H-3), 7.58(1H, d, J = 3.0 Hz, H-8), 7.46(1H, d, J = 9.0 Hz, H-5), 7.33(1H, dd, J = 9.0, 3.0 Hz, H-6), 7.09(1H, d, J = 8.4 Hz, H-4), 6.95(1H, d, J = 8.4 Hz, H-2), 3.95(3H, s, -OCH_3), 3.90(3H, s, -OCH_3)。;^{13}C-NMR数据见表 1。经与文献对照[4],鉴定此化合物为 1,7-二甲氧基呫酮。

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Chemical constituents of basidiomycete *Hydnum repandum*

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Abstract: Objective To study the chemical constituents of the fruiting bodies of *Hydnum repandum*. **Methods** Separation and purification were performed on silica gel, Sephadex LH-20 and ODS CC. Their sturctures were established by 2D-NMR (^{1}H-^{1}HCOSY, HMQC, HMBC, and NOESY), MS, HR-MS spectra, and ORD data. **Results** Eleven compounds were obtained and identified as sarcodonin A (Ⅰ), scabronine B (Ⅱ), 3β-hydroxy-5α, 8α-epidioxyergosta-6, 22-dien (Ⅲ), (22*E*, 24*R*)-ergosta-7, 22-diene-3β, 5α, 6β-triol (Ⅳ), (22*E*, 24*R*)-ergosta-7, 22-diene-3β-ol (Ⅴ), benzoic acid (Ⅵ), 4-hydroxylbenzaldehyde (Ⅶ), 4-monopropanoylbenzenediol (Ⅷ), ethyl-β-*D*-glucopyranoside (Ⅸ), thioacetic anhydride (Ⅹ), (2*S*, 2′*R*, 3*S*, 4*R*)-2-(2-hydroxyoctadecanoylamino) docosane-1, 3, 4-triol (Ⅺ). **Conclusion** All of the compounds are isolated from this fungus for the first time.

Key words: *Hydnum repandum* L. Fr.; basidiomycete; diterpenoids

担子菌黄卷缘齿菌的化学成分

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摘 要: 目的 研究担子菌黄卷缘齿菌 *Hydnum repandum* 的化学成分。**方法** 通过硅胶、Sephadex LH-20、反相硅胶柱色谱分离化合物, 运用氢谱、碳谱、二维核磁共振(^{1}H-^{1}HCOSY, HMQC, HMBC, NOESY)、质谱、高分辨质谱、旋光鉴定结果。**结果** 共分离鉴定了 11 个化合物, 分别是: sarcodonin A (Ⅰ)、scabronine B (Ⅱ)、3β-羟基-5α, 8α-过氧麦角甾-6, 22-二烯-3β-醇 (Ⅲ)、(22*E*, 24*R*)-麦角甾-7, 22-二烯-3β, 5α, 6β-三醇 (Ⅳ)、(22*E*, 24*R*)-麦角甾-7, 22-二烯-3β-醇 (Ⅴ)、苯甲酸 (Ⅵ)、对羟基苯甲醛 (Ⅶ)、对羟基苯甲酸乙酯 (Ⅷ)、乙基-β-*D*-吡喃葡萄糖苷 (Ⅸ)、硫代乙酸酐 (Ⅹ)、(2*S*, 2′*R*, 3*S*, 4*R*)-2-(2-羟基-十八碳酰胺) 二十二碳烷-1, 3, 4-三醇 (Ⅺ)。**结论** 所有化合物都是首次在黄卷缘齿菌中分到。

关键词: 黄卷缘齿菌; 担子菌; 二萜

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Hydnum repandum L. ex Fr., an edible mushroom, grows under conifers or hardwoods in summer and autumn and distributes widely all around the world[1]. In previous studies, many fatty acids, sterols[2], and a diepoxide[3] which has cytotoxic activity against various tumor cells were isolated from *H. repandum*. As a part of our search for naturally occurring bioactive metabolites of the higher fungi in Yunnan Province, further isolation was carried out and 11 compounds were isolated from its alcohol extracts, including two diterpenoids (Ⅰ, Ⅱ), three sterols (Ⅲ — Ⅴ), three benzoic derivatives (Ⅵ — Ⅷ), a glucoside (Ⅸ), thioacetic anhydride (Ⅹ), and a ceramide (Ⅺ) of which compound Ⅱ was reported to stimulate the synthesis of nerve growth factor[4].

