# Four New Triterpene Glycosides from *Schefflera bodinieri* Roots

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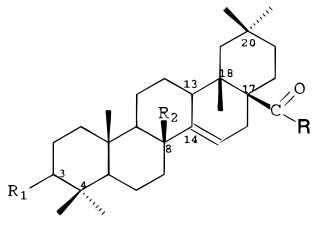
*Received February 7, 1996*[⊗]

Four novel triterpene glycosides named bodinitins A (**1**), B (**2**), C (**3**), and D (**4**) were isolated from the roots of *Schefflera bodinieri*. Based on spectroscopic data, especially $^1$H−$^1$H COSY and $^{13}$C−$^1$H COSY NMR, the structures of the glycosides have been determined as 28-*O*-[α-L-rhamopyranosyl-(1→4)-*O*-*β*-D-glucopyranosyl-(1→6)]-*β*-D-glucopyranoside of demethylisoaleuritolic acid (**1**), 28-*O*-[α-L-rhamopyranosyl(1→4)-*O*-*β*-D-glucopyranosyl(1→6)]-*β*-D-glucopyranoside of isoaleuritolic acid (**2**), 28-*O*-[α-L-rhamnopyranosyl(1→4)-*O*-*β*-D-glucopyranosyl(1→6)]-*β*-D-glucopyranoside of 3-oxo-8-demethylisoaleuritolic acid (**3**), and 28-*O*-[α-L-rhamopyranosyl(1→4)-*O*-*β*-D-glucopyranosyl(1→6)]-*β*-D-glucopyranoside of 3-oxoisoaleuritolic acid (**4**).

Several species of *Schefflera* (Araliaceae) are used as folk remedies for the treatment of pain, rheumatic arthritis, fracture, sprains, lumbago, and stomach ache in the southwest of China[1] and in certain Asian countries, such as Vietnam and India.[2,3] Two species, *S. octophylla* and *S. capitata*, have been chemically investigated to isolate a series of triterpenes, triterpene glycosides, and oligosaccharides.[3−13] *Schefflera bodinieri* (Levi.) Rehd. root, which has not previously been investigated, was selected for the present study. The 70% EtOH extract showed strong binding to 5HT and GABA receptors in radioligand-receptor binding assays, then the bioassay-guided isolation resulted in obtaining four novel triterpene glycosides. This paper deals the structure elucidation of these compounds.

## Results and Discussion

The 70% EtOH root extract was fractionated by repeated flash chromatography ($SiO_2$), and the fractions were further purified with Sephadex columns and HPLC to isolate four triterpene glycosides, termed as bodinitins A (**1**), B (**2**), C (**3**), and D (**4**).




1 R1= , R2=H
2 R1= , R2=CH3
3 R1=O, , R2=H
4 R1=O, , R2=CH3

R= α-L-Rham-*β*-D-Glc-*β*-D-Glc-
1→4 1→6

The molecular weight of compound **1** was found to be 912.5085 (required 912.5083), and the molecular formula was established as $C_{47}H_{76}O_{17}$ by HRFABMS spectrum. The $^1$H−NMR spectrum suggested the presence of three sugar moieties, and the anomeric proton signals appeared at *δ* 5.35 (1H, d, *J* = 7 Hz), 4.40 (1H, d, *J* = 7 Hz), 4.85 (1H, br s), respectively. The hydrolysis of the compound gave glucose and rhamnose as sugar components as indicated by TLC (in three different solvent systems, also with mannose, arabinose, galactose, and xylose as additional references). The anomeric proton signal at *δ* 4.85 (br s) and a methyl group signal at *δ* 1.29 (3H, d, *J* = 6.5 Hz) indicated that there was only one rhamnose in the molecule. The $^{13}$C-NMR spectrum confirmed the presence of the three sugar moieties (signals for anomeric C-atoms: *δ* 95.7, 102.9, 104.2). The $^{13}$C−$^1$H COSY spectrum showed a cross peak between the proton at *δ* 5.35 ppm (glucose−H-1) and the carbon at *δ* 95.7 (glucose−C-1), indicating that the glucose unit was linked to the genin via a carboxylic group because the chemical shift of the carbon was about 10 ppm downfield compared with that of glucose linked to $C_3$−OH.[14] The FABMS data showed the peaks at *m*/*z* 934 [M + Na − 1]$^+$, 788 [M + Na − 1 − Rham]$^+$, 604 [M − Rham − Glc]$^+$, and 442 [M − Rham − Glc − Glc]$^+$, which gave the possible link order of the sugar moieties. The $^{13}$C-NMR−DEPT data of compound **1** showed that the chemical shift of C-6 of the glucose linked with genin and that of C-4 of the second glucose were both 7 ppm downfield; this suggested that the linkage position between the two glucoses was 6→1, and that between the second glucose and the rhamnose was 4→1. The long-range $^{13}$C−$^1$H COSY spectrum further confirmed that the rhamnose linked with the second glucose at C-4 position, showing a cross peak between the proton at *δ* 4.85 (rham − 1) and the carbon at 78.6 (glc − 4) (Table 1). The coupling-constant data of the anomeric protons in $^1$H NMR indicated the configuration of the glucoses was *β*-oriented (d, *J* = 7 Hz), and that of rhamnose was α-oriented (br s).[15] Therefore, the structure of the sugar moieties of **1** was established as α-L-rhamopyranosyl-(1→4)-*O*-*β*-D-glucopyranosyl(1→6)-*O*-*β*-D-glucopyranoside. Moreover, this sugar residue was of the same type

