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FIVE DITERPENOID ALKALOIDS FROM *DELPHINIUM CARDIOPETALUM*

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Key Word Index—*Delphinium cardiopetalum*; Ranunculaceae; diterpenoid alkaloids; cardiopine; cardiopinine; cardiopimine; cardiopidine; cardiodine.

Abstract—A further study of the alkaloidal constituents of *Delphinium cardiopetalum* led to the isolation of five new highly functionalized diterpenoid alkaloids, cardiopine, cardiopinine, cardiopimine, cardiopidine and cardiodine. Their structures were established by 1D and 2D NMR spectroscopy, ^{1}HCOSY, HMQC, HMBC and ROESY, and chemical transformations.

INTRODUCTION

Plants of the *Aconitum*, *Delphinium*, and *Consolida* genera are recognised as rich sources of biologically active and structurally complex norditerpenoid and diterpenoid alkaloids [1–4]. In previous papers [5, 6], we have reported on the isolation from the aerial parts of *Delphinium cardiopetalum* D.C. of seven norditerpenoid alkaloids, cardiopetaline, cardiopetalidine, dihydrogadesine, 14-benzoyldihydrogadesine, 14-benzoylgadesine, karacoline, and 14-acetylnudicaulidine, and eight diterpenoid alkaloids, cardiopetamine, 15-acetylcardiopetamine, hetisine, hetisinone, 13-acetylhetisinone, cardionidine, and atisinium chloride. In the on-going investigation of the minor constituents of this plant, we have now isolated five new highly oxygenated hetisine-type diterpenoid alkaloids, cardiopine (**1**), cardiopinine (**2**), cardiopimine (**3**), cardiopidine (**4**) and cardiodine (**5**).

RESULTS AND DISCUSSION

The molecular formulae of the new alkaloids were derived from their HR-mass spectrometry and ^{13}C NMR spectra. The NMR spectra indicated that they belong to the hetisine subtype of diterpenoid alkaloids and are highly functionalized [7–12]. It was evident that the compounds each have an exocyclic double bond (δ_H 4.84–4.87 and 4.97–5.01 (each *br s*), δ_C 110.3–110.6 *t* and 141.5–142.7 *s*), an angular methyl group (δ_H 0.99–1.14 *s*, δ_C 25.3–25.7 *q*), a benzoate group (δ_H 7.45–7.50 *t*, 7.55–7.57 *t*, 8.11–8.23 *d*, δ_C 128.5–128.7 *d*, 129.6–130.0 *d*, 130.0–130.1 *s*, 133.2–133.5 *d* and 165.6–165.9 *s*) and at least two acetate groups [δ_H 1.97–2.00 *s*, 2.02–2.09 *s*, δ_C 171.0–171.5 (two *s*)]. The alkaloids cardiopine (**1**), $C_{36}H_{43}NO_9$, cardiopidine (**4**), $C_{36}H_{43}NO_9$, and cardiodine (**5**), $C_{38}H_{45}NO_{11}$, also bear a 2-methylbutyrate group (δ_H 0.85–1.12 *d*, 0.57–0.87 *t*, δ_C 10.7–11.6 *q*, 15.7–16.7 *q*, 24.9–26.6 *t*, 39.6–41.2 *d*, and 174.5–177.2 *s*) and the alkaloids cardiopinine (**2**), $C_{35}H_{45}NO_9$, and cardiopimine (**3**), $C_{35}H_{45}NO_9$, an isobutyrate group [δ_H 0.59–1.15 (two *d*), δ_C 17.9–18.2 *q*, 19.2–19.3 *q*, and 33.1–34.1 *d*, and 177.4–176.3 *s*].

The signals at δ_H 2.37 and 3.10 (each *d*, AB-system) for cardiopine (**1**) (Tables 1 and 6), which showed one-bond correlation with the methylene carbon resonance at δ_C 59.5 (*t*) in the HMQC spectrum [13] (Table 1), were assigned to the non-equivalent C-19 methylene protons because of the three-bond connectivity with the C-18 resonance observed in the HMBC spectrum [14] (Table 1). In that spectrum, three-bond correlations were observed between the H-18 signal and δ_C 59.5 (*d*) (δ_H 2.15 *s* from HMQC) and 70.8 (*d*) (δ_H 3.87, *d*), and between the H-19α signal and δ_C 66.2 (*d*) (δ_H 3.67, *s*), 63.9 (*d*) (δ_H 3.30, *br s*) and 70.8 (*d*) (δ_H 3.87, *d*). Also the proton signal at δ_H 3.30 showed scalar coupling to δ_H 2.15 (*s*) and to the methylene protons (AB-system) at δ_H 1.66 (*dd*) and 1.88 (*dd*) (δ_C 35.9 *t* from HMQC) in the ^{1}HCOSY spectrum (Table 6). Therefore, the one-proton signals at δ_H 2.15 (*s*), 3.30 (*br s*), 3.67 (*s*), 1.66 (*dd*) and 1.88 (*dd*) were assigned to H-5, H-6, H-20, H-7β and H-7α, respectively, and the carbon signals at δ_C 59.5 (*d*), 63.9 (*d*), 66.2 (*d*) and 35.9 (*t*), to C-5, C-6, C-20 and C-7, respectively. Furthermore, the one-proton signal at δ_H 3.87 (*d*) and its correlated methine carbon resonance at δ_C 70.8 were assigned to H-C (3) and clearly indicated the existence of a secondary hydroxyl group at C-3 in cardiopine (**1**). Since the H-3 signal gave NOEs with the H-5 and H-18 signals in the

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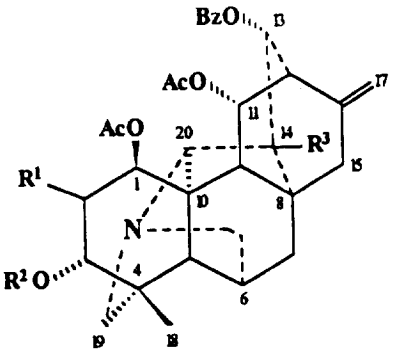
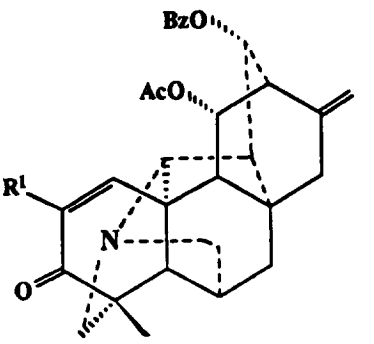


