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Synthesis and antifeedant properties of *N*-benzoylphenylisoserinates of *Lactarius* sesquiterpenoid alcohols

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Abstract

The esterification of various sesquiterpenoid alcohols of *Lactarius* origin with *N*-benzoyl-[2*R*,3*S*]-phenylisoserine (side chain of Taxol®) produced compounds whose antifeedant properties against storage pests *Tribolium confusum, Trogoderma granarium* and *Sitophylus granarius* were measured. The introduction of the taxol side chain in these molecules, in comparison to original compounds, moderately enhanced their antifeedant activities, as well as changed their selectivity of activity towards the test insects.

Keywords: *N*-Benzoylphenylisoserinates; *Lactarius* sesquiterpenes; Paclitaxel; Antifeedant activity; Storage pests; *Tribolium confusum*; *Trogoderma granarium*; *Sitophilus granarius*; *Rhizopertha dominica*

1. Introduction

In our recent paper (Daniewski et al., 1998) we have identified a group of compounds responsible for the resistance of *Taxus baccata* to the attack of insects. It appeared that the taxanes 10-deacetylbaccatin III (**1**) and its 7α isomer (**2**), contained in the needles of *T. baccata* and possessing a very strong antifeedant activity, protect them from the attack of insects (Fig. 1).

This fact prompted us to investigate the antifeedant activity against the storage pests, of paclitaxel (**3**), the very important anticancer compound isolated from *Taxus brevifolia*. The antifeedant activity tests of paclitaxel (**3**) revealed its very potent activity, and perhaps, its role in the bark of *T. brevifolia* in defence against insects. In our previous papers (Daniewski et al., 1993, 1995) we studied the antifeedant properties of sesquiterpenoid alcohols from *Lactarius* species. The sesquiterpenes, as in the case of 10-deacetylbaccatin III (**1**) or paclitaxel (**3**), are responsible for chemical defence of the mushrooms against several predators. Since paclitaxel (**3**) is the 10-acetyl-13-*N*-benzoylphenylisoserine ester of 10-deacetylbaccatin III, we decided to attach the paclitaxel side chain to a series of sesquiterpenoid alcohols to produce *N*-benzoylphenylisoserine esters and to investigate their biological properties.

2. Results and discussion

There are many methods of attachment of *N*-benzoylphenylisoserine to the baccatin core to produce Taxol® (Farina, 1995); among them, a very simple one, involves the synthesis of the oxazoline derivative (**5**) of *RS* (natural) phenylisoserine (**4**) (Scheme 1):

Originally the synthesis of oxazoline (**5**) required as starting material the phenylisoserine with unnatural configuration at asymmetric center 2. In order to simplify the procedure and to use the phenylisoserine with natural configuration, which is commercially available, we decided to use trimethyl *ortho*-benzoate for the cyclisation, as recently described (Kamata et al., 1998). The hydrolysis of the ester **5** to the free acid **6** as well as its esterification with properly protected baccatin III was described by Kingston et al. (1994) in the semisynthesis of paclitaxel (**3**). The same esterification procedure was applied for the acid **6** and sesquiterpenoid alcohols and it is exemplified by the following scheme where lactarorufin A (**31**) was used as sesquiterpenoid alcohol (Scheme 2).

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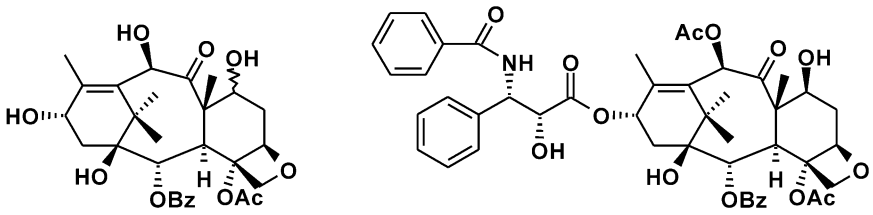
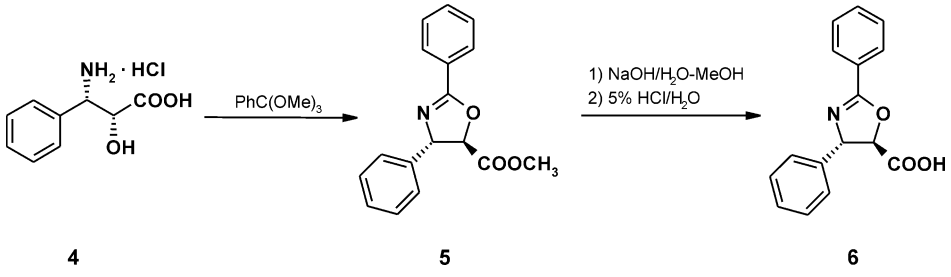


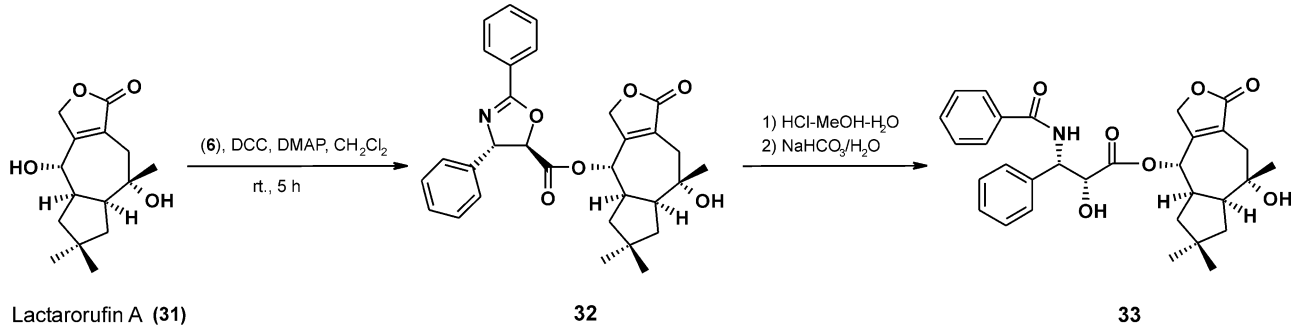
Fig. 1. **1**, R = β-OH (10-deacetylbaccatin III); **2**, R = α-OH (7-*epi*-10-deacetylbaccatin III).

The esterification reaction went smoothly to give the cyclic ester **32**. The hydrolysis of the cyclic ester to form the *N*-benzoylphenylisoserinate (**33**) required different conditions from those used for the synthesis of paclitaxel. To avoid elimination of the side chain low temperature and methanol as solvent had to be used.

Using the above general method described in the experimental part a series of *N*-benzoylphenylisoserinates of various *Lactarius* sesquiterpenoid alcohols was prepared. (Scheme 2). The series included esters of marasmane, isolactarane and lactarane sesquiterpenes. The structures of all the compounds were substantiated by their ^{1}H NMR and ^{13}C NMR spectra which are included in the experimental part. The marasmane esters (**8**, **9**) possess very characteristic signals which allow their identification. The geminal cyclopropane protons at C-4 give rise to a pair of doublets with $J = 4$–5 Hz. The geminal methyl groups at C-11 appear as singlets at ca. δ 0.90–1.1, while the C-12 methyl resonates at lower field (ca. δ 1.15–1.5). Similarly isolactarane esters (**11, 12, 14, 15**) exhibited ^{1}H NMR spectra showing three methyl group singlets, one of them (C-12) resonating at lower field. The cyclopropane protons at C-5, as in the case of marasmane sesquiterpenes produced a pair of doublets (gem. coupling $J = 5.5$ Hz). An important and characteristic ^{1}H NMR spectral feature of isolactarane esters is involving the ABq system with $J = 10$ Hz, typical of saturated γ-lactone ring, In case of ^{1}H NMR spectra of lactarane esters, signals of methyl groups appear as in the previously discussed groups. Depending on heterocyclic rings (furans or lactones), characteristic signals are exhibited. The C-13 or C-5 methylene protons of lactones form an ABq system with a large coupling constant (15–20 Hz). The value of H-8, H-9



Scheme 1.



Scheme 2.

coupling constants are indicative of the *cis* or *trans* stereochemistry. As general feature the signals of protons on carbons bearing the ester groups, in the ^{1}H NMR spectra, are down field shifted in comparison with those of free alcohols (Fig. 2).

The ^{13}C NMR spectra of all the phenylisoserinates confirmed their structures and are included in the experimental part.

3. Antifeedant properties

As it was already mentioned in the introduction, we wanted to check the antifeedant properties of the synthesised compounds in order to find the influence of introduction of paclitaxel side chain into their molecules. First we checked paclitaxel (**3**) (Item 1, R = c, R' = Ac) that has a very potent antifeedant activity to the storage pests mentioned in Table 1. Therefore one can assume that its role in *Taxus brevifolia* is to protect the plant against insects. 10-Deacetyl baccatin III (**1**) (Item 1, R = H, R' = H), which is a good antifeedant, demonstrated lower activity than paclitaxel, especially against *Trogoderma granarium* and *Sitophylus granarius*. The bonding of paclitaxel side chain to the molecule of isovellerol (Item 2) decreased its activity. Introduction of paclitaxel side chain into the molecule of isolactarorufin (**10**) (Item 3, R = H) (which is an attractant) enhanced its antifeedant properties. Change of stereochemistry at C-8 (Item 4) did not influence activity. Similarly esterification of furanol (Item 5) did not have important effect on antifeedant activity. In case of furandiol (**19**) (Item 6), the esterification gave a compound **21** with twice as high activity. Introduction of the paclitaxel side chain into "artifact" (Item 7) as well as into lactarorufin A (Item 8) influenced only the selectivities of antifeedant activity. Esterification of 8-*epi*-lactarorufin A (**34**) (Item 9), which is inactive, caused some activity. Introduction of the side chain into 5-deoxy-lactarolid B (Item 10) did not increase its activity but changed its selectivity towards storage pests. Our procedure was verified with azadirachtin (Item 11) test.

4. Experimental

4.1. General

All melting points were measured on a Koffler hot plate and are uncorrected. ^{1}H and ^{13}C NMR spectra were run at 500 and 125 MHz respectively (Bruker 500 MHz spectrometer) in $CDCl_3$ as otherwise noted, using TMS as internal standard. Column chromatography (CC) was carried out using silica gel, and the TLC were conducted on silica gel or RP-18.

The phenylisoserinates were prepared from sesquiterpenoid alcohols isolated from mushrooms (*Lactarius rufus, Lactarius vellereus,* voucher numbers 33550, and 32260 respectively, specimen deposited at the Department of Systematics and Geography of Plants of the University of Warsaw) or synthesized by transformation of natural products. The references on the procedures of isolation or preparation of all the sesquiterpenes (**7**, **10**, **13**, **16**, **19**, **22**, **25**, **28**, **31**, **34**, **37**, **40**) can be found in the recent review (Daniewski and Vidari, 1999).

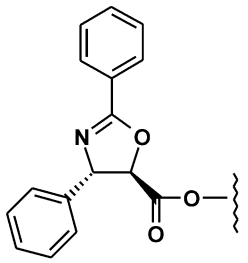
4.2. Preparation of oxazoline methyl ester (*5*)

Phenylisoserine (*R*,*S*) (2.87 g, 0.013 mol) was suspensed in dry toluene (50 ml) in round bottom flask (200 ml) equipped with magnetic stirrer and a still head. The reaction was heated to boiling and 15 ml of toluene was distilled off. Subsequently trimethylorthobenzoate (5 ml, 0.029 mol) was added and the volatile components were removed slowly by distillation during 8 h. Residual solids were filtered off and the filtrate evaporated in rotavap. The resulting oil was purified by chromatography over silica-gel in hexane–ethyl acetate gradient solvent system. Proper fractions were collected and gave pure ester **5** (1.5 g, 41% theoretical yield). $[\alpha]_D = +14.2^\circ$ (EtOH, *c* 1.0); ^{1}H NMR (200 MHz): δ_H 3.90 (3H *s*), 4.96 (1H, *d*, J = 6.5 Hz,), 5.50 (1H, *d*, J = 6.5 Hz,), 7.30–7.62 (8H, *m*), 8.10–8.20 (2H,*m*); ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 52.68, 74.59, 83.07, 126.39, 126.72, 127.97, 128.15, 128.22, 128.39, 128.64, 128.79, 131.86, 141.04, 163.89, 170.55.

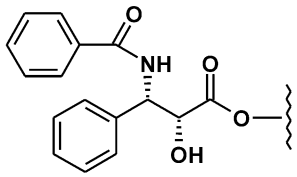
The unidentified residual solids, by treatment with another portion of trimethyl ortho benzoate in presence of *p*-toluenesulphonic acid in toluene, can be converted into the desired ester **5**. In this way overall yield can be improved up to 66%.