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⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1996.

S0163-3864(96)00235-2 CCC: $12.00 

**Table 1.** $^{13}C$ and $^{1}H$−NMR Spectral Data of Compound **1** ($\delta$ ppm)[a]

| aglycone | δC | DEPT | δH | $^{1}H-^{1}H$ COSY | $^{13}C-^{1}H$ COSY | $^{13}C-^{1}H$ COSY (long range) |
|---|---|---|---|---|---|---|
| aglycone | | | | | | |
| 1 | 34.4 | $CH_2$ | 1.39, 1.41 (m) | 1.39→1.41, 1.55, 1.98 | 34.4→1.39, 1.41 | 34.4 (C-1)→1.55 (H-2), 1.01 (H-25) |
| 2 | 25.2 | $CH_2$ | 1.98, 1.55 | 1.98→1.39, 1.55 | 25.2→1.98, 1.55 | 25.2 (C-2)→1.41 (H-1) |
| 3 | 76.7 | CH | 3.32 (overlapped with H-2 of Glc1[b]) | 3.31→1.55, 1.98 | 76.7→3.32 | 76.7 (C-3)→0.90 (H-23) |
| 4 | 38.3 | C | | | | 38.3 (C-4)→0.91 (H-24) |
| 5 | 49.2 | CH | 2.20 (dd, 10, 2;) | 2.20→1.95, 2.00 | 49.2→2.20 | 49.2 (C-5)→0.91 (H-24) |
| 6 | 25.2 | $CH_2$ | 1.95, 2.00 (m) | 1.95→2.00, 2.20 | 25.2→1.95, 2.00 | 25.2 (C-6)→1.23 (H-7) |
| 7 | 34.7 | $CH_2$ | 1.21, 1.23 (m) | 1.21→1.19, 1.23 | 34.7→1.21, 1.23 | |
| 8 | 48.1 | CH | 1.19 (m) | 1.19→1.23, 1.30 | 48.1→1.19 | |
| 9 | 50.8 | CH | 1.30 (m) | 1.30→1.19 | 50.8→1.30 | 50.8 (C-9)→1.01 (H-25) |
| 10 | 38.3 | C | | | | 38.3 (C-10)→1.01 (H-25), 1.30 (H-9) |
| 11 | 19.3 | $CH_2$ | 1.30, 1.32 (m) | 1.32→1.18, 1.45 | 19.3→1.30, 1.32 | |
| 12 | 44.7 | $CH_2$ | 1.18, 1.45 (m) | 1.45→1.18, 1.32, 2.92 | 44.7→1.18, 1.45 | |
| 13 | 44.5 | CH | 2.92 (dd, 8, 2) | 2.92→1.18, 1.45 | 44.5→2.92 | 44.5 (C-13)→0.96 (H-27) |
| 14 | 137.5 | C | | | | |
| 15 | 127.9 | CH | 5.65 (t, 4) | 5.65→1.95, 1.98 | 127.9→5.65 | |
| 16 | 23.9 | $CH_2$ | 1.95, 1.98 (m) | 1.98→1.95, 5.65 | 23.9→1.95, 1.98 | |
| 17 | 57.3 | C | | | | 57.3 (C-17)→0.96 (H-27), 5.65 (H-15) |
| 18 | 40.9 | C | | | | 40.9 (C-18)→0.96 (H-27) |
| 19 | 32.8 | $CH_2$ | 1.30 (m), 1.58 (m) | 1.30→1.58 | 32.8→1.30, 1.58 | 32.8 (C-19)→0.92 (H-29), 0.96 (H-27) |
| 20 | 31.5 | C | | | | 31.5 (C-20)→0.85 (H-30), 0.92 (H-29) |
| 21 | 37.7 | $CH_2$ | 1.63, 1.73 (m) | 1.73→1.63, 2.08 | 37.7→1.63, 1.73 | 37.7 (C-21)→0.85 (H-30) |
| 22 | 25.7 | $CH_2$ | 2.06, 2.08 (m) | 2.08→1.63, 1.73, 2.06 | 25.7→2.06, 2.08 | |
| 23 | 33.0 | $CH_3$ | 0.90 (s) | | 33.0→0.90 | 33.0 (C-23)→0.91 (H-24) |