1	$R^1 = \alpha$ OCOCH(Me)CH$_2$Me	R^2 = H	R^3 = H
2	$R^1 = \alpha$ OCOCH(Me)$_2$	R^2 = H	R^3 = H
3	$R^1 = \alpha$ OH	R^2 = COCH(Me)$_2$	R^3 = H
4	$R^1 = \alpha$ OH	R^2 = COCH(Me)CH$_2$Me	R^3 = H
5	$R^1 = \alpha$ OCOCH(Me)CH$_2$Me	R^2 = Ac	R^3 = OH
6	$R^1 = \alpha$ OCOCH(Me)CH$_2$Me	R^2 = Ac	R^3 = H
7	$R^1 = \alpha$ OCOCH(Me)$_2$	R^2 = Ac	R^3 = H
10	R^1 = O	R^2 = COCH(Me)$_2$	R^3 = H
11	$R^1 = \alpha$ OH	R^2 = H	R^3 = H



8 R^1 = OCOCH(Me)CH$_2$Me

9 R^1 = OCOCH(Me)$_2$

ROESY spectrum (Table 6) [15], the secondary hydroxyl group at C-3 must be in an equatorial α configuration (Ring A chair). Moreover, upon acetylation of cardiopine (**1**) the one-proton signal at δ_H 3.87 (*d*) shifted to 5.11 (*d*), and by oxidation with Cornforth's reagent yielded the α,β-unsaturated ketone (**8**) [M^+, 571; δ_C 193.4 (*s*), 128.5 (*s*) and 138.4 (*d*)], the structure of which was subsequently deduced by comparison of its NMR spectra with those of cardiopine (**1**).

In the ^{1}HCOSY spectrum of cardiopine (**1**) the H-3β resonance at δ_H 3.87 (*d*, J = 5 Hz) showed coupling with the one-proton signal at δ_H 5.60 (*dd*, J = 5.2 and 2.9 Hz) and this in turn with the one-proton signal at δ_H 6.09 (*d*, J = 2.9 Hz). On the other hand, the signals at δ_H 5.60 and 6.09 gave, among others, a three-bond connectivity with the quaternary carbon resonances at δ_C 177.2 (carbonyl 2-methylbutyrate) and 171.0 (carbonyl acetate), respectively, in the HMBC experiment; and in the ROESY spectrum the signal at δ_H 6.09 showed spatial correlation to the H-20 signal at δ_H 3.67 (*s*). These findings together with the chemical shifts and coupling constants of the involved protons, allowed the location of the 2-methylbutyrate group at C-2 in the α configuration and an acetate group at C-1 in the β configuration.

Since both H-6 and H-2β proton signals at δ_H 3.30 and 5.60, respectively, gave a three-bond connectivity with the quaternary carbon resonance at δ_C 53.9 in the HMBC spectrum of cardiopine (**1**), this carbon resonance was assigned to C-10. The second acetate group in cardiopine (**1**) was placed at C-11 because the one-proton signal at δ_H 5.42 (*d*, J = 9.5 Hz) (δ_C 75.4 from HMQC) displayed three-bond connectivities with the carbon signals at δ_C 171.5 *s*, 53.9 (*s*, C-10), and 142.7 (*s*, C-16). Also the afore mentioned signal at δ_H 5.42 was coupled to the one-proton signal at δ_H 2.33 (*dd*, J = 9.6 and 2.1 Hz), which was assigned to H-9 owing to its NOE effects with the H-5 and H-7β protons at δ_H 2.15 (*s*) and 1.66 (*dd*), respectively. The H-11 proton must be in the β configuration, and the acetate group should be α. For analogous reasons, the benzoate group was situated at C-13 in a Ψ-axial (α) configuration in the molecule of **1**: the one-proton signal at δ_H 5.51 (*dt*, J = 9.7 and 2.6 Hz) (δ_C 73.8 from HMQC) gave three-bond connectivities with the carbon resonances at δ_C 165.9 (*s*, carbonyl benzoate) and 75.4 (*d*, C-11) in the HMBC experiment; in the ^{1}HCOSY spectrum the signal at δ_H 5.51 was coupled to the one-proton signal at δ_H 2.53 (*dd*, J = 9.9 and 1.9 Hz), assigned to H-14 from its spatial correlations to the H-7α and H-20 signals in the ROESY spectrum; the benzoate group showed spatial correlation with the C-11 α acetate methyl at δ_H 2.00 (*s*) and the H-1α signal in the 2D NOE spectrum.

Hydrolysis of cardiopine (**1**) gave the amino alcohol (**11**) (M^+, 549) with loss of the 2-methylbutyryl group, as inferred from the ^{13}C and ^{1}H NMR spectra; δ_H 4.15 (*br s*, $W_{1/2}$ = 7.5 Hz, H-2β) and 3.52 (*d*, J = 5.2 Hz, H-3β).

The NMR spectra of cardiopinine (**2**) (Tables 2 and 13) almost fit those of cardiopine (**1**), indicating that both compounds have the same set of functional groups. However, cardiopinine (**2**) has an isobutyrate group instead of a 2-methylbutyrate. The isobutyrate group was easily located at C-2 in an α configuration on account of the three-bond connectivities observed between the one-proton signal at δ_H 5.59 (*dd*, J = 5.1 and 2.8 Hz) (δ_C 68.9 from HMQC) and the quaternary carbon resonances at δ_C 177.4 (carbonyl isobutyrate), 42.7 (C-4) and 53.9 (C-10) in the HMBC spectrum (Table 2), and the coupling constants between the H-2β and H-1α (δ_H 6.08, *d*, J = 2.9 Hz) and H-3β (δ_H 3.85, *d*, J = 5 Hz). The acetylation and oxidation of cardiopinine (**2**) yielded an acetate (**7**) and an α,β-unsaturated ketone (**9**), respectively, in a similar manner to cardiopine (**1**).

The similarity of the NMR spectra of cardiopine (**1**), cardiopimine (**3**) and cardiopidine (**4**) as well as the NMR data from the 2D NMR spectra of **3** and **4** permitted the two acetate groups at C-1β and C-11α and the benzoate group at C-13α, to be located in both alkaloids. The one-proton signal at δ_H 4.91–4.94 (*d*, J = 4.7–4.8 Hz) (δ_C 73.3 *d* from HMQC) in **3** and **4** showed three-bond correlations with the carbonyl ester (δ_C 176.3–175.7), and with the C-18 and C-19 carbon resonances, indicating that the isobutyrate group in **3** and the 2-methylbutyrate group in **4** are at C-3. As the one-proton signal at C-3, δ_H 4.91–4.94 (*d*, J = 4.7–4.8 Hz) showed coupling with the one-proton signal at δ_H 4.28 (*dd*, J = 4.6–4.7 and 3.2–3.4 Hz) (δ_C 67.0–67.1 from HMQC), and this signal in turn coupled with the one-proton signal at δ_H 6.04–6.05 (*d*, J = 3.3 Hz) (δ_C 74.1–74.2 from HMQC), in the ^{1}HCOSY spectra of **3** and **4**, clearly the aliphatic ester is in the α configuration at C-3, the secondary hydroxyl group is in the α configuration at C-2 and one acetate group is in the β configuration at C-1. Cardiopimine (**3**) did not give an acetyl derivative on treatment with acetic anhydride and pyridine but oxidation gave the ketone **10**, the structure of which was derived from its ^{1}H NMR spectra (table 12). These results confirmed the existence of a secondary hydroxyl group at C-2 in the molecule.