4.3. (4S,5R) 2,4-Diphenyl-4,5-dihydro-oxazol-5-carboxylic acid (*6*)

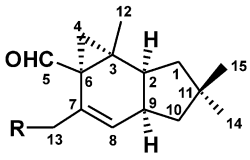
Compound **5** (1.52 g, 0.0054 mol) dissolved in methanol (8 ml) was treated with sodium hydroxide (0.33 g, 0.00835 mol) dissolved in methanol (20 ml) and water (0.5 ml) at room temperature. The reaction was followed by TLC and when no starting material was detected (5 h), hydrochloric acid (6 ml, 5%) was added to the reaction mixture to obtain the pH value equal 6. Precipitated solid was filtered, washed with water and dried to give 1.23 g of the desired product with 86% yield. mp. = 207–211 °C, $[\alpha]_D = -9.97^\circ$ (0.05 *N* NaOH aq., c 1.01),^{1}H NMR (200 MHz, DMSO-d_6,): δ_H 5.00 (1H, *d*, J = 6.4 Hz,), 5.41 (1H *d*, J = 6.4 Hz,), 7.20–7.70 (8H,*m*), 7.90–8.10 (2H,*m*); ^{13}C NMR (DMSO-d_6, 50 MHz) δ_C 73.78, 82.42, 126 53, 126.64, 127.79, 128.18, 128.71, 128.80, 132.09, 141.54, 162.86, 171.45.



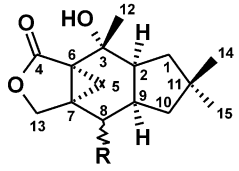
a



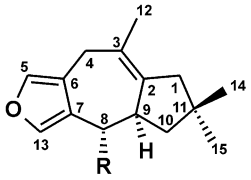
b



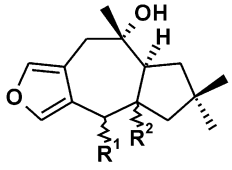
7 R = H
8 R = a
9 R = b



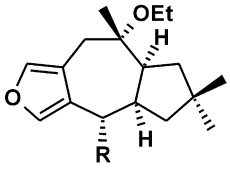
10 R = α-H
11 R = α-a
12 R = α-b
13 R = β-H
14 R = β-a
15 R = β-b



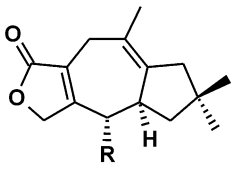
16 R = H
17 R = a
18 R = b



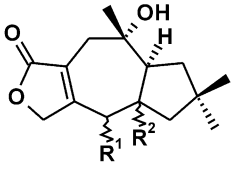
19 R^1 = α-H, R^2 = α-H
20 R^1 = α-a, R^2 = α-H
21 R^1 = α-b, R^2 = α-H
22 R^1 = β-H, R^2 = β-H
23 R^1 = β-a, R^2 = β-H
24 R^1 = β-b, R^2 = β-H



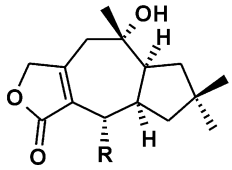
25 R = H
26 R = a
27 R = b



28 R = H
29 R = a
30 R = b



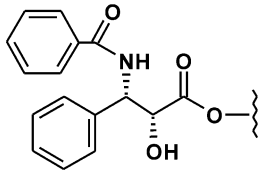
31 R^1 = α-H, R^2 = α-H
32 R^1 = α-a, R^2 = α-H
33 R^1 = α-b, R^2 = α-H
34 R^1 = β-H, R^2 = α-H
35 R^1 = β-a, R^2 = α-H
36 R^1 = β-b, R^2 = α-H
37 R^1 = β-H, R^2 = β-H
38 R^1 = β-a, R^2 = β-H
39 R^1 = β-b, R^2 = β-H

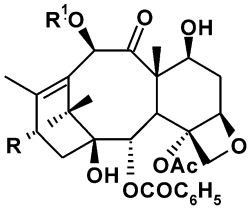
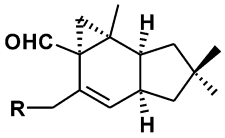
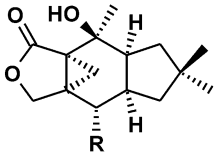
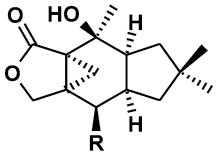
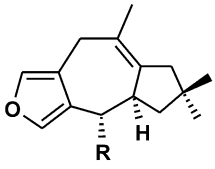
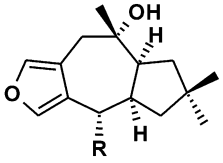
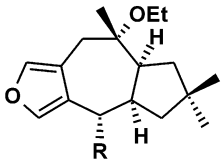


40 R = H
41 R = a
42 R = b

Fig. 2. *N*-benzoylphenyllsoserinates of *Lactarius* sesquiterpenoid alcohols and their oxazdine synthatic intermediates.

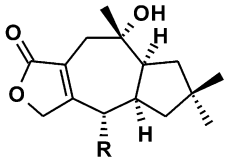
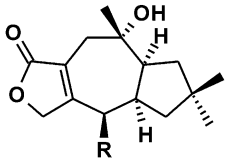
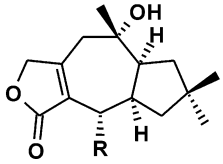
Table 1
Antifeedant activity of 10-deacetyl baccatin III (**1**) and Taxol® (**3**) and *N*-benzoyl phenylisoserinates of several sesquiterpenoid alcohols of *Lactarius* origin



Compound			*Trogoderma granarium*, larvae	*Sitophilus granarius*, adults	*Tribolium confusum*, larvae	*Rhizopertha dominica*, adults	Average activity class[a]
Item 1		R = H R^1 = H (1)	115.5	185.0	149.4	–	150.0 III
		R = b R^1 = Ac (3)	178.9	190.8	122.6	131.5	156.0 IV
Item 2		R = H (7)	200	176	161.9	–	179.3 IV
		R = b (9)	99.2	165.5	95.1	132.7	123.1 III
Item 3		R = H (10)	−50.4	−7.0	15.3	–	-42.1 atr.
		R = b (12)	70.1	122.4	164.9	70.0	106.9 III
Item 4		R = H (13)	42.6	35.3	−22.8	–	18.4 I
		R = b (15)	92.9	111.1	67.9	−23.0	62.2 II
Item 5		R = H (16)	21.0	137.0	152.7	–	103.6 III
		R = b (18)	43.5	102.3	103.6	141.2	97.7 II
Item 6		R = H (19)	9.2	60.0	95.7	–	55.0 II
		R = b (21)	78.1	118.5	84.1	125.1	101.5 III
Item 7		R = H (25)	41.6	173.7	163.8	–	126.4 III
		R = b (27)	119.6	115.9	91.0	172.3	124.7 III

(*continued on next page*)

Table 1 (*continued*)

Compound		*Trogoderma granarium*, larvae	*Sitophilus granarius*, adults	*Tribolium confusum*, larvae	*Rhizopertha dominica*, adults	Average activity class[a]
Item 8 	R = H (31)	148.6	88.6	144.9	–	127.4 III
	R = b (33)	118.9	162.9	11.7	51.2	86.2 II
Item 9 	R = H (34)	−17.4	−11.9	59.3	–	10.0 I
	R = b (36)	79.9	94.6	42.7	-46.6	42.7 I
Item 10 	R = H (40)	93.3	73.4	150.0	–	105.6 III
	R = b (42)	123.0	129.3	66.4	133.8	113.1 III
Item 11 Azadirachtin		190.0	170.0	185.0	–	181.7 IV

[a] Below "0", attractant; class I (0–50), poor antifeedant; class II (51–100), medium antifeedant; class III (101–150), good antifeedant; class IV (151–200), very good antifeedant.

4.4. General method for the synthesis of esters of (4S,5R)-2,4-diphenyl-4,5-dihydro-oxazol-5-carboxylic acid and sesquiterpenoid alcohols of Lactarius origin

A sesquiterpenoid alcohol (1 mmol), the acid (**6**) (1.1 mmol), DMAP (18.3 mg, 0.15 mmol) and DCC (247.2 mg, 1.2 mmol) were dissolved in methylene chloride (25 ml) in a round bottom flask. The reaction was carried out at room temperature and was monitored by TLC. When the reaction was completed (3–12 h) the content of the flask was fitered, the solution evaporated in vacuo and the residue purified by chromatography to give the desired esters.

*4.4.1. Compound **8***

TLC $R_f = 0.72$ (CH_2Cl_2–Me_2CO 96:4); Oil; $[\alpha]_D^{20} = +2.62^\circ$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 204 (ε 9664); IR ν_{max} ($CHCl_3$) cm^{-1}: 2955, 1753, 1702,1654; ^1H NMR: δ 0.97 (3H, *s*, H-15), 1.00 (3H, *s*, H-14), 1.23 (3H, *s*, H-12), 1.25 (1H, *d*, $J_{10\beta,10\alpha} = 12.2$ Hz, H-10β), 1.27 (1H, *d*, $J_{4\beta,4\alpha} = 4.4$ Hz, H-4β), 1.35 (1H, *dd*, $J_{1\beta,1\alpha} = 13.3$ Hz and $J_{1\beta,2\alpha} = 7.9$ Hz, H-1β), 1.60 (1H, *dd*, $J_{10\alpha,10\beta} = 12.2$ Hz and $J = 7.4$ Hz, H-10α), 1.68 (1H, *d*, $J_{4\alpha,4\beta} = 4.4$ Hz, H-4α), 1.77 (1H, *dd*, $J_{1\alpha,1\beta} = 13.3$ Hz and $J_{1\alpha,2\alpha} = 1.1$ Hz, H-1α), 2.46–2.52 (2H, *m*, H-2α and H-9α), 4.86–4.89 (1H, *m*, H-13β and H-2′), 5.28 (1H, *d*, $J_{13\alpha,13\beta} = 12.2$ Hz, H-13α), 5.39 (1H, *br s*, H-8), 5.40 (1H, *d*, $J_{2',3'} = 6.0$ Hz, H-3′), 7.28–7.55 (8H, *m*, H-Ph) 8.08–8.11 (2H, *m*, H-Ph), 9.45 (1H, *s*, H-5); ^{13}C NMR: δ 19.9 (*q*, C-12), 30.7 (*t*, C-4), 31.6 (*q*, C-15), 31.7 (*q*, C-14), 35.5 (*s*, C-11), 36.8 (*s*, C-3), 37.4 (*s*, C-6), 38.2 (*d*, C-2), 42.5 (*d*, C-9), 44.8 (*t*, C-10), 47.5 (*t*, C-1), 67.8 (*t*, C-13), 74.5 (*d*, C-3′), 83.0 (*d*, C-2′), 126.4 (*d*, C-Ph), 126.8 (*s*, C-Ph), 127.9 (*d*, C-Ph), 128.4 (*d*, C-Ph), 128.7 (*d*, C-Ph), 128.8 (*d*, C-Ph), 130.2 (*s*, C-7), 131.2 (*d*, C-8), 131.8 (*d*, C-Ph), 141.1 (*s*, C-Ph), 164.0 (*s*, NCO), 169.6 (*s*, C-1′), 200.1 (*s*, C-5); EIMS 70 eV, *m*/*z* (rel. int.): 483 $[M]^+$ (19.3), 269 (17.7), 268 (100.0), 22 (6), 193 (11), 173 (2.4), 165 (2.5), 146 (2), 120 (6), 119 (8), 105 (22), 91 (17), 90 (7), 89 (4), 77 (5), 69 (2), 55 (2), 43 (1) 41 (4); HR EIMS *m*/*z*: $[M]^+$ calc. for $C_{31}H_{33}O_4N$: 483.24096, found: 483.23978.