1 Instruments and materials

Optical rotations were measured with Horiba SEPA — 300 Digital Polarimeter. ^{1}H-NMR and ^{13}C-NMR spectra were recorded by Bruker AM — 400 spectrometers (TMS as internal standard) while ^{1}H-^{1}HCOSY, HMQC, HMBC, and NOESY were performed on Bruker AM—500. MS and HR-MS were obtained with VG Autospec—3000 Spectrometer. Column chromatography (CC) were carried out with silica gel (200 — 300 meshes), Sephadex LH-20 and RP-18.

The fresh fruiting bodies of *H. repandnum* were collected at Ailao Mountain of Yunnan Province, China, in July, 2003 and identified by Prof. MU Zang, Kunming Institute of Botany, the Chinese Academy of Sciences. The voucher specimen was deposited in the Herbarium of the Kunming Institute of Botany, the Chinese Academy of Sciences.

2 Extraction and isolation

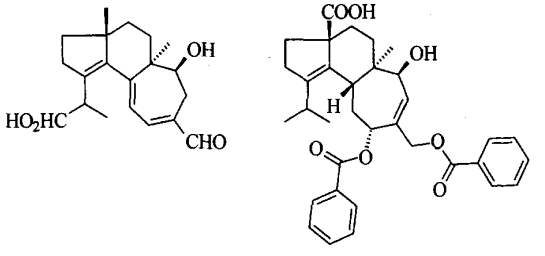
The fresh fruiting bodies of *H. repandnum* were extracted with 95% EtOH at room temperature for four times. The combined extracts were concentrated *in vacuo* to give a syrup (250 g), which was subjected to silica gel CC gradient eluted with chloroform-methanol (100 ∶ 0—0 ∶ 100) to give five fractions. From the fraction Ⅰ (chloroform-methanol, 98 ∶ 2), compounds Ⅰ, Ⅲ, and Ⅵ were isolated by repeated silica gel chromatography. Fraction Ⅱ (chloroform-methanol, 95 ∶ 5) was passed through ODS and Sephadex LH-20 columns and compounds Ⅱ, Ⅴ, Ⅶ, and Ⅷ were obtained. Fraction Ⅲ (chloroform-methanol, 85 ∶ 15) afford compounds Ⅳ, Ⅸ, Ⅹ, and Ⅺ by silica gel CC eluted with ethyl acetate-methanol.

3 Identification

Compound Ⅰ: Sarcodonin A[5], yellow-green syrup. $[\alpha]_D^{25} = +91.7°$ (c 0.1, $CHCl_3$). EI-MS *m/z*: 316 ($[M]^+$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.74 (2H, m, H-1), 2.38 (2H, m, H-2), 2.51 (1H, m, H-7a), 1.34 (1H, dt, J=14.0, 3.6 Hz, H-7b), 1.67 (2H, m, H-8), 6.18 (1H, d, J=8.2 Hz, H-10), 6.82 (1H, dd, J=8.5, 2.4 Hz, H-11), 3.13 (1H, dd, J=18.2, 5.8 Hz, H-13a), 2.54 (1H, br.d, J=18.2 Hz, H-13b), 3.71 (1H, d, J=5.2 Hz, H-14), 9.43 (1H, s, H-15), 0.93 (3H, s, H-16), 1.01 (3H, s, H-17), 2.94 (1H, m, H-18), 0.95 (3H, d, J=4.7 Hz, H-19), 3.56 (1H, dd, J=2.2 Hz, H-20a), 3.57 (1H, dd, J=3.8 Hz, H-20b). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 38.1 (t, C-1), 28.8 (t, C-2), 141.0 (s, C-3), 145.7 (s, C-4), 137.7 (s, C-5), 47.9 (s, C-6), 33.2 (t, C-7), 36.1 (t, C-8), 49.2 (s, C-9), 119.6 (d, C-10), 145.0 (d, C-11), 154.1 (s, C-12), 29.2 (t, C-13), 73.7 (d, C-14), 194.4 (d, C-15), 26.2 (q, C-16), 23.9 (q, C-17), 34.9 (d, C-18), 157.7 (q, C-19), 66.0 (t, C-20). The sturcture (Fig. 1-A) was proved by ^{1}H-^{1}HCOSY, HMQC, HMBC, and NOESY spectra.

