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NERVOSANIN A AND B, AND *ENT*-KAURANOIDS FROM *ISODON NERVOSUS*

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Key Word Index—*Isodon nervosus*; Labiatae; *ent*-kauranoids; nervosanin A; nervosanin B.

Abstract—Two new diterpenoids nervosanin A and nervosanin B were isolated, together with the known neorabdosin, nervosin, odonicin, effusanin A and effusanin E, from the leaves of *Isodon nervosus* and their structures were elucidated from spectral and chemical evidence.

INTRODUCTION

Diterpene constituents of *Isodon nervosus* Kudo have been isolated and characterized as nervosin [1], neorabdosin [2], odonicin [1], effusanin A [3] and effusanin E [3]. In the course of the investigations on biologically active substances in *Isodon* plants, we have examined the constituents of *I. nervosus* collected in the southern district of Anhui, China and isolated two new diterpenes, nervosanin A and B. This paper describes the isolation and structure elucidation of these two diterpenes.

RESULTS AND DISCUSSION

Dry leaves of *I. nervosus* were extracted with ethanol. Silica gel column chromatography of the extract yielded nervosanin A (**1**) and nervosanin B (**2**) along with known neorabdosin (**5**), odonicin (**6**), effusanin A (**3**) and effusanin E (**4**).

Nervosanin A (**1**), $C_{21}H_{32}O_6$, had a five-membered ketone group [ν_{max} 1705, δ224.3 (*s*)]. The ^{1}H NMR spectrum of **1** showed the presence of two tertiary methyl groups (δ1.10 and δ1.23, each 3H, *s*), two oxygenated methyl groups (δ3.76, 1H, *dd*, J = 4.7, 10.1 Hz; 3.64, 1H, *dd*, J = 8.8, 10.1 Hz; 4.34, 1H, *dd*, J = 1.0, 10.0 Hz and 4.69, 1H, *d*, J = 10.0 Hz) three hydroxy groups (δ4.95, 5.85 and 6.44, each 1H, *s*) and two methine protons attached to hydroxy group bearing carbons (δ3.68, 1H, *dd*, J = 5.4, 11.5 Hz and 4.16, 1H, *dd*, J = 5.4, 11.4 Hz, changed to *d*, J = 5.4 Hz on adding D_2O). The ^{13}C NMR spectrum exhibited a signal due to an acetal carbon (δ95.7, *s*) along with the signals due to two primary carbinyl carbons (δ64.0 and 69.0) and two secondary carbinyl carbons (δ73.1 and 74.8). From the examination of the spectral data, coupled with the consideration of the structures of diterpenoids isolated so far from the genus *Isodon*, the *ent*-7α-hydroxy-7β,20-epoxy-kaur-15-one structure was inferred as the basic skeleton [4] of this substance. This inference was supported by the fact that the nervosanin A shows a negative Cotton effect $[\theta]_{300}$ −4684 (MeOH) in the CD spectrum.

Acetylation of **1** with acetic anhydride and pyridine gave the monoacetate (**7**). In the ^{1}H NMR spectrum of **7**, a signal for 1-H appeared downfield at δ4.71 compared with that of **1**. This proton was assigned to the C-1 β position for the following reasons: (i) the coupling pattern of the proton (δ4.71, 1H, *dd*, J = 5.4, 11.4 Hz) in the ^{1}H–^{1}H COSY spectrum of **7**; (ii) comparison of the ^{13}C NMR spectrum of **7** with that of **1** revealing that the chemical shift value of C-1 shifted downfield by 1 ppm, while that of C-2, C-10 and C-11 shifted upfield by 3.4, 1.7 and 1.8 ppm, respectively, because of the α- and β-substituent effects and space-steric effect of the C-1α acetyl group. Another secondary hydroxy group of **1** was located at the C-6β position because the secondary carbinyl proton (δ4.16, 1H, *dd*, J = 5.4, 11.4 Hz changed to *d*, on adding D_2O) is coupled with the C-5β proton (δ1.45, *dd*, J = 1.5, 5.6 Hz), the latter is further coupled by the long range interaction across the W-path with the C-20 proton (δ4.34, 1H, *dd*, J = 1.5, 10.0 Hz).

