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云南割舌树的化学成分*

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摘要：从云南割舌树（*Walsura yunnanensis* C. Y. Wu.）树皮的乙醇提取物中分离鉴定了12个化合物，它们分别是walsurol（1），tocopherol（2），sitoindoside I（3），3β－stigmast－5－en－3－yl－β－D－xylopyranoside（4），stigmast－4－en－6β－ol－3－one（5），7－oxositosterol（6），3β－hydroxy－5α，8α－epidioxyergosta－6，22－diene（7），（－）epicatechin（8），3，5－dihydroxy－4－methoxylphenylethanol（9），间三甲氧基苯，（β－谷甾醇和胡萝卜甙。新化合物1命名为割舌醇（walsurol）。

关键词：云南割舌树；楝科；割舌醇
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Chemical Constituents from *Walsura yunnanensis*

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Abstract：A new compound walsurol（**1**），along with known compounds，tocopherol（**2**），sitoindoside I（**3**），3β－stigmast－5－en－3－yl－β－D－xylopyranoside（**4**），stigmast－4－en－6β－ol－3－one（**5**），7－oxositosterol（**6**），3β－hydroxy－5α，8α－epidioxyergosta－6，22－diene（**7**），（－）epicatechin（**8**），and 3，5－dihydroxy－4－methoxylphenylethanol（**9**），were isolated from the EtOH extract from the bark of Walsura yunnanensis C. Y. Wu. Their structures were identified on the basis of spectral methods.

Key words：*Walsura yunnanensis*；Meliaceae；Walsurol

The genus *Walsura* Roxb.（Meliaceae），comprising 30－40 species，is naturally distributed in the People's Republic of China，India，and Indonesia（Wu *et al*，1977）. In previous literature，triterpenoids and tetranortriterpenoids were isolated from species in this genus（Balakrishna *et al*，1995；Govindachari et al，1995；Purushothaman *et al*，1985）. In the course of study on chemical constituents from the family Meliaceae（Luo *et al*，1999），we undertook the investigation of *W. yunnanensis* C. Y. Wu. as there was no chemical constituents reported from this plant. A new

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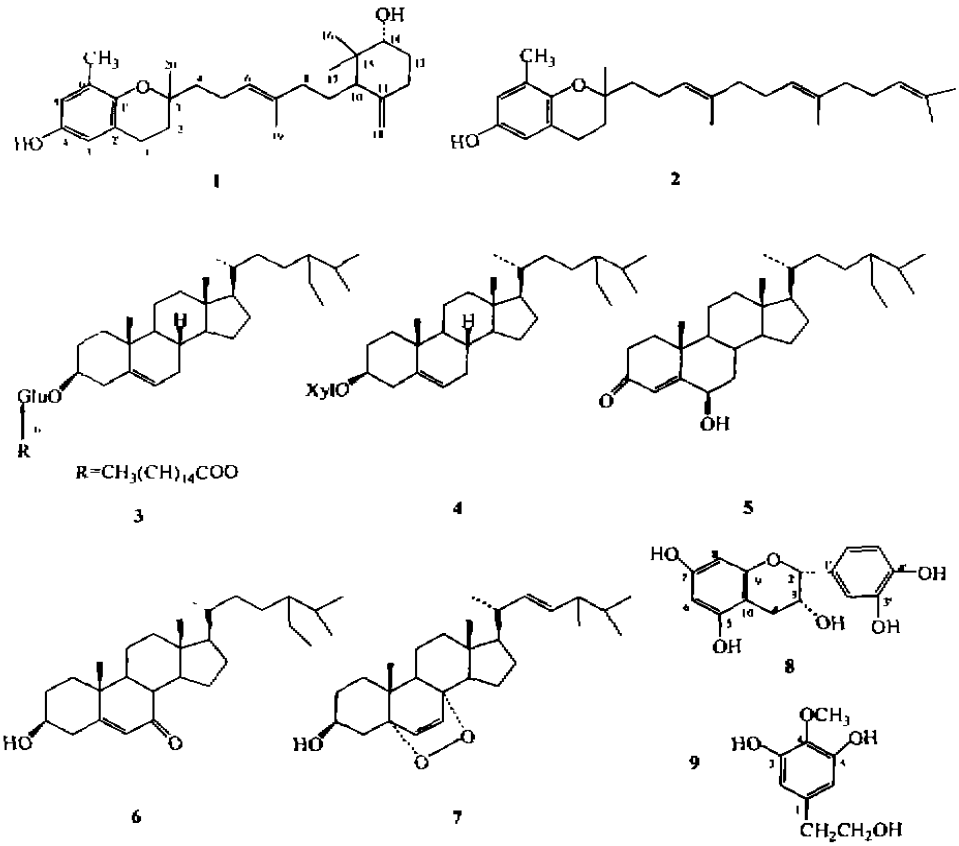
compound named walsurol (1) together with known compounds, tocopherol (2) (Rao *et al*, 1972), sitoindoside I (3)(Kiribuchi *et al*, 1967), 3β – stigmast – 5 – en – 3 – yl – β – D – xylopyranoside (4) (Tin – Wa *et al*, 1971), stigmast – 4 – en – 6β – ol – 3 – one (5), 7 – oxositosterol (6) (Greca *et al*, 1990), 3β – hydroxy – 5α, 8α – epidioxyergosta – 6, 22 – diene (7) (Ma *et al*, 1994), (–) epicatechin (8) (Zhang *et al*, 1994), 3, 5 – dihydroxy – 4 – methoxylphenylethanol (9), were isolated from the EtOH extract from the bark of *Walsura yunnanensis* C. Y. Wu.