Comparison of the ^{1}H and ^{13}C NMR spectra of cardiodine (**5**) (Tables 5 and 13) with those of cardiopine (**1**) (Tables 1 and 13) and 3-acetylcardiopine (**6**) (Tables 11 and 13), and consideration of the connectivities observed in the 2D NMR spectra (Tables 5 and 10), led to the conclusion that cardiodine (**5**) has the same functional groups and configuration as 3-acetylcardiopine (**6**). Cardiodine (**5**) possesses an additional tertiary hydroxyl group as seen by the signal at δ_C 78.6 (*s*). The location of an hydroxyl group at C-14 in **5** was consistent with the α, β and γ effects observed on C-14, C-13 and C-20, and C-15 and C-7 carbon resonances, respectively. This was supported by the three-bond connectivities observed between the one-proton resonances at δ_H 1.49 (*dd*, H-7β), 2.40 (*d*, H-9) and 2.47 (*d*, H-12) and the C-14 carbon resonance at δ_C 78.6 (*s*) in the HMBC experiment (Table 5).

The remaining correlations between proton and carbon resonances observed in the 2D NMR spectra of the new alkaloids are in agreement with the proposed structures.

EXPERIMENTAL

General. Mp: uncorr., mixtures of hexane–EtOAc were used for crystallization; OR: EtOH, 1 dm cell; EI-MS and

exact mass measurements: Hewlett Packard-5995 and VG-Micromass-ZAB-2F instruments, respectively: 70 eV; NMR: Bruker-AMX-400 spectrometer, $CDCl_3$, TMS as int. standard. The programs used for DEPT, HMQC, HMBC ($J = 7$ Hz) and ROESY (spin lock 700 ms) experiments were those furnished in the Bruker manual. CC, TLC, PTLC: Alumina Merck, Art. 1077 and 5581, respectively. Visualization was effected with Dragendorff's reagent. Cornforth's reagent was prepared by adding dropwise a soln of CrO_3 (100 mg) in H_2O (0.1 ml) to pyridine (1 ml) at 0°.

Plant material. The plants were collected in the Cadí-Moixeró Natural Park, Lerida Province, Spain, growing on a calcareous and clayey soil, and authenticated by Professors J. Molero and C. Blanché, Botany Department, University of Barcelona, where a voucher specimen has been deposited.

Extraction and isolation. Aerial parts of *Delphinium cardiopetalum* DC (2.25 kg) were extracted with 80% EtOH by percolation for 4 days. After removing the solvent under vacuum, the EtOH extract (238 g) was treated with 0.5 HCl [6]. The acid sol was extracted with $CHCl_3$ to provide a crude material (32.6 g). The $CHCl_3$ extract, since it gave a positive test with Dragendorff's reagent, was treated with 0.5 M H_2SO_4, filtered, basified with NH_4OH (pH 10) and extracted with $CHCl_3$ to give a crude alkaloidal material (2.6 g). This material was chromatographed over alumina and eluted with hexane–EtOAc gradient. The frs eluted with hexane–EtOAc (7:3) were combined (91 mg), and repeatedly crystallized to give cardiopine (**1**) (35 mg). Frs eluted with hexane–EtOAc (1:1) afforded a mixture of alkaloids (150 mg) which after PTLC on 10 layers of alumina, elution with hexane–EtOAc (4:1) six times, gave cardiopinine (**2**) (27 mg), cardiopimine (**3**) (17 mg), cardiopidine (**4**) (10 mg), and cardiodine (**5**) (7 mg).

Cardiopine (**1**). Mp 194–197°, $[\alpha]_D - 26.3°$ ($C = 0.06$). $[M]^+$, m/z 633.2848 for $C_{36}H_{43}NO_9$ (calc. 633.2842); IR ν_{max}^{KBr} cm^{-1}: 3367, 3026, 2931, 1733, 1693, 1601, 1451, 1361, 1292, 1245, 1141, 1107, 1034, 979, and 712; EIMS m/z (rel. int.), 633 (1) $[M]^+$, 574 (100), 560 (4), 532 (2), 490 (14), 472 (8), 452 (3), 430 (2), 410 (2), 308 (5), 105 (28), 77 (5), 57 (7), 43 (3); ^1H and ^{13}C NMR: Tables 1 and 13.

Acetylcardiopine (**6**). A mixture of cardiopine (**1**) (5 mg), pyridine (0.15 ml) and Ac_2O (0.2 ml) was kept at room temperature for 24 hr. Toluene was then added and the solvent removed under vacuum. The residue was chromatographed over alumina with hexane–EtOAc (7:3) to give acetylcardiopine (**6**) as a resin (4 mg, 75%). EIMS m/z (rel. int.), 675 (1) $[M]^+$, 632 (2), 616 (100), 574 (4), 555 (6), 532 (17), 472 (8), 452 (8), 436 (4), 392 (5), 350 (6), 308 (6), 105 (32), 85 (3), 77 (6), 57 (10) and 43 (5); ^1H and ^{13}C NMR: Tables 11 and 13.

Cornforth oxidation of cardiopine to give the ketone (**8**). A mixture of cardiopine (10 mg), pyridine (0.3 ml) and Cornforth's reagent (0.4 ml) was stirred at room temp. for 6 days. The excess of reagent was decomposed with EtOH, the solvent removed and the residue percolated with hexane–EtOAc (1:1) on a short alumina column. PTLC on one layer of alumina, eluting with hexane–EtOAc (3:1), afforded the starting material **1** (4 mg) and the amorphous ketone (**8**) (3 mg, 55%). EIMS m/z (rel. int.), 571 (27) $[M]^+$, 487 (19), 486 (42), 459 (6), 426 (3), 364 (12), 322 (11), 306 (7), 294 (8), 278 (4), 157 (7), 144 (6), 128 (7), 126 (5), 122 (9), 105 (100), 77 (22), 57 (12) and 44 (10); ^1H and ^{13}C NMR: Tables 11 and 13.

Hydrolysis of cardiopine (**1**) *to give the amino alcohol* (**11**). To a soln of **1** (10 mg) in MeOH (2 ml), 5% methanolic KOH (0.4 ml) was added and the reaction mixture stirred at room temp. for 24 hr. Ice water was added and reaction product extracted with EtOAc. PTLC on one layer of Al_2O_3 and elution with EtOAc–MeOH (19:1) gave the amorphous amino alcohol **11** (7 mg, 80.7%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 2900, 1725, 1655, 1455, 1375, 1320, 1275, 1250, 1115, 1075, 1035, 905 and 715; EIMS m/z (rel. int.) 549 (2) $[M]^+$, 532 (11), 490 (100), 472 (7), 430 (5), 368 (8), 326 (12), 308 (18), 144 (8), 105 (89), 77 (9) and 43 (13); ^1H and ^{13}C NMR: Tables 12 and 13.