| 24 | 18.3 | $CH_3$ | 0.91 (s) | 0.91→1.01 (H-25) weak | 18.3→0.91 | 18.3 (C-24)→0.90 (H-23) |
| 25 | 16.5 | $CH_3$ | 1.01 (s) | | 16.5→1.01 | 16.5 (C-25)→1.41 (H-1) |
| 26 | | | | | | |
| 27 | 23.6 | $CH_3$ | 0.96 (s) | 0.96→1.45 (H-12) weak | 23.6→0.96 | 23.6 (C-27)→0.85 (H-30), 1.30 (H-19), 1.45 (H-12) |
| 28 | 178.1 | C | | | | 178.1 (C-28)→2.08 (H-22) |
| 29 | 28.5 | $CH_3$ | 0.92 (s) | | 28.5→0.92 | 28.5 (C-29)→0.85 (H-30) |
| 30 | 22.3 | $CH_3$ | 0.85 (s) | | 22.3→0.85 | 22.3 (C-30)→0.92 (H-29), 1.30 (H-19) |
| sugar moiety | | | | | | |
| Glc1 | | | | | | |
| 1 | 95.7 | CH | 5.35 (d, 7) | 5.35→3.32 | 95.7→5.35 | |
| 2 | 73.7 | CH | 3.32 (overlapped with H-3 of aglycon) | 3.32→3.65, 5.35 | 73.7→3.32 | |
| 3 | 79.5 | CH | 3.65 (t, 6.5) | 3.65→3.32, 3.43 | 79.5→3.65 | 79.5 ($C_{glc\text{-}1}$-3)→3.55 ($H_{glc\text{-}1}$-5) |
| 4 | 71.0 | CH | 3.43 (t, 6.5) | 3.43→3.55, 3.65 | 71.0→3.43 | |
| 5 | 76.8 | CH | 3.55 (m) | 3.55→3.43, 3.83, 4.12 | 76.8→3.55 | |
| 6 | 69.4 | $CH_2$ | 3.83 (dd, 10, 2)<br>4.12 (dd, 10, 3) | 3.83→3.55, 4.12 | 69.4→3.83, 4.12 | |
| Glc2 | | | | | | |
| 1 | 104.1 | CH | 4.40 (d, 7) | 4.40→3.28 | 104.1→4.40 | |
| 2 | 75.3 | CH | 3.28 (t, 8) | 3.28→3.50, 4.40 | 75.3→3.28 | |
| 3 | 76.7 | CH | 3.50 (t, 8) | 3.50→3.28, 3.42 | 76.7→3.50 | |
| 4 | 78.6 | CH | 3.42 (t, 6) | 3.42→3.30, 3.50 | 78.6→3.42 | 78.6 ($C_{glc\text{-}2}$-4)→3.50 ($H_{glc\text{-}2}$-3), 4.85 ($H_{rham}$-1) |
| 5 | 78.1 | CH | 3.30 (m) | 3.30→3.42, 3.67, 3.82 | 78.1→3.30 | 78.1 ($C_{glc\text{-}2}$-5)→3.67 ($H_{glc\text{-}2}$-6) |
| 6 | 61.9 | $CH_2$ | 3.67 (dd, 12, 3)<br>3.82 (dd, 11.5, 4) | 3.82→3.67, 3.30 | 61.9→3.67, 3.82 | |
| Rham | | | | | | |
| 1 | 102.9 | CH | 4.85 (br s) | 4.85→3.87 | 102.9→4.85 | |
| 2 | 72.4 | CH | 3.87 (br s) | 3.87→3.67, 4.85 | 72.4→3.87 | 72.4 ($C_{rham}$-2)→4.85 ($H_{rham}$-1) |
| 3 | 72.2 | CH | 3.67 (dd, 5, 1) | 3.67→3.43, 3.87 | 72.2→3.67 | 72.2 ($C_{rham}$-3)→3.87 ($H_{rham}$-2) |
| 4 | 73.8 | CH | 3.43 (dd, 8, 3) | 3.43→3.67, 4.00 | 73.8→3.43 | |
| 5 | 70.6 | CH | 4.00 (m) | 4.00→1.29, 3.43 | 70.6→4.00 | 70.6 ($C_{rham}$-5)→4.85 ($H_{rham}$-1) |
| 6 | 17.9 | $CH_3$ | 1.29 (d, 6.5) | 1.29→3.43, 4.00 | 17.9→1.29 | |