The location of one of the two oxygenated methyl groups, the signal of which appears at δ4.69 and 4.34, was easily assigned to the C-20 position. Another oxygenated methyl group, whose signal was found at δ3.76 (1H, *dd*, J = 4.7, 10.1 Hz) and δ3.64 (1H, *dd*, J = 8.8, 10.1 Hz) was assigned to the C-16β position, because the protons were coupled with the C-16α proton (δ2.90, 1H, *dd*, J = 5.0, 13.0 Hz, 16α-H), which was further coupled with C-13α proton (δ2.71, 1H, *dd*, J = 5.0, 12.0 Hz). The methoxyl group was located to the C-17 position of **1** because of the upfield chemical shift of C-12. The data suggest that nervosanin A has the structure **1**.

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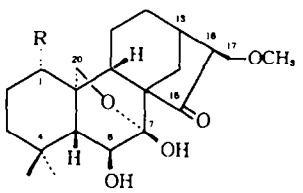

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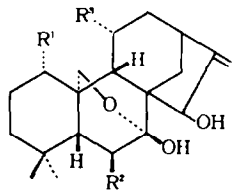

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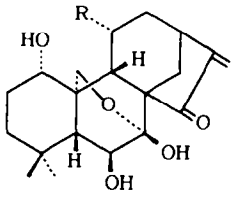

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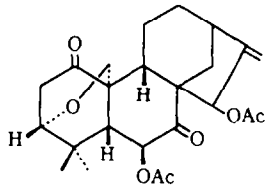

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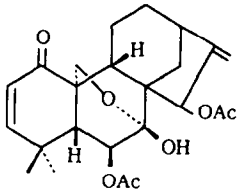

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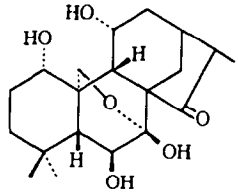

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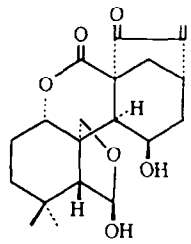

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The presumed structure was supported by the NOESY spectrum described below. In the NOESY spectrum of **1**, NOE cross peaks were observed in the following ways: (i) 4α-Me and 4β-Me, 6α-H, 20-H_a and 2α-H; (ii) 4β-Me and 4α-Me, 3β-H and 5β-H; (iii) 9β-H and 1β-H and 5β-H; (iv) 16α-H and 13α-H, 17-H_a; (v) 17-H_2 and 12β-H, 16α-H and OMe.

Nervosanin B (**2**), $C_{20}H_{30}O_6$, was shown to contain two tertiary methyl groups (δ_H1.26, 1.18, each 3H, *s*; δ_C33.7 *q*, 22.4 *q*), an exo-methylene group (ν_{max} 1660 cm^{-1}; δ_H5.34, 5.21, each 1H, *br s*; δ_C106.3 *t*, 162.5 *s*) and five hydroxy groups (ν_{max} 3280 cm^{-1}; δ_H8.25, 7.90, 7.52, 6.75 and 6.42, each 1H, disappeared on adding D_2O). The signals due to four methine protons attached to hydroxy group-bearing carbons at δ5.46 (1H, *br s*), 4.71 (1H, *t*, J = 4.2 Hz), 4.37 (1H, *d*, J = 6.3 Hz) and 3.98 (1H, *dd*, J = 6.0, 11.0 Hz) in the ^{1}H NMR spectrum and five signals at δ97.7 (*s*), 75.7 (*d*), 73.9 (*d*), 66.7 (*d*), 75.2 (*d*) in the ^{13}C NMR spectrum of **2** suggested that four of the five hydroxy groups were secondary and the fifth was tertiary. The data suggested that nervosanin B had the same structure as that of effusanin E (**4**) except for the absence of the ketone and the presence of a secondary hydroxyl group [5].