Cardiopinine (**2**). Mp 218–220°, $[\alpha]_D - 26.6°$ ($C = 0.08$). $[M]^+$ m/z 619.2776 for $C_{35}H_{45}NO_9$ (calc. 619.2780). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3411, 3025, 2980, 1734, 1719, 1657, 1450, 1370, 1272, 1237, 1149, 1109, 1069, 1034, 980, 901, and 713; EIMS m/z (rel. int.), 619 (2) $[M]^+$, 560 (100), 532 (5), 490 (17), 472 (5), 438 (6), 396 (6), 368 (4), 326 (6), 308 (16), 296 (4), 280 (10), 250 (3), 208 (3), 196 (3), 121 (3), 105 (71) and 77 (15); ^1H and ^{13}C NMR: Tables 2 and 13.

Acetylcardiopinine (**7**). A mixture of cardiopinine (**2**) (5 mg), pyridine (0.1 ml) and Ac_2O (0.1 ml) was kept for 24 hr at room temp. Usual work-up as for **6** gave 3-acetylcardiopinine (**7**) (5.0 mg, 94%) as a resin. EIMS m/z (int. rel.), 661 (1) $[M]^+$, 618 (2), 602 (100), 543 (2), 533 (4), 532 (11), 514 (1), 480 (2), 472 (7), 438 (8), 378 (4), 350 (7), 308 (3), 290 (2), 105 (31), 77 (39), and 43 (5); ^1H and ^{13}C NMR: Tables 11 and 13.

Ketocompound (**9**) *from cardiopinine* (**2**). A mixture of **2** (15 mg), pyridine (0.3 ml) and Cornforth's reagent (0.4 ml) was stirred at room temp. for 10 days. Work-up as for **8** gave the starting material (**2**) (7 mg) and the amorphous ketocompound **9** (7 mg, 78%). EIMS m/z (rel. int.), 557 (1) $[M]^+$, 504 (19), 466 (72), 454 (54), 442 (81), 364 (20), 322 (21), 105 (100), 77 (35), and 43 (47); ^1H and ^{13}C NMR: Tables 12 and 13.

Cardiopimine (**3**). Isolated as a resin, $[\alpha]_D - 81.3°$ ($C = 0.2$). $[M]^+$ m/z 619.2784 for $C_{35}H_{45}NO_9$ (calc. 619.2780). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3367, 3029, 1729, 1657, 1272, 1239, 1151, 1110 and 776; EIMS m/z (rel. int.), 619 (2) $[M]^+$, 560 (69), 532 (76), 490 (15), 472 (12), 396 (12), 308 (30), 280 (11), 105 (100), and 77 (25); ^1H and ^{13}C NMR: Tables 3 and 13. Cardiopimine (**3**) (5 mg) was treated with pyridine (0.1 ml) and Ac_2O (0.1 ml) at room temp. for 24 hr. Work-up in the usual way gave only the starting material.

Ketocompound (**10**) *from cardiopimine* (**3**). A mixture of cardiopimine (**3**) (5 mg), pyridine (0.15 ml) and Cornforth's reagent (0.3 ml) was stirred at room temp. for a week. Work-up as for **8** gave the amorphous ketocompound **10** (3.5 mg, 70%). EIMS m/z (rel. int.), 617 (2) $[M]^+$, 574 (2), 572 (3), 558 (100), 530 (46), 486 (3), 470 (3), 436 (3), 428 (4), 400 (6), 394 (15), 306 (9), 278 (4), 233 (3), 105 (100), 77 (12), 71 (13), and 43 (38); ^1H NMR: Table 12.

Table 1. ^{1}H, HMQC and HMBC NMR data of cardiopine (**1**)*

H		Correlated C-atom	
		HMQC	HMBC
1α	6.09 *d* (2.9)	73.2 *d*	171.0, C-2, C-3, C-5, C-10
2β	5.60 *dd* (5.2, 2.9)	68.9 *d*	177.2, C-1, C-3, C-4, C-10
3β	3.87 *d* (5.0)	70.8 *d*	C-2, C-4, C-5, C-18, C-19
5	2.15 *s*	59.5 *d*	C-18, C-19, C-20
6	3.30 *br s* ($W_{1/2}$ = 6.0)	63.9 *d*	C-8, C-10, C-20
7α	1.88 *dd* (13.6, 3.6)	35.9 *t*	C-8
7β	1.66 *dd* (13.6, 2.6)	35.9 *t*	C-8, C-14
9	2.33 *dd* (9.6, 2.1)	51.7 *d*	C-5, C-12, C-14, C-20
11β	5.42 *d* (9.5)	75.4 *d*	171.5, C-10, C-13, C-16
12	2.38 *d* (2.7)	46.6 *d*	
13β	5.51 *dt* (9.7, 2.6)	73.8 *d*	165.9, C-11
14	2.53 *dd* (9.9, 1.9)	50.4 *d*	C-9, C-10
15α	2.18 *dt* (17.8, 2.1)	33.9 *t*	C-8, C-9
15β	2.39 *dt* (17.8, 2.1)	33.9 *t*	
17z	4.97 *br s*	110.3 *t*	C-12, C-15
17e	4.87 *br s*	110.3 *t*	C-12, C-15
18	1.14 *s*	25.7 *q*	C-3, C-4, C-5
19α	3.10 *d* (12.8)	59.5 *t*	C-3, C-6, C-18, C-20
19β	2.37 *d* (12.8)	59.5 *t*	
20	3.67 *s*	66.2 *d*	C-5, C-6, C-8, C-9, C-13, C-14
2′	1.10 *m*	39.6 *d*	
3′	1.08 *m*	25.0 *t*	
4′	0.57 *t* (7.5)	10.8 *q*	C-2′, C-3′
5′	0.85 *d* (6.5)	15.7 *q*	C-1′, C-2′, C-3′
	8.14 *d* (7.2)	129.8 *d*	165.9
13α-OBz	7.47 *t* (7.0)	128.7 *d*	
	7.57 *t* (7.4)	133.4 *d*	
1β-OAc	2.06 *s*	21.2 *q*	171.0
11α-OAc	2.00 *s*	21.5 *q*	171.5

*Chemical shifts in ppm rel. to TMS; coupling constants *J* in Hz. C-Multiplicities were established by DEPT data.

