-1 and -18), 3.53 (3H, s, OMe-16), 3.96 (1H, d,  $J=6.5$  Hz, H-6 $\beta$ ), 4.88 (1H, d,  $J=4.5$  Hz, H-14 $\beta$ ), 5.35 (4H, m, H-9", 10", 12", and 13"), 7.42 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.54 (1H, t,  $J=7.2$  Hz, H-4'), and 8.06 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 2.

**14-BENZOYLDELPHONINE-8-LINOLENATE [8].**—Delphinine (150 mg, 0.25 mmol) and linolenic acid (300 mg, 1.07 mmol) were mixed thoroughly. The usual reaction and workup furnished compound **8** ( $C_{49}H_{71}NO_9$ , 94 mg, 45.5%) as an oil,  $[\alpha]^{22}_D + 20.02^\circ$  ( $c=0.31$ );  $\nu$  max 3450, 1726, 1280, 1130, 1093, and 710  $cm^{-1}$ ; eims  $m/z$  508  $[M-R^3-OH-OMe]^+$  (7), 237 (21), 105 (57), and 44 (100);  $^1H$  nmr  $\delta$  0.95 (3H, t,  $J=7.2$  Hz, H-18"), 2.31 (3H, s,  $N-CH_3$ ), 3.12 (3H, s, OMe-6), 3.25 (6H, s, OMe-1 and -18), 3.51 (3H, s, OMe-16), 3.94 (1H, d,  $J=6.5$  Hz, H-6 $\beta$ ), 4.87 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 5.35 (6H, m, H-9", 10", 12", 13", 15", and 16"), 7.41 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.53 (1H, t,  $J=7.2$  Hz, H-4'), and 8.05 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 2.

**14-BENZOYLDELPHONINE-8-OLEATE [9].**—Delphinine (150 mg, 0.25 mmol) and oleic acid (300 mg, 1.07 mmol) were thoroughly mixed. The usual reaction and workup gave compound **9** ( $C_{49}H_{75}NO_9$ , 85 mg, 41.3%) as an oil,  $[\alpha]^{20}_D + 20.08^\circ$  ( $c=0.40$ );  $\nu$  max 1730, 1280, 1116, and 1093  $cm^{-1}$ ; eims  $m/z$  791  $[M-31]^+$  (3), 508 (25), 237 (40), 105 (55), and 55 (100);  $^1H$  nmr  $\delta$  0.87 (3H, t,  $J=7.2$  Hz, H-18"), 2.31 (3H, s,  $N-CH_3$ ), 3.13 (3H, s, OMe-6), 3.27 (6H, s, OMe-1 and -18), 3.53 (3H, s, OMe-16), 3.95 (1H, d,  $J=6.9$  Hz, H-6 $\beta$ ), 4.88 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 5.33 (2H, m, H-9" and 10"), 7.42 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.51 (1H, t,  $J=7.2$  Hz, H-4'), and 8.06 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 2.

**14-BENZOYLDELPHONINE-8-PALMITATE [10].**—Delphinine (100 mg, 0.166 mmol) and palmitic acid (200 mg, 0.78 mmol) were thoroughly mixed. The usual reaction and workup gave compound **10** ( $C_{47}H_{73}NO_9$ , 56 mg, 35.0%) as an oil,  $[\alpha]^{22}_D 0^\circ$  ( $c=0.10$ );  $\nu$  max 1730, 1280, 1115, and 1093  $cm^{-1}$ ; eims  $m/z$  765  $[M-31]^+$  (5), 508 (21), 237 (35), and 43 (100);  $^1H$  nmr  $\delta$  0.87 (3H, t,  $J=7.2$  Hz, H-16"), 2.31 (3H, s,  $N-CH_3$ ), 3.13 (3H, s, OMe-6), 3.26 (6H, s, OMe-1 and -18), 3.52 (3H, s, OMe-16), 3.95 (1H, d,  $J=6.9$  Hz, H-6 $\beta$ ), 4.88 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 7.42 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.54 (1H, t,  $J=7.2$  Hz, H-4'), and 8.06 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 2.