[a] The data were obtained from $^{1}H$ NMR (500 MHz) and $^{13}C$ NMR (125.7 MHz) in $CD_3OD$. [b] Glc1: the first glucose linked with the aglycon, Glc2: the second glucose linked with Glc1, Rham: rhamnose linked with Glc2.

as those found in other triterpene glycosides isolated from *Schefflera*.[7−9]

The $^{13}C$-NMR−DEPT spectrum of **1** substantiated the presence of 29 carbon atoms of the aglycon including an ester carbonyl carbon ($\delta$ 178.1), a carbon linked with a hydroxyl group ($\delta$ 76.7), and olefinic carbons ($\delta$ 137.5, 127.9). The $^{1}H$-NMR spectrum exhibited the presence of one olefinic proton ($\delta$ 5.65), a proton linked with a hydroxyl group ($\delta$ 3.32), and six tertiary methyl groups ($\delta$ 0.85−1.01) in the aglycon. From the biogenetic point of view, the hydroxyl group should be assigned to the C-3 position, and this was further substantiated by the $^{1}H-^{1}H$ COSY spectrum (Table 1). The C-3−OH of compound **1** had $\beta$-equatorial orientation, which was mainly determined by the chemical shifts of C-3 ($\delta$ 76.7, $\beta$-OH) and H-3 ($\delta$ 3.32, α-H), and by comparison with related compounds.[16] Hydrolysis of compound **1** gave its aglycon. The EIMS of the aglycon showed the $M^+$ at *m/z* 442. These data suggested that the aglycon might have a $\beta$-amyrane-type structure with one double bond in the molecule.

The EIMS spectrum of compound **1** was identical to that of the hydrolyzed aglycon. The MS fragmentation of the aglycon was not the same as those of olean-12-en-oic or urs-12-en-oic acids that commonly occur in nature.[17,18] The retro-Diels−Alder (RDA) fragmentation suggested the presence of a 14:15 double bond in ring D of compound **1**, which exhibited a peak at *m/z* 275. The fragments formed by collapse of ring C were also observed at *m/z* 207 and 234 and their fragmentation ions at *m/z* 189 and 190. Comparison was made with the MS fragmentation of the related compound 3$\beta$-acetoxy-D-friedoolean-14-en-28-oic acid,[19] suggesting that **1** contained a C-18−Me, and there was no methyl group