Compound Ⅱ: Scabronine B[4], yellowish oil. $[\alpha]_D^{25} = +10.3°$ (c 0.01, MeOH). FAB-MS (neg.) *m/z* (rel. int., %): 557 (25), 436 (6), 121 (100). HR-ESI-MS (neg.): 557.254 7 (cal. for $C_{34}H_{37}O_7$ as 557.253 9). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.61 (1H, m, H-1a), 2.10 (1H, m, H-1b), 2.48 (2H, m, H-2), 3.22 (1H, br.d, J=11.7 Hz, H-5), 1.16 (2H, br.d, J=11.0 Hz, H-7), 1.44 (1H, br.t, J=13.3 Hz, H-8a), 2.24 (1H, m, H-8b), 2.50 (2H, m, H-10), 6.42 (1H, br.d, J=10.2 Hz, H-11), 6.07 (1H, d, J=6.7 Hz, H-13), 3.92 (1H, d, J=6.7 Hz, H-14), 4.84 (1H, d, J=12.8 Hz, H-15a), 4.87 (1H, d,

J=12.8 Hz, H-15b), 0.85 (3H, s, H-16), 2.98 (1H, m, H-18), 0.98 (3H, d, J=6.8 Hz, H-19), 0.98 (3H, d, J=6.8 Hz, H-20), 7.96 (2H, d, J=7.3 Hz, H-3′ and H-7′), 7.93 (2H, d, J=7.3 Hz, H-3″ and H-7″), 7.36 (2H, br.t, J=7.3 Hz, H-4′ and H-6′), 7.33 (2H, br.t, J=7.3 Hz, H-4″ and H-6″), 7.50 (1H, br.t, J=7.3 Hz, H-5′), 7.49 (1H, br.t, J=7.3 Hz, H-5″). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 34.2 (t, C-1), 30.4 (t, C-2), 144.1 (s, C-3), 134.0 (s, C-4), 42.8 (d, C-5), 41.3 (s, C-6), 34.9 (t, C-7), 32.7 (t, C-8), 61.5 (s, C-9), 34.0 (t, C-10), 73.5 (d, C-11), 139.6 (s, C-12), 130.9 (d, C-13), 75.6 (d, C-14), 65.8 (t, C-15), 16.7 (q, C-16), 181.8 (q, C-17), 26.95 (d, C-18), 21.8 (q, C-19), 21.7 (q, C-20), 165.9 (s, C-1′), 166.1 (s, C-1″), 129.99 (s, C-2′), 129.95 (s, C-2″), 129.6 (d, C-3′), 129.5 (d, C-3″), 128.3 (d, C-4′), 128.2 (d, C-4″), 133.0 (d, C-5′), 132.8 (d, C-5″). The sturcture (Fig. 1-B) was proved by ^{1}H-^{1}HCOSY, HMQC, HMBC, and NOESY spectra.



sarcodonin A　　sarbronine B

Fig. 1 Structures of sarcodonin (A) and sarbronine (B)

Compound Ⅲ: 3β-Hydroxy-5α, 8α-epidioxyergosta-6, 22-dien[6], colorless needle. EI-MS m/z (rel. int.,%): 428 (5), 395 (100), 362 (30). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.92 (1H, m, H-3), 6.24 (1H, d, J=8.4 Hz, H-6), 6.46 (1H, d, J=8.4 Hz, H-7), 5.25 (1H, m, H-22), 5.13 (1H, m, H-23), 0.78—2.05 (other). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 34.8 (t, C-1), 30.2 (t, C-2), 66.4 (d, C-3), 37.0 (t, C-4), 79.4 (s, C-5), 135.4 (d, C-6), 130.7 (d, C-7), 82.1 (s, C-8), 51.2 (d, C-9), 36.9 (s, C-10), 20.6 (t, C-11), 39.4 (t, C-12), 44.6 (s, C-13), 51.7 (d, C-14), 28.6 (t, C-15), 23.4 (t, C-16), 56.3 (d, C-17), 12.97 (q, C-18), 18.1 (q, C-19), 39.6 (d, C-20), 20.9 (q, C-21), 135.2 (d, C-22), 132.4 (d, C-23), 42.8 (d, C-24), 33.1 (d, C-25), 19.6 (q, C-26), 19.9 (q, C-27), 17.54 (q, C-28).