Acetylation of **2** with acetic anhydride and pyridine gave the triacetate (**8**). Comparison of the ^{13}C NMR spectrum of **8** with that of **2**, showed that the chemical shift values of C-1, C-6 and C-11 were shifted downfield by 1, 2 and 3.4 ppm, respectively, while the chemical shift values of C-2, C-10, C-5, C-7, C-9 and C-12 were shifted upfield by 4.3, 1.8, 1.1, 1.9, 4.8 and 1.8 ppm, respectively, because of the α- and β-substituent effect of the 1-, 6- and 11-acetyl groups. Based on these data, together with the coupling pattern of 1-H, 6-H and 11-H, three hydroxy groups of **2** were located at the C-1α, C-6β and C-11α positions. Another secondary hydroxyl group was located to the 15β-position of **2** from the fact that dihydroeffusanin E (**9**) was obtained on treatment of **2** with 15% HCl–MeOH under the conditions for the garryfoline–cuauchichicine rearrangement [6] and that nodosin (**10**) was obtained on the oxidation of **2** with MnO_2. Accordingly, nervosanin B was shown to have structure **2**.

EXPERIMENTAL

General. Mps: uncorr. IR spectra were recorded on a Shimadazu IR-435 spectrometer for KBr disks. ^{1}H NMR spectra were taken on a JEOL JNM-FX 200 or AC-300 or AM-600 spectrometer with TMS as int. standard; chemical shifts are given in δ (ppm) values. Mass spectra

were determined with a JEOL JMS-01 SG-2 spectrometer. UV spectra were taken with a Shimadzu 435 or Hitachi 240 double beam spectrophotometer. Optical rotations were measured with a JASCO DIP-181 digital polarimeter. CD curves were measured with a JASCO J 500 A spectropolarimeter. Silica gel 60 (70–230 mesh, Merck) was used for chromatography and precoated silica gel plates F_{254} (0.25 and 0.5 mm in thickness) were used for TLC. Extracts were dried over dry Na_2SO_4.

Isolation of diterpenoids from the dried leaves of the plant. The ethanolic extract obtained from the dried leaves of *I. nervosus* (10 kg) collected at Jixi, Anhui, China in late August 1986, was concd under red. pres. to *ca* 10 l. The extract was diluted with EtOH to make a 90% EtOH soln and treated with charcoal. After evapn of the solvent, the residue was dissolved in EtOAc. The soln was shaken with aq. Na_2CO_3 to remove the acidic substance. The organic layer, after drying, was evapd under red. pres. to give a residue (210 g), which was chromatographed on a silica gel column with $CHCl_3$–Me_2CO as eluent with stepwise increase of the Me_2CO content. The $CHCl_3$ eluate gave neorabdosin and odonicin, the $CHCl_3$–Me_2CO (9:1) eluate gave effusanin A and nervosanin A, and the $CHCl_3$–Me_2CO (8:2) eluate gave effusanin E and nervosanin B.