at C-8 or C-13. The presence of H-8 ($\delta$ 1.19) and H-13 ($\delta$ 2.92) was revealed by the $^1$H−$^1$HCOSY and $^{13}$C−$^1$H COSY spectra (Table 1), and the chemical shift of C-13 ($\delta$ 44.5) was confirmed by long-range $^{13}$C−$^1$H spectrum as the carbon showed coupling with H-27 methyl group. The presence of a $\beta$ $C_{18}$−Me ($\delta$ 23.6) was also demonstrated by the long-range $^{13}$C−$^1$H spectrum as the methyl carbon was coupling with $\beta$ H-19, $\beta$ H-12, and $\beta$ H-30. With the aid of a molecular model, it was found that when compound **1** had α C-13−H and $\beta$ C-18−Me, the protons of C-18−Me were able to couple with $\beta$ C-12−H ($\delta$1.45) through space. This weak coupling can be observed in the $^1$H−$^1$H COSY spectrum (Table 1). On the other hand, if the compound has either $\beta$ C-13−H and $\beta$ C-18−Me, α C-13−H and α C-18−Me, or $\beta$ C-13−H and α C-18−Me, the long-range coupling cannot be present. Therefore, the stereochemistry of **1** belongs to the teraxerane type. The presence of the C14:15 double bond can also be proved by the long-range $^{13}$C−$^1$H spectrum because the olefinic proton at C-15 coupled with the carbon of C-17. Based on the results and compared with the related data in the literature,[20,21] the assignment of protons and carbons of **1** has been achieved (Table 1). The structure is found to be novel and established as 28-*O*-[α-L-rhamopyranosyl(1→4)-*O*-$\beta$-D-glucopyranosyl(1→6)-]-$\beta$-D-glucopyranoside of demethylisoaleuritolic acid, which is named bodinitin A.

Compounds **2**, **3**, and **4** were structurally related to compound **1** as indicated by EIMS, FABMS, and $^1$H NMR. They were all triterpene glycosides with the same sugar moieties as **1** showing in their $^1$H-NMR spectra. The anomeric proton signals appeared around $\delta$ 5.35 (1H, d, $J$ = 7 Hz), 4.40 (1H, d, $J$ = 7 Hz), 4.85 (1H, br s), respectively. Hydrolysis of the compounds followed by TLC examination indicated the presence of glucose and rhamnose as the sugar residues. Hence, the major difference in the structures of **1**−**4** lies in their aglycons.

The aglycon structure of compound **2** is closely related to compound **1**, except for the presence of an additional tertiary methyl group as shown in the $^1$H NMR. This was confirmed by the EIMS showing $M^+$ of the aglycon at $m/z$ 456 and the CIMS showing the $M^+$ of **2** at $m/z$ 926 (both were 14 mass units higher than those of compound **1**). The additional tertiary methyl group was located at C-8, as indicated by the fragment $m/z$ 289 and $m/z$ 221. An ion peak at $m/z$ 275, which was formed by loss of the allylic methyl group at C-8, was also observed. Therefore, the structure of **2** is represented by 28-*O*-[α-L-rhamopyranosyl(1→4)-*O*-$\beta$-D-glucopyranosyl(1→6)-]-$\beta$-D-glucopyranoside of isoaleuritolic acid, which is new and named bodinitin B.

The HRFABMS spectrum of compound **3** established the molecular formula as $C_{47}H_{74}O_{17}$ and indicated the molecular weights as 910.4929 (requires 910.4926), which was 2 mass units less than compound **1**. In the EIMS spectrum, the $M^+$ of the aglycon was at $m/z$ 440, indicating that the difference between **3** and **1** was at their aglycon. The RDA cleavage produced an ion at $m/z$ 273, and ring C cleavage gave ions at $m/z$ 205 and 234. These MS fragmentations suggested that compound **3** had a carbonyl group at C-3. The $^1$H-NMR spectrum showed that **3** exhibited the same sugar moiety signals as **1** and a similar aglycon spectral pattern to **1** except for the absence of proton at $C_3$. The IR spectrum also indicated the presence of a ketone group ($\nu$ max 3050, 1670). Therefore, the structure of this new glycoside was determined as 28-*O*-[α-L-rhamnopyranosyl(1→4)-*O*-$\beta$-D-glucopyranosyl(1→6)-$\beta$-D-glucopyranoside of 3-oxo-8-demethylisoaleuritolic acid, which is named bodinitin C.

