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SHINJULACTONE C, A NEW QUASSINOID WITH A 1α,12α:5α,13α-DICYCLO-9βH-PICRASANE SKELETON FROM AILANTHUS ALTISSIMA SWINGLE

Masami Ishibashi, Tatsushi Murae, Hiroshi Hirota, Takahiko Tsuyuki, Takeyoshi Takahashi,* Akiko Itai,+ and Yoichi Iitaka+
Department of Chemistry, Faculty of Science, and +Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Summary: A new non-bitter quassinoid, named shinjulactone C (1), was isolated from the root bark of Ailanthus altissima SWINGLE and shown to be 1α,12α:5α,13α-dicyclo-1β,12β,20-trihydroxy-9βH-picras-3-ene-2,11,16-trione by X-ray diffraction method.

Several investigations on bitter principles of Ailanthus altissima SWINGLE (= A. glandulosa DESF.) have been reported.[1] In previous papers[1b,c] we reported isolation of new bitter quassinoids, shinjudilactone and shinjulactone B, from this plant (Japanese name: Shinju) grown in Japan, together with seven known quassinoids. Further investigation on the constituents of the root bark of the plant led to the isolation of a new non-bitter quassinoid, shinjulactone C (1). This paper deals with the structure determination of 1.

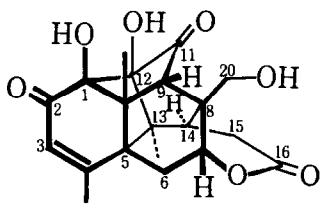
The aqueous extract of the root bark was continuously extracted with CH_2Cl_2 and the organic layer was evaporated and subjected to separation by SiO_2 column chromatography. A fraction eluted with 16% CH_3OH-CH_2Cl_2 was rechromatographed and crystallized from acetone to give shinjulactone C (1; ca. 0.001% yield), mp 292 °C (decomp); $[\alpha]_D^{23}$ -344° (C_5H_5N); IR (KBr) ca. 3480, 1775, 1720, and 1650 cm^{-1}; UV (MeOH) 248 nm (ε 10600); ^1H and ^{13}C NMR[2]; MS m/e (%) 374 (M^+; 100), 356 (5), 343 (20), 315 (10), and 151 (60); Found: m/e 374.1379. Calcd for $C_{20}H_{22}O_7$: M, 374.1366.

On treatment with acetic anhydride in pyridine at room temperature for 20 hr, 1 gave a monoacetate (2) and a diacetate (3) in a ratio of 3:7. The monoacetate (2) showed mp 131-134 °C (acetone-hexane); $[\alpha]_D^{22}$ -222° ($CHCl_3$); IR (Nujol) ca. 3450, 1770, 1740, and 1660 cm^{-1}; UV (EtOH) 245 nm (ε 14000); ^1H NMR[3]; MS m/e (%) 416 (M^+; 25), 398 (10), 388 (8), 374 (8), 356 (100), 193 (30), and 151 (10); Found: m/e 416.1464. Calcd for $C_{22}H_{24}O_8$: M, 416.1469. The diacetate (3) gave mp 152-154 °C (acetone-hexane); $[\alpha]_D^{21}$ -200° ($CHCl_3$); IR (Nujol) ca. 3450, 1780, 1740, and 1665 cm^{-1}; UV (EtOH) 245.5 nm (ε 9600); ^1H and ^{13}C NMR[4]; MS m/e (%) 458 (M^+; 12), 430 (10), 416 (100), 398 (20), 193 (60), and 151 (58); Found: m/e 458.1590. Calcd for $C_{24}H_{26}O_9$: M, 458.1587.