Compound Ⅳ: (22E, 24R)-Ergosta-7, 22-diene-3β, 5α, 6β-triol[7], colorless needle. EI-MS m/z (rel. int.,%): 412 ([M-H_2O]$^+$, 14), 394 (12), 379 (22), 251 (35), 69 (100). FAB-MS (pos.) m/z (rel. int.,%): 412 (18), 395 (100), 377 (65). ^{1}H-NMR (400 MHz, MDSO) δ: 5.03 (1H, m, H-3), 3.72 (1H, m, H-6), 5.07 (1H, br.d, J=2.4 Hz, H-7), 0.53 (3H, s, H-18), 0.89 (3H, s, H-19), 0.97 (3H, d, J=6.6 Hz, H-21), 5.15 (1H, dd, J=15.3, 7.9 Hz, H-22), 5.22 (1H, dd, J=15.3, 7.0 Hz, H-23), 0.79 or 0.78 (3H, d, J=6.6 Hz, H-26 or 27), 0.87 (1H, d, J=6.6 Hz, H-28). ^{13}C-NMR (100 MHz, DMSO) δ: 31.2 (t, C-1), 32.5 (t, C-2), 66.0 (d, C-3), 40.0 (t, C-4), 74.5 (s, C-5), 72.2 (d, C-6), 119.5 (d, C-7), 139.8 (s, C-8), 42.3 (d, C-9), 36.7 (s, C-10), 21.4 (t, C-11), 39.0 (t, C-12), 43.0 (s, C-13), 54.2 (d, C-14), 22.6 (t, C-15), 37.8 (t, C-16), 55.4 (d, C-17), 12.1 (q, C-18), 17.6 (q, C-19), 40.1 (d, C-20), 21.0 (q, C-21), 135.4 (d, C-22), 131.4 (d, C-23), 42.1 (d, C-24), 32.5 (d, C-25), 19.6 (q, C-26), 19.9 (q, C-27), 17.3 (q, C-28).

Compound Ⅴ: (22E, 24R)-Ergosta-7, 22-diene-3β-ol[8], colorless needle. EI-MS m/z: 398, 383, 365. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.60 (1H, m, H-3), 5.18 (2H, m, H-22 and H-23), 0.53—2.03 (other). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 37.1 (t, C-1), 31.4 (t, C-2), 71.0 (d, C-3), 37.9 (t, C-4), 40.2 (d, C-5), 29.6 (t, C-6), 117.4 (d, C-7), 139.6 (s, C-8), 49.4 (d, C-9), 34.1 (s, C-10), 21.5 (t, C-11), 39.4 (t, C-12), 44.6 (s, C-13), 55.0 (d, C-14), 22.9 (t, C-15), 28.1 (t, C-16), 55.9 (d, C-17), 12.1 (q, C-18), 13.0 (q, C-19), 40.4 (d, C-20), 21.1 (q, C-21), 135.6 (d, C-22), 131.8 (d, C-23), 42.7 (s, C-24), 33.0 (d, C-25), 19.6 (q, C-26), 19.9 (q, C-27), 17.5 (q, C-28).

Compound Ⅵ: Benzoic acid, colorless needle. EI-MS m/z (rel. int.,%): 122 (65), 105 (55), 96 (68). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.14

(2H, m, H-2 and 6), 7.47 (2H, m, H-3 and 5), 7.61 (1H, m, H-4). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 172.6 (s, C-1′), 129.3 (s, C-1), 130.2 (d, C-2 and 6), 128.4 (d, C-3 and 5), 133.8 (d, C-4).