**14-BENZOYLDELPHONINE-8-STEARATE [11].**—Delphinine (100 mg, 0.166 mmol) and stearic acid (200 mg, 0.7 mmol) were mixed thoroughly. The usual reaction and workup furnished compound **11** ( $C_{49}H_{77}NO_9$ , 80 mg, 58.2%) as an oil,  $[\alpha]^{22}_D + 21.97^\circ$  ( $c=0.40$ );  $\nu$  max 1730, 1280, 1117, and 1095  $cm^{-1}$ ; eims  $m/z$  793  $[M-31]^+$  (0.2), 539 (2), 508 (18), 237 (25), 105 (54), and 43 (100);  $^1H$  nmr  $\delta$  0.87 (3H, t,  $J=7.2$  Hz, H-18"), 2.31 (3H, s,  $N-CH_3$ ), 3.15 (3H, s, OMe-6), 3.27 (6H, s, OMe-1 and -18), 3.53 (3H, s, OMe-16), 3.95 (1H, d,  $J=6.9$  Hz, H-6 $\beta$ ), 4.88 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 7.42 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.54 (1H, t,  $J=7.2$  Hz, H-4'), and 8.06 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 2.

**14-BENZOYLDELPHONINE-8-PROPIONATE [12].**—Delphinine (100 mg, 0.166 mmol) and propionic

acid (0.3 ml) were mixed. The usual reaction and workup gave compound **12** ( $C_{34}H_{47}NO_9$ , 67.3 mg, 65.9%) as an amorphous solid,  $[\alpha]^{22D} + 32.2^\circ$  ( $c=0.1$ );  $ir \nu$  max 1722, 1280, and  $720\text{ cm}^{-1}$ ; eims  $m/z$  582  $[M-31]^+$  (41), 568 (6), 540 (3), 508 (20), and 105 (100);  $^1H$  nmr  $\delta$  0.62 (3H, t,  $J=7.2$  Hz, H-3 $''$ ), 2.31 (3H, s, N-CH $_3$ ), 3.12 (3H, s, OMe-6), 3.26 (6H, s, OMe-1 and -18), 3.52 (3H, s, OMe-16), 3.95 (1H, d,  $J=6.9$  Hz, H-6 $\beta$ ), 4.89 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 7.42 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.54 (1H, t,  $J=7.2$  Hz, H-4'), and 8.05 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 2.

**PYRODELPHININE [13].**—The known compound **13** ( $C_{31}H_{41}NO_7$ , 13–14%) (14) was obtained as a byproduct in all the reactions of delphinine with fatty acids, mp 209–211°,  $[\alpha]^{22D} + 156.46^\circ$  ( $c=0.46$ );  $ir \nu$  max 3460, 1700, 1285, 1099, and  $720\text{ cm}^{-1}$ ; eims  $m/z$  539  $[M]^+$  (6), 524  $[M-15]^+$  (4), 508 (43), 237 (58), and 105 (100);  $^1H$  nmr  $\delta$  2.39 (3H, s, N-CH $_3$ ), 3.27 (3H, s, OMe-6), 3.30 (3H, s, OMe-1), 3.31 (3H, s, OMe-18), 3.40 (3H, s, OMe-16), 4.20 (1H, d,  $J=6.8$  Hz, H-6 $\beta$ ), 4.98 (1H, d,  $J=3.0$  Hz, H-14 $\beta$ ), 5.58 (1H, d,  $J=6.3$  Hz, H-15), 7.42 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.55 (1H, t,  $J=7.2$  Hz, H-4'), and 8.06 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 2.

