Bitter Principles of *Picrasma ailanthoides* Planchon. Nigakihemiacetals A and B, and Nigakilactones G and H.

Tatsushi MURAE, Tôru IKEDA, Takahiko TSUYUKI, Tadaaki NISHIHAMA and Takeyoshi TAKAHASHI

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo

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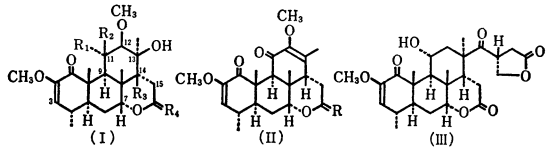
In addition to the previously reported nigakilactones A, B, C, D,[1] E and F,[2] four bitter principles (nigakihemiacetals A and B, and nigakilactones G and H) have been isolated from *Picrasma ailanthoides* Planchon (= *P. quassioides* Bennett). Recently, isolation of picrasin B[3] and A[4] from the same plant was recorded by Hikino *et al.*

Nigakihemiacetal A, mp 262—263°C, $C_{22}H_{34}O_7$, M^+ 410, $[\alpha]_D$+20° (*c* 0.22, in EtOH), λ_{max}^{MeOH} 272 nm (ε 5800), IR (nujol): 3560, 3470, 3360, 1668, 1634 cm^{-1}, PMR (Table 1), is a new bitter substance which has a hemiacetal instead of a lactone grouping. On oxidation with Ag_2O, this hemiacetal gave nigakilactone F[2] (I, R_1=OH, R_2=H, R_3=H, R_4=O). Thus, structure I (R_1=OH, R_2=H, R_3=H, R_4=OH, H) is given for nigakihemiacetal A.

Spectral data of nigakihemiacetal B, mp 230.5—231°C, $C_{22}H_{30}O_6$, M^+ 390, $[\alpha]_D$+20° (*c* 0.21, in EtOH), λ_{max}^{MeOH} 256 nm (ε 11400), IR (nujol): 3400, 1690, 1674, 1640, 1621 cm^{-1}, suggest that this substance would be neoquassin. Indeed, nigakihemiacetal B was shown to be identical with neoquassin[5] (II, R=OH, H) by the formation of quassin[5] (II, R=O) on oxidation of this hemiacetal with Ag_2O.

Nigakilactone H, mp 274.5—275.5°C, $C_{22}H_{32}O_8$, M^+ 424, $[\alpha]_D$+67° (*c* 0.14, in EtOH), λ_{max}^{MeOH} 271 nm (ε 4260), IR (nujol): 3450, 1725, 1675, 1640 cm^{-1}, is a new bitter principle containing one hydroxyl group more than nigakilactone F[2]. In the PMR spectrum, C_9-H (1H, δ 2.05) resonates as doublet (J=11 Hz), C_{11}-H (1H, δ 3.96) as quartet (J=11; 9 Hz), C_{12}-H (1H, δ 3.02) as doublet (J=9 Hz), C_3-H (1H, δ 5.51) as doublet (J=2.5 Hz) and C_7-H (1H, δ 4.56) as multiplet. These observations are best interpreted on the basis of the skeletal structure of known nigakilactone F[2] (I, R_1=OH, R_2=H, R_3=H, R_4=O). Nigakilactone H, when treated with $Na_2Cr_2O_7$, afforded a ketone, mp 161—163°C, $C_{22}H_{30}O_8$, M^+ 422, λ_{max}^{MeOH} 264 nm (ε 5920), IR (nujol): 3450, 1720, 1690, 1625 cm^{-1}. The PMR spectrum shows signals due to C_9-H (1H, δ 2.61, singlet), C_{12}-H (1H, δ 3.38, singlet), C_3-H (1H, δ 5.42, doublet, J=2.5 Hz) and C_7-H (1H, δ 4.53, multiplet); no signal due to C_{11}-H is observed. In the PMR spectra of nigakilactone H and its ketone, a signal due to two protons on C_{15} appears as *singlet* at δ 2.67 and at δ 2.89, respectively. This shows that the C_{14}-carbon is tertiary, and leads to the location of an extra hydroxyl group on C_{14} for nigakilactone H. Thus, nigakilactone H and its ketone should be represented by I (R_1=OH, R_2=H, R_3=OH, R_4=O, for nigakilactone H; R_1, R_2=O, R_3=OH, R_4=O, for its ketone) except for absolute configuration.



(I) (II) (III)

TABLE 1. PMR SPECTRAL DATA (δ in ppm,* in $CDCl_3$)

	Nigakihemiacetals		Nigakilactones	
	A	B	H	F
s-C<u>H</u>$_3$	1.11 d	1.07 d	1.15 d	1.11 d
	J=7	J=6	J=7.5	J=7
t-C<u>H</u>$_3$	1.20 s	1.05 s	1.27 s	1.22 s
	1.34 s	1.49 s	1.35 s	1.46 s
	1.44 s		1.50 s	1.46 s
C=C-C<u>H</u>$_3$		1.83 s		
<u>H</u>-C-OCH$_3$	2.98 d		3.02 d	3.03 d
	J=9		J=9	J=9
-O-C<u>H</u>$_3$	3.58 s	3.55 s	3.63 s	3.58 s
	3.69 s	3.61 s	3.77 s	3.73 s
<u>H</u>-C-OH	3.52 q		3.96 q	4.00 q
	J=11; 9		J=11; 9	J=11; 9
C<u>H</u>-O-	3.88 m	3.95 m	4.56 m	4.13 m
C=C<u>H</u>	5.40 d	5.25 d	5.51 d	5.43 d
	J=2.5	J=2.5	J=2.5	J=2

* internal standard; TMS

Spectral and some chemical data of nigakilactone G, mp 305—305.5°C, $C_{26}H_{34}O_8$, M^+ 474, $[\alpha]_D$+41° (c 0.29, in EtOH), λ_{max}^{MeOH} 271 nm (ε 5300), IR (Nujol): 3430, 1778, 1734, 1678, 1640 cm^{-1}, suggest that this substance would be identical with picrasin A[4] (III), whose structure was recently determined.[4] Confirmation of this identity is under way.

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4) H. Hikino, T. Ohta and T. Takemoto, *ibid.*, **18**, 1082 (1970).

5) Z. Valenta, S. Papadopoulos and C. Podešva, *Tetrahedron*, **15**, 100 (1961).