Table 2. ^{1}H, HMQC and HMBC NMR data of cardiopinine (**2**)*

H		Correlated C-atom	
		HMQC	HMBC
1α	6.08 *d* (2.9)	73.1 *d*	170.2, C-2, C-3, C-5, C-10
2β	5.59 *dd* (5.1, 2.8)	68.9 *d*	177.4, C-1, C-3, C-4, C-10
3β	3.85 *d* (5.1)	70.6 *d*	C-2, C-4, C-18, C-19
5	2.16 *s*	59.3 *d*	C-18, C-19, C-20
6	3.32 *br s* ($W_{1/2}$ = 6.4)	63.8 *d*	C-8
7α	1.90 *dd* (13.4, 3.2)	35.7 *t*	C-8
7β	1.69 *dd* (13.4, 2.4)	35.7 *t*	C-8, C-14
9	2.30 *dd* (9.6, 2.0)	51.7 *d*	C-12, C-14, C-20
11β	5.43 *d* (10.4)	75.3 *d*	171.0, C-9, C-10, C-12, C-13, C-16
12	2.40 *d* (2.6)	46.2 *d*	
13β	5.48 *dt* (10.0, 2.0)	73.7 *d*	165.8, C-11
14	2.54 *dd* (9.9, 2.0)	50.4 *d*	C-9, C-10, C-20
15α	2.19 *br d* (17.5)	33.7 *t*	C-8, C-9
15β	2.39 *br d* (17.5)	33.7 *t*	
17z	4.97 *br s*	110.3 *t*	C-12, C-15
17e	4.84 *br s*	110.3 *t*	C-12, C-15
18	1.14 *s*	25.7 *q*	C-3, C-4, C-5
19α	3.10 *d* (12.8)	59.3 *t*	C-3, C-6, C-18, C-20
19β	2.35 *d* (12.8)	59.3 *t*	
20	3.67 *s*	66.1 *d*	C-1, C-5, C-6, C-8, C-9, C-13
2′	1.25 *sept* (6.6)	33.1 *d*	C-1′, C-3′, C-4′
3′	0.59 *d* (7.0)	17.9 *q*	C-1′, C-2′, C-4′
4′	0.90 *d* (7.0)	19.3 *q*	C-1′, C-2′, C-3′
	8.15 *dd* (8.0, 1.0)	129.8 *d*	165.8
13α-OBz	7.47 *t* (7.6)	128.7 *d*	
	7.55 *t* (8.0)	133.4 *d*	
1β-OAc	2.05 *s*	21.2 *q*	170.2
11α-OAc	1.99 *s*	21.4 *q*	171.0

*Chemical shifts in ppm rel. to TMS; coupling constants *J* in Hz. C-Multiplicities were established by DEPT data.

Table 3. ^{1}H, HMQC and HMBC NMR data of cardiopimine (3)*

H		Correlated C-atom	
		HMQC	HMBC
1α	6.04 *d* (3.2)	74.2 *d*	170.4, C-2, C-3, C-5, C-10
2β	4.28 *dd* (4.7, 3.2)	67.0 *d*	
3β	4.91 *d* (4.7)	73.3 *d*	176.3, C-4, C-18, C-19
5	2.21 *s*	59.6 *d*	C-18, C-19, C-20
6	3.33 *br s* ($W_{1/2}$ = 6.3)	63.7 *d*	
7α	1.91 *dd* (13.8, 3.3)	35.7 *t*	
7β	1.67 *dd* (13.8, 2.4)	35.7 *t*	C-8, C-14
9	2.30 *dd* (9.6, 2.2)	51.6 *d*	C-12, C-14, C-20
11β	5.41 *d* (9.6)	75.2 *d*	171.0, C-10, C-13, C-16
12	2.55 *m*	46.0 *d*	C-9, C-14, C-15, C-17
13β	5.33 *dt* (9.6, 3.0)	73.7 *d*	C-11
14	2.55 *m*	50.2 *d*	C-9, C-15
15α	2.15 *br d* (17.5)	33.7 *t*	C-9
15β	2.39 *br d* (17.5)	33.7 *t*	
17z	5.01 *br s*	110.4 *t*	C-12, C-15
17e	4.85 *br s*	110.4 *t*	C-12, C-15
18	1.01 *s*	25.5 *q*	C-3, C-4, C-5
19α	3.43 *d* (12.6)	60.0 *t*	C-3, C-6, C-20
19β	2.41 *d* (12.6)	60.0 *t*	C-18
20	3.95 *s*	66.1 *s*	C-1, C-6, C-8, C-13, C-14
2′	2.55 *m*	34.1 *d*	C-1′, C-3′, C-4′
3′	1.12 *d* (6.8)	18.8 *q*	C-1′, C-2′, C-4′
4′	1.15 *d* (6.8)	19.2 *q*	C-1′, C-2′, C-3′
	8.23 *dd* (8.0, 1.0)	129.9 *d*	165.8
13α-OBz	7.50 *t* (7.2)	128.5 *d*	
	7.57 *t* (7.0)	133.2 *d*	
1β-OAc	2.02 *s*	21.3 *q*	170.4
11α-OAc	1.97 *s*	21.4 *q*	171.0

*Chemical shifts in ppm rel. to TMS; coupling constants *J* in Hz. C-Multiplicities were established by DEPT data.

Table 4. ^{1}H, HMQC and HMBC NMR data of cardiopidine (4)*

H		Correlated C-atom	
		HMQC	HMBC
1α	6.05 *d* (3.2)	74.1 *d*	170.4, C-2, C-3, C-5, C-10
2β	4.28 *dd* (4.6, 3.4)	67.1 *d*	C-3, C-10
3β	4.94 *d* (4.8)	73.3 *d*	175.7, C-4, C-18, C-19
5	2.20 *s*	59.5 *d*	C-18, C-19, C-20
6	3.27 *br s* ($W_{1/2} = 6.5$)	63.6 *d*	
7α	1.89 *dd* (13.6, 3.1)	35.7 *t*	
7β	1.70 *dd* (13.6, 2.2)	35.7 *t*	
9	2.30 *dd* (9.6, 2.2)	51.5 *d*	C-20
11β	5.41 *d* (9.2)	75.2 *d*	171.0, C-10, C-13, C-16
12	2.53 *d* (2.5)	46.0 *d*	C-9, C-16
13β	5.36 *dt* (9.5, 2.0)	73.9 *d*	C-11
14	2.50 *dd* (9.0, 2.1)	50.2 *d*	C-9
15α	2.15 *br d* (18.0)	33.7 *t*	
15β	2.40 *br d* (18.0)	33.7 *t*	
17z	5.01 *br s*	110.4 *t*	C-12, C-15
17e	4.85 *br s*	110.4 *t*	C-12, C-15
18	0.99 *s*	25.6 *q*	C-3, C-4, C-5, C-19
19α	3.39 *d* (12.6)	60.0 *t*	
19β	2.40 *d* (12.6)	60.0 *t*	
20	3.91 *s*	66.1 *d*	
2′	2.65 *m*	41.2 *d*	C-1′, C-3′
3′	1.25 *m*	26.6 *t*	C-1′, C-2′
4′	0.87 *t* (7.4)	11.6 *q*	C-2′, C-3′
5′	1.12 *d* (6.9)	16.7 *q*	C-1′, C-2′ C-3′
	8.23 *d* (8.0)	130.0 *d*	165.7
13α-OBz	7.50 *t* (7.5)	128.5 *d*	
	7.56 *t* (7.5)	133.2 *d*	
1β-OAc	2.02 *s*	21.3 *q*	170.4
11α-OAc	1.97 *s*	21.4 *q*	171.0

*Chemical shifts in ppm rel. to TMS; coupling constants *J* in Hz. C-Multiplicities were established by DEPT data.