**16-DEMETHOXY-15,16-DIDEHYDRO-14-BENZOYLDDELPHONINE-8-PALMITATE [14].**—Compound **14** ( $C_{46}H_{69}NO_8$ , 19–21%) was an oil and was isolated from the reaction of delphinine with palmitic acid,  $[\alpha]^{22D} - 3.15^\circ$  ( $c=0.37$ );  $ir \nu$  max 3430, 1723, 1278, 1112, 1092, and  $710\text{ cm}^{-1}$ ; eims  $m/z$  733  $[M-31]^+$  (8), 476 (2), 237 (13), 105 (61), and 43 (100);  $^1H$  nmr  $\delta$  0.88 (3H, t,  $J=7.0$  Hz, H-16 $''$ ), 2.27 (3H, s, N-CH $_3$ ), 2.94 (1H, br s, H-17), 3.14 (3H, s, OMe-1), 3.26 (3H, s, OMe-6), 3.29 (3H, s, OMe-18), 3.22 and 3.64 (1H each, d,  $J=8.6$  Hz, H-18), 4.10 (1H, d,  $J=6.7$  Hz, H-6 $\beta$ ), 4.93 (1H, d,  $J=3.8$  Hz, H-14 $\beta$ ), 6.04 (1H, dd,  $J=10.5$  and 1.3 Hz, H-16), 6.53 (1H, d,  $J=10.5$  Hz, H-15), 7.41 (2H, t,  $J=7.6$  Hz, H-3', 5'), 7.55 (1H, t,  $J=7.2$  Hz, H-4'), and 8.00 (2H, d,  $J=7.5$  Hz, H-2', 6'); for  $^{13}C$ -nmr data, see Table 2.

**N-DEMETHYL-N,19-DIDEHYDRODELPHININE [15].**—Compound **15** ( $C_{31}H_{39}NO_9$ , 10–12%) was an amorphous solid,  $ir \nu$  max 3390, 1725, 1280, 1100, 815,  $652\text{ cm}^{-1}$ ;  $^1H$  nmr  $\delta$  1.25 (3H, s, -COMe), 2.72 (1H, m, H-9), 3.07 (3H, s, OMe-6), 3.19 (3H, s, OMe-1), 3.31 (3H, s, OMe-18), 3.55 (3H, s, OMe-16), 3.75 (1H, br s, H-17), 3.47 and 3.78 (each 1H, d,  $J=8.8$  Hz, H-18), 3.92 (1H, d,  $J=7.0$  Hz, H-6 $\beta$ ), 4.94 (1H, d,  $J=4.8$  Hz, H-14 $\beta$ ), 7.34 (1H, br s, H-19), 7.43 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.56 (1H, t,  $J=7.2$  Hz, H-4'), and 8.06 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}C$  nmr data, see Table 2.

**1-ACETYL-8-DEACETYLDDELPHISINE-8-LINOLEATE [16].**—14-Acetyl delphisine (70 mg, 0.124 mmol) and linoleic acid (140 mg, 0.5 mmol) were thoroughly mixed. The usual reaction and workup gave compound **16** ( $C_{46}H_{73}NO_9$ , 50 mg, 51.4%) as an oil,  $[\alpha]^{22D} - 6.83^\circ$  ( $c=0.25$ );  $ir \nu$  max 3432, 1740, and  $1240\text{ cm}^{-1}$ ; eims  $m/z$  725  $[M-59]^+$  (4), 444 (49), 412 (7), and 43 (100);  $^1H$  nmr  $\delta$  0.88 (3H, t,  $J=7.0$  Hz, H-18 $''$ ), 1.08 (3H, t,  $J=7.0$  Hz, N-CH $_2$ CH $_3$ ), 2.03 (6H, s, OAc-1 and -14), 3.22 (3H, s, OMe-6), 3.27 (3H, s, OMe-18), 3.30 (3H, s, OMe-16), 3.61 (1H, d,  $J=8.5$  Hz, H-18), 4.02 (1H, d,  $J=6.5$  Hz, H-6 $\beta$ ), 4.73 (1H, d,  $J=4.8$  Hz, H-14 $\beta$ ), 4.83 (1H, dd,  $J=10.4$  and 7.0 Hz, H-1 $\beta$ ), and 5.34 (4H, m, H-9 $''$ , 10 $''$ , 12 $''$ , and 13 $''$ ); for  $^{13}C$ -nmr data, see Table 1.