*4.4.2. Compound **11***

TLC $R_f = 0.24$, (hexane–EtOAc 77:23); mp 170–172 °C; $[\alpha]_D^{20} = -43.7^\circ$ ($CHCl_3$ *c* 1.1); UV λ_{max} (EtOH) nm: 243 (ε 20541); IR ν_{max} (KBr) cm^{-1}: 3475, 2957, 1957, 1895, 1769, 1740, 1656; ^1H NMR: δ 0.95 (3H, *s*, H-15), 1.10 (3H, *s*, H-14), 1.11 (1H, *d*, $J_{5\beta,5\alpha} = 6.2$ Hz, H-5β), 1.36 (1H, *t*, $J_{10\beta,10\alpha} = 11.3$ Hz, H-10β), 1.50 (1H, *dd*, $J_{1\beta,1\alpha} = 12.4$ Hz and $J_{1\beta,2\alpha} = 7.8$ Hz, H-1β), 1.64 (1H, *d*, $J_{5\alpha,5\beta} = 6.2$ Hz, H-5α), 1.68–1.74 (2H, *m*, H-1α and H-10α), 2.08–2.19 (2H, *m*, H-2α and H-9α), 4.16 (1H, *d*, $J_{13\beta,13\alpha} = 9.4$ Hz, H-13β), 4.41 (1H, *d*, $J_{13\alpha,13\beta} = 9.4$ Hz, H-13α), 4.90 (1H, *d*, $J_{2',3'} = 6.6$ Hz, H-2′), 5.37 (1H, *d*, $J_{3',2'} = 6.6$ Hz, H-3′), 5.66 (1H, *d*, $J_{8\beta,9\alpha} = 8.0$ Hz, H-8β), 7.30–7.65 (8H, *m*, H-Ph), 8.07–8.12 (2H, *m* H-Ph); ^{13}C NMR: δ 18.3 (*t*, C-5), 24.6 (*q*, C-12), 26.8 (*q*, C-15), 28.7 (*q*, C-14), 31.6 (*s*, C-11), 38.5 (*s*, C-6), 38.9 (*s*, C-7), 39.9

(*t*, C-1), 40.7 (*d*, C-2), 45.9 (*d*, C-9), 47.3 (*t*, C-10), 71.0 (*s*, C-3), 71.4 (*t*, C-13), 75.0 (*d*, C-8), 79.4 (*d*, C-3′), 83,1 (*d*, C-2′), 126.5 (*d*, C-Ph), 126.7 (*s*, C-Ph), 128.2 (*d*, C-Ph), 128.5 (*d*, C-Ph), 128.7 (*d*, C-Ph), 128.9 (*d*, C-Ph), 132.1 (*d*, C-Ph), 140.9 (*s*, C-Ph), 164.2 (*s*, NCO), 170.1 (*s*, C-1′), 175.1 (*s*, C-4); LSIMS *m/z* (rel. int.): 516 $[M+H]^+$ (38), 498 (15), 460 (4), 307 (29), 268 (29), 231 (6), 222 (6), 154 (100); HR LSIMS *m/z*: $[M+H]^+$ calc. for $C_{31}H_{34}O_6N$: 516.23859, found: 516.23813.

4.4.3. Compound **14**

TLC $R_f = 0.25$ (hexane–EtOAc 8:2); mp 86–91 °C; $[\alpha]_D^{20} = +35.24°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 243 (ε 16937); IR ν_{max} ($CHCl_3$) cm^{-1}: 3555, 3434, 2957, 1772, 1746,1655; ^1H NMR: δ 0.67 (3H, *s*, H-15), 0.85 (3H, *s*, H-14), 0.95 (1H, *t*, $J_{10\beta,10\alpha} = 11.8$ Hz, H-10β), 1.18 (1H, *d*, $J_{5\beta,5\alpha} = 6.3$ Hz, H-5β), 1.30–1.42 (3H, *m*, H-1α, H-1β and H-10α), 1.60 (3H, *s*, H-12), 1.61 (1H, *d*, $J_{5\alpha,5\beta} = 6.3$ Hz, H-5α), 1.99–2.05 (1H, *m*, H-2α), 2.25-2.32 (1H, *m*, H-9α), 4.08 (1H, *d*, $J_{13\beta,13\alpha} = 9.4$ Hz, H-13β), 4.21 (1H, *d*, $J_{13\alpha,13\beta} = 9.4$ Hz, H-13α), 5.02 (1H, *d*, $J_{2',3'} = 5.9$ Hz, H-2′), 5.56 (1H, *d*, $J_{3',2'} = 5.9$ Hz, H-3′), 5.83 (1H, *d*, $J_{8\alpha,9\alpha} = 4.5$ Hz, H-8α), 7.30–7.56 (8H, *m*, H-Ph), 8.11–8.13 (2H, *m*, H-Ph); ^{13}C NMR: δ 19.5 (*t*, C-5), 24.7 (*q*, C-12), 26.5 (*q*, C-14), 28.1 (*q*, C-15), 32.0 (*s*, C-11), 35.2 (*s*, C-6), 37.6 (*d*, C-9), 37.6 (*s*, C-7), 39.6 (*t*, C-1), 42.1 (*t*, C-10), 44.3 (*d*, C-2), 68.0 (*t*, C-13), 69.3 (*s*, C-3), 71.2 (*d*, C-8), 74.7 (*d*, C-3′), 82.9 (*d*, C-2′), 125.9 (*s*, C-Ph), 126.4 (*d*, C-Ph), 128.2 (*d*, C-Ph), 128.5 (*d*, C-Ph), 128.9 (*d*, C-Ph), 129.0 (*d*, C-Ph), 132.2 (*d*, C-Ph), 140.6 (*s*, C-Ph), 163.4 (*s*, NCO), 170.1 (*s*, C-1′), 173.6 (*s*, C-4); LSIMS *m/z* (rel. int.): 516 $[M+H]^+$ (100), 498 (26), 474 (2), 403 (2), 307 (12), 289 (7), 268 (100), 225 (52), 193 (8), 154 (92); HR LSIMS *m/z*: $[M+H]^+$ calc. for $C_{31}H_{34}O_6N$: 516.23861, found: 516.23963.

4.4.4. Compound **17**

TLC $R_f = 0.62$ (hexane–EtOAc 8:2); mp 127–131 °C; $[\alpha]_D^{20} = -57.83°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 241 (ε 15984); IR ν_{max} ($CHCl_3$) cm^{-1}: 3066, 2955, 2867, 1960, 1748, 1654; ^1H NMR: δ 0.90 (3H, *s*, H-15), 1.12 (3H, *s*, H-14), 1.46 (1H, *dd*, $J_{10\beta,10\alpha} = 12.6$ Hz, $J_{10\beta,9\alpha} = 8.3$ Hz, H-10β), 1.75 (3H, *s*, H-12), 1.91 (1H, *ddd*, $J_{10\alpha,10\beta} = 12.6$ Hz, $J_{10\alpha,9\alpha} = 7.9$ Hz and $J = 2.0$ Hz, H-10α), 2.07 (1H, *d*, $J_{1\beta,1\alpha} = 15.0$ Hz, H-1β), 2.20 (1H, *d*, $J_{1\alpha,1\beta} = 15.0$ Hz, H-1α), 2.91 (1H, *d*, $J_{4\beta,4\alpha} = 16.1$ Hz, H-4β), 3.25–3.31 (1H, *m*, H-9α), 3.40 (1H, *d*, $J_{4\alpha,4\beta} = 16.1$ Hz, H-4α), 4.94 (1H, *d*, $J_{2',3'} = 6.3$ Hz, H-2′), 5.47 (1H, *d*, $J_{3',2'} = 6.3$ Hz, H-3′), 5.82 (1H, *d*, $J_{8\beta,9\alpha} = 11.4$ Hz, H-8β), 7.13 (1H, *t*, $J = 1.5$ Hz, H-5α), 7.28–7.55 (9H, *m*, H-13 and H-Ph), 8.07–8.12 (2H, *m*, H-Ph); ^{13}C NMR: δ 21.5 (*q*, C-12), 27.5 (*q*, C-14), 28.7 (*q*, C-15), 29.4 (*t*, C-4), 37.6 (*s*, C-11), 44.6 (*d*, C-9), 45.8 (*t*, C-10), 46.5 (*t*, C-1), 73.6 (*d*, C-8), 74.7 (*d*, C-3′), 83,2 (*d*, C-2′), 121.3 (*s*, C-6), 124.2 (*s*, C-7), 126.4 (*d*, C-Ph), 128.0 (*d*, C-Ph), 128.4 (*d*, C-Ph), 128.7 (*d*, C-Ph), 128.8 (*d*, C-Ph), 130.0 (*s*, C-3), 131.9 (*d*, C-Ph), 135.7 (*s*, C-2), 135.7 (*s*, C-Ph), 137.8 (*d*, C-13), 141.1 (*s*, C-Ph), 141.8 (*d*, C-5), 164.1 (*s*, NCO), 170.1 (*s*, C-1′); EIMS 70 eV, m/z (rel. int.): 481 $[M]^+$ (6), 268 (100), 223 (8), 222 (42), 215 (14), 214 (72), 199 (41), 193 (33), 158 (28), 145 (5), 143 (7), 119 (10), 105 (23), 91 (17), 77 (8); HR EIMS *m/z*: $[M]^+$ calc. for $C_{31}H_{31}O_4N$: 481.22531, found: 481.22887.

4.4.5. Compound **20**

TLC $R_f = 0.63$ (C_6H_6–Me_2CO 8:2); mp 58–63 °C; $[\alpha]_D^{20} = -31.38°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 242 (ε 24950); IR ν_{max} (KBr) cm^{-1}: 3439, 3063, 2952, 2869, 1758, 1655; ^1H NMR: δ 1.09 (3H, *s*, H-15), 1.15 (3H, *s*, H-14), 1.29 (3H, *s*, H-12), 1.58–1.59 (2H, *m*, H-10), 1.63 (2H, *dd*, $J_{1\alpha,1\beta} = 13.5$ Hz and $J = 5.9$ Hz, H-1), 2.35–2.41 (1H, *m*, H-2α), 2.49–2.55 (1H, *m*, 9α), 2.56 (1H, *d*, $J_{4\beta,4\alpha} = 15.0$ Hz, H-4β), 2.82 (1H, *d*, $J_{4\alpha,4\beta} = 15.0$ Hz, H-4α), 5.00 (1H, *d*, $J_{2',3'} = 6.2$ Hz, H-2′), 5.52 (1H, *d*, $J_{3',2'} = 6.2$ Hz, H-3′), 6.06 (1H, *d*, $J_{8\beta,9\alpha} = 10.8$ Hz, H-8β), 7.13 (1H, *br s*, H-5), 7.24 (1H, *br s*, H-13), 7.28–7.57 (8H, *m*, H-Ph), 8.08–8.13 (2H, *m*, H-Ph); ^{13}C NMR: δ 30.6 (*q*, C-12), 31.8 (*q*, C-14), 32.1 (*q*, C-15), 32.5 (*t*, C-4), 35.3 (*s*, C-11), 42.6 (*t*, C-1), 43.6 (*t*, C-10), 44.8 (*d*, C-9), 53.9 (*d*, C-2), 70.7 (*d*, C-8), 71.3 (*s*, C-3), 74.7 (*d*, C-3′), 83,1 (*d*, C-2′), 118.1 (*s*, C-6), 125.1 (*s*, C-7), 126.4 (*d*, C-Ph), 126.6 (*s*, C-Ph), 128.1 (*d*, C-Ph), 128.5 (*d*, C-Ph), 128.7 (*d*, C-Ph), 128.9 (*d*, C-Ph), 132.0 (*d*, C-Ph), 138.9 (*d*, C-5), 140.9 (*s*, C-Ph), 141.9 (*d*, C-13), 164.1 (*s*, NCO), 169.1 (*s*, C-1′); EIMS 70 eV, *m/z* (rel. int.): 499 $[M]^+$ (3), 481 (6), 464 (7), 446 (5), 268 (16), 232 (32), 223 (16), 222 (100), 217 (14), 199 (7), 193 (58), 189 (13), 165 (6), 145 (2), 137 (3), 119 (4), 105 (15), 91 (9), 77 (6), 43 (4); HR LSIMS *m/z*: $[M+H]^+$ calc. for $C_{31}H_{34}O_5N$: 500.24371, found: 500.24270.