Compound Ⅶ: 4-Hydroxylbenzaldehyde, colorless needle. EI-MS *m/z* (rel. int.,%): 122 (15), 105 (100), 77 (28). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.80 (1H, s, H-1′), 7.80 (2H, d, J= 8.2 Hz,H-2 and 6), 6.98 (2H, d, J=8.2 Hz,H-3 and 5). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 191.5 (d, C-1′), 129.4 (s, C-1), 132.6 (d, C-2 and 6), 116.1 (d, C-3 and 5), 162.3 (s, C-4).

Compound Ⅷ: 4-Monopropanoylbenzenediol, colorless crystal. FAB-MS (neg.) *m/z*: 165. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.37 (3H, t, J= 7.1 Hz,H-3′), 4.34 (2H, q, J=7.1 Hz,H-2′), 7.94 (2H, m, H-2 and 6), 6.87 (2H, m, H-3 and 5). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.3 (q, C-3′), 60.8 (t, C-2′), 166.8 (s, C-1′), 122.6 (s, C-1), 131.8 (d, C-2 and 6), 115.2 (d, C-3 and 5), 160.3 (s, C-4).

Compound Ⅸ: Ethyl-β-*D*-glucopyranoside[9], yellow oil. ^{1}H-NMR (500 MHz, CD_3OD) δ: 1.22 (3H, m, H-2′), 3.95 (2H, m, H-1′), 4.25 (1H, d, J=7.8 Hz,H-1), 3.16 (1H, q, J=9.0, 8.1 Hz,H-2), 3.33 (1H, m, H-3), 3.27 (1H, m, H-4), 3.38 (1H, m, H-5), 3.62 (1H, m, H-6a), 3.85 (1H, m, H-6b). ^{13}C-NMR (100 MHz, CD_3OD) δ: 66.1 (t, C-1′), 15.4 (q, C-2′), 103.9 (d, C-1), 74.9 (d, C-2), 77.9 (d, C-3), 71.4 (d, C-4), 77.7 (d, C-5), 62.6 (t, C-6).

Compound Ⅹ: Thioacetic anhydride[9], white powder. EI-MS *m/z* (rel. int.,%): 100 (60), 74 (100), 56 (53). FAB-MS (pos.) *m/z*: 119, 101. ^{1}H-NMR (400 MHz, CD_3OD) δ: 2.55 (6H, s, H-1 and 1′). ^{13}C-NMR (100 MHz, CD_3OD) δ: 176.1 (s, C-2 and 2′), 29.8 (q, C-1), 29.5 (q, C-1′).

Compound Ⅺ: (2*S*, 2′*R*, 3*S*, 4*R*)-2-(2-hydroxyoctadecanoylamino) docosane-1, 3, 4-triol[10], white powder. FAB-MS (neg.) *m/z*: 655, 396. ^{1}H-NMR (400 MHz, C_5D_5N) δ: 4.60 (1H, dd, J=10.5, 4.5 Hz, H-1a), 4.38 (1H, dd, J= 10.5, 4.5 Hz, H-1b), 5.01 (1H, m, H-2), 4.28 (1H, dd, J=6.5, 4.5 Hz, H-3), 4.24 (1H, m, H-4), 1.92 (2H, m, H-15), 1.72 (2H, m, H-6), 1.30－1.50 (18H, m, H-7－15), 0.90 (3H, t, J=6.8 Hz, H-16), 4.57 (1H, J=7.6, 3.7 Hz, H-2′), 2.21 (2H, m, H-3′), 1.76 (2H, m, H-4′), 1.30－1.50 (36H, m, H-5′－22′), 0.90 (3H, t, J= 6.8 Hz, H-23′), 8.56 (NH). ^{13}C-NMR (100 MHz, C_5D_5N) δ: 62.2 (t, C-1), 53.2 (d, C-2), 77.0 (d, C-3), 73.1 (d, C-4), 35.8 (t, C-5), 29.6 (t, C-6), 29.7－30.4 (t, C-7－21), 14.2 (q, C-22), 175.3 (s, C-1′), 72.6 (d, C-2′), 35.7 (t, C-3′), 26.6 (t, C-4′), 30.0－30.4 (t, C-5′－17′), 14.2 (q, C-18′).

4 Discussion

Cyathane diterpenoids are currently attracting more attention because of their unique biological activities. Compounds Ⅰ and Ⅱ are cyathane diterpenoids.