The difference between compounds **4** and **1** included the presence of a carbonyl group at C-3 and an additional tertiary methyl group in **4** as indicated by IR, EIMS, and $^1$H-NMR spectra. The HRFABMS spectrum established the molecular formula as $C_{48}H_{76}O_{17}$ and gave the molecular weight as 924.5086 (requires 924.5083). In the EIMS spectrum, the $M^+$ of the aglycon was at $m/z$ 454, and there were diagnostic peaks at $m/z$ 287 and 219, indicating the presence of the additional tertiary methyl group at C-8 and the carbonyl group at C-3. The $^1$H-NMR spectrum showed the presence of seven tertiary methyl groups, the absence of the proton at C-3, and the same signals for the sugars' protons. On the basis of these data, the new compound is 28-*O*-[α-L-rhamnopyranosyl(1→4)-*O*-$\beta$-D-glucopyranosyl(1→6)-$\beta$-D-glucopyranoside of $\beta$-oxoisoaleuritolic acid, which is named bodinitin D.

The findings in this study indicate that the triterpene glycosides of *Schefflera bodinieri*, which grows in China, have different structures from those present in *S. octophylla* (grown, in Vietnam) and *S. capitata* (grown in India). The chemical constituents in the latter two species include $\beta$-amyrane with C-12 double-bond and lupane types. In *S. bodinieri*, there are also $\beta$-amyrane-type triterpenes, but the double bond exhibits at a less usual position: C-14. From our knowledge, this is the first time that $\beta$-amyrane-type compounds with a C-14 double bond have been found in the Araliaceae.

## Experimental Section

**General Experimental Procedures.** $^1$H-NMR, $^1$H−$^1$H COSY, and $^{13}$C−$^1$H COSY spectra were measured at 500 MHz, and the $^{13}$C-NMR spectra-DEPT was measured at 125.7 MHz on an AMX-500, at room temperature with MeOH-$d_4$ solution with TMS as internal standard; EIMS (70 eV), FABMS, and HRFAB were obtained with a direct probe on an Analytical ZAB-2F (VG, Micromass Ltd.). The isolation was conducted on the following chromatographic columns: Si gel C60 (40−60A, May and Baker); Sephadex LH-20 (Sigma), and reversed-phase ODS column (dp 5 $\mu$m, 4.6 mm × 25 cm, Beckman) in HPLC (Waters 991, photodiode array detector). TLC examination was carried out with Si gel 60 $F_{254}$ plates (Merck). Spray reagent was vanillin−$H_2SO_4$ for glycosides, aglycons, and sugars. Solvent systems for examining sugars were $CHCl_3$−MeOH−HOAc (2:2:1), BuOH−HOAc−$H_2O$ (5:1:2), and EtOAc−MeOH−HOAc (3:2:1). Reference compounds for sugar detection included glucose, rhamnose, arabinose, galactose, mannose, and xylose.

**Plant Material.** *S. bodinieri* was collected on Jinfo Mountain, Sichuan province, People's Republic of China, in November 1990, and identified by Professor Z. Liu. The voucher specimen is kept in the herbarium of the Institute of Medicinal Plant Cultivation, Sichuan province, China.

**Extraction and Isolation.** The air-dried root of *Schefflera bodinieri* (1 kg) was extracted by 70% EtOH at room temperature to yield an extract (70 g). This extract (20 g) was subjected to a flash column on Si gel eluting with solvents of increasing polarity. The MeOH

fraction (3 g) was purified by Sephadex LH-20 column and reversed-phase HPLC to give compound **1** (100 mg), compound **2** (5 mg), compound **3** (5 mg), and compound **4** (4 mg).

**Hydrolysis of Glycosides.** Each glycoside (2 mg) was dissolved in 10 mL of MeOH with 10% HCl and heated at 80 °C for 1 h. The reaction solution was diluted with $H_2O$ and extracted with $CHCl_3$. The extract was dried over anhydrous $Na_2SO_4$ and filtered. Removal of the organic solvent resulted in the aglycon. The $H_2O$ layer was neutralized by NaOH and dried *in vacuo* to give the sugar moieties of the glycoside. The dry sugar residue was dissolved in MeOH and identified by co-TLC with authentic samples.