4.4.6. Compound **23**

TLC $R_f = 0.27$, (hexane–EtOAc 7:3); mp 64–68 °C; $[\alpha]_D^{20} = -21.2°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 242 (ε 16768); IR ν_{max} ($CHCl_3$) cm^{-1}: 3066, 2955, 2867, 1960, 1748, 1654; ^1H NMR: δ 0.95 (3H, *s*, H-15), 1.00 (3H, *s*, H-14), 1.05 (3H, *s*, H-12), 1.41 (1H, *dd*, $J_{10\alpha,10\beta} = 12.6$ Hz and $J_{10\alpha,9\beta} = 10.6$ Hz, H-10α), 1.50 (1H, *dd*, $J_{1\beta,1\alpha} = 12.9$ Hz and $J_{1\beta,2\alpha} = 10.8$ Hz, H-1β), 1.70 (1H, *dd*, $J_{10\beta,10\alpha} = 12.6$ Hz and $J_{10\beta,9\beta} = 7.0$ Hz, H-10β), 1.80 (1H, *dd*, $J_{1\alpha,1\beta} = 12.9$ Hz and $J_{1\alpha,2\alpha} = 8.1$ Hz, H-1α), 2.02–2.10 (1H, *m*, H-9β), 2.13–2.19 (1H, *m*, H-2α), 2.59 (1H, *d*, $J_{4\beta,4\alpha} = 14.1$ Hz, H-4β), 2.69 (1H, *d*, $J_{4\alpha,4\beta} = 14.1$ Hz, H-4α), 4.98 (1H, *d*, $J_{2',3'} = 6.4$ Hz, H-2′), 5.49 (1H, *d*, $J_{3',2'} = 6.4$ Hz, H-3′), 5.86 (1H, *d*, $J_{8\alpha,9\beta} = 10.3$ Hz, H-8α), 7.16 (1H, *s*, H-5), 7.20 (1H, *s*, H-13), 7.30–7.57 (8H, *m*, H-Ph), 8.09–8.14 (2H, *m*, H-Ph); ^{13}C NMR: δ 20.7 (*q*, C-12), 31.0 (*q*, C-15), 31.2 (*q*, C-14), 34.7 (*s*, C-11), 40.1 (*t*, C-4), 43.2 (*t*, C-1), 46.1 (*t*, C-10), 46.5 (*d*, C-9), 55.1 (*d*, C-2), 73.3 (*s*, C-3), 74.8 (*d*, C-3′), 75.7 (*d*, C-8), 83.3 (*d*, C-2′), 119.1 (*s*, C-6), 124.9 (*s*, C-7), 126.5 (*d*, C-Ph), 126.7 (*s*, C-Ph), 128.2 (*d*, C-Ph), 128.5 (*d*, C-Ph),

128.7 (*d*, C-Ph), 128.9 (*d*, C-Ph), 132.0 (*d*, C-Ph), 138.2 (*d*, C-5), 140.8 (*s*, C-Ph), 140.9 (*d*, C-13), 164.0 (*s*, NCO), 169.3 (*s*, C-1′); EIMS 70 eV, *m*/*z* (rel. int.): 499 $[M]^+$ (1.5), 269 (17), 268 (98), 266 (20), 234 (51), 222 (40), 217 (10), 194 (12), 193 (71), 189 (28),165 (19), 145 (7), 143 (4), 137 (10), 119 (35), 105 (56), 91 (100), 77 (40), 43 (97); HR EIMS *m*/*z*: $[M]^+$ calc. for $C_{31}H_{33}O_5N$: 499.23587, found: 499.23743.

4.4.7. Compound **26**

TLC $R_f = 0.46$ (hexane–EtOAc 8:2); mp 50–53 °C; $[\alpha]_D^{20} = -46.43°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 242 (ε 10297); IR ν_{max} ($CHCl_3$) cm^{-1}: 2955, 2872, 1755, 1654; ^1H NMR: δ 0.90 (3H, *t*, $J_{CH_2CH_3} = 6.9$ Hz, $-OCH_2CH_3$), 1.08 (3H, *s*, H-15), 1.16 (3H, *s*, H-14), 1.20 (3H, *s*, H-12), 1.57–1.61 (3H, *m*, H-1α, H-10α and H-10β), 1.69 (1H, *t*, $J_{1\beta,1\alpha} = 12.8$ Hz, H-1β), 2.37-2.42 (1H, *m*, H-2α), 2.58 (1H, *dd*, $J_{4\beta,4\alpha} = 15.2$ Hz and $J = 1.2$ Hz, H-4β), 2.59–2.64 (1H, *m*, H-9α), 2.75 (1H, *d*, $J_{4\alpha,4\beta} = 15.2$ Hz, H-4α), 3.28 (1H, *qn*, $J_{CH_2CH_3} = 6.9$ Hz, $-OCH_2CH_3$), 3.36 (1H, *qn*, $J_{CH_2CH_3} = 6.9$ Hz, $-OCH_2CH_3$), 5.00 (1H, *d*, $J_{2',3'} = 6.4$ Hz, H-2′), 5.54 (1H, *d*, $J_{3',2'} = 6.4$ Hz, H-3′), 6.06 (1H, *d*, $J_{8\beta,9\alpha} = 11.4$ Hz, H-8β), 7.05 (1H, *s*, H-5), 7.13 (1H, *t*, $J = 1.3$ Hz, H-13), 7.29–7.57 (8H, *m*, H-Ph), 8.09–8.13 (2H, *m*, H-Ph); ^{13}C NMR: δ 15.7 (*q*, $-CH_2CH_3$), 25.5 (*q*, C-12), 28.9 (*t*, C-4), 32.2 (*q*, C-14), 32.7 (*q*, C-15), 34.9 (*s*, C-11), 41.7 (*t*, C-1), 43.5 (*t*, C-10), 44.5 (*d*, C-9), 52.5 (*d*, C-2), 55.6 (*t*, $-CH_2CH_3$), 75.4 (*s*, C-3), 74.8 (*d*, C-3′), 77.2 (*d*, C-8), 83.2 (*d*, C-2′), 119.3 (*s*, C-6), 125.6 (*s*, C-7), 126.4 (*d*, C-Ph), 126.7 (*s*, C-Ph), 128.0 (*d*, C-Ph), 128.4 (*d*, C-Ph), 128.7 (*d*, C-Ph), 128.9 (*d*, C-Ph), 131.9 (*d*, C-Ph), 137.7 (*d*, C-5), 140.3 (*d*, C-13), 141.1 (*s*, C-Ph), 164.1 (*s*, NCO), 169.3 (*s*, C-1′); EIMS 70 eV, *m*/*z* (rel. int.): 527 $[M]^+$ (4), 512 $[M\text{-}CH_3]^+$ (2), 498 $[M\text{-}C_2H_5]^+$ (2), 269 (18), 268 (100), 260 (12), 223 (11), 222 (40), 215 (20), 193 (32), 165 (6), 137 (6), 105 (20), 91 (26) 77 (11), 43 (16); HR EIMS *m*/*z*: $[M-C_2H_5]^+$ calc. for $C_{31}H_{32}O_5N$: 498.22805, found: 498.22811.

4.4.8. Compound **29**

TLC $R_f = 0.57$ (hexane–EtOAc 7:3); mp 62–64 °C; $[\alpha]_D^{20} = -47.90°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 196 (ε 76709); 242 (ε 20511); IR ν_{max} (KBr) cm^{-1}: 3448, 2952, 2866, 1758, 1655; ^1H NMR: δ 0.92 (3H, *s*, H-15), 1.13 (3H, *s*, H-14), 1.44 (1H, *dd*, $J_{10\beta,10\alpha} = 12.5$ Hz and $J_{10\beta,9\alpha} = 9.0$ Hz, H-10β), 1.86 (1H, *dd*, $J_{10\alpha,10\beta} = 12.5$ Hz and $J_{10\alpha,9\alpha} = 4.7$ Hz, H-10α), 1.77 (3H, *s*, H-12), 2.13 (1H, *d*, $J_{1\beta,1\alpha} = 15.8$ Hz, H-1β), 2.28 (1H, *d*, $J_{1\alpha,1\beta} = 15.8$ Hz, H-1α), 2.97 (1H, *d*, $J_{4\beta,4\alpha} = 20.3$ Hz, H-4β), 3.18 (1H, *d*, $J_{4\alpha,4\beta} = 20.3$ Hz, H-4α), 3.15-3.28 (1H, *m*, H-9α), 4.64 (2H, *ABq*, $J_{AB} = 17.0$ Hz, H-13α and H-13β), 4.96 (1H, *d*, $J_{2',3'} = 6.1$ Hz, H-2′), 5.47 (1H, *d*, $J_{3',2'} = 6.1$ Hz, H-3′), 5.69 (1H, *d*, $J_{8\beta,9\alpha} = 10.9$ Hz, H-8β), 7.31–7.58 (8H, *m*, H-Ph), 8.08–8.11 (2H, *m*, H-Ph); ^{13}C NMR: δ 22.6 (*q*, C-12), 27.1 (*q*, C-15), 28.5 (*q*, C-14), 30.3 (*t*, C-4), 37.2 (*s*, C-11), 45.0 (*d*, C-9), 45.4 (*t*, C-1), 46.5 (*t*, C-10), 69.6 (*t*, C-13), 73.3 (*d*, C-8), 74.8 (*d*, C-3′), 82.8 (*d*, C-2′), 126.4 (*s*, C-2), 126.4 (*s*, C-3), 127.0 (*s*, C-6), 128.3 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.7 (*d*, C-Ph), 128.8 (*d*, C-Ph), 129.0 (*d*, C-Ph), 132.2 (*d*, C-Ph), 135.5 (*s*, C-Ph), 140.6 (*s*, C-Ph), 155.9 (*s*, C-7), 163.9 (*s*, NCO), 169.8 (*s*, C-5), 173.6 (*s*, C-1′); LSIMS *m*/*z* (rel. int.): 498 $[M+H]^+$ (60), 460 (2), 313 (2), 307 (23), 289 (11), 268 (67), 231 (6), 229 (6), 166 (6), 154 (100), 137 (76), 120 (18), 105 (26); HR LSIMS *m*/*z*: $[M+H]^+$ calc. for $C_{31}H_{32}O_5N$: 498.22806, found: 498.23098.

4.4.9. Compound **32**

TLC $R_f = 0.41$ (C_6H_6-Me_2CO 8:2); mp 83–86 °C; $[\alpha]_D^{20} = -20.45°$ ($CHCl_3$, *c* 1.0,); IR ν_{max} ($CHCl_3$) cm^{-1}: 3592, 3507, 2958, 2871, 1756, 1655; ^1H NMR: δ 1.05 (3H, *s*, H-15), 1.14 (3H, *s*, H-14), 1.28 (3H, *s*, H-12), 1.39 (1H, *dd*, $J_{10\beta,10\alpha} = 13.3$ Hz and $J_{10\beta,9\alpha} = 7.1$ Hz, H-10β), 1.55 (1H, *t*, $J = 12.9$ Hz, H-1β), 1.66 (1H, *dd*, $J_{10\alpha,10\beta} = 13.3$ Hz and $J_{10\alpha,9\alpha} = 6.0$ Hz, H-10α), 1.70 (1H, *dd*, $J_{1\alpha,1\beta} = 12.9$ Hz and $J_{1\alpha,2\alpha} = 6.9$ Hz, H-1α), 2.49-2.55 (1H, *m*, H-2α), 2.62 (2H, *ABq*, $J = 17.3$ Hz, H-4α and H-4β), 2.73-2.80 (1H, *m*, H-9α), 4.56 (1H, *d*, $J_{13\beta,13\alpha} = 17.3$ Hz, H-13β), 4.70 (1H, *d*, $J_{13\alpha,13\beta} = 17.3$ Hz, H-13α), 4.96 (1H, *d*, $J_{2',3'} = 6.2$ Hz, H-2′), 5.47 (1H, *d*, $J_{3',2'} = 6.2$ Hz, H-3′), 6.00 (1H, *d*, $J_{8\beta,9\alpha} = 10.3$ Hz, H-8β), 7.30–7.57 (8H, *m*, H-Ph), 8.06–8.10 (2H, *m*, H-Ph); ^{13}C NMR: δ 28.6 (*q*, C-14), 29.5 (*q*, C-12), 30.7 (*q*, C-15), 35.8 (*t*, C-4), 35.9 (*s*, C-11), 42.6 (*d*, C-9), 42.7 (*t*, C-10), 47.7 (*t*, C-1), 52.1 (*d*, C-2), 69.5 (*t*, C-13), 71.5 (*s*, C-3), 72.5 (*d*, C-8), 74.7 (*d*, C-3′), 82.8 (*d*, C-2′), 125.7 (*s*, C-6), 126.3 (*s*, C-Ph), 126.4 (*d*, C-Ph), 128.3 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.7 (*d*, C-Ph), 129.0 (*d*, C-Ph), 132.2 (*d*, C-Ph), 140.5 (*s*, C-Ph), 157.1 (*s*, C-7), 163.9 (*s*, NCO), 169.5 (*s*, C-5), 173.9 (*s*, C-1′); LSIMS *m*/*z* (rel. int.): 516 $[M+H]^+$ (60), 498 (4), 307 (14), 289 (8), 268 (77), 225 (15), 154 (100), 136 (77), 105 (44); HR LSIMS *m*/*z*: $[M+H]^+$ calc. for $C_{31}H_{34}O_6N$: 516.23859, found: 516.23648.