**1-ACETYL-8-DEACETYL-16-DEMETHOXY-15,16-DIDEHYDRODELPHISINE-8-LINOLEATE [17].**—The compound was an oil,  $ir \nu$  max 3436, 1735, and  $1240\text{ cm}^{-1}$ ; eims  $m/z$  693  $[M-59]^+$  (16), 414 (16), 412, and 43 (100);  $^1H$  nmr  $\delta$  0.89 (3H, t,  $J=6.8$  Hz, H-18 $''$ ), 1.05 (3H, t,  $J=7.1$  Hz, N-CH $_2$ CH $_3$ ), 2.00 (6H, s, OAc-1 and -14), 3.21 (3H, s, OMe-6), 3.29 (3H, s, OMe-18), 4.17 (1H, d,  $J=6.5$  Hz, H-6 $\beta$ ), 4.65 (1H, d,  $J=4.5$  Hz, H-14 $\beta$ ), 4.82 (1H, dd,  $J=10.4$  and 7.0 Hz, H-1 $\beta$ ), 5.36 (4H, m, H-9 $''$ , 10 $''$ , 12 $''$ , and 13 $''$ ), 6.05 (1H, dd,  $J=10.0$  and 6.3 Hz, H-16), and 6.53 (1H, d,  $J=10.0$  Hz, H-15); for  $^{13}C$ -nmr data, see Table 1.

**FALCONERINE-8-PALMITATE [18].**—8-Acetylfalconerine (30 mg, 0.044 mmol) and palmitic acid (60 mg, 0.234 mmol) were thoroughly mixed. The usual reaction and workup furnished compound **18** ( $C_{50}H_{79}NO_{11}$ , 30 mg, 77.5%) as an oil,  $[\alpha]^{24D} + 11.1^\circ$  ( $c=0.32$ );  $ir \nu$  max 1728, 1600, 1512, and  $1270\text{ cm}^{-1}$ ; eims  $m/z$  613  $[M-R^3-OH]^+$  (0.8), 598 (3), 582 (9), 432 (25), 266 (21), 165 (81), and 43 (100);  $^1H$  nmr  $\delta$  0.87 (3H, t,  $J=6.8$  Hz, H-16 $''$ ), 1.07 (3H, t,  $J=7.2$  Hz, N-CH $_2$ CH $_3$ ), 2.12 (1H, d,  $J=6.4$  Hz, H-5), 2.42 (1H, m, H-13), 2.78 (1H, br s, H-17), 3.03 (1H, s, H-7), 3.16 (3H, s, OMe-1), 3.24 (3H, s, OMe-16), 3.29 (3H, s, OMe-6), 3.39 (3H, s, OMe-18), 3.43 and 3.61 (1H each, d,  $J=8.8$  Hz, H-18), 3.79 (1H, m, H-3 $\beta$ ), 3.89 and 3.91 (each 3H, s, OMe-3' and -4'), 4.09 (1H, d,  $J=6.2$  Hz, H-6 $\beta$ ), 5.02 (1H, t,  $J=4.7$  Hz, H-14 $\beta$ ), 6.87 (1H, d,  $J=8.5$  Hz, H-5'), 7.62 (1H, d,  $J=1.6$  Hz, H-2'), and 7.69 (1H, dd,  $J=8.0$  and 1.6 Hz, H-6'); for  $^{13}C$ -nmr data, see Table 1.

**14-BENZOYLMESACONINE-8-PALMITATE [19].**—Mesaconitine (30 mg, 0.047 mmol) and palmitic acid (60 mg, 0.234 mmol) were thoroughly mixed. The usual reaction and workup gave compound **19** ( $C_{47}H_{73}NO_{11}$ , 16 mg, 40.7%) as an oil,  $ir \nu$  max 1730 and  $1712\text{ cm}^{-1}$ ; eims  $m/z$  554  $[M-R^3-OH-OH]$  (14), 540 (34), 105 (100), and 43 (98);  $^1H$  nmr  $\delta$  0.88 (3H, t,  $J=6.7$  Hz, H-16 $''$ ), 2.34 (3H, s, N-CH $_3$ ), 3.15 (3H, s, OMe-6), 3.28 (3H, s, OMe-1), 3.30 (3H, s, OMe-18), 3.75 (3H, s, OMe-16), 4.03 (1H, d,  $J=6.7$



Hz, H-6 $\beta$ ), 4.45 (2H, m, H-15 $\beta$  and OH-15), 4.86 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 7.45 (2H, t,  $J=7.2$  Hz, H-3', 5'), 7.57 (1H, t,  $J=7.2$  Hz, H-4'), and 8.03 (2H, d,  $J=7.2$  Hz, H-2', 6'); for  $^{13}\text{C}$ -nmr data, see Table 2.

