Fevicordin A and Fevicordin A Glucoside, Novel Norcucurbitacins from *Fevillea cordifolia*

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From the seeds of the Central American *Fevillea cordifolia* (Cucurbitaceae) fevicordin A glucoside (**1**) and fevicordin A (**2**), members of the novel norcucurbitacin group, were isolated.

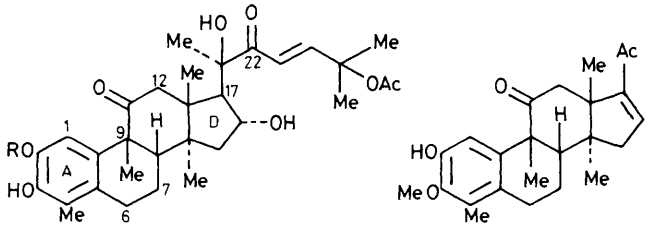
The seeds of the Central American plant *Fevillea cordifolia* (Cucurbitaceae) have given fevicordin A glucoside (**1**) and fevicordin A (**2**),† which are the first members of the novel norcucurbitacin group. Their structures were assigned as follows.

The desorption chemical ionisation mass spectra (NH_3) of (**1**) and (**2**) show the $[M + NH_4]^+$ ions at *m/z* 722 and 560, respectively. The glycosidic linkage of (**1**) can be cleft by cellulase yielding (**2**), which constitutes only a minor natural component. The glucose moiety in (**1**) was evident from the ^1H and ^{13}C n.m.r. spectra of the isolated compound and its acetyl derivative as was the β-configuration at the anomeric centre.[1,2]

The u.v. spectrum of (**1**) exhibits maxima at 224 (log ε 4.15) and 285 (3.35) nm. On catalytic hydrogenation a dihydro-derivative is produced, in which only the short-wave maximum shifts to $\lambda_{max.}$ 228 nm with a simultaneous significant decrease in the value of the extinction coefficient (log ε 4.15 → 3.86). These data can be explained by the presence of an α,β-unsaturated carbonyl group and a benzene ring system. The latter is hydroxy-substituted because of the bathochromic shift of the long wavelength maximum on addition of NaOH.

N.m.r. studies, particularly comparison with the ^{13}C n.m.r. data published for cucurbitacin E,[1,3] helped to establish the structure of rings B, C, and D, and the structure of the side chain at C-17. The structure of the aromatic ring A was mainly assigned from n.m.r. studies of the 2,3-di-*O*-methyl derivative of (**2**) and of 2,3-dimethoxy-1-methyltetralin, which was synthesized for comparison. Evidence for C-1 being unsubstituted and for the presence of the methyl group at C-4 comes from heteronuclear two-dimensional n.m.r. (shift correlated) studies, which showed long-range coupling between 1-H and C-9, C-3, C-5, between the 4-Me group and C-3, C-4, C-5, and between CH_2-6 and C-4, C-5. The direct proximity of the hydroxy-groups in ring A is