Nervosanin A (**1**). Needles (0.4 g). mp 200–202° (from MeOH); $[\alpha]_D^{25}$ −82.09° (MeOH; *c* 0.2); IR ν_{max} cm^{-1} 3400, 3350, 1705; ^1H NMR (C_5D_5N): δ6.44 (1H, *d*, *J* = 11.0 Hz, OH), 5.85 (1H, *d*, *J* = 5.0 Hz, OH), 4.95 (1H, *br s*, OH), 4.69 (1H, *d*, *J* = 10.0 Hz, H_a-20), 4.34 (1H, *dd*, *J* = 1.5, 10.0 Hz, H_b-20), 4.16 (1H, *dd*, *J* = 5.4, 11.4 Hz, H-6α), 3.76 (1H, *dd*, *J* = 4.7, 10.1 Hz, H_a-17), 3.64 (1H, *dd*, *J* = 8.8, 10.1 Hz, H_b-17), 3.68 (1H, *dd*, *J* = 5.4, 11.5 Hz, H-1β), 3.29 (3H, *s*, –OMe), 2.90 (1H, *dd*, *J* = 5.0, 13.0 Hz, H-16α, 2.71 (1H, *dd*, *J* = 5.0, 12.0 Hz, H-13α), 1.45 (1H, *d*, *J* = 5.6 Hz, H-5β), 1.10, 1.23 (each 3H, *s*, 4-Me_2). ^{13}C NMR (C_5D_5N): δ74.8 (C-1, *d*), 28.8 (C-2, *t*), 39.5 (C-3, *t*), 34.7 (C-4, *s*), 62.2 (C-5, *d*), 73.1 (C-6, *d*), 95.7 (C-7, *s*), 61.3 (C-8, *s*), 52.1 (C-9, *d*), 41.5 (C-10, *s*), 19.9 (C-11, *t*), 20.0 (C-12, *t*), 29.8 (C-13, *d*), 30.4 (C-14, *t*), 224.3 (C-15, *s*), 57.5 (C-16, *d*), 69.0 (C-17, *t*), 33.0 (C-18, *q*), 21.9 (C-19, *q*), 64.0 (C-20, *t*), 58.6 (–OMe). HRMS *m/z* found: 380.2192. $C_{21}H_{32}O_6$ requires: 380.2198. Found: C, 66.49; H, 8.71. $C_{21}H_{32}O_6$ requires: C, 66.31; H, 8.42. CD $[\theta]_{300}$ −4684 (MeOH).

Nervosanin B (**2**). Needles (0.5 g). mp 258–260° (from MeOH); $[\alpha]_D^{25}$ −54.73° (pyridine; *c* 0.33); IR ν_{max} cm^{-1}: 3280, 1660; ^1H NMR (C_5D_5N): δ8.25, 7.90, 7.52, 6.75, 6.42 (each 1H, *br s*, OH), 5.46 (1H, *br s*, H-15α), 5.36, 4.43 (each 1H, AB, *d*, *J* = 10.0 Hz, H_2-20), 5.34, 5.21 (each 1H, *br s*, H_2-17), 4.71 (1H, *t*, *J* = 4.2 Hz, H-11β), 4.37 (1H, *d*, *J* = 6.3 Hz, H-6α), 3.98 (1H, *dd*, *J* = 6.0, 11.0 Hz, H-1β), 3.29 (1H, *d*, *J* = 11.5 Hz, H-14α), 2.91 (1H, *dd*, *J* = 4.5, 9.0 Hz, H-13α), 2.67 (1H, *dd*, *J* = 9.5, 14.0 Hz, H-12α), 2.50 (1H, *d*, *J* = 4.5 Hz, H-9β), 2.22 (1H, *dd*, *J* = 4.5, 11.5 Hz, H-14β), 1.94 (1H, *dd*, *J* = 5.0, 14.0 Hz, H-12β), 1.78 (1H, *d*, *J* = 6.3 Hz, H-5β), 1.26, 1.18 (each 3H, *s*, 4-Me_2). ^{13}C NMR (C_5D_5N): δ75.7 (C-1, *d*), 29.6 (C-2, *t*), 39.2 (C-3, *t*), 33.9 (C-4, *s*), 47.7 (C-5, *d*), 73.9 (C-6, *d*), 97.7 (C-7, *s*), 52.2 (C-8, *s*), 58.2 (C-9, *d*), 42.7 (C-10, *s*), 66.7 (C-11, *d*), 42.8 (C-12, *t*), 37.3 (C-13, *d*), 26.8 (C-14, *t*), 75.2 (C-15, *d*), 162.5 (C-16, *s*), 106.3 (C-17, *t*), 33.7 (C-18, *q*), 22.4 (C-19, *q*), 65.7 (C-20, *t*), HRMS found: 366.20324. $C_{20}H_{30}O_6$ requires: 366.2042. Found: C, 65.29; H, 8.44. $C_{20}H_{30}O_6$ requires: C, 65.57; H, 8.20.

