STRUCTURE OF FUROBINORDENTATIN, A NOVEL BICOUMARIN FROM *CITRUS YUKO*

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The structure of furobinordentatin, isolated from the root of *Citrus yuko* (Rutaceae), has been elucidated by spectroscopic studies and a single crystal X-ray analysis as **1**.

Furobinordentatin is a novel type of bicoumarin composed of two nordentatin (**2**) units linked with the forming of a dihydrofuran ring.

KEYWORDS bicoumarin; furobinordentatin; *Citrus yuko*; Rutaceae; dimer; crystal structure

Many new coumarins and acridone alkaloids have been isolated from *Citrus* plants.[1] In particular, novel type acridone-coumarin dimers (acrimarines[2] and neoacrimarines[3]) and bicoumarins[4] were characteristic constituents of *Citrus* plants. As part of our studies on the constituents of this family,[1] we studied the constituents of the root of *C. yuko* Hort. ex Tanaka[5] (Rutaceae) and isolated a novel bicoumarin, named furobinordentatin (**1**). This paper deals with the structure elucidation of this new bicoumarin on the basis of spectroscopic data and X-ray crystal analysis.

Furobinordentatin (**1**), mp 225-227°C was obtained as racemic colorless cubes (from acetone) in 2.9×10^{-6}% yield. The molecular formula $C_{38}H_{40}O_9$ [M^+ 640.2675. Calcd. 640.2672] was established by HR-MS. The UV [λ_{max}(EtOH): 228 (sh), 265, 283 and 329 nm] and IR [ν_{max} ($CHCl_3$): 1720 and 1625 cm^{-1}] absorptions indicated the presence of a 5,7-dioxygenated coumarin nucleus.[6] The ^1H and ^{13}C-NMR spectra including ^1H-^1H COSY and HMQC technique indicated the presence of two pairs of characteristic signals of H-4 and H-3 [δ_H 8.19, 6.19, 8.03, 6.12 (each 1H, d, J= 9.5 Hz)] of coumarin skeleton, two geminal dimethyls [δ_H 1.43, 1.22, 1.46, 1.58 (each 3H, s)], and two 1,1-dimethylallyl groups [δ_H 6.23, 6.22 (each 1H, dd, J= 11.0, 17.6 Hz), 4.84 (1H, d, J= 17.6 Hz), 4.82 (1H, d, J= 11.0 Hz), 4.81 (1H, d, J= 17.6 Hz), 4.80 (1H, d, J= 11.0 Hz), 1.61, 1.58 (each 3H, s), 1.57 (6H, s)]. The partial structure of -(O)-C(11)H-C(10)H-C(10')H-C(11')-(O)- was shown by the four proton signals [δ_H 4.72 (1H, d, J=11.0 Hz), 1.90 (1H, dd, J=8.1, 11.0 Hz), 2.70 (1H, t, J=8.1 Hz), 5.17 (1H, d, J= 8.1 Hz)] and four carbon signals [δ_C 73.86, 52.08, 45.60, 74.40]. In HMBC spectrum, ^2J and ^3J correlations were observed for H-11' (δ_H 5.17)/C-6' (δ_C 106.61), C-7' (δ_C 155.23), C-9' (δ_C 77.87) and C-10' (δ_C 45.60), which indicated the linear orientation of pyranocoumarin nucleus. Treatment of **1** with diazomethane afforded O,O'-dimethylether (**3**). In NOE experiment on **3**, irradiation of the methoxy signal at δ 4.12 showed increments on the signal at δ 7.93 (H-4') and 5.13 (H-11') and irradiation the signal at δ 3.75 showed increments on the signal at δ 7.87 (H-4) and 4.69 (H-11), supporting the estimation of the linear orientations of two pyranocoumarin nuclei. The NOEs were also observed between the signal at δ 5.13 (H-11'), 2.41 (H-10') and 4.69 (H-11) indicating the

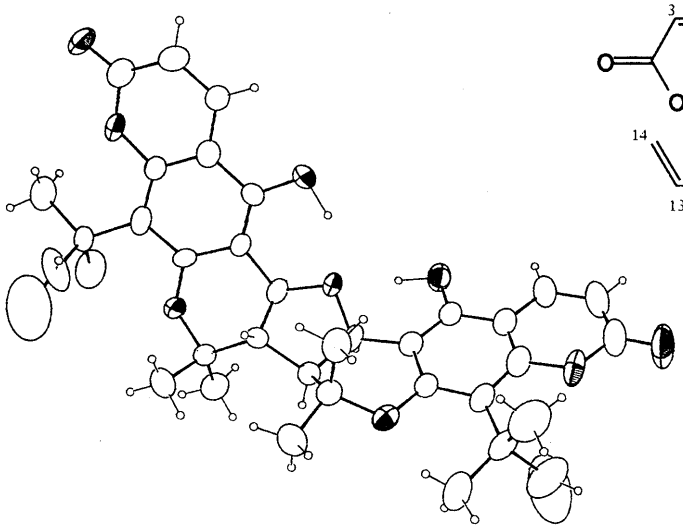
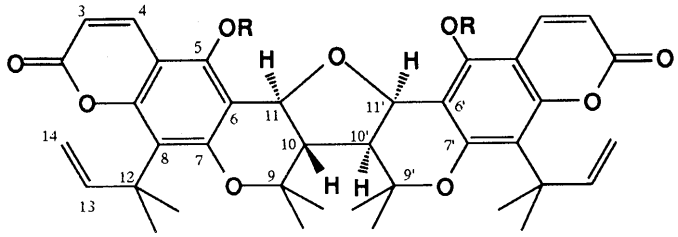
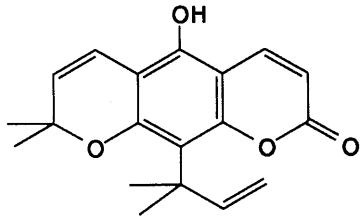


Fig.1



(1) R=H

(3) R=CH_3



(2)

cis relationships of these three protons. On the basis of these results, the structure of furobinordentatin was assigned to **1** composed of two nordentatin (**2**)[7] units linked with the forming of dihydropyran ring. The complete structure and the relative stereochemistry were unequivocally established by X-ray analysis[8] as shown in Fig. **1**.

Furobinordentatin is the first bicoumarin linked with the forming of dihydrofuran ring between pyran ring of linear pyranocoumarin.

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8) Crystal data for **1**. $C_{38}H_{40}O_9$, M= 640.7, triclinic, a=9.768 (1), b= 12.706 (1), c= 13.847 (3)Å^3, α=80.79 (1), β= 81.87 (1), γ=82.07 (1)°, V= 1667 (4)Å^3, Z=2, space group $P\bar{1}$, Dc=1.276 g/cm^3. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation. The structure was solved by direct methods using MULTAN 82 and refined by least-squares techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Final cycles of two-blocked matrix least-squares refinement were carried to convergence at R= 0.079.

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