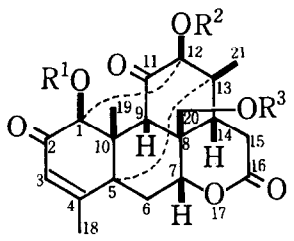
In order to determine the structure of shinjulactone C (1), a single crystal of 1 was subjected to X-ray diffraction analysis. Crystals of 1 belong to an orthorhombic space group $P2_12_12_1$ with the cell parameters of a=13.247, b=13.331, and c=9.596 Å, Z=4, and D_c=1.47 g cm^{-3}. The final R-factor was

0.073. Figure 1 is a computer-generated perspective drawing of the molecule of 1. Thus the structure of shinjulactone C (1) was shown to be formulated as 1α,12α:5α,13α-dicyclo-1β,12β,20-trihydroxy-9βH-picras-3-ene-2,11,16-trione.[5]

The unusual hexacyclic 1α,12α:5α,13α-dicyclo-9βH-picrasane skeleton is unprecedented and its biogenetic pathway is unknown. However, an inversion of a chiral center at the $C_{(9)}$-position in common picrasanes must occur prior to the bond formation, and a participation of a double bond between $C_{(12)}$ and $C_{(13)}$ in ring C with ring A must be necessary to form the $C_{(1)}$- $C_{(12)}$ and $C_{(5)}$- $C_{(13)}$ linkages. The investigation in this direction is under way.



1



1 $R^1 = R^2 = R^3 = H$
2 $R^1 = R^2 = H$; $R^3 = Ac$
3 R^1 or $R^2 = H$;
R^2 or $R^1 = Ac$;
$R^3 = Ac$

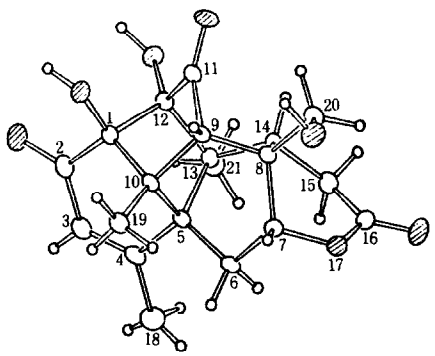


Figure 1

References and notes

1) a) J. Polonsky, Fortschr. Chem. Org. Naturst., 30, 101 (1973) and references cited therein; b) M. Ishibashi, T. Murae, H. Hirota, H. Naora, T. Tsuyuki, T. Takahashi, A. Itai, and Y. Iitaka, Chem. Lett., 1981, 1597; c) T. Furuno, H. Naora, T. Murae, H. Hirota, T. Tsuyuki, T. Takahashi, A. Itai, Y. Iitaka, and K. Matsushita, Chem. Lett., 1981, 1797.

2) ^{1}H NMR (90 MHz, C_5D_5N) δ 1.08 (3H, s), 1.28 (3H, s), 2.02 (3H, br s), 2.85 (1H, s), 4.03 (2H, s), 5.18 (1H, m), and 6.45 (1H, br s); ^{13}C NMR (22.5 MHz, C_5D_5N) δ 12.7 (q), 14.5 (q), 22.7 (q), 30.0 (t), 30.2 (t), 36.2 (d), 45.4 (s), 50.7 (s), 51.7 (d), 55.3 (s), 55.5 (s), 60.2 (t), 72.6 (d), 88.3 (s), 93.6 (s), 127.8 (d), 165.9 (s), 170.8 (s), 195.2 (s), and 209.8 (s).

3) ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.99 (3H, s), 1.03 (3H, s), 2.08 (6H, s), 4.07 (2H, s), 4.63 (1H, m), and 6.35 (1H, br s).

4) ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.99 (3H, s), 1.00 (3H, s), 2.06 (3H, s), 2.10 (3H, br s), 2.13 (3H, s), 4.10 (2H, s), 4.63 (1H, m), and 6.37 (1H, br s); ^{13}C NMR (22.5 MHz, C_5D_5N) δ 12.3 (q), 13.3 (q), 20.0 (q), 20.3 (q), 22.6 (q), 29.8 (t), 29.8 (t), 35.4 (d), 42.4 (s), 51.0 (s), 52.7 (d), 55.0 (s), 56.2 (s), 63.5 (t), 72.6 (d), 86.4 (s), 97.5 (s), 128.4 (d), 165.5 (s), 169.7 (s), 170.0 (s), 170.0 (s), 193.2 (s), and 201.0 (s).

5) Numbering of picrasane refers to the nomenclature described in the Chemical Abstracts.

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