Effusanin A (**3**). Needles (5.5 g). mp 264–266° (from MeOH); IR ν_{max} cm^{-1} 3220, 1700, 1638, 1060; ^1H NMR (C_5D_5N): δ6.80, 5.70 (OH), 5.85, 5.15 (each 1H, *br s*, H_2-17), 4.62, 4.22 (each 1H, AB, *d*, *J* = 10.0 Hz, H_2-20), 4.15 (1H, *t*, *J* = 5.0 Hz, H-6α), 3.53 (1H, *t*, *J* = 8.0 Hz, H-1β), 2.77 (1H, *d*, *J* = 9.5 Hz, H-13α), 1.14, 0.98 (each 3H, *s*, 4-Me_2); HRMS *m/z* found 348.19269. $C_{20}H_{28}O_5$ requires: 348.19365.

Effusanin E (**4**). Needles (4.5 g). mp 240–242° (from MeOH); IR ν_{max} cm^{-1}: 3240, 1700, 1640, 1060; ^1H NMR (C_5D_5N): δ7.76, 6.93, 6.48 (OH), 5.97, 5.30 (each 1H, *br s*, H_2-17), 5.13 (1H, AB, *dd*, *J* = 1.0, 11.0 Hz, H_a-20), 4.57 (1H, *t*, *J* = 4.0 Hz, H-11β), 4.38 (1H, AB, *d*, *J* = 11.0 Hz, H_b-20), 4.23 (1H, *dd*, *J* = 11.0, 7.0 Hz, H-6α), 3.80 (1H, *dd*, *J* = 10.0, 6.0 Hz, H-1β), 3.70 (1H, *d*, *J* = 11.8 Hz, H-14α), 3.15 (1H, *dd*, *J* = 4.0, 9.0 Hz, H-13α), 1.33, 1.14 (each 3H, *s*, 4-Me_2); HRMS found: 364.1880. $C_{20}H_{28}O_6$ requires: 364.1886.

Neorabdosin (**5**). Needles (0.35 g). mp 222° (from MeOH); IR ν_{max} cm^{-1}: 1738, 1720, 1240; ^1H NMR ($CDCl_3$): δ6.14 (1H, *t*, *J* = 2.5 Hz, H-15α), 5.65 (1H, *d*, *J* = 12.5 Hz, H-6α), 5.06, 5.03 (each 1H, *d*, *J* = 2.0 Hz, H_2-17), 4.73, 4.18 (each 1H, *d*, *J* = 10.0 Hz, H_2-20), 3.71 (1H, *t*, *J* = 2.5 Hz, H-3β), 2.96 (1H, *d*, *J* = 8.0 Hz, H-9β), 2.84 (1H, *m*, H-13α), 2.72 (1H, *d*, *J* = 4.5 Hz, H_2-2), 2.19, 2.13 (each 3H, *s*, 2 × OAc), 1.28, 1.08 (each 3H, *s*, 4-Me_2). HRMS *m/z* found: 430.19931. $C_{24}H_{30}O_7$ requires: 430.1991.

Odonicin (**6**). Needles. (1.3 g). mp 187°; IR ν_{max} cm^{-1}: 3400, 1738, 1660, 1645, 1235, 1060; ^1H NMR ($CDCl_3$): δ6.73 (1H, *d*, *J* = 10.0 Hz, H-3), 5.93 (1H, *d*, *J* = 10.0 Hz, H-2), 5.66 (1H, *t*, *J* = 2.3 Hz, H-15), 5.32 (1H, *d*, *J* = 9.0 Hz, H-6), 5.06, 4.86 (each 1H, *br s*, H_2-17), 4.37, 4.05 (each 1H, *d*, *J* = 10.0 Hz, H_2-20), 2.63 (1H, *dd*, H = 1.5, 8.8 Hz, H-5), 2.18, 2.09 (each 3H, *s*, 2 × OAc), 1.23, 1.10 (each 3H, *s*, 4-Me_2); HRMS *m/z* found: 430.1987. $C_{24}H_{30}O_7$ requires: 430.1991.