Compound Ⅰ was obtained as an oily solid, $[\alpha]_D^{25}$ = +91.7° (c0.1, $CHCl_3$). EI-MS gave an ion peak at *m/z*: 316 ($[M]^+$). ^{13}C-NMR (DEPT) of compound Ⅰ showed 20 carbon signals of which an aldehyde (δ: 194.4), one oxymethine (δ: 73.7), and one oxymethylene (δ: 65.9) carbons, one tetrasubstituted double bond (δ: 145.8, C; 141.0, C) and two trisubstituted double bonds (δ: 137.7, 154.1, C; 119.6, 145.8, CH) were presented. ^{1}H-NMR spectrum of compound Ⅰ showed one secondary methyl and two tertiary methyl hydrogen signals at δ: 0.93 (3H, d, J=6.8 Hz), 0.95 (3H, s), and 1.01 (3H, s), respectively. The former methyl hydrogen signal and another methylene protons (3.56 and 3.57, 2H, m) were spin-coupled with a methine hydrogen signal at δ: 2.94 (1H, m), demonstrating the presence of an isolated system $NCH(CH_3)$-CH_2OH.

Based on the above partial structures, the cyathane diterpenoid structure of compound Ⅰ was deduced from ^{1}H-^{1}HCOSY, HMQC, HMBC, and NOESY spectra.

Compared with the data of the literature[5], compound Ⅰ was identified as sarcodonin A.

Compound Ⅱ was obtained as yellowish oil,

$[\alpha]_D^{25} = +10.3°$ (c 0.01, MeOH). High-resolution ESI-MS (pos.) gave an ion peak at m/z: 557.254 7 (cal. for $C_{34}H_{37}O_7$ as 557.253 9). ^{13}C-NMR signal at δ: 181.8 suggested the presence of a carboxyl group. Aromatic ^{1}H-NMR signals at δ: 7.35－7.96 and twelve ^{13}C-NMR signals between δ: 128.2 and δ: 134.1 and two carbonyl carbon signals at δ: 166.1 and δ: 165.9 showed two benzoate moieties. Interpretation of the ^{1}H-NMR, ^{13}C-NMR revealed the structure of compound Ⅱ[4].

Comparison of physicochemical properties with the reported data allowed to identify compounds Ⅲ－Ⅺ, isolated from the same fungus, as 3β-hydroxy-5α, 8α-epidioxyergosta-6, 22-dien (Ⅲ)[6], (22*E*, 24*R*)-ergosta-7, 22-diene-3β, 5α, 6β-triol (Ⅳ)[7], (22*E*, 24*R*)-ergosta-7, 22-diene-3β-ol (Ⅴ)[8], benzoic acid (Ⅵ), 4-hydroxylbenzaldehyde (Ⅶ), 4-monopropanoylbenzenediol (Ⅷ), ethyl-β-*D*-glucopyranoside (Ⅸ)[9], thioacetic anhydride (Ⅹ)[9], and (2*S*, 2′*R*, 3*S*, 4*R*)-2-(2-hydroxyoctadecanoylamino) docosane-1, 3, 4-triol (Ⅺ)[10], respectively.

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耙齿菌糖蛋白 $I_{1\text{-}2\text{-}1}$ 的化学研究

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摘 要：目的 对均一耙齿菌 *Irpex lacteus* 糖蛋白 $I_{1\text{-}2\text{-}1}$ 进行化学研究。**方法** 利用化学方法和光谱方法分析其结构特征。**结果** $I_{1\text{-}2\text{-}1}$ 的相对分子质量为40 000，由 Ara、Xyl、Man、Gal、Glu 组成，甲基化分析表明 $I_{1\text{-}2\text{-}1}$ 的主链主要以 1→2，1→6 linked Manp 为主。**结论** $I_{1\text{-}2\text{-}1}$ 为结构复杂的糖蛋白，为首次从耙齿菌中获得。

关键词：耙齿菌；糖蛋白；甲基化分析

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Glycoprotein $I_{1\text{-}2\text{-}1}$ from *Irpex lacteus*

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Abstract: Objective To study the chemical structure of a pure glycoprotein $I_{1\text{-}2\text{-}1}$ from *Irpex lacteus*.

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