4.4.10. Compound **35**

TLC $R_f = 0.28$ (hexane–EtOAc 6:4); mp 83–87 °C; $[\alpha]_D^{20} = -66.59°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 194 (ε 52202); IR ν_{max} ($CHCl_3$) cm^{-1}: 3593, 3030, 2958, 2868, 1751, 1655; ^1H NMR: δ 0.91 (3H, *s*, H-15), 0.97 (3H, *s*, H-14), 1.04 (1H, *t*, $J_{1\beta,1\alpha} = 12.7$ Hz, H-1β), 1.12 (1H, *t*, $J = 12.2$ Hz, H-10β), 1.28 (3H, *s*, H-12), 1.43 (1H, *dd*, $J_{10\alpha,10\beta} = 12.2$ Hz and $J_{10\alpha,9\alpha} = 7.0$ Hz, H-10α), 1.55 (1H, *dd*, $J_{1\alpha,1\beta} = 12.7$ Hz and $J_{1\alpha,2\alpha} = 7.9$ Hz, H-1α), 2.47 (1H, *d*, $J_{4\beta,4\alpha} = 19.2$ Hz, H-4β), 2.57–2.63 (1H, *m*, H-2α), 2.64 (1H, *dq*, $J_{4\alpha,4\beta} = 19.2$ Hz and $J = 3.0$ Hz, H-4α), 2.93–3.01 (1H, *m*, H-9α), 4.65 (2H, *br s*, H-13), 4.93 (1H, *d*, $J_{2',3'} = 6.0$ Hz, H-2′), 5.39 (1H, *d*, $J_{3',2'} = 6.0$ Hz, H-3′) 6.96 (1H, *br s*, H-8α), 7.30–7.57 (8H, *m*, H-Ph), 8.06–8.09 (2H, *m*, H-Ph); ^{13}C NMR: δ 26.2 (*q*, C-15), 28.9 (*q*, C-14), 32.4 (*q*, C-12), 34.9 (*t*, C-4), 37.7 (*s*, C-11), 43.9 (*d*, C-9), 42.2 (*t*, C-10), 44.6 (*t*, C-1), 49.1 (*d*, C-2), 70.4 (*t*, C-13), 73.8 (*s*, C-3), 74.0 (*d*, C-8), 75.0 (*d*, C-

3′), 83.1 (*d*, C-2′), 122.6 (*s*, C-6), 126.4 (*d*, C-Ph), 126.4 (*s*, C-Ph), 128.3 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.6 (*d*, C-Ph), 129.0 (*d*, C-Ph), 132.2 (*d*, C-Ph), 140.4 (*s*, C-Ph), 157.9 (*s*, C-7), 163.9 (*s*, NCO), 174.3 (*s*, C-5), 174.3 (*s*, C-1′); LSIMS *m/z* (rel. int.): 516 $[M+H]^+$ (24), 369 (3), 307 (16), 268 (25), 222 (4), 154 (100), 137 (76); HR LSIMS *m/z*: $[M+H]^+$ calc. for $C_{31}H_{34}O_6N$: 516.23861, found: 516.23900.

4.4.11. Compound **38**

TLC $R_f = 0.26$ (hexane–Me_2CO 7:3); mp 90–92 °C; $[\alpha]_D^{20} = -41.2°$ ($CHCl_3$, *c* 1.0); UV no peaks found; IR ν_{max} (KBr) cm^{-1}: 3448, 3064, 2953, 2866, 1758, 1655; ^1H NMR: δ 0.96 (3H, *s*, H-15), 1.06 (3H, *s*, H-14), 1.09 (3H, *s*, H-12), 1.38 (1H, *dd*, $J_{10\alpha,10\beta} = 12.6$ Hz and $J_{10\alpha,9\beta} = 10.7$ Hz, H-10α), 1.53 (1H, *dd*, $J_{1\beta,1\alpha} = 13.3$ Hz and $J_{1\beta,2\alpha} = 10.5$ Hz, H-1β), 1.66 (1H, *dd*, $J_{10\beta,10\alpha} = 12.6$ Hz and $J_{10\beta,9\beta} = 6.9$ Hz, H-10β), 1.86 (1H, *dd*, $J_{1\alpha,1\beta} = 13.3$ Hz and $J_{1\alpha,2\alpha} = 8.3$ Hz, H-1α), 2.13–2.21 (1H, *m*, H-9), 2.24–2.31 (1H, *m*, H-2α), 2.36 (1H, *dq*, $J_{4\beta,4\alpha} = 15.1$ Hz and $J = 3.0$ Hz, H-4β), 2.81 (1H, *d*, $J_{4\alpha,4\beta} = 15.1$ Hz, H-4α), 4.63 (1H, *ddd*, $J_{13\beta,13\alpha} = 17.6$ Hz, $J = 3.1$ Hz and $J = 1.3$ Hz, H-13β), 4.75 (1H, *dq*, $J_{13\alpha,13\beta} = 17.6$ Hz and $J = 1.6$ Hz, H-13α), 4.98 (1H, *d*, $J_{2',3'} = 6.2$ Hz, H-2′), 5.44 (1H, *d*, $J_{3',2'} = 6.2$ Hz, H-3′), 5.89 (1H, *dd*, $J_{8\alpha,9\beta} = 10.7$ Hz and $J = 1.9$ Hz, H-8α), 7.31–7.59 (8H, *m*, H-Ph), 8.08–8.10 (2H, *m*, H-Ph); ^{13}C NMR: δ 20.7 (*q*, C-12), 30.8 (*q*, C-15), 31.2 (*q*, C-14), 34.3 (*s*, C-11), 39.5 (*t*, C-4), 43.4 (*t*, C-10), 44.0 (*d*, C-9), 46.2 (*t*, C-1), 54.4 (*d*, C-2), 68.9 (*t*, C-13), 72.1 (*s*, C-3), 75.0 (*d*, C-3′), 76.7 (*d*, C-8), 83.0 (*d*, C-2′), 124.5 (*s*, C-6), 126.3 (*s*, C-Ph), 126.4 (*d*, C-Ph), 128.4 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.6 (*d*, C-Ph), 129.0 (*d*, C-Ph), 132.2 (*d*, C-Ph), 140.3 (*s*, C-Ph), 159.1 (*s*, C-7), 163.8 (*s*, NCO), 169.4 (*s*, C-1′), 173.6 (*s*, C-5); LSIMS *m/z* (rel. int.): 1031 $[2M+H]^+$ (3), 516 $[M+H]^+$ (95), 499 (18), 307 (11), 268 (100), 222 (18), 193 (5), 154 (77), 137 (53), 105 (45); HR LSIMS *m/z*: $[M+H]^+$ calc. for $C_{31}H_{34}O_6N$: 516.23861, found: 516.23779.

4.4.12. Compound **41**

TLC $R_f = 0.26$ (hexane–EtOAc 4:6); mp 76–80 °C; $[\alpha]_D^{20} = -36.29°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 194 (ε 57717); IR ν_{max} ($CHCl_3$) cm^{-1}: 3566, 2958, 2869, 1764, 1654; ^1H NMR: δ 0.99 (3H, *s*, H-15), 1.06 (3H, *s*, H-14), 1.16 (1H, *t*, $J_{10\beta,10\alpha} = 11.9$ Hz, H-10β), 1.23 (3H, *s*, H-12), 1.25 (1H, *t*, $J_{1\beta,1\alpha} = 7.2$ Hz, H-1β), 1.62 (1H, *t*, $J_{10\alpha,10\beta} = 11.9$ Hz, H-10α), 1.67–1.74 (1H, *m*, H-1α), 2.56 (1H, *d*, $J_{4\beta,4\alpha} = 18.8$ Hz, H-4β), 2.62–2.69 (1H, *m*, H-2α), 2.80 (1H, *d*, $J_{4\alpha,4\beta} = 18.8$ Hz, H-4α), 2.85–2.91 (1H, *m*, H-9α), 4.61 (2H, *ABq*, $J_{AB} = 17.0$ Hz, H-5α and H-5β), 4.97 (1H, *d*, $J_{2',3'} = 6.5$ Hz, H-2′), 5.50 (1H, *d*, $J_{3',2'} = 6.5$ Hz, H-3′), 5.96 (1H, *d*, $J_{8\beta,9\alpha} = 5.2$ Hz, H-8β), 7.26–7.55 (8H, *m*, H-Ph), 8.08–8.11 (2H, *m*, H-Ph); ^{13}C NMR: δ 26.9 (*q*, C-15), 29.4 (*q*, C-14), 29.6 (*q*, C-12), 36.5 (*s*, C-11), 38.6 (*t*, C-4), 42.5 (*d*, C-9), 45.1 (*t*, C-10), 45.2 (*t*, C-1), 50.6 (*d*, C-2), 73.1 (*s*, C-3), 69.6 (*d*, C-8), 71.9 (*t*, C-5), 74.3 (*d*, C-3′), 83.1 (*d*, C-2′), 122.9 (*s*, C-7), 126.6 (*d*, C-Ph), 126.6 (*s*, C-Ph), 128.0 (*d*, C-Ph), 128.3 (*d*, C-Ph), 128.7 (*d*, C-Ph), 128.8 (*d*, C-Ph), 131.9 (*d*, C-Ph), 140.7 (*s*, C-Ph), 151.9 (*s*, C-6), 163.9 (*s*, NCO), 168.4 (*s*, C-13), 172.5 (*s*, C-1′); LSIMS *m/z* (rel. int.): 516 $[M+H]^+$ (58), 403 (1), 379 (1), 359 (1), 337 (1), 307 (3), 268 (85), 249 (11), 222 (12), 154 (42), 136 (38), 105 (73), 81 (100); HR LSIMS *m/z*: $[M+H]^+$ calc. for $C_{31}H_{34}O_6N$: 516.23861, found: 516.23737.

4.5. General method for the hydrolysis of esters of (4S,5R)-2,4-diphenyl-4,5-dihydro-oxazol-5-carboxylic acid and sesquiterpenoid alcohols of Lactarius origin into (2S,3R)-phenyl-isoserinates

A sesquiterpenoid alcohol (4*S*,5*R*)-2,4-diphenyl-oxazol-5-carboxylate (0.2 mmol) dissolved in methanol (25 ml) was chilled to 0 °C and treated with 0.5 N aq. HCl solution (2.5 ml). The reaction must be carried out at 0 °C. After completion of the reaction the solution was neutralised with saturated aq. sodium hydrogen carbonate solution (pH = 7) and left for 15 min. Subsequently the solution was diluted with water (75 ml) and extracted with chloroform (3×40 ml). The chloroform extract was dried over magnesium sulphate, filtered and evaporated to dryness leaving a residue, which was purified by chromatography in proper solvent system and gave the desired *N*-benzoylphenylisoserinate.

4.5.1. Compound **9**

TLC $R_f = 0.21$ (hexane–EtOAc 7:3); mp 60–63 °C; $[\alpha]_D^{20} = +15.83°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 226 (ε 17509); IR ν_{max} ($CHCl_3$) cm^{-1}: 3683, 3519, 3440, 2955, 2866, 1731, 1702, 1664, 1511; ^1H NMR: δ 0.95 (3H, *s*, H-15), 0.98 (3H, *s*, H-14), 1.23 (1H, *t*, $J_{10\beta,10\alpha} = 13.0$ Hz, H-10β), 1.26 (3H, *s*, H-12), 1.29 (1H, *d*, $J_{4\beta,4\alpha} = 4.5$ Hz, H-4β), 1.30 (1H, *dd*, $J_{1\alpha,1\beta} = 13.3$ Hz and $J_{1\alpha,2\alpha} = 1.8$ Hz, H-1α), 1.59 (1H, *dd*, $J_{10\alpha,10\beta} = 13.0$ Hz and $J_{10\alpha,9\alpha} = 7.6$ Hz, H-10α), 1.72 (1H, *dd*, $J_{1\beta,1\alpha} = 13.3$ Hz and $J_{1\beta,2\alpha} = 8.0$ Hz, H-1β), 1.80 (1H, *d*, $J_{4\alpha,4\beta} = 4.5$ Hz, H-4α), 2.42–2.50 (2H, *m*, H-2α and H-9α), 4.58 (1H, *d*, $J_{2',3'} = 2.2$ Hz, H-2′), 4.84 (1H, *d*, $J_{13\beta,13\alpha} = 12.1$ Hz, H-13β), 5.29 (1H, *d*, $J_{13\alpha,13\beta} = 12.1$ Hz, H-13α), 5.33 (1H, br *s*, H-8), 5.63 (1H, *dd*, $J_{3',NH} = 8.9$ Hz and $J_{3',2'} = 2.2$ Hz, H-3′), 7.05 (1H, *d*, $J_{NH,3'} = 8.9$ Hz, NH), 7.26–7.52 (8H, *m*, H-Ph), 7.74–7.77 (2H, *m*, H-Ph), 9.40 (1H, *s*, H-5); ^{13}C NMR: δ 20.0 (*q*, C-12), 31.0 (*t*, C-4), 31.6 (*q*, C-14), 31.7 (*q*, C-15), 35.5 (*s*, C-11), 36.9 (*s*, C-3), 37.3 (*s*, C-6), 38.3 (*d*, C-2), 42.5 (*d*, C-9), 44.8 (*t*, C-10), 47.5 (*t*, C-1), 54.5 (*d*, C-3′), 68.5 (*t*, C-13), 73.2 (*d*, C-2′), 126.9 (*d*, C-Ph), 127.0 (*s*, C-Ph), 127.9 (*d*, C-Ph), 128.5 (*d*, C-Ph), 128.6 (*d*, C-Ph), 129.9 (*s*, C-7), 131.7 (*d*, C-Ph), 131.8 (*s*, C-8), 134.1 (*s*, C-Ph), 138.8 (*s*, C-Ph), 166.7 (*s*, NCO), 172.6 (*s*, C-1′), 200.6 (*s*, C-5); LSIMS *m/z* (rel. int.): 524 $[M+Na]^+$ (9), 484 (4), 446 (12), 330 (5), 308 (28), 286 (14), 231

(28), 215 (16), 154 (20), 111 (21), 105 (100); HR LSIMS *m/z*: $[M+Na]^+$ calcd for $C_{31}H_{33}O_5NNa$: 524.24129, found: 524.24127.