Nervosanin A 1-acetate (**7**). Acetylation of nervosanin A (**1**) (43 mg) with a mixt. of Ac_2O (1 ml) and pyridine (1 ml) gave the monoacetate (**7**) (40 mg) as needles, mp 208–210° (from MeOH); IR ν_{max} cm^{-1}: 3400–3350, 1720, 1250; ^1H NMR (C_5D_5N): δ8.75 (1H, *br s*, OH), 6.33 (1H, *d*, *J* = 11.2 Hz, OH), 4.71 (1H, *dd*, *J* = 5.4, 11.4 Hz, H-1β), 4.39 (1H, *d*, *J* = 10.1 Hz, H_a-20), 4.22 (1H, *dd*, *J* = 1.55, 10.1 Hz, H_b-20), 4.07 (1H, *dd*, *J* = 5.7, 11.2 Hz, H-6α), 3.72 (1H, *dd*, *J* = 4.7, 10.3 Hz, H_a-17), 3.60 (1H, *dd*, *J* = 8.8, 10.1 Hz, H_b-17), 3.24 (3H, *s*, –OMe), 2.86 (1H, *dd*, *J* = 4.0, 10.0 Hz, H-16α), 2.66 (1H, *m*, H-13α), 2.43 (1H, *dd*, *J* = 3.3, 12.5 Hz, H-14β), 2.37 (1H, *dd*, *J* = 1.0, 10.0 Hz, H-14α), 2.03 (3H, *s*, OAc), 2.05 (1H, *m*, H-11β), 1.78 (1H, *m*, H-12β), 1.75 (1H, *m*, H-2β), 1.65 (1H, *dd*, *J* = 4.5, 13.0 Hz, H-9β), 1.64 (1H, *m*, H-2α), 1.45 (1H, *dd*, *J* = 1.5, 5.6 Hz, H-5β), 1.34 (1H, *m*, H-12α), 1.33 (2H, *m*, H_2-3), 1.20 (1H, *m*, H-11β), 1.16 (3H, *s*, Me-4β), 1.04 (3H, *s*, Me-4α). ^{13}C NMR (C_5D_5N): δ75.8 (C-1, *d*), 25.4, (C-2, *t*), 38.5 (C-3, *t*), 33.8 (C-4, *s*), 62.0 (C-5, *d*), 74.3 (C-6, *d*) 95.4 (C-7, *s*), 60.7 (C-8, *s*), 50.9 (C-9, *d*), 39.8 (C-10, *s*), 18.1 (C-11, *t*), 19.4 (C-12, *t*), 29.5 (C-13, *d*), 28,6 (C-14, *t*), 223.8 (C-15, *s*), 57.4 (C-16, *d*),

68.0 (C-17, *t*), 32.6 (18-Me), 21.6 (19-Me), 63.4 (C-20, *t*), 58.6 (OMe), 169.9, 21.4 (OAc), HRMS *m/z* found: 422.23023. $C_{23}H_{34}O_7$ requires: 422.23042.