8-DEACETYLPSEUDAONITINE-8-PALMITATE [20].—Pseudoaconitine (30 mg, 0.043 mmol) and palmitic acid (60 mg, 0.234 mmol) were thoroughly mixed. The usual reaction and workup gave compound 20 ( $\text{C}_{50}\text{H}_{79}\text{NO}_{12}$ , 14 mg, 36.4%) as an oil [ $\alpha$ ] $^{24}\text{D} + 17.19^\circ$  ( $c=0.13$ ); eims  $m/z$  629 [ $\text{M}-\text{R}^3-\text{OH}$ ] $^+$  (3), 614 (3), 598 (11), 268 (38), 165 (92), and 43 (100);  $^1\text{H}$  nmr  $\delta$  0.87 (3H, t,  $J=6.8$  Hz, H-16 $\alpha$ ), 1.08 (3H, t,  $J=7.2$  Hz, N- $\text{CH}_2\text{CH}_3$ ), 3.02 (1H, br s, H-17), 3.14 (3H, s, OMe-6), 3.24 (3H, s, OMe-1), 3.29 (3H, s, OMe-18), 3.39 (1H, m, H-16 $\alpha$ ), 3.52 (3H, s, OMe-16), 3.77 (1H, m, H-3 $\beta$ ), 3.89 and 3.92 (3H each, s, OMe-3' and -4'), 4.00 (1H, d,  $J=6.2$  Hz, H-6 $\beta$ ), 4.84 (1H, d,  $J=5.0$  Hz, H-14 $\beta$ ), 6.87 (1H, d,  $J=8.4$  Hz, H-5'), 7.59 (1H, d,  $J=1.8$  Hz, H-2'), and 7.69 (1H, dd,  $J=8.2$  and 1.8 Hz, H-6'); for  $^{13}\text{C}$ -nmr data, see Table 1.

#### ACKNOWLEDGMENTS

This work was supported by Grant HL32562 from the National Institutes of Health. We thank Mr. Courtney Pape for the mass spectra.

#### LITERATURE CITED

1. M.H. Benn and J.M. Jacyno, in: "Alkaloids: Chemical and Biological Perspectives." Ed. by S.W. Pelletier, John Wiley and Sons, New York, 1983, Vol. 1, pp. 153-210.
2. N.G. Bisset, *J. Ethnopharmacol.*, **4**, 247 (1981).
3. I. Kitagawa, M. Yoshikawa, Z.L. Chen, and K. Kobayashi, *Chem. Pharm. Bull.*, **30**, 758 (1982).
4. S.A. Ross and S.W. Pelletier, *Heterocycles*, **27**, 1381 (1988).
5. S.A. Ross and S.W. Pelletier, *Heterocycles*, **31**, 671 (1990).
6. S.A. Ross and S.W. Pelletier, *Heterocycles*, **32**, 1307 (1991).
7. R. Majima and H. Sugimoto, *Ber. Dtsch. Chem. Ges.*, **57B**, 1468 (1924).
8. B.S. Joshi, J.K. Wonderlich, and S.W. Pelletier, *Can. J. Chem.*, **65**, 99 (1987).
9. J.B. Hanuman and A. Katz, *J. Nat. Prod.*, **56**, 801 (1993).
10. J.G. Batchelor, R.J. Cushley, and J.H. Prestegard, *J. Org. Chem.*, **39**, 1698 (1974).
11. S.W. Pelletier, J. Finer-Moore, R.C. Desai, N.V. Mody, and H.K. Desai, *J. Org. Chem.*, **47**, 5290 (1982).
12. S.W. Pelletier, H.K. Desai, Q.P. Jiang, and S.A. Ross, *Phytochemistry*, **29**, 3649 (1990).
13. H.K. Desai, E.R. Trumbull, and S.W. Pelletier, *J. Chromatogr.*, **366**, 439 (1986).
14. S.W. Pelletier, N.V. Mody, B.S. Joshi, and L.C. Schramm, in: "Alkaloids: Chemical and Biological Perspectives." Ed. by S.W. Pelletier, John Wiley & Sons, New York, 1984, Vol. 2, pp. 205-462.

Received 4 March 1994