**Bodinitin A (1):** white amorphous powder, $[\alpha]^{25}_D$ +7.96° (*c* 1.0, MeOH); IR (KBr) $\nu$ max 3480 (OH), 3090 (C=C, trisubs), 1694 (COOR), 827 (C=CH, trisubs) $cm^{-1}$; HRFABMS *m/z* $[M]^+$ 912.5085, $C_{47}H_{76}O_{17}$, requires 912.5083; $^1H$ NMR and $^{13}C$ NMR, Table 1; EIMS (70 eV) *m/z* 442, aglycon(17), 427 (35), 409 (15), 381 (9), 363 (36), 275 (27), 273 (21), 234 (11), 219 (7), 229 (32), 207 (29), 190 (81), 189 (45), 175 (43), 69 (100); FABMS *m/z* 934 $[M + Na - 1]^+$, 788 $[M + Na - 1 - Rham]^+$, 604 $[M - Rham - Glc]^+$, 442 $[M - Rham - Glc - Glc]^+$.

**Aglycon of bodinitin A (hydrolysis product):** white amorphous powder, $[\alpha]^{25}_D$ +54.32° (*c* 0.8, $CHCl_3$); IR (KBr) $\nu$ max 3280 (OH), 3091 (C=C, trisubs), 1700 (COOH), 825 (C=CH, trisubs) $cm^{-1}$; EIMS (70 eV) *m/z* 442 ($M^+$, 25), 427 (49), 409 (23), 396 (5), 382 (11), 363 (28), 275 (24), 229 (22), 207 (28), 190 (100), 175 (52), 135 (55).

**Bodinitin B (2):** white amorphous powder, $[\alpha]^{25}_D$ +8.72° (*c* 0.3, MeOH); IR (KBr) $\nu$ max 3478 (OH), 3090 (C=C, trisubs), 1689 (COOR), 828 (C=CH, trisubs) $cm^{-1}$; $^1H$ NMR ($CD_3OD$, 500 MHz), aglycon $\delta$ 0.75 (3H, s, tert−Me), 0.87 (6H, s, tert−Me), 0.90 (9H, s, tert−Me), 0.95 (3H, s, tert−Me), 3.32 (1H, m, H-3α), 5.65 (1H, br s, H-15); sugar residue, $Glc_1$ 5.35 (d, $J$ = 7 Hz, H-1), 3.34 (t, $J$ = 7 Hz, H-2), 3.67 (t, $J$ = 8 Hz, H-3), 3.45 (t, $J$ = 8 Hz, H-4), 3.56 (m, H-5), 3.82 (dd, $J$ = 10, 1 Hz, H-$6_a$), 4.10 (dd, $J$ = 10, 2 Hz, H-$6_b$); $Glc_2$ 4.40 (d, $J$ = 7 Hz, H-1), 3.27 (t, $J$ = 7 Hz, H-2), 3.51 (t, $J$ = 8 Hz, H-3), 3.44 (t, $J$ = 6 Hz, H-4), 3.30 (m, H-5), 3.65 (dd, $J$ = 10, 1 Hz, H-$6_a$), 3.80 (dd, $J$ = 12, 2 Hz, H-$6_b$); Rham 4.85 (br s, H-1), 3.82 (br s, H-2), 3.64 (dd, $J$ = 8, 2 Hz, H-3), 3.44 (t, $J$ = 3 Hz, H-4), 3.98 (m, H-5), 1.27 (d, $J$ = 6.5 Hz, rham−Me); EIMS (70 eV) *m/z* 457, aglycon + 1, (7), 443 (15), 428 (53), 410 (25), 382 (13), 364 (18), 289 (3), 275 (37), 273 (45), 234 (8), 219 (53), 207 (43), 190 (34), 189 (62), 175 (53), 81 (100); CIMS *m/z* 926 $[M]^+$, 780 $[M - Rham]^+$, 618 $[M - Rham - Glc]^+$, 456 $[aglycon]^+$.