Nervosanin B 1,6,11-acetate (**8**). Acetylation of nervosanin B (**2**) (50 mg) with a mixt. of Ac_2O (1 ml) and pyridine (1 ml) gave the triacetate (**8**) (25 mg) as needles. mp 210–212° (from MeOH); IR ν_{max} cm^{-1}: 3410–3360, 1736, 1725, 1660; ^1H NMR (C_5D_5N): δ5.88 (1H, *d*, *J* = 8.0 Hz, H-6α), 5.45 (1H, *br s*, H-15α), 5.17, 4.95 (each 1H, *s*, H_2-17), 5.13 (1H, *dd*, *J* = 6.0, 11.0 Hz, H-1β), 5.12 (1H, *d*, *J* = 4.1 Hz, H-11β), 4.75, 4.20 (each 1H, *d*, *J* = 8.5 Hz, H_2-20), 2.55 (1H, *dd*, *J* = 4.0, 9.0 Hz, H-13α), 2.18, 2.11 2.08 (each 3H, *s*, 3 × OAc), 1.18, 0.98 (each 3H, *s*, 2 × Me). ^{13}C NMR (C_5D_5N): δ76.7 (C-1), 25.3 (C-2), 38.3 (C-3), 33.5 (C-4), 46.6 (C-5), 75.9 (C-6), 95.8 (C-7), 52.1 (C-8), 53.4 (C-9), 40.9 (C-10), 70.1 (C-11), 41.0 (C-12), 35.4 (C-13), 27.0 (C-14), 75.0 (C-15), 160.9 (C-16), 108.8 (C-17), 32.5 (C-18), 22.3 (C-19), 65.3 (C-20), 170.3, 170.1, 169.7, 21.1, 21.4, 22.1 (3 × OAc). HRMS found: 492.2341. $C_{26}H_{36}O_9$ requires: 492.2359.

Acid treatment of nervosanin B (**2**), *garryfoline–cuauchichicine rearrangement*. To a soln of nervosanin B (**2**) (21 mg) in MeOH and $CHCl_3$ (2 ml), conc. HCl (6 ml) was added and the mixt. was refluxed for 3 hr. After neutralization with aq. Na_2CO_3, the reaction mixt. was concd *in vacuo*. The residue was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, dried and concd to leave 12 mg of residue, which was crystallized from MeOH to give 8 mg of dihydroeffusanin E (**9**). mp 234°, IR ν_{max} cm^{-1}: 3200, 1724, 1065. ^1H NMR (C_5D_5N): δ5.15, 4.30 (each 1H, *d*, *J* = 9.0 Hz, H_2-20), 4.54 (1H, *m*, H-11β), 4.20 (1H, *m*, H-6α), 3.90 (1H, *dd*, *J* = 6.0, 10.0 Hz, H-1β), 3.65 (1H, *d*, *J* = 11.0 Hz, H-14α), 1.25 (3H, *d*, *J* = 8.1 Hz, Me-17), 1.10 (6H, *s*, 2 × Me). HRMS *m/z* found: 366.20518. $C_{20}H_{30}O_6$ requires: 366.20422.

Manganese dioxide oxidation of nervosanin B. To a soln of nervosanin B (**2**) (20 mg) in Me_2CO (30 ml), MnO_2 was added. After stirring at room temp. for 24 hr, the MnO_2 was filtered off and the solvent was removed under red. pres. to leave a residue, which was recrystallized from MnO_2 to give 15 mg of nodosin (**10**). mp > 290°; IR ν_{max} cm^{-1}: 3500, 3300, 1740, 1690, 1640; ^1H NMR (C_5D_5N): δ5.93, 5.28 (each 1H, *s*, H_2-17), 5.77 (1H, *s*, H-6α), 5.75 (1H, *dd*, *J* = 8.0, 10.0 Hz, H-1β), 5.11, (1H, *br s*, H-11α), 4.50, 4.30 (each 1H, *d*, *J* = 9.0 Hz, H_2-20), 3.68 (1H, *m*, H-13α), 1.03, 1.00 (each 3H, *s*, 4-Me_2). ^{13}C NMR (C_5D_5N): δ78.4 (C-1), 24.0 (C-2), 37.4 (C-3), 31.5 (C-4), 55.6 (C-5), 101.9 (C-6), 172.0 (C-7), 56.5 (C-8), 48.5 (C-9), 49.9 (C-10), 65.9 (C-11), 41.3 (C-12), 35.4 (C-13), 34.1 (C-14), 200.9 (C-15), 151.0 (C-16), 117.0 (C-17), 33.0 (C-18), 23.0 (C-19), 73.9 (C-20), HRMS *m/z* found: 362.1756. $C_{20}H_{26}O_6$ requires: 362.17292.

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