Table 5. ^{1}H, HMQC and HMBC NMR data of cardiodine (**5**)*

H		Correlated C-atom	
		HMQC	HMBC
1α	6.08 *d* (3.2)	72.4 *d*	170.0, C-2, C-3, C-5, C-10
2β	5.70 *dd* (5.0, 3.1)	65.8 *d*	C-1, C-3, C-4, C-10
3β	5.12 *d* (4.9)	70.9 *d*	169.9, C-2, C-4, C-18 C-19
5	2.23 *s*	58.0 *d*	C-9, C-18, C-19, C-20
6	3.21 *br s* ($W_{1/2}$ = 6.0)	62.5 *d*	C-19, C-20
7α	2.00 *m*		
7β	1.49 *dd* (13.9, 2.2)		C-8, C-14
9	2.40 *d* (9.4)	49.7 *d*	C-1, C-5, C-10, C-12, C-14, C-20
11β	5.40 *d* (9.4)	74.9 *d*	170.0, C-10, C-13
12	2.47 *d* (2.8)	47.9 *d*	C-14, C-16
13β	5.55 *t* (2.4)	80.4 *d*	165.6, C-11, C-14
15α	2.30 *dt* (18.0, 2.0)	30.7 *d*	
15β	2.18 *dt* (18.0, 2.0)	30.7 *d*	
17z	5.01 *br s*	110.6 *t*	C-12, C-15
17e	4.87 *br s*	110.6 *t*	C-12, C-15
18	1.05 *s*	25.3 *q*	C-3, C-4, C-5
19α	3.23 *d* (12.5)	59.1 *t*	C-3, C-6, C-18, C-20
19β	2.41 *d* (12.5)	59.1 *t*	C-4, C-18, C-20
20	3.68 *s*	67.0 *d*	C-5, C-6, C-8, C-10, C-13, C-14
2′	1.30 *m*	39.6 *d*	C-1′
3′	1.20 *m*	24.9 *t*	
4′	0.57 *t* (7.4)	10.7 *q*	C-2′, C-3′
5′	0.88 *d* (7.4)	15.8 *q*	C-1′, C-2′ C-3′
	8.11 *dd* (7.6, 1.6)	129.6 *d*	165.6
13α-OBz	7.45 *t* (7.6)	128.7 *d*	
	7.56 *t* (7.6)	133.5 *d*	
1β-OAc	2.09 *s*	21.2 *q*	170.0
3α-OAc	1.87 *s*	20.6 *q*	169.9
11α-OAc	1.90 *s*	21.4 *q*	171.0

*Chemical shifts in ppm rel. to TMS; coupling constants *J* in Hz. C-Multiplicities were established by DEPT data.

Table 6. Scalar and spatial correlation of the protons of cardiopine (1)

H	COSY	ROESY
1α	H-2β	H-2β, H-20, $H_{2,6}$-13α-OBz, 11α-OAc
2β	H-1α, H-3β	H-1α, H-2β
3β	H-2β	H-2β, H-5, H-18
5	H-6	H-3β, H-6, H-9, H-18
6	H-5, H-7α, H-7β	H-5, H-7α, H-7β, H-18, H-19β
7α	H-6, H-7β	H-6, H-7β, H-14, H-15α
7β	H-6, H-7α	H-5, H-6, H-7α, H-9
9	H-11β, H-14	H-5, H-7β, H-11β
11β	H-9	H-9, H-12, H-15β
12	H-13β	H-11β, H-13β, Hz-17
13β	H-12, H-14	H-12, H-14
14	H-9, H-13β	H-7α, H-13β, H-20
15α	H-15β	H-7α, H-14, H-15β
15β	H-15α	H-11β, H-15α, He-17
17z	He-17	H-12
17e	Hz-17	H-15β
18		H-3β, H-5, H-6, H-19β
19α	H-19β	H-19β, H-20, H-5′
19β	H-19α	H-6, H-18, H-19α
20		H-1α, H-14, H-19α, H-5′
2′	H-5′	
3′	H-4′	
4′	H-3′	H-3′
5′	H-2′	H-2′
11α-OAc		$H_{-2,6}$-13α-OBz

Table 7. Scalar and spatial correlation of the protons of cardiopinine (2)

H	COSY	ROESY
1α	H-2β	H-2β, H-20, $H_{2,6}$-13α-OBz, 11α-OAc
2β	H-1α, H-3β	H-1α, H-3β
3β	H-2β	H-2β, H-5, H-18
5	H-6	H-3β, H-6, H-9, H-18
6	H-5, H-7α, H-7β, H-20	H-5, H-7α, H-7β, H-18, H-19β
7α	H-6, H-7β	H-6, H-7β
7β	H-6, H-7α	H-5, H-6, H-7α
9	H-11β, H-14	H-5, H-7β, H-11β
11β	H-9, H-12	H-9, H-12, H-15β
12	H-11β, H-11β	H-11β, H-13β, H-17z
13β	H-12, H-14	H-12, H-14
14	H-9, H-13β	H-13β, H-20
15α	H-15β	H-15β
15β	H-15α, H-17z, H-17e	H-15α
17z	H-17e	H-12
17e	H-17z	H-15β
18		H-3β, H-5, H-6, H-19β
19α	H-19β	H-19β, H-20, H-4′
19β	H-19α	H-6, H-18, H-19α
20	H-6	H-1α, H-14, H-19α
2′	H-3′, H-4′	H-3′, H-4′
3′	H-2′	H-2′, H-4′
4′	H-2′	H-2′, H-3′
11α-OAc		$H_{2,6}$-13α-OBz

Table 8. Scalar and spatial correlation of the protons of cardiopimine (3)

H	COSY	ROESY
1α	H-2β	H-2β, H-20, $H_{2,6}$-13α-OBz, 11α-OAc
2β	H-1α, H-3β	H-1α, H-3β
3β	H-2β	H-2β, H-5, H-18
5		H-3β, H-6, H-18
6	H-7α, H-7β	H-5, H-18, H-19β
7α	H-6, H-7β	H-6, H-7β
7β	H-6, H-7α	H-6, H-7α
9	H-11β, H-14	H-7β, H-11β
11β	H-9, H-12	H-9, H-12,
12	H-11β, H-13β	H-11β, H-13β, H-17e, H-17z
13β	H-12, H-14	H-12, H-14
14	H-9, H-13β	H-13β, H-20
15α	H-15β, H-17e, H-17z	H-15β
15β	H-15α, H-17e, H-17z	H-15α
17z	H-15α, H-15β, H-17e	H-12
17e	H-15α, H-15β, H-17z	H-12
18		H-3β, H-5, H-6, H-19β
19α	H-19β	H-19β, H-20
19β	H-19α	H-19α
20	H-6	H-1α, H-14, H-19α
2′	H-3′, H-4′	H-3′, H-4′
3′	H-2′	H-2′
4′	H-2′	H-2′
11α-OAc		$H_{2,6}$-13α-OBz, H-1α