**Bodinitin C (3):** white amorphous powder, $[\alpha]^{25}_D$ + 10.52° (*c* 0.3, MeOH); IR (KBr) $\nu$ max 3090 (C=C, trisubs), 3050, 1670 (C=O, ketone), 1691 (COOR), 827 (C=CH, trisubs) $cm^{-1}$; HRFABMS *m/z* $[M]^+$ 910.4929, $C_{47}H_{74}O_{17}$, requires 910.4926; $^1H$ NMR ($CD_3OD$, 500 MHz), aglycon $\delta$ 0.90, 0.92, 0.94, 1.02, 1.07, 1.07 (3H, each, s, tert−Me), 5.65 (1H, t, $J$ = 2 Hz, H-15); sugar residues, $Glc_1$ 5.35 (1H, d, $J$ = 7 Hz, H-1), 3.32 (m, H-2), 3.66 (t, $J$ = 8 Hz, H-3), 3.42 (t, $J$ = 7 Hz, H-4), 3.57 (m, H-5), 3.80 (dd, $J$ = 10, 1 Hz, H-$6_a$), 4.10 (dd, $J$ = 10, 1 Hz, H-$6_b$); $Glc_2$ 4.40 (d, $J$ = 7 Hz, H-1), 3.26 (t, $J$ = 8 Hz, H-2), 3.49 (t, $J$ = 8 Hz, H-3), 3.40 (t, $J$ = 6 Hz, H-4), 3.29 (m, H-5), 3.65 (dd, $J$ = 11, 3 Hz, H-$6_a$), 3.80 (dd, $J$ = 8, 2 Hz, H-$6_b$); Rham 4.82 (1H, br s, H-1), 3.84 (br s H-2), 3.65 (dd, $J$ = 8, 2 Hz, H-3), 3.41 (t, $J$ = 3 Hz, H-4), 3.98 (m, H-5), 1.28 (3H, d, $J$ = 6.5 Hz, rham − Me); EIMS (70 eV) *m/z* 440 (24), 425 (53), 394 (11), 379 (41), 273 (20), 261 (5), 227 (19), 207 (25), 190 (27), 189 (25), 177 (47), 55 (100).

**Bodinitin D (4):** white amorphous powder; $[\alpha]^{25}_D$ +11.43° (*c* 0.3, MeOH); IR (KBr) $\nu$ max 3091 (C=C, trisubs), 3050, 1669 (C=O, ketone), 1691 (COOR), 827 (C=CH, trisubs) $cm^{-1}$; HRFABMS *m/z* $[M]^+$ 924.5086, $C_{48}H_{76}O_{17}$, requires 924.5083; $^1H$ NMR ($CD_3OD$, 500 MHz), aglycon $\delta$ 0.87, 0.90, 0.97, 1.00, 1.02, 1.04, 1.10 (3H, each, s, tert−Me), 5.75 (1H, t, $J$ = 2 Hz, H-15), sugar residues, $Glc_1$ 5.35 (d, $J$ = 7 Hz, H-1), 3.32 (m, H-2), 3.66 (t, $J$ = 8 Hz, H-3), 3.43 (t, $J$ = 7 Hz, H-4), 3.56 (m, H-5), 3.79 (dd, $J$ = 10, 1 Hz, H-$6_a$), 4.10 (dd, $J$ = 10, 1 Hz, H-$6_b$); $Glc_2$ 4.40 (d, $J$ = 7 Hz, H-1), 3.26 (t, $J$ = 8 Hz, H-2), 3.49 (t, $J$ = 8 Hz, H-3), 3.39 (t, $J$ = 6 Hz, H-4), 3.29 (m, H-5), 3.65 (dd, $J$ = 10, 2 Hz, H-$6_a$), 3.80 (dd, $J$ = 10, 2 Hz, H-$6_b$); Rham 4.82 (1H, br s, H-1), 3.84 (br s H-2), 3.65 (dd, $J$ = 8, 2 Hz, H-3), 3.41 (t, $J$ = 3 Hz, H-4), 3.98 (m, H-5), 1.28 (3H, d, $J$ = 6.5 Hz, rham−Me); EIMS (70 eV) *m/z* 454 (14), 440 (2), 426 (3), 408 (15), 379 (3), 335 (10), 287 (13), 239 (21), 234 (7), 219 (8), 207 (46), 190 (9), 189 (8), 169 (90), 69 (100).

**Acknowledgements.** The authors thank Professor Z. Liu, the head of the Department of Medicinal Plants, Institute of Cultivation of Medicinal Plants, Sichuan province, China, for helping to collect the plant material and identifying the species. Thanks are also due to the mass spectrum laboratory in the School of Pharmacy and NMR service in King's College, University of London. The project was supported by Pfizer Ltd.

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NP960235H