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STRUCTURE OF SHINJULACTONE B, A NEW BITTER PRINCIPLE FROM AILANTHUS ALTISSIMA

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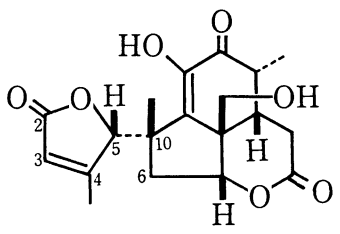
A new bitter principle, shinjulactone B was isolated from the stem bark of Ailanthus altissima SWINGLE and the structure was established.

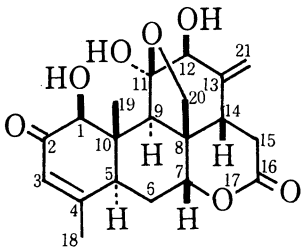
Bitter principles of plants belonging to Simaroubaceae including Ailanthus altissima SWINGLE have been extensively investigated from the interest in both anti-tumor activity and structure determination.[1] In connection with our studies on bitter principles of Picrasma ailanthoides PLANCHON (Simaroubaceae),[2] constituents of A. altissima SWINGLE (Japanese name: Shinju or Niwaurushi) were examined and the isolation of shinjudilactone, a new 13(12→11α)abeo-picrasane derivative, from the root bark and the structure determination were reported.[3] This paper deals with the isolation of a new bitter principle, shinjulactone B (1) from the stem bark of the plant and the structure elucidation of 1.

Concentrated aqueous extract of the stem bark of this plant was continuously extracted with CH_2Cl_2 and the residue obtained from the CH_2Cl_2 layer was separated by SiO_2 column chromatography. A fraction eluted with 4% CH_3OH-$CHCl_3$ was purified by recrystallization from CH_3OH-$CHCl_3$ to give shinjulactone B (1) in ca. 0.001% yield. Shinjulactone B (1), mp 265.5-268 °C, $[\alpha]_D^{25}$ +167.3° (c 0.65, CH_3OH), showed IR (KBr) 3570, 3420, 1770, 1750, 1695, 1680, 1660, and 1635 cm^{-1}; UV (EtOH) 279 nm (ε 8100), which shifted to 330 nm on addition of alkali (pH ca. 11); ^1H and ^{13}C NMR[4]; MS m/e (%) 362 (M^+; 0.4), 344 (0.4), 332 (2.3), 265 (8.4), 235 (34), and 191 (100); M^+ 362.1395 ($C_{19}H_{22}O_7$). Found: C, 60.81; H, 6.38%. Calcd for $C_{19}H_{22}O_7 \cdot 1/2\ H_2O$: C, 60.96; H, 6.19%. Acetylation of 1 with acetic anhydride in pyridine gave a diacetate, mp 194-198 °C; IR (Nujol) 1770, 1750, 1720, 1685, 1660, and 1640 cm^{-1}; UV (EtOH) 278 nm; ^1H and ^{13}C NMR[5]; MS (CI) m/e 447 $(M + H)^+$, 405, 387, and 345. The structure of the C_{19}-bitter principle, shinjulactone B (1), was determined by X-ray diffraction method[6] and a computer-generated perspective drawing of the molecule is given in Figure 1.

Shinjulactone B (1) seems to be derived biogenetically from a picrasane-type derivative, such as ailanthone (2),[7,8] via a 1,2-dioxo derivative (3). Under oxidative conditions, 3 would suffer successively a $C_{(1)}$-$C_{(2)}$ bond cleavage, decarboxylation, a contraction of the B-ring, and a formation of the α,β-unsaturated γ-lactone to afford 1 (Scheme 1). Shinjulactone B (1) is the first example of natural bitter principles with a 1,2-seco-1-nor-6(5→10)abeo-picrasane skeleton isolated from plants of the family Simaroubaceae.