Table 9. Scalar and spatial correlation of the protons of cardiopidine (4)

H	COSY	ROESY
1α	H-2β	H-2β, H-20, $H_{2,6}$-13α-OBz, 11α-OAc
2β	H-1α, H-3β	H-1α, H-3β
3β	H-2β	H-5, H-18
5		H-3β, H-18
6	H-7α	H-5, H-18, H-19β
7α	H-6, H-7β	H-7β
7β	H-7α	H-7α
9	H-11β	H-5, H-11β
11β	H-9	H-9, H-12
12	H-13β	H-17z, H-17e
13β	H-12, H-14	H-12, H-14
14	H-13β	H-13β, H-20
15α	H-15β	H-15β
15β	H-15α, H-17z,	H-15α
17z	H-15β, H-17e	H-12β
17e	H-17z	H-12β
18		H-3β, H-5, H-6, H-19β
19α	H-19β	H-19β, H-20
19β	H-19α	H-19α
20		H-1α, H-14, H-19α
2′	H-5′	H-5′
3′	H-4′	
4′	H-3′	H-5′
5′	H-2′	
11α-OAc		$H_{2,6}$-13α-OBz

Table 10. Scalar and spatial correlation of the protons of cardiodine (**5**)

H	COSY	ROESY
1α	H-2β	H-2β, H-20, $H_{2,6}$-13α-OBz, 11α-OAc
2β	H-1α, H-3β	H-1α, H-3β
3β	H-2β	H-2β, H-5, H-18
5		H-3β, H-6, H-7β, H-9, H-18
6	H-7α, H-7β	H-5, H-7α, H-7β, H-18
7α	H-6, H-7β	H-6, H-7β, H-15α
7β	H-6, H-7α	H-5, H-6, H-7α, H-9, H-15β
9	H-11β	H-5, H-7β, H-11β, H-15β
11β	H-9, H-12	H-9, H-12
12	H-11β, H-13β	H-11β, H-13β, H-17z, H-17e
13β	H-12	H-12, H-20
15α	H-15β	H-15β
15β	H-15α	H-7β, H-9, H-15α
17z	H-15α, H-15β, H-17e	H-12β
17e	H-15α, H-15β, H-17z	H-12β
18		H-3β, H-5, H-6, H-19β
19α	H-19β	H-19β, H-20, H-5′
19β	H-19α	H-6, H-18, H-19α
20		H-1α, H-13β, H-19α, H-5′
2′	H-3′, H-5′	
3′	H-2′, H-4′	
4′	H-3′	
5′	H-2′	
11α-OAc		$H_{2,6}$-13α-OBz

Table 11.[1]H NMR data of compounds (**6–8**)

H	6	7	8
1α	6.09 *d* (3.0)	6.10 *d* (3.0)	7.75 *s*
2β	5.69 *dd* (4.3, 3.2)	5.71 *dd* (5.0, 3.0)	
3β	5.11 *d* (4.8)	5.10 *d* (5.0)	
5	2.31 *s*	2.30 *s*	3.01 *s*
6	3.46 *br s* ($W_{1/2} = 6.2$)	3.61 *br s* ($W_{1/2} = 6.2$)	3.45 *br s* ($W_{1/2} = 6.3$)
7β	1.73 *d* (13.6)	1.74 *dd* (14.0, 2.3)	
9		2.42 *m*	2.37 *br d* (9.0)
11β	5.43 *d* (9.4)	5.45 *d* (9.6)	5.35 *d* (10.0)
12	2.37 *d* (9.9)	2.42 *d* (2.4)	2.80 *d* (2.8)
13β	5.52 *d* (9.9)	5.55 *dt* (10.0, 2.0)	5.35 *d* (10.0)
14	2.63 *d* (10.1)	2.70 *d* (10.0)	2.43 *br d* (10.0)
15α	2.22 *br d* (18.0)	2.25 *br d* (17.9)	2.15 *br d* (18.0)
15β	2.37 *m*	2.40 *br d* (17.9)	
17z	4.99 *br s*	5.01 *br s*	5.09 *br s*
17e	4.86 *br s*	4.87 *br s*	4.90 *br s*
18	1.04 *s*	1.06 *s*	1.21 *s*
19α	3.29 *d* (12.8)	3.35 *d* (12.8)	3.27 *d* (13.2)
19β	2.53 *d* (12.8)	2.66 *d* (12.8)	2.75 *d* (13.2)
20	3.85 *s*	3.95 *s*	3.61 *s*
2′		1.50 *sept* (6.7)	
3′		0.58 *d* (6.8)	
4′	0.57 *t* (7.4)	0.93 *d* (6.8)	0.94 *t* (7.4)
5′	0.88 *d* (7.0)		1.23 *d* (6.3)
	8.11 *d* (8.0)	8.10 *d* (7.2)	8.02 *dd* (8.4, 1.0)
Bz	7.46 *t* (7.8)	7.50 *t* (7.0)	7.50 *t* (8.2)
	7.57 *t* (7.1)	7.56 *t* (7.4)	7.56 *t* (8.0)
Ac	1.89 *s*	1.90 *s*	1.87 *s*
	1.96 *s*	1.95 *s*	
	2.04 *s*	2.10 *s*	

Chemical shifts in ppm rel. to TMS; coupling constants *J* in Hz.

Table 12. ^{1}H NMR data of compounds (9–11)*

H	9		10	11
1α	7.73 *s*	138.2 *d*†	5.99 *s*	6.03 *d* (3.0)
2β				4.15 *br s* ($W_{1/2}$ = 7.5)
3β			5.50 *s*	3.52 *d* (5.2)
5	3.00 *s*	67.7 *d*	2.57 *s*	2.08 *s*
6	3.46 *br s* ($W_{1/2}$ = 6.3)	66.6 *d*	3.40 *br s* ($W_{1/2}$ = 6.0)	3.26 *br s* ($W_{1/2}$ = 5.0)
7α	1.94 *dd* (13.4, 3.2)	35.2 *t*		1.85 *dd* (13.6, 3.2)
7β	1.84 *dd* (13.4, 2.4)	35.2 *t*		1.65 *dd* (13.6, 2.3)
9	2.38 *dd* (10.4, 1.9)	49.5 *d*		2.27 *dd* (9.5, 2.1)
11β	5.35 *br d* (10.0)	74.9 *d*	5.37 *d* (8.3)	5.42 *d* (9.5)
12	2.84 *d* (2.6)	44.5 *d*	2.63 *d* (3.2)	2.53 *d* (2.7)
13β	5.35 *br d* (10.0)	73.4 *d*	5.39 *dt* (10.0)	5.36 *dt* (9.6, 2.0)
14	2.44 *dd* (9.4, 2.8)	51.2 *d*		2.49 *dd* (9.6, 2.0)
15α	2.21 *br d* (17.8)	33.6 *t*	2.30 *br d* (17.0)	2.17 *dt* (17.9, 2.1)
15β	2.43 *br d* (17.8)	33.6 *t*		2.37 *dt* (17.9, 2.6)
17z	5.10 *br s*	111.2 *t*	5.07 *br s*	5.01 *s*
17e	4.91 *br s*	111.2 *t*	4.89 *br s*	4.85 *s*
18	1.21 *s*	20.9 *q*	1.17 *s*	1.13 *s*
19α	3.28 *d* (13.0)	64.9 *t*		3.09 *d* (12.6)
19β	2.75 *d* (13.0)	64.9 *t*		2.31 *d* (12.6)
20	3.62 *s*	75.0 *d*	3.20 *s*	3.67 *s*
2′	2.68 *sept* (7.0)			
3′	1.23 *d* (7.0)	18.7 *q*	1.20 *d* (4.5)	
4′	1.26 *d* (7.0)	19.0 *q*	1.22 *d* (4.5)	
	8.04 *dd* (8.0, 1.2)	129.6 *d*	8.30 *dd* (7.2, 1.8)	8.22 *d* (7.0)
Bz	7.45 *t* (8.0)	128.6 *d*	7.59 *t* (7.4)	7.60 *t* (7.2)
	7.58 *t* (8.0)	133.1 *d*	7.59 *t* (7.4)	7.53 *t* (7.2)
Ac	1.86 *s*		1.69 *s*	2.00 *s*
			2.14 *s*	2.05 *s*