4.5.2. Compound ***12***

TLC $R_f = 0.21$ (hexane–EtOAc 1:1); mp 104–108 °C; $[\alpha]_D^{20} = -9.82°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 223 (ε 16399); IR ν_{max} (KBr) cm^{-1}: 3431, 2953, 2865, 1768, 1745,1651; ^1H NMR: δ 0.68 (3H, *s*, H-15), 0.80 (3H, *s*, H-14), 1.07–1.12 (2H, *m*, H-5β and H-10β), 1.36–1.45 (2H, *m*, H-1β and H-10α), 1.56 (1H, *dd*, $J = 11.9$ Hz and $J = 2.5$ Hz, H-1α), 1.58 (3H, *s*, H-12), 1.69 (1H, *d*, $J_{5\alpha,5\beta} = 6.2$ Hz, H-5α), 2.03–2.12 (2H, *m*, H-2α and H-9α), 4.10 (1H, *d*, $J_{13\beta,13\alpha} = 9.3$ Hz, H-13β), 4.23 (1H, *d*, $J_{13\alpha,13\beta} = 9.3$ Hz, H-13α), 4.65 (1H, *d*, $J_{2',3'} = 2.0$ Hz, H-2′), 5.67 (1H, *d*, $J_{8\beta,9\alpha} = 8.0$ Hz, H-8β), 5.77 (1H, *dd*, $J_{3',NH} = 9.1$ Hz, $J_{3',2'} = 2.0$ Hz, H-3′), 7.15 (1H, *d*, $J_{NH,3'} = 9.1$, NH), 7.25–7.53 (8H, *m*, H-Ph), 7.76–7.80 (2H, *m*, H-Ph); ^{13}C NMR: δ 18.4 (*t*, C-5), 24.4 (q, C-12), 26.2 (*q*, C-15), 28.4 (*q*, C-14), 31.3 (*s*, C-11), 38.1 (*s*, C-6), 38.7 (*s*, C-7), 39.9 (*t*, C-1), 40.0 (*d*, C-2), 46.1 (*d*, C-9), 46.6 (*t*, C-10), 54.6 (*d*, C-3′), 71.0 (*s*, C-3), 71.2 (*t*, C-13), 73.5 (*d*, C-8), 80,2 (*d*, C-2′), 126.9 (*d*, C-Ph), 127.1 (*d*, C-Ph), 127.8 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.6 (*d*, C-Ph), 131.9 (*d*, C-Ph), 133.7 (*s*, C-Ph), 138.6 (*s*, C-Ph), 166.4 (*s*, NCO), 172.6 (*s*, C-1′), 175.1 (*s*, C-4); LSIMS m/z (rel. int.): 534 $[M+H]^+$ (4), 516 (3), 307 (8), 286 (100), 249 (3), 231 (12), 210 (20), 176 (2), 154 (56), 137 (46), 123 (24), 105 (60); HR LSIMS *m/z*: $[M+Na]^+$ calc. for $C_{31}H_{35}O_7NNa$: 556.23114, found: 556.23308.

4.5.3. Compound ***15***

TLC $R_f = 0.25$ (hexane–EtOAc 55:45); mp 176–183 °C; $[\alpha]_D^{20} = +49.6°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 228 (ε 14420); IR ν_{max} ($CHCl_3$) cm^{-1}: 3555, 3436, 2935, 2858, 1769, 1730,1657; ^1H NMR: δ 0.73 (3H, *s*, H-15), 0.80 (3H, *s*, H-14), 0.91 (1H, *t*, $J_{10\beta,10\alpha} = 11.7$ Hz, H-10β), 1.05 (1H, *d*, $J_{5\beta,5\alpha} = 6.2$ Hz, H-5β), 1.20–1.30 (2H, *m*, H-1α and H-10α), 1.31 (3H, *s*, H-12), 1.41 (1H, *t*, $J_{1\beta,2\alpha} = 12.1$ Hz, H-1β), 1.48 (1H, *d*, $J_{5\alpha,5\beta} = 6.2$ Hz, H-5α), 1.86–1.92 (1H, *m*, H-2α), 2.14–2.21 (1H, *m*, H-9α), 3.87 (1H, *d*, $J_{13\beta,13\alpha} = 9.3$ Hz, H-13β), 4.02 (1H, *d*, $J_{13\alpha,13\beta} = 9.3$ Hz, H-13α), 4.86 (1H, *d*, $J_{2',3'} = 2.1$ Hz, H-2′), 5.65 (1H, *d*, $J_{8\alpha,9\alpha} = 4.5$ Hz, H-8α), 5.83 (1H, *dd*, $J_{3',NH} = 9.3$ Hz, $J_{3',2'} = 2.1$ Hz, H-3′), 7.23–7.51 (9H, *m*, NH and H-Ph), 7.80–7.84 (2H, *m*, H-Ph); ^{13}C NMR: δ 19.4 (*t*, C-5), 24.9 (*q*, C-12), 26.3 (*q*, C-14), 28.6 (*q*, C-15), 32.0 (*s*, C-7), 32.1 (*s*, C-6), 34.6 (*s*, C-11), 37.5 (*d*, C-9), 39.5 (*t*, C-1), 41.9 (*t*, C-10), 44.2 (*d*, C-2), 54.8 (*d*, C-3′), 68.2 (*t*, C-13), 69.7 (*s*, C-3), 70.4 (*d*, C-8), 73,8 (*d*, C-2′), 127.0 (*d*, C-Ph), 127.3 (*d*, C-Ph), 127.8 (*d*, C-Ph), 128.5 (*d*, C-Ph), 128.6 (*d*, C-Ph), 131.6 (*d*, C-Ph), 134.2 (*s*, C-Ph), 138.7 (*s*, C-Ph), 166.9 (*s*, NCO), 172.0 (*s*, C-1′), 174.2 (*s*, C-4); LSIMS m/z (rel. int.): 556 $[M+Na]^+$ (22), 534 $[M+H]^+$ (4), 516 (3), 338 (8), 312 (16), 286 (20), 240 (3), 225 (18), 210 (5), 154 (16), 136 (17), 105 (100); HR LSIMS *m/z*: $[M+Na]^+$ calc. for $C_{31}H_{35}O_7NNa$: 556.23114, found: 556.23175.

4.5.4. Compound ***18***

TLC $R_f = 0.23$ (hexane–EtOAc 8:2); mp 68–70 °C; $[\alpha]_D^{20} = -4.55°$ ($CHCl_3$, c 1.0); UV λ_{max} (EtOH) nm: no peaks found above threshold; IR ν_{max} ($CHCl_3$) cm^{-1}: 3423, 2952, 2864, 1736, 1645; ^1H NMR: δ 0.78 (6H, *s*, H-14 and H-15), 1.16 (1H, *dd*, $J_{10\beta,10\alpha} = 12.9$ Hz and $J_{10\beta,9\alpha} = 8.1$ Hz, H-10β), 1.73 (3H, *s*, H-12), 1.83 (1H, *dd*, $J_{10\alpha,10\beta} = 12.9$ Hz and $J_{10\alpha,9\alpha} = 7.9$ Hz, H-10α), 1.94 (1H, *d*, $J_{1\beta,1\alpha} = 15.0$ Hz, H-1β), 2.11 (1H, *d*, $J_{1\alpha,1\beta} = 15.0$ Hz, H-1α), 2.89 (1H, *d*, $J_{4\beta,4\alpha} = 15.9$ Hz, H-4β), 3.25–3.31 (1H, *m*, H-9α), 3.42 (1H, *d*, $J_{4\alpha,4\beta} = 15.9$ Hz, H-4α), 4.60 (1H, *d*, $J_{2',3'} = 2.0$ Hz, H-2′), 5.73 (1H, *dd*, $J_{3',NH} = 8.8$ Hz and $J_{3',2'} = 2.0$ Hz, H-3′), 5.81 (1H, *d*, $J_{8\beta,9\alpha} = 11.1$ Hz, H-8β), 7.12 (1H, *d*, $J_{NH,3'} = 8.8$ Hz, NH), 7.13 (1H, br *s*, H-5), 7.23 (1H, *s*, H-13), 7.26–7.53 (8H, *m*, H-Ph), 7.79–7.81 (2H, *m*, H-Ph); ^{13}C NMR: δ 21.5 (*q*, C-12), 27.2 (*q*, C-14), 28.2 (*q*, C-15), 29.3 (*t*, C-4), 37.5 (*s*, C-11), 44.4 (*d*, C-9), 45.8 (*t*, C-10), 45.8 (*t*, C-1), 54.7 (*d*, C-3′), 73.8 (*d*, C-8), 74.9 (*d*, C-2′), 121.6 (*s*, C-6), 124.8 (*s*, C-7), 126.8 (*d*, C-Ph), 127.1 (*d*, C-Ph), 127.8 (*d*, C-Ph), 128.5 (*d*, C-Ph), 128.6 (*d*, C-Ph), 130.1 (*s*, C-3), 131.7 (*d*, C-Ph), 134.0 (*s*, C-2), 136.0 (*s*, C-Ph), 137.8 (*d*, C-5), 138.9 (*s*, C-13), 141.8 (*d*, C-13), 166.4 (*s*, NCO), 172.8 (*s*, C-1′); LSIMS *m/z* (rel. int.): 522 $[M+Na]^+$ (14), 338 (5), 329 (26), 308 (43), 286 (48), 258 (4), 240 (4), 215 (44), 199 (6), 187 (4), 176 (100), 154 (78), 136 (56), 120 (12), 105 (37); HR LSIMS *m/z*: $[M+Na]^+$ calc. for $C_{31}H_{33}O_5NNa$: 522.22565, found: 522.22465.

4.5.5. Compound ***21***

TLC $R_f = 0.31$ (C_6H_6–Me_2CO 8:2); mp 72–75 °C; $[\alpha]_D^{20} = -5.67°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 193 (ε 64656); IR ν_{max} (KBr) cm^{-1}: 3401, 3065, 2929, 2856, 1757, 1646; ^1H NMR (CD_3OD): δ 0.80 (3H, *s*, H-15), 0.87 (3H, *s*, H-14), 1.21 (3H, *s*, H-12), 1.28–1.38 (2H, *m*, H-10), 1.51 (1H, *dd*, $J_{1\beta,1\alpha} = 13.0$ Hz and $J_{1\beta,2\alpha} = 7.4$ Hz, H-1β), 1.58 (1H, *dd*, $J_{1\alpha,1\beta} = 13.0$ Hz and $J_{1\alpha,2\alpha} = 1.3$ Hz, H-1α), 2.28–2.33 (1H, *m*, H-2α), 2.46–2.51 (1H, *m*, H-9α), 2.57 (1H, *d*, $J_{4\beta,4\alpha} = 15.0$ Hz, H-4β), 2.73 (1H, *d*, $J_{4\alpha,4\beta} = 15.0$ Hz, H-4α), 4.73 (1H, *d*, $J_{2',3'} = 3.4$ Hz, H-2′), 5.65 (1H, *d*, $J_{3',2'} = 3.4$ Hz, H-3′), 5.96 (1H, *dd*, $J_{8\beta,9\alpha} = 11.0$ Hz and $J = 1.2$ Hz, H-8β), 7.19 (1H, *br s*, H-5), 7.22 (1H, *br s*, H-13), 7.25–7.57 (8H, *m*, H-Ph), 7.85–7.92 (2H, *m*, H-Ph); ^{13}C NMR: δ 31.1 (*q*, C-12), 32.0 (*q*, C-15), 32.4 (*q*, C-14), 33.6 (*t*, C-4), 35.8 (*s*, C-11), 43.3 (*t*, C-1), 44.4 (*t*, C-10), 45.9 (*d*, C-9), 54.7 (*d*, C-2), 54.7 (*d*, C-3′), 72.1 (*d*, C-8), 72.5 (*s*, C-3), 74.9 (*d*, C-2′), 120.5 (*s*, C-6), 126.6 (*s*, C-7), 128.2 (*d*, C-Ph), 128.5 (*d*, C-Ph), 128.6 (*d*, C-Ph), 129.5 (*d*, C-Ph), 129.6 (*d*, C-Ph), 133.0 (*d*, C-Ph), 135.2 (*s*, C-Ph), 139.9 (*d*, C-13), 140.6 (*s*, C-Ph), 142.3 (*d*, C-5), 169.4 (*s*, NCO), 172.9 (*s*, C-1′); LSIMS *m/z* (rel. int.): 1057 $[2M+Na]^+$ (1), 540 $[M+Na]^+$ (24), 413 (5), 391 (3), 330 (22), 308 (100), 286

(95), 240 (8), 215 (24), 176 (95), 136 (60), 158 (28), 105 (98); HR LSIMS *m/z*: $[M+Na]^+$ calc. for $C_{31}H_{35}O_6NNa$: 540.23621, found: 540.23982.

