The Structures of Nigakilactones E and F

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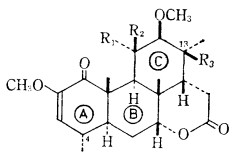
The isolation and determination of the structure of bitter principles (nigakilactones A, B, C and D (quassin)) of *Picrasma ailanthoides* Planchon have already been reported.[1] Two additional bitter principles have now been isolated from the same plant. These new bitter principles, nigakilactones E ($C_{24}H_{34}O_8$) and F($C_{22}H_{32}O_7$), contain one hydroxyl group more than nigakilactones C and B, respectively.

Nigakilactone F (I, R_1=OH, R_2=H, R_3=OH), mp 265—265.5°C, M^+ 408, $[\alpha]_D$ +46° (*c* 0.20, in EtOH), λ_{max}^{MeOH} 272 nm (ε 4500), IR (Nujol): 3530, 3470 sh, 3450, 1732, 1684, 1675, 1642, 1634 cm^{-1}, was obtained by the alkaline hydrolysis of nigakilactone E (I, R_1=OAc, R_2=H, R_3=OH), mp 280°C, M^+ 450, $[\alpha]_D$ +36° (*c* 0.22, in EtOH), λ_{max}^{MeOH} 264 nm (ε 4600), IR (Nujol): 3460, 1740, 1725 sh, 1717, 1642, 1255 cm^{-1}, which was not acetylated with acetic anhydride and pyridine.

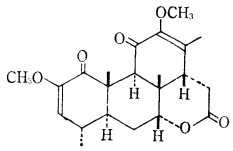
The NMR spectra (Table 1) of nigakilactones E and F are best interpreted on the basis of the skeletal structures of two known nigakilactones C (I, R_1=OAc, R_2=H, R_3=H) and B (I, R_1=OH, R_2=H, R_3=H), respectively. The spectra of nigakilactones C and B show the presence of two secondary and two tertiary methyls. However, those of nigakilactones E and F indicate the presence of one secondary and three tertiary methyls.

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

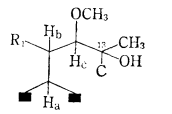
Nigakilactones	E	F	B	C
s-C<u>H</u>$_3$	1.08 d *J*=7	1.11 d *J*=7	1.00 d *J*=6.5 1.13 d *J*=6.5	1.01 d *J*=6 1.06 d *J*=7
t-C<u>H</u>$_3$	1.25 s 1.27 s 1.53 s	1.22 s 1.46 s 1.46 s	1.21 s 1.45 s	1.27 s 1.27 s
–O–CO–C<u>H</u>$_3$	1.98 s			1.95 s
<u>H</u>–C–OCH$_3$	3.38 d *J*=9	3.03 d *J*=9		
–O–C<u>H</u>$_3$	3.55 s 3.57 s	3.58 s 3.73 s	3.60 s 3.65 s	3.42 s 3.54 s
<u>H</u>–C–OH		4.00 q *J*=11; 9		
C–C<u>H</u>–O–	4.21 m	4.13 m	4.15 m	4.14 m
<u>H</u>–C–OAc	5.54 q *J*=11; 9			5.22 q *J*=11; 9
C=C<u>H</u>	5.17 d *J*=2.5	5.43 d *J*=2	5.45 d *J*=2.5	5.10 d *J*=2.5



I



II



III-a: R_1=OAc
III-b: R_1=OH
(■ indicates carbon with no proton)

These observations, along with the spectral data (Table 1), show that a hydroxyl group is located on C-13 (not on C-4) and lead to partial structures of III-a and -b for the ring C of nigakilactones E and F, respectively. The coupling costants of H_a–H_b (*J*=11 Hz) and H_b–H_c (*J*=9 Hz) indicate that two adjacent protons are in axial-axial relationships. One secondary methyl of nigakilactone E (and F) should be located on C-4. The facile dehydration of the ketone (I, R_1, R_2=O, R_3=OH) to yield II suggests that the hydroxyl group at C-13 is in axial conformation.

Thus, the structures of nigakilactones E and F are shown to be I (R_1=OAc, R_2=H, R_3=OH) and I(R_1=OH, R_2=H, R_3=OH), respectively.

1) T. Murae, T. Tsuyuki, T. Nishihama, S. Masuda and T. Takahashi, *Tetrahedron Lett.*, **1969**, 3013.

2) Z. Valenta, A. H. Gray, D. E. Orr, S. Papadopoulos and C. Podešva, *Tetrahedron*, **18**, 1433 (1962).