1



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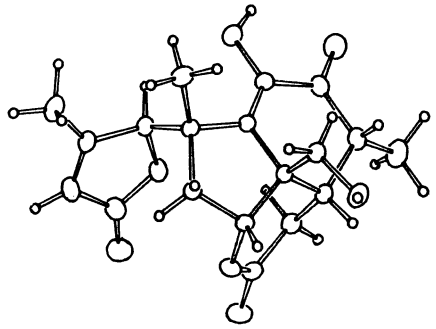
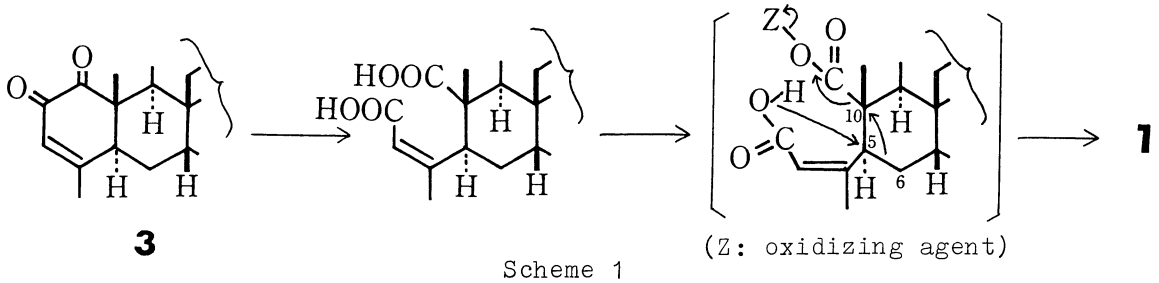


Figure 1



3

(Z: oxidizing agent)

Scheme 1

References

1) J. Polonsky, Fortschr. Chem. Org. Naturst., 30, 101 (1973) and references cited therein.

2) T. Murae, A. Sugie, T. Tsuyuki, and T. Takahashi, Chem. Pharm. Bull., 23, 2188 (1975) and references cited therein.

3) M. Ishibashi, T. Murae, H. Hirota, H. Naora, T. Tsuyuki, T. Takahashi, A. Itai, and Y. Iitaka, Chem. Lett., 1981, 1597.

4) ^{1}H NMR (100 MHz, C_5D_5N) δ 1.03 (3H, d, J=6.8 Hz), 1.61 (3H, s), 1.94 (3H, d, J=1.0 Hz), 1.97 (1H, d, J=1.5 Hz), 2.11 (1H, d, J=5.9 Hz), ca. 2.6 (2H, m), ca. 3.3 (2H, m), 3.89 and 4.10 (each 1H, A and B part of an ABq, J=11 Hz), 5.25 (1H, dd, J=5.9 and J=1.5 Hz), 5.95 (1H, m), and 6.13 (1H, m); ^{13}C NMR (25.0 MHz, C_5D_5N) δ 12.3 (q), 16.3 (q), 23.8 (q), 28.3 (t), 37.4 (d), 39.7 (d), 40.4 (t), 48.8 (s), 51.6 (s), 64.3 (t), 85.2 (d), 87.1 (d), 120.4 (d), 138.5 (s), 145.1 (s), 167.7 (s), 168.8 (s), 171.5 (s), and 195.9 (s).

5) ^{1}H NMR (100 MHz, C_5D_5N) δ 1.11 (3H, d, J=6.8 Hz), 1.49 (3H, s), 1.93 (3H, d, J=0.7 Hz), 2.13 (3H, s), 2.31 (3H, s), 2.0-3.0 (5H, m), ca. 3.4 (1H, m), 4.41 and 4.73 (each 1H, A and B part of an ABq, J=12.2 Hz), 4.98 (1H, d, J=5.4 Hz), 5.63 (1H, br s), and 5.96 (1H, m); ^{13}C NMR (25.0 MHz, C_5D_5N) δ 12.2 (q), 16.0 (q), 20.3 (q), 20.6 (q), 24.4 (q), 28.3 (t), 38.1 (d), 40.5 (d), 40.5 (t), 49.1 (s), 50.9 (s), 64.8 (t), 83.7 (d), 87.6 (d), 120.9 (d), 142.6 (s), 153.0 (s), 166.8 (s), 167.4 (s), 168.5 (s), 170.4 (s), 170.8 (s), and 192.0 (s).

6) Orthorhombic, space group: $P2_12_12_1$, z=4; a=12.594(5), b=19.016(8), and c=7.755(3) Å; D_c=1.36 g cm^{-3}; a final R factor=0.036.

7) J. Polonsky and J.-L. Fourrey, Tetrahedron Lett., 1964, 3983; C. G. Casinovi, P. Ceccherelli, G. Grandolini, and V. Bellavita, ibid., 1964, 3991.

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

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