4.5.6. Compound ***24***

TLC $R_f = 0.29$ (hexane–EtOAc 1:1); mp 95–98 °C; $[\alpha]_D^{20} = -17.80°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 195 (ε 51825); IR ν_{max} ($CHCl_3$) cm^{-1}: 3597, 3516, 3438, 2955, 2867, 1733, 1664; ^1H NMR: δ 0.98 (3H, *s*, H-15), 1.01 (3H, *s*, H-14), 1.02 (3H, *s*, H-12), 1.28 (1H, *dd*, $J_{10\alpha,10\beta} = 12.7$ Hz and $J_{10\alpha,9\beta} = 9.9$ Hz, H-10α), 1.50 (1H, *dd*, $J_{1\beta,1\alpha} = 13.0$ Hz and $J_{1\beta,2\alpha} = 10.5$ Hz, H-1β), 1.63 (1H, *dd*, $J_{10\beta,10\alpha} = 12.7$ Hz and $J_{10\beta,9\beta} = 6.4$ Hz, H-10β), 1.80 (1H, *dd*, $J_{1\alpha,1\beta} = 13.0$ Hz and $J_{1\alpha,2\alpha} = 7.6$ Hz, H-1α), 2.07–2.14 (2H, *m*, H-2α and H-9β), 2.53 (1H, *d*, $J_{4\beta,4\alpha} = 14.0$ Hz, H-4β), 2.67 (1H, *d*, $J_{4\alpha,4\beta} = 14.0$ Hz, H-4α), 4.68 (1H, *dd*, $J_{2',3'} = 3.6$ Hz and $J_{2',OH} = 2.3$ Hz, H-2′), 5.81 (1H, *d*, $J_{8\alpha,9\beta} = 10.0$ Hz, H-8α), 5.82 (1H, *dd*, $J_{3',NH} = 9.1$ Hz and $J_{3',2'} = 3.6$ Hz, H-3′), 7.12 (1H, *t*, $J = 1.5$ Hz, H-5), 7.19 (1H, *d*, $J_{NH,3'} = 9.1$ Hz, N*H*), 7.22 (1H, *t*, $J = 1.0$ Hz, H-13), 7.28–7.51 (8H, *m*, H-Ph), 7.74–7.79 (2H, *m*, H-Ph); ^{13}C NMR: δ 20.7 (*q*, C-12), 31.0 (*q*, C-15), 31.1 (*q*, C-14), 34.7 (*s*, C-11), 40.1 (*t*, C-4), 43.2 (*t*, C-1), 46.2 (*t*, C-10), 46.4 (*d*, C-9), 54.6 (*d*, C-3′), 54.9 (*d*, C-2), 73.3 (*s*, C-3), 73.6 (*d*, C-2′), 77.1 (*d*, C-8), 118.8 (*s*, C-6), 123.9 (*s*, C-7), 126.9 (*d*, C-Ph), 127.0 (*d*, C-Ph), 127.9 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.7 (*d*, C-Ph), 131.8 (*d*, C-Ph), 133.9 (*s*, C-Ph), 138.9 (*s*, C-Ph), 139.2 (*d*, C-13), 140.7 (*d*, C-5), 166.9 (*s*, NCO), 172.1 (*s*, C-1′); LSIMS *m/z* (rel. int.): 540 $[M+Na]^+$ (18), 481 (3), 425 (6), 329 (18), 308 (19), 286 (40), 225 (19), 176 (100), 154 (55), 136 (42), 105 (40), 91 (81); HR LSIMS *m/z*: $[M+Na]^+$ calc. for $C_{31}H_{35}O_6NNa$: 540.23621, found: 540.23494.

4.5.7. Compound ***27***

TLC $R_f = 0.31$ (hexane–EtOAc 7:3); mp 69–74 °C; $[\alpha]_D^{20} = -21.16°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 196 (ε 60975); 218 (ε 21513); IR ν_{max} ($CHCl_3$) cm^{-1}: 3517, 3440, 2956, 2871, 1731, 1667; ^1H NMR: δ 0.84 (3H, *s*, H-15), 0.87 (3H, *s*, H-14), 0.90 (3H, *t*, $J = 6.9$ Hz, -OCH_2CH_3), 1.17 (3H, *s*, H-12), 1.32 (1H, *dd*, $J_{10\alpha,10\beta} = 14.0$ Hz and $J_{10\alpha,9\alpha} = 2.5$ Hz, H-10α), 1.43 (1H, *dd*, $J_{10\beta,10\alpha} = 14.0$ Hz and $J_{10\beta,9\alpha} = 6.8$ Hz, H-10β), 1.49 (1H, *dd*, $J_{1\alpha,1\beta} = 12.6$ and $J_{1\alpha,2\alpha} = 6.6$ Hz, H-1α), 1.55 (1H, *t*, $J = 12.6$ Hz, H-1β), 2.34–2.40 (1H, *m*, H-2α), 2.56 (1H, *d*, $J_{4\beta,4\alpha} = 15.4$ Hz, H-4β), 2.58-2.63 (1H, *m*, H-9α), 2.74 (1H, *d*, $J_{4\alpha,4\beta} = 15.4$ Hz, H-4α), 3.27 (1H, *qn*, $J = 6.9$ Hz, -OCH_2CH_3), 3.36 (1H, *qn*, $J = 6.9$ Hz, -OCH_2CH_3), 4.68 (1H, *d*, $J_{2',3'} = 2.2$ Hz, H-2′), 5.79 (1H, *dd*, $J_{3',NH} = 8.9$ Hz and $J_{3',2'} = 2.2$ Hz, H-3′), 6.01 (1H, *d*, $J_{8\beta,9\alpha} = 11.2$ Hz, H-8β), 6.93 (1H, *s*, H-5), 7.13 (1H, *t*, $J = 2.0$ Hz, H-13), 7.23 (1H, *d*, $J_{NH,3'} = 8.9$ Hz, N*H*), 7.26-7.53 (8H, *m*, H-Ph), 7.78-7.83 (2H, *m*, H-Ph); ^{13}C NMR: δ 15.7 (*q*, -CH_2CH_3), 25.5 (*q*, C-12), 29.1 (*t*, C-4), 31.6 (*q*, C-15), 32.1 (*q*, C-14), 34.7 (*s*, C-11), 41.8 (*t*, C-1), 43.8 (*t*, C-10), 44.2 (*d*, C-9), 51.9 (*d*, C-2), 54.7 (*d*, C-3′), 55.6 (*t*, -CH_2CH_3), 72.6 (*d*, C-8), 73.6 (*d*, C-2′), 75.4 (*s*, C-3), 119.4 (*s*, C-6), 125.2 (*s*, C-7), 126.9 (*d*, C-Ph), 127.1 (*d*, C-Ph), 127.8 (*d*, C-Ph), 128.5 (*d*, C-Ph), 128.6 (*d*, C-Ph), 131.7 (*d*, C-Ph), 133.9 (*s*, C-Ph), 138.0 (*d*, C-5), 138.8 (*s*, C-Ph), 140.4 (*d*, C-13), 166.3 (*s*, NCO), 172.1 (*s*, C-1′); LSIMS *m/z* (rel. int.): 568 $[M+Na]^+$ (18), 413 (2), 338 (2), 330 (18), 308 (95), 286 (26), 261 (19), 240 (6), 215 (100), 176 (46), 154 (23), 136 (21), 105 (66), 95 (17); HR LSIMS *m/z*: $[M+Na]^+$ calc. for $C_{33}H_{39}O_6NNa$: 568.26751, found: 568.26825.

4.5.8. Compound ***30***

TLC $R_f = 0.11$ (hexane–EtOAc 7:3); mp 80–83 °C; $[\alpha]_D^{20} = +5.23°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 204 (ε 53790); 220 (ε 41181); IR ν_{max} ($CHCl_3$) cm^{-1}: 3528, 3440, 2956, 2867, 1752, 1667; ^1H NMR: δ 0.75 (3H, *s*, H-15), 0.77 (3H, *s*, H-14), 1.12 (1H, *dd*, $J_{10\beta,10\alpha} = 12.8$ Hz and $J_{10\beta,9\alpha} = 8.8$ Hz, H-10β), 1.64 (1H, *ddd*, $J_{10\alpha,10\beta} = 12.8$ Hz, $J_{10\alpha,9\alpha} = 7.8$ Hz and $J = 1.8$ Hz, H-10α), 1.74 (3H, *br s*, H-12), 2.01 (1H, *d*, $J_{1\beta,1\alpha} = 15.0$ Hz, H-1β), 2.29 (1H, *d*, $J_{1\alpha,1\beta} = 15.0$ Hz, H-1α), 2.89 (1H, *d*, $J_{4\beta,4\alpha} = 19.9$ Hz, H-4β), 3.13–3.24 (2H, *m*, H-4α and H-9α), 4.59 (1H, *d*, $J_{13\beta,13\alpha} = 17.3$ Hz, H-13β), 4.69 (1H, *d*, $J_{2',3'} = 3.8$ Hz, H-2′), 4.70 (1H, *dd*, $J_{13\alpha,13\beta} = 17.3$ Hz and $J = 3.6$ Hz, H-13α), 5.60 (1H, *dd*, $J_{3',NH} = 11.2$ Hz and $J_{3',2'} = 3.8$ Hz, H-3′), 5.61 (1H, *d*, $J_{8\beta,9\alpha} = 11.2$ Hz, H-8β), 7.25–7.88 (9H, m, N*H* and H-Ph), 8.10–8.15 (2H, *m*, H-Ph); ^{13}C NMR: δ 22.6 (*q*, C-12), 27.2 (*q*, C-14), 28.6 (*q*, C-15), 30.9 (*t*, C-4), 36.2 (*s*, C-11), 46.1 (*d*, C-9), 45.9 (*t*, C-10), 47.5 (*t*, C-1), 57.5 (*d*, C-8), 57.5 (*d*, C-3′), 71.4 (*t*, C-13), 74.8 (*d*, C-2′), 127.2 (*s*, C-2), 128.3 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.7 (*d*, C-Ph), 129.4 (*s*, C-6), 129.5 (*d*, C-Ph), 129.6 (*d*, C-Ph), 133.0 (*d*, C-Ph), 135.2 (*s*, C-Ph), 137.4 (*s*, C-Ph), 140.4 (*s*, C-3), 159.0 (*s*, C-7), 169.4 (*s*, NCO), 173.3 (*s*, C-1′), 175.9 (*s*, C-5); LSIMS *m/z* (rel. int.): 538 $[M+Na]^+$ (18), 516 $[M+H]^+$ (8), 443 (2), 338 (5), 308 (29), 286 (100), 253 (5), 231 (15), 210 (8), 176 (70), 154 (59), 136 (42), 105 (83); HR LSIMS *m/z*: $[M+Na]^+$ calc. for $C_{31}H_{33}O_6NNa$: 538.22056, found: 538.22162.

4.5.9. Compound ***33***

TLC $R_f = 0.33$, (C_6H_6–Me_2CO 8:2); mp 101–103 °C; $[\alpha]_D^{20} = -18.40°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 218 (ε 26218); IR ν_{max} (KBr) cm^{-1}: 3428, 2955, 2867, 1746, 1649; ^1H NMR: δ 0.71 (3H, *s*, H-15), 0.90 (3H, *s*, H-14), 1.06 (1H, *dd*, $J_{10\beta,10\alpha} = 12.6$ Hz and $J_{10\beta,9\alpha} = 10.0$ Hz, H-10β), 1.22 (3H, *s*, H-12), 1.20–1.27 (1H, *m*, H-1β), 1.48 (1H, *dd*, $J_{10\alpha,10\beta} = 12.6$ Hz and $J_{10\alpha,9\alpha} = 6.8$ Hz, H-10α), 1.54 (1H, *dd*, $J_{1\alpha,1\beta} = 11.8$ Hz and $J_{1\alpha,2\alpha} = 7.2$ Hz, H-1α), 2.44–2.50 (1H, *m*, H-2α), 2.53-2.62 (3H, *m*, H-4α, 4-β and H-9α), 4.41 (1H, *br d*, $J_{13\beta,13\alpha} = 17.3$ Hz, H-13β), 4.65 (1H, *dt*, $J_{13\alpha,13\beta} = 17.3$ Hz and $J = 2.5$ Hz, H-13α), 4.71 (1H, *d*, $J_{2',3'} = 2.3$ Hz, H-2′), 5.64 (1H, *d*, $J = 5.9$ Hz, H-8β), 5.78 (1H, *dd*, $J_{3',NH} = 9.3$ Hz and $J_{3',2'} = 2.3$ Hz, H-3′), 7.25–7.54 (9H, *m*, N*H* and H-Ph), 7.78-7.81 (2H, *m*, H-Ph); ^{13}C NMR: δ 22.6 (*q*, C-15), 27.1 (*q*, C-14), 29.4 (*q*, C-12),

34.7 (*t*, C-4), 36.0 (*s*, C-11), 42.4 (*d*, C-9), 44.6 (*t*, C-1), 45.0 (*t*, C-10), 50.2 (*d*, C-2), 54.7 (*d*, C-3′), 70.6 (*t*, C-13), 71.7 (*d*, C-8), 72.3 (*s*, C-3), 73.2 (*d*, C-2′), 126.9 (*d*, C-Ph), 127.1 (*d*, C-Ph), 127.8 (*s*, C-6), 127.9 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.7 (*d*, C-Ph), 132.1 (*d*, C-Ph), 133.3 (*s*, C-Ph), 138.0 (*s*, C-Ph), 154.0 (*s*, C-7), 167.0 (*s*, NCO), 172.2 (*s*, C-1′), 174.3 (*s*, C-5); LSIMS *m*/*z* (rel. int.): 534 $[M+H]^+$ (10), 391 (3), 369 (5), 307 (19), 286 (24), 225 (10), 215 (8), 176 (5), 154 (100), 137 (71), 105 (39); HR LSIMS *m*/*z*: $[M+H]^+$ calc. for $C_{31}H_{36}O_7N$: 534.24921, found: 534.25325.

