# Cucurbitacin F in Seeds of *Kageneckia angustifolia* (Rosaceae)

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Cucurbitacin F and the cyanogenetic compounds prunasin were isolated and identified from the seeds of *Kageneckia angustifolia*.

## Introduction

*Kageneckia angustifolia* D. Don (Rosaceae) is an endemic 3 m tall tree of a sclerophyll forest from Central Chile, and protected by law (Benoit, 1989). Vernacular name of this plant is ölivillo“ and it appears edible for livestocks. Birds eat the seeds of Chilean *Kageneckia*. We observe no plants growing underneath the tree canopy, allelopathic and toxic effects probably affects also insects. On the other hand Peñaloza *et al.* (2001) have observed a nurture intra-specific effect of *K. angustifolia* on the germination of seeds and survival of the plant lets in the mountain sclerophyll forest.

Previous works in Chilean *Kageneckia* species reports the occurrence of several cucurbitacins and triterpenoids in *K. oblonga*, as well as the determination of biological activities including antineoplastic assays (Muñoz *et al.*, 2000).

Continuing the investigations and our research on the pharmacologically active compounds, we report the isolation and structure elucidation of cucurbitacin and prunasin of the seeds of *Kageneckia angustifolia.*

## Materials and Methods

$H^1$ NMR and $^{13}$CNMR were run in $CDCl_3$, DMSO-$d_6$ at 200 MHz and 500 MHz, respectively, with TMS as int. Standard HMBC and HMQC were recorded by a Bruker AMX 400 spectrometer.

### *Seed material*

*Kageneckia angustifolia* D. Don seeds were collected in December 1993 and 1994 in Farellones (Metropolitan Region Chile), and identified by Prof. A. Peñaloza (Univ. de Chile). A voucher sample is kept in Faculty of Sciences of our University.

### *Extraction and isolation*

Ground seeds of *K.angustifolia* were extracted with MeOH-$H_2O$ (3.0 l : 0.8) at room temperature and the extract (0.12 kg) was partitioned between *n*-BuOH and water.

The concentrated *n*-BuOH soluble portion was subjected to silica gel CC with $CH_2Cl_2$-MeOH-$H_2O$(9:1:0.1 v/v/v) to afford three fractions (1, 2, 3). Frs. 1 and 2 were repeatedly chromatographed on silica gel ($CH_2Cl_2$-MeOH-$H_20$) (8:2:0.1 v/v) and $CH_2Cl_2$-MeOH (1:1 v/v) to afford compound **1** (121 mg). Acetylation of compound 1 (1.25 mg) was treated with $Ac_2O$-pyridine (1:1.5 ml) at room temperature overnight. Work-up in the usual manner afforded a triacetate (2.15 mg) as an amorphous powder. Compound **2** was identified as 2, 3, 16-tri-acetyl cucurbitacin F by comparison with reported spectral data (Fang *et al.*, 1989). Fraction 3 was chromatographed on silica gel ($CH_2Cl_2$-MeOH) (1:1 v/v) and affords compound **3** (1.2 g).

## Results

Repeated chromatography of the MeOH extract of *K. angustifolia* seeds, followed by crystalliza-

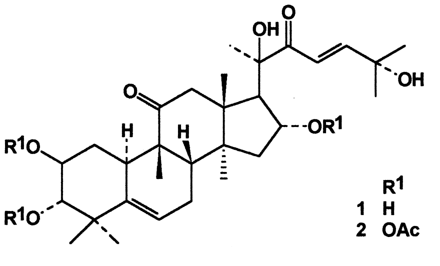

Fig. 1. **1**, Cucurbitacin F and **2**. 2, 3,16 triacetate-15-oxo-23,24-dihydroxycucurbitacin.

tion, led to the isolation of a small amount of a compound **1** identified as cucurbitacin F by comparison with previously reported $^1$H and $^{13}$C NMR spectral data (Fang *et al.*, 1984, Mata *et al.*, 1988). Further the triacetate **2** was derived from **1**, and also identified by comparison with reported spectral data (Konoshima *et al.*, 1993). Curcubitacin F 1(121 mg), $^1$HNMR (400 MHz, pyridine-$d_5$) 1. 210 (s, -$CH_3$),1.240 (s, -$CH_3$), 1.296 (s, -$CH_3$), 1.430 (s, -$CH_3$), 1.453 (s,-$CH_3$), 1.474 (s,-$CH_3$), 1.502 (s, -$CH_3$), 1.547 (d, $J$ = 10.2 Hz, H-1 β), 1.599 (s,-$CH_3$), 1.717 (d, $J$ = 13.0 Hz, H-15β), 1.901 (m, H-7β), 1.927 (d, $J$ = 8.1 Hz, H-8), 2.333 (dm, H-7α), 2.449 (ddd, $J$ = 3.8, 3.9, 12.0 Hz, H-1α) , 2.714 (br d, $J$ = 12.4 Hz, H-10), 2.784 (d, $J$ = 14.5 Hz, H-12β), 2.992 (d, $J$ = 7.0Hz, H-17), 3.164 (d, $J$ = 14.6 Hz, H-12α) 3.426 (dd, $J$ = 4.8, 9.0 Hz, H-3), 4.139 (m, H-2), 4.988 (m, H-16), 5.716 (br d, $J$ = 5.4 Hz, H-6), 5.902 (s, 0H-20 or OH-25), 6.185 (d, $J$ = 5.0 Hz, OH-2), 6.255 (d, $J$ = 4.8 Hz, OH-16), 6.368 (d, $J$ = 4.7 Hz, OH-3), 6.731 ( s, OH-20 or OH-25) , 7.482 (d, $J$ = 15.5 Hz, H-23), 7.555 (d, $J$ = 15.4 Hz, H-24).

Direct comparison of NMR spectrum of **1** with those 15-oxo-23, 24-dihydroxycurcubitacin F (Konoshima *et al.*, 1993) revealed the structural similarity of both compounds showing that the A-B ring residue and the side-chain at C-17 were similar. A detailed structural elucidation of **1** was carried out using two dimensional (2D)-NMR spectra and difference nuclear Overhauser effect (NOE) experiments. All the proton and carbon signals of **1** could be assigned using $^1$H-H correlation spectroscopy (COSY) and 2D (COSY, HMQC, HMBC, ROESY) experiments. Compound **3** was identified as prunasin (Maldonado *et al.*, 1997).

Although none of the compounds isolated in this study were new natural products, this is the first time that the occurrence is reported in Chilean *Kageneckia*, and could explain the allelopathic effect of the seeds.

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