*Chemical shifts in ppm rel. to TMS; coupling constants *J* in Hz.
†One-bond connectivities observed in a HMQC experiment.

Table 13. ^{13}C NMR assignments for compounds (**1–9**) and (**11**)

C	1	2	3	4	5	6	7	8	9	11
1	73.2	73.1	74.2	74.1	72.4	72.3	72.0	138.4	138.2	73.9
2	68.9	68.9	67.0	67.1	65.8	65.7	65.5	128.5	128.5	68.4
3	70.8	70.6	73.3	73.3	70.9	70.8	70.6	193.4	193.9	70.4
4	42.7	42.7	41.8	41.8	42.5	41.3	41.0	37.5	38.1	43.3
5	59.5	59.3	59.6	59.5	58.0	58.9	58.4	67.6	67.7	59.2
6	63.9	63.8	63.7	63.6	62.5	63.5	63.4	66.5	66.6	63.8
7	35.9	35.7	35.7	35.7	31.3	35.2	34.7	35.2	35.2	35.9
8	44.2	44.1	43.6	43.6	44.9	44.1	44.0	45.9	45.9	43.8
9	51.7	51.7	51.6	51.5	49.7	51.5	51.4	49.5	49.5	51.5
10	53.9	53.9	53.9	53.7	49.5	54.1	54.2	49.2	49.1	53.7
11	75.4	75.3	75.2	75.2	74.9	75.0	74.9	75.0	74.9	75.3
12	46.6	46.2	46.0	46.0	47.9	46.4	46.2	44.6	44.5	46.0
13	73.8	73.7	73.7	73.9	80.4	73.3	73.2	73.4	73.4	74.5
14	50.4	50.4	50.2	50.2	78.6	49.5	48.8	51.3	51.2	50.2
15	33.9	33.7	33.7	33.7	30.7	33.6	33.5	33.6	33.6	33.9
16	142.7	142.8	142.7	142.7	141.5	141.5	141.8	142.0	142.0	142.8
17	110.3	110.3	110.4	110.4	110.6	110.6	110.9	111.2	111.2	110.4
18	25.7	25.7	25.5	25.6	25.3	25.1	25.1	21.0	20.9	25.9
19	59.5	59.3	60.0	60.0	59.1	58.8	58.4	65.0	64.9	59.5
20	66.2	66.1	66.1	66.1	67.0	65.7	65.7	75.0	75.0	66.3
1′	177.2	177.4	176.3	175.7	174.5	174.4	174.8	176.0	175.0	—
2′	39.6	33.1	34.1	41.2	39.6	39.5	33.2	40.7	33.5	—
3′	25.0	17.9	18.8	26.6	24.9	25.0	18.1	26.6	18.7	—
4′	10.8	19.3	19.2	11.6	10.7	10.7	19.5	11.6	19.0	—
5′	15.7	—	—	16.7	15.8	15.7	—	16.5	—	—
	165.9	165.8	165.8	165.7	165.6	165.9	165.8	165.9	166.0	165.5
	130.1	130.0	130.1	130.1	130.0	129.8	129.7	129.7	129.6	130.2
13α-OBz	129.8	129.8	129.9	130.0	129.6	129.6	129.6	129.6	129.6	129.9
	128.7	128.7	128.5	128.5	128.7	128.8	128.8	128.6	128.6	128.6
	133.4	133.4	133.2	133.2	133.5	133.5	133.6	133.1	133.1	133.4
1β-OAc	171.0	170.2	170.4	170.4	170.0	170.0	169.9	170.0	—	170.6
	21.2	21.2	21.3	21.3	21.2	21.2	21.2	20.8	—	21.5
3αOAc	—	—	—	—	169.9	170.0	169.8	—	—	—
	—	—	—	—	20.6	20.5	20.5	—	—	—
11α-OAc	171.5	171.0	171.0	171.0	171.0	171.0	171.0	—	169.5	170.1
	21.5	21.4	21.4	21.4	21.4	21.5	21.4	—	20.8	21.3

Chemical shifts in ppm rel. to TMS. Carbon multiplicities were established by DEPT data.

Cardiopidine (**4**). Isolated as a resin, $[\alpha]_D$ −22.5° ($C = 0.05$). $[M]^+$ *m/z* 633.2991 for $C_{36}H_{43}NO_9$ (calc. 633.2938). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3371, 2935, 1729, 1653, 1451, 1371, 1272, 1240, 1090, 710; EIMS *m/z* (rel. int.) 633 (3) $[M]^+$, 574 (45), 532 (100), 490 (10), 472 (15), 410 (13), 308 (32), 280 (11), 278 (11), 105 (70), 77 (16), and 71 (15); ^1H and ^{13}C NMR: Tables 4 and 13.

Cardiodine (**5**). Isolated as a resin, $[\alpha]_D$ −26° ($C = 0.05$). $[M]^+$ *m/z* 691.2952 for $C_{38}H_{45}NO_{11}$ (calc. 691.2992). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 2900, 1745, 1740, 1730, 1725, 1650, 1370, 1270, 1240, 1140, 1040, 910; EIMS *m/z* (rel. int.), 691 (3) $[M]^+$, 632 (96), 590 (6), 586 (6), 574 (6), 570 (8), 560 (12), 548 (12), 530 (6), 510 (11), 498 (6), 488 (8), 470 (6), 366 (22), 324 (18), 306 (13), 280 (4), 105 (100), 77 (18) and 57 (44); ^1H and ^{13}C NMR: Tables 5 and 13.

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