4.5.10. Compound **36**

LC $R_f = 0.16$ (hexane–Me_2CO 7:3); mp 114–117 °C; $[\alpha]_D^{20} = -11.63°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 194 (ε 59567), 220 (ε 25610); IR ν_{max} ($CHCl_3$) cm^{-1}: 3593, 3440, 2958, 2868, 1738, 1662; ^1H NMR: δ 0.88 (3H, *s*, H-15), 0.99 (3H, *s*, H-14), 1.03 (1H, *t*, $J = 12.2$ Hz, H-1β), 1.19 (1H, *t*, $J = 12.3$ Hz, H-10β), 1.21 (3H, *s*, H-12), 1.46 (1H, *dd*, $J_{10\alpha,10\beta} = 12.3$ Hz and $J_{10\alpha,9\alpha} = 8.9$ Hz, H-10α), 1.51 (1H, *dd*, $J_{1\alpha,1\beta} = 12.2$ Hz and $J_{1\alpha,2\alpha} = 7.8$ Hz, H-1α), 2.43 (1H, *d*, $J_{4\beta,4\alpha} = 19.2$ Hz, H-4β), 2.53–2.60 (1H, *m*, H-2α), 2.60 (1H, *dq*, $J_{4\alpha,4\beta} = 19.2$ Hz and $J = 2.9$ Hz, H-4α), 2.83–2.91 (1H, *m*, H-9α), 4.61 (1H, *d*, $J_{2',3'} = 2.2$ Hz, H-2′), 4.77 (2H, *br s*, H-13), 5.65 (1H, *dd*, $J_{3',NH} = 9.0$ Hz and $J_{3',2'} = 2.2$ Hz, H-3′), 6.88 (1H, *br s*, H-8α), 7.15 (1H, *d*, $J_{NH,3'} = 9.0$ Hz, N*H*), 7.28–7.48 (8H, *m*, H-Ph), 7.72–7.75 (2H, *m*, H-Ph); ^{13}C NMR: δ 26.2 (*q*, C-15), 28.9 (*q*, C-14), 29.4 (*q*, C-12), 34.8 (*t*, C-4), 37.7 (*s*, C-11), 42.3 (*t*, C-10), 43.8 (*d*, C-9), 44.6 (*t*, C-1), 48.9 (*d*, C-2), 55.0 (*d*, C-3′), 70.8 (*t*, C-13), 73.3 (*d*, C-2′), 73.6 (*s*, C-3), 74.8 (*d*, C-8), 122.2 (*s*, C-6), 127.0 (*d*, C-Ph), 127.0 (*d*, C-Ph), 128.0 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.8 (*d*, C-Ph), 131.9 (*d*, C-Ph), 133.6 (*s*, C-Ph), 138.5 (*s*, C-Ph), 158.5 (*s*, C-7), 167.5 (*s*, NCO), 174.8 (*s*, C-5), 174.8 (*s*, C-1′); LSIMS *m*/*z* (rel. int.): 534 $[M+H]^+$ (2), 524 (1), 460 (1), 391 (2), 369 (1), 338 (3), 307 (14), 286 (12), 231 (2), 154 (100), 136 (77), 120 (14), 105 (42); HR LSIMS *m*/*z*: $[M+Na]^+$ calc. for $C_{31}H_{35}O_7NNa$: 556.23112, found: 556.23110.

4.5.11. Compound **39**

TLC $R_f = 0.31$ (hexane–Me_2CO 6:4); mp 116–120 °C; $[\alpha]_D^{20} = -47.20°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 221 (ε 24542); IR ν_{max} (KBr) cm^{-1}: 3423, 2952, 2865, 1747, 1649; ^1H NMR: δ 0.97 (3H, *s*, H-15), 1.01 (3H, *s*, H-14), 1.07 (3H, *s*, H-12), 1.28 (1H, *dd*, $J_{10\alpha,10\beta} = 12.6$ Hz and $J_{10\alpha,9\beta} = 10.3$ Hz, H-10α), 1.51 (1H, *dd*, $J_{1\beta,1\alpha} = 13.2$ Hz and $J_{1\beta,2\alpha} = 10.1$ Hz, H-1β), 1.60 (1H, *dd*, $J_{10\beta,10\alpha} = 12.6$ Hz and $J_{10\beta,9\beta} = 6.4$ Hz, H-10β), 1.83 (1H, *dd*, $J_{1\alpha,1\beta} = 13.2$ Hz and $J_{1\alpha,2\alpha} = 7.8$ Hz, H-1α), 2.14-2.25 (2H, *m*, H-2α and H-9β), 2.28 (1H, *dd*, $J_{4\beta,4\alpha} = 15.1$ Hz and $J = 2.3$ Hz, H-4β), 2.75 (1H, *d*, $J_{4\alpha,4\beta} = 15.1$ Hz, H-4α), 4.56 (1H, *dd*, $J_{13\beta,13\alpha} = 18.1$ Hz and $J = 2.9$ Hz, H-13β), 4.66 (1H, *d*, $J_{2',3'} = 2.4$ Hz, H-2′), 4.78 (1H, *br d*, $J_{13\alpha,13\beta} = 18.1$ Hz, H-13α), 5.71 (1H, *dd*, $J_{3',NH} = 9.0$ Hz and $J_{3',2'} = 2.4$ Hz, H-3′), 5.79 (1H, *br d*, $J_{8\alpha,9\alpha} = 8.7$ Hz, H-8α), 7.21 (1H, *d*, $J_{NH,3'} = 9.0$ Hz, N*H*), 7.29–7.52 (8H, *m*, H-Ph), 7.75–7.78 (2H, *m*, H-Ph); ^{13}C NMR: δ 20.6 (*q*, C-12), 30.8 (*q*, C-15), 31.1 (*q*, C-14), 34.2 (*s*, C-11), 39.3 (*t*, C-4), 43.4 (*t*, C-1), 44.0 (*d*, C-9), 46.2 (*t*, C-10), 54.4 (*d*, C-2), 54.9 (*d*, C-3′), 69.3 (*t*, C-13), 72.1 (*s*, C-3), 73.5 (*d*, C-2′), 77.5 (*d*, C-8), 124.1 (*s*, C-6), 127.0 (*d*, C-Ph), 127.0 (*d*, C-Ph), 128.2 (*d*, C-Ph), 128.7 (*d*, C-Ph), 128.8 (*d*, C-Ph), 132.1 (*d*, C-Ph), 133.4 (*s*, C-Ph), 138.4 (*s*, C-Ph), 159.7 (*s*, C-7), 167.2 (*s*, NCO), 172.0 (*s*, C-1′), 174.1 (*s*, C-5); ESI-MS *m*/*z* (rel. int.): 1623.7016 $[3M+Na]^+$ (20), 1089.4559 $[2M+Na]^+$ (100), 556.2276 $[M+Na]^+$ (95); HR ESI-MS *m*/*z*: $[M+Na]^+$ calc. for $C_{31}H_{35}O_7NNa$: 556.23112, found: 556.23060.

4.5.12. Compound **42**

TLC $R_f = 0.34$ (hexane–Me_2CO 6:4); mp 102–105 °C; $[\alpha]_D^{20} = -3.80°$ ($CHCl_3$, *c* 1.0); UV λ_{max} (EtOH) nm: 194 (ε 64173), 217 (ε 23025); IR ν_{max} ($CHCl_3$) cm^{-1}: 3429, 2958, 2868, 1757, 1727, 1650; ^1H NMR: δ 0.52 (3H, *s*, H-15), 0.78 (3H, *s*, H-14), 1.06 (1H, *t*, $J = 12.4$ Hz, H-1β), 1.31 (3H, *s*, H-12), 1.51 (1H, *ddd*, $J_{1\alpha,1\beta} = 12.4$ Hz, $J_{1\alpha,2\alpha} = 7.8$ Hz and $J = 2.1$ Hz, H-1α), 1.54 (1H, *ddd*, $J_{10\alpha,10\beta} = 12.3$ Hz, $J_{10\alpha,9\alpha} = 6.8$ Hz and $J = 2.2$ Hz, H-10α), 2.48-2.58 (2H, *m*, H-2α and H-9α), 2.56 (1H, *d*, $J_{4\beta,4\alpha} = 19.4$ Hz, H-4β), 2.76 (1H, *d*, $J_{4\alpha,4\beta} = 19.4$ Hz, H-4α), 4.68 (2H, *br s*, H-5α and H-5β), 4.76 (1H, *d*, $J_{2',3'} = 1.9$ Hz, H-2′), 5.83 (1H, *d*, $J_{8\beta,9\alpha} = 2.3$ Hz, H-8β), 5.86 (1H, *dd*, $J_{3',NH} = 9.9$ Hz, $J_{3',2'} = 2.3$ Hz, H-3′), 7.21 (1H, *d*, $J_{3',NH} = 9.9$ Hz, N*H*), 7.24–7.55 (8H, *m*, H-Ph), 7.81–7.83 (2H, *m*, H-Ph); ^{13}C NMR: δ 25.3 (*q*, C-15), 28.9 (*q*, C-14), 32.2 (*q*, C-12), 36.2 (*s*, C-11), 36.8 (*t*, C-4), 42.3 (*d*, C-9), 45.8 (*t*, C-10), 46.3 (*t*, C-1), 48.8 (*d*, C-2), 54.0 (*d*, C-3′), 70.1 (*d*, C-8), 72.3 (*t*, C-5), 72.7 (*d*, C-2′), 73.0 (*s*, C-3), 122.5 (*s*, C-7), 126.9 (*d*, C-Ph), 127.1 (*d*, C-Ph), 127.7 (*d*, C-Ph), 128.6 (*d*, C-Ph), 128.8 (*d*, C-Ph), 132.3 (*d*, C-Ph), 133.3 (*s*, C-Ph), 137.9 (*s*, C-Ph), 164.2 (*s*, C-6), 167.3 (*s*, NCO), 172.5 (*s*, C-1′), 173.9 (*s*, C-13); LSIMS *m*/*z* (rel. int.): 1067 $[2M+H]^+$ (1), 534 $[M+H]^+$ (26), 460 (1), 286 (100), 240 (8), 210 (20), 167 (7), 154 (76), 136 (56), 105 (76); HR LSIMS *m*/*z*: $[M+H]^+$ calc. for $C_{31}H_{36}O_7N$: 534.24918, found: 534.24918.

4.6. Antifeedant activity test

The test is described in detail in Błoszyk et al. (1995). Insects (adults and larvae) used for the test were reared under laboratory conditions at temp. of 26 °C and 75% humidity. All compounds investigated were dissolved in EtOH at concentration of 10 mg ml^{-1}. Air dry wheat wafer discs were used as test food. The discs (1 cm in diameter) were saturated with EtOH solutions of pure compounds to produce 0.5% (by weight) contamination of the wafer in every test. Feeding of insects was recorded under three conditions: (1) on pure food (control); (2) on food with possibility of choice (choice test); on food with the compounds tested (no choice test). The wafer discs were weighed after saturation and drying in

air for 30 min before the experiments and again after 7 days of feeding by beetles or larvae. On the basis of eaten food, the index of activity of the compounds tested was calculated in the following way: three values of the food eaten were obtained in the control KK, in the no-choice test EE, and in the choice test K, E.

Thus, the relative coefficient of antifeedancy:

$$R = \frac{K - E}{K + E} \times 100$$

The total coefficient of antifeedancy is equal to $T = A + R$, and the maximum value of the coefficient can reach 200 for a perfect antifeedant.

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