Compound 1 was isolated as viscous oil. Negative – ion HRFABMS spectrum gave molecular ion peak at m/z 411.2823 $[M-1]^-$, corresponding to a molecular formula $C_{27}H_{40}O_3$. The ^{13}C and ^1H NMR of 1 displayed signals due to five tertiary methyls, two of which were connected to an olefinic linkage or phenyl [δ_H 1.57 (s), 2.10 (s)], eight methylenes, two methines,

in which one was oxygenated, two quaternary carbons, four olefinic carbons [δ_c 108.3 (t), 124.5 (d), 135.3 (s), 147.2 (s)], a tetrasubstituted phenyl signals [δ_c 148.0 (s), 145.9 (s), 127.3 (s), 121.2 (s), 115.8 (d), 112.7 (d)].



Signals for δ_H 6.46 (d, J = 2.9 Hz, H – 5'), 6.37 (d, J = 2.9 Hz, H – 3'), 2.10 (6' – Me), 1.75 (2H, m, H – 2) and 1.24 (20 – Me) in the ^1H NMR spectrum indicated the presence of a 2, 8 – dimethyl – 6 – hydroxychromane fragment (Zafra – Polo *et al*, 1996). In the HMBC

spectrum (Fig. 1), δ_H 6.37 (H-3') showed cross peaks to δ_c 148.0 (C-4'), 115.8 (C-5') and 22.5 (C-1), and δ_H 6.46 (H-5') also showed cross peaks to δ_c 148.0 (C-4'), 145.9 (C-1') and 16.0 (6'-*Me*), respectively, also supported these assignments.

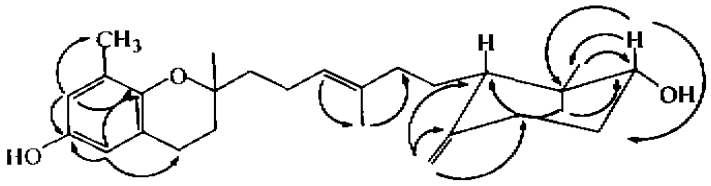


Fig. 1 selected HMBC of compound 1 (from H to C)

The remaining portion of 1 was elucidated by examination of the ^{13}C, ^1H NMR, HMQC and HMBC spectra. Besides the 2, 8-dimethyl-6-hydroxychromane fragment, the remaining possessed sixteen carbons having two double bonds and a ring required by the molecular formula. The formation of six-membered ring between C_{10} and C_{15} was determined by cross signals between δ_H 4.56, 4.84 (each 1H, H-18) to δ_c 50.7 (d, C-10), 0.97 (H-16) to C-10, and 0.67 (H-17) to C-10 in the HMBC spectrum. The hydroxyl was placed C-14 by the presence of cross signals between δ_H 3.35 (dd, J = 10.1, 4.2 Hz, H-14) to 15.4 (C-17), H-14 to 25.8 (C-16), H-14 to 32.2 (C-13), H-14 to 40.5 (C-15), and H-14 to 50.7 (C-10) in the HMBC spectrum of 1. A large and a small coupling constants (J = 10.1, 4.2 Hz) of H-14 due to *aa* and *ae* coupling, placed 14-OH at equatorial bond. Therefore, the structure of 1 was determined as a prenylated benzopyran compound similar to tocopherol.

Experimental Section

Melting points were obtained on a Sichuan Micromelting apparatus and are uncorrected. Optical rotations were taken with a Horiba SEAP-300 spectropolarimeter. UV spectra were measured with a Shimadzu double-beam 210A spectrophotometer in MeOH solution. IR spectra (KBr) were obtained on a Bio-Rad FTS-135 infrared spectrophotometer. ^1H, ^{13}C NMR and 2D-NMR spectra were recorded on a Bruker AM-400 and a DRX-500 NMR spectrometer with TMS as internal standard. MS data were obtained on a VG Autospec-3000 spectrometer, at 70 eV for EI. Si gel (200-300 mesh) for column chromatography and GF_{254} for TLC were obtained from the Qindao Marine Chemical Factory.

The bark of *W. yunnanensis* was collected from Mengla County, Yunnan Province, People's Republic of China, in December 1996. It was identified by Prof. G. D. Tao, Xishuangbanna Botanical Garden. A voucher specimen has been deposited in the herbarium of the Department of Plant Taxonomy, Kunming Institute of Botany Chinese Academy of Sciences (KUN).

The air-dried and powdered bark (4.2 kg) of *W. yunnanensis* was extracted with EtOH three times under reflux. After removal of the solvent *in vacuo*, the residue was suspended in H_2O and extracted EtOAc. The EtOAc fraction was concentrated *in vacuo* to give 66 g of a residue, which was

subjected to column chromatography on Si gel, eluted with gradient mixtures of $CHCl_3 - Me_2CO$ (from $CHCl_3$ to $CHCl_3 - Me_2CO$, 2: 1). According to differences in composition monitored by TLC (Si gel GF_{254}), ten fractions were obtained. Then, they were further purified on silica gel CC with various eluent system and on Reversed – phase C_{18} silica gel using $CH_3OH - H_2O$ (3: 1 – 1: 1) as eluent to yield (**1**) (3.16 g), (**2**) (18 mg), (**3**) (32 mg), (**4**) (16 mg), (**5**) (8 mg), (**6**) (48 mg), (**7**) (18 mg), (**8**) (684 mg) and (**9**) (9 mg).

Walsurol (**1**): Viscous oil; $[\alpha]_D^{28} = -15.8°$ (c 0.36, $CHCl_3$); UV (MeOH) λ_{max} 206, 296 nm; IR ν_{max}^{KBr} cm^{-1}: 3388, 2869, 1707, 1646, 1611, 1470, 1379, 1222, 1095, 1024, 893, 855, 792; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.46 (1H, d, J = 2.9 Hz, H – 5'), 6.37 (1H, d, J = 2.9 Hz, H – 3'), 5.06 (1H, t, J = 6.2 Hz, H – 6), 4.84, 4.56 (each 1H, s, H – 18), 3.33 (1H, dd, J = 10.1, 4.2 Hz, H – 14), 2.66 (2H, t, J = 6.8 Hz, H – 1), 2.28, 1.93 (each 1H, m, H – 12), 2.10 (3H, s, CH_3 – 6'), 2.05 (2H, m, H – 5), 2.05, 1.82 (each 1H, m, H – 8), 1.75 (2H, m, H – 2), 1.60 (2H, m, H – 9), 1.55 (3H, s, H – 19), 1.48 (2H, m, H – 4), 1.45 (2H, m, H – 13), 1.24 (3H, s, H – 20), 0.97 (3H, s, H – 16), 0.67 (3H, s, H – 17); ^{13}C NMR ($CDCl_3$, 100 MHz) δ148.0 (s, C – 4'), 147.2 (s, C – 11), 145.9 (s, C – 1'), 135.3 (s, C – 7), 127.3 (s, C – 6') 124.5 (d, C – 6), 121.2 (s, C – 2'), 115.8 (d, C – 5'), 112.9 (d, C – 3'), 108.3 (t, C – 18), 77.4 (d, C – 14), 75.3 (s, C – 3), 50.7 (d, C – 10), 40.5 (s, C – 15), 39.5 (t, C – 4), 38.5 (t, C – 8), 33.1 (t, C – 12), 32.2 (t, C – 13), 31.5 (t, C – 2), 25.8 (q, C – 17), 24.1 (q, C – 20), 23.5 (t, C – 9), 22.5 (t, C – 1), 22.1 (t, C – 5), 16.0 (q, CH_3 – 6') 15.8 (q, C – 19), 15.4 (q, C – 16); EIMS m/z 412 $[M]^+$ (50), 394 (3), 351 (1), 260 (8), 203 (10), 192 (18), 175 (60), 163 (15), 147 (21), 135 (60), 121 (78), 109 (60), 95 (70), 78 (60), 68 (75); HRFABMS m/z 411.2824 $[M - 1]^-$ (calcd. for $C_{27}H_{39}O_3$, 411.2899).

Tocopherol (**2**): Viscous oil; UV (MeOH) λ_{max} 206, 297 nm; IR ν_{max}^{KBr} cm^{-1}: 3344, 2971, 2926, 2754, 1668, 1611, 1471, 1378, 1222, 1147, 1103, 1048, 993, 935, 854; ^1H NMR (CD_3Cl, 400 MHz) δ 6.44 (1H, d, J = 2.8 Hz, H – 5'), 6.35 (1H, d, J = 2.9 Hz, H – 3'), 5.10 (3H, m, H – 6, H – 10, H – 14), 2.64 (2H, t, J = 6.8 Hz, H – 1), 2.12 (3H, s, 6' – CH_3), 2.05 (6H, m, H – 5, H – 9, H – 13), 1.98 (4H, m, H – 8, H – 12), 1.75 (2H, dd, J = 13.0, 6.5 Hz, H – 2), 1.66 (3H, s, H – 16), 1.60 (2H, m, H – 4), 1.58 (9H, s, H – 17, H – 18, H – 19), 1.23 (3H, s, C – 20); ^{13}C NMR ($CDCl_3$, 100 MHz) δ147.7 (s, C – 4'), 146.0 (s, C – 1'), 135.1 (s, C – 11), 134.9 (s, C – 7), 131.2 (s, C – 15), 127.3 (s, C – 6'), 124.4 (d, C – 6), 124.3 (d, C – 14), 124.2 (d, C – 10), 121.2 (s, C – 2'), 115.8 (d, C – 5'), 112.7 (d, C – 3'), 75.3 (s, C – 3), 39.7 (t, C – 12, C – 4, C – 8), 31.4 (t, C – 2), 26.7 (t, C – 13), 26.6 (t, C – 9), 25.6 (q, C – 17), 24.0 (q, C – 20), 22.5 (t, C – 1), 22.2 (t, C – 5), 17.6 (q, C – 16), 16.0 (q, C – 18), 16.0 (q, CH_3 – 6'), 15.8 (q, C – 19); EIMS m/z 396 $[M]^+$ (65), 272 (5), 260 (15), 245 (10), 217 (13), 204 (25), 192 (70), 175 (85), 161 (52), 149 (57), 137 (92), 121 (88), 105 (65), 93 (87), 79 (97), 69 (100).

Sitoindoside I (3): Viscous oil; IR ν_{max}^{KBr} cm^{-1}: 3417, 2927, 2854, 1740, 1466, 1379, 1174, 1083, 1021, 723; ^1H, ^{13}C NMR and TLC were identical to authentic sample.

3β-Stigmast-5-en-3-yl-β-D-xylopyranoside (4): White powder (Me_2CO); mp 232-234 ℃; IR ν_{max}^{KBr} cm^{-1}: 3403, 2960, 2937, 1464, 1380, 1239, 1164, 1072, 1084, 974, 897, 801; ^1H NMR (pyridine-d_5, 400 MHz) δ5.36 (1H, brs, H-6), 4.92 (1H, d, J = 9.5 Hz, H-1'), 4.38 (2H, dd, J = 11.0, 5.6 Hz, H-5'), 4.27 (1H, dd, J = 9.2, 4.4 Hz, H-4'), 4.21 (1H, t, J = 8.6 Hz, H-2'), 4.04 (1H, t, J = 8.1 Hz, H-3'), 3.89 (1H, m, H-3), 3.75 (1H, t, J = 10.4 Hz, H-5'), 1.01 (3H, d, J = 6.5 Hz, H-21), 0.97 (3H, s, H-19), 0.89 (3H, d, J = 7.0 Hz, H-27), 0.86 (3H, d, J = 7.0 Hz, H-26), 0.86 (3H, t, J = 7.0 Hz, H-29), 0.64 (3H, s, H-18); ^{13}C NMR (pyridine-d5, 100 MHz) δ141.1 (s, C-5), 122.0 (d, C-6), 103.4 (d, C-1'), 78.5 (d, C-3), 78.3 (d, C-3'), 75.1 (d, C-2'), 71.3 (d, C-4'), 67.2 (t, C-5'), 56.9 (d, C-14), 56.4 (d, C-17), 50.5 (d, C-9), 46.2 (d, C-24), 42.6 (s, C-13), 40.0 (t, C-12), 39.4 (t, C-4), 37.0 (t, C-1), 36.5 (s, C-10), 36.5 (d, C-20), 34.3 (t, C-22), 32.2 (t, C-2), 32.2 (d, C-8), 30.5 (t, C-7), 29.7 (d, C-25), 29.7 (t, C-16), 25.6 (t, C-15), 23.5 (t, C-28), 21.4 (t, C-11), 20.0 (q, C-27), 19.3 (q, C-19), 19.1 (q, C-21), 19.0 (q, C-26), 12.2 (q, C-29), 12.1 (q, C-18); EIMS m/z 546 $[M]^+$ (1), 414 (5), 397 (100), 384 (37), 255 (38), 213 (14), 187 (7), 173 (12), 159 (30), 149 (18), 133 (38), 119 (23), 107 (47), 95 (56), 83 (51), 73 (89).

Stigmast-4-en-6β-ol-3-one (5): Crystalline solids (Me_2CO); mp 192-194 ℃; UV (MeOH) λ_{max} (logε) 217.5 (4.32), 232.5 (4.28), 249 (3.84) nm; IR ν_{max}^{KBr} cm^{-1}: 3500, 3403, 2958, 2869, 1681, 1466, 1384, 1232, 1194, 1039, 1018, 971, 879; EIMS m/z 428 $[M]^+$ (75), 414 (15), 399 (5), 365 (10), 314 (8), 286 (10), 269 (15), 248 (6), 227 (13), 213 (5), 185 (5), 161 (7), 152 (24), 107 (18), 95 (30), 81 (40), 69 (52), 55 (100); ^1H and ^{13}C NMR spectral data were identical to the published (Greca *et al*, 1990).

7-Oxositosterol (6): Colorless needles (Me_2CO); mp 108-110℃; UV (MeOH) λ_{max} 202 nm; IR ν_{max}^{KBr} cm^{-1}: 3533, 3344, 2958, 2939, 2871, 1673, 1464, 1382, 1295, 1184, 1067, 1017, 948, 864 cm-1; EIMS m/z 428 $[M]^+$ (14), 414 (70), 396 (10), 383 (30), 328 (12), 314 (37), 287 (60), 247 (23), 205 (26), 192 (45), 161 (42), 149 (31), 135 (42), 121 (26), 109 (29), 93 (38), 84 (50), 69 (47); ^1H and ^{13}C NMR spectral data were identical to the published (Greca *et al*, 1990).

3β-Hydroxy-5α, 8α-epidioxyergosta-6, 22-diene (7): Colorless needles (Me_2CO); mp 152-155 ℃; IR ν_{max}^{KBr} cm^{-1}: 3526, 3305, 2857, 2932, 2873, 1660, 1460, 1378, 1076, 1047, 968, 935, 858; EIMS m/z 410 $[M]^+$ (4), 396 (100), 376 (5), 363 (17), 152 (3), 337 (8), 271 (4), 253 (8), 197 (2), 175 (2), 143 (3), 107 (3), 95 (4), 69 (10), 58 (15); ^1H and ^{13}C NMR spectral data were identical to the published (Ma *et al*, 1994).

(-) **Epicatechin (8)**: Colorless needles (MeOH); mp 248-249 ℃; UV (MeOH) λ_{max} 206,

222.5, 280.5 nm; IR ν_{max}^{KBr} cm^{-1}: 3501, 3174, 2932, 2592, 2558, 2358, 1877, 1626, 1522, 1469, 1441, 1389, 1313, 1290, 1260, 1226, 1185, 1147, 1096, 1046, 1017, 979; ^1H and ^{13}C NMR spectral data were identical to the published (Zhang *et al*, 1994).

3, 5 – Dihydroxy – 4 – methoxylphenylethnol (9): Crystalline solids (MeOH); ^1H NMR (pyridine – d_5, 400 MHz) δ 6.90 (2H, s, H – 2, H – 6), 4.12 (2H, t, J = 7.0 Hz, α – H) 3.97 (3H, s, OCH_3), 3.00 (2H, t, J = 7.0 Hz, β – H); ^{13}C NMR (pyridine – d_5, 100 MHz) δ 152.2 (s, C – 3, C – 5), 136.4 (s, C – 4), 123.8 (s, C – 1), 109.4 (d, C – 2, C – 6), 63.8 (t, α – C), 40.5 (t, β – C), 60.3 (q, OCH_3); EIMS m/z 184 $[M]^+$ (88), 169 (8), 153 (100), 139 (65), 123 (13), 110 (70), 94 (8), 84 (38), 69 (14), 64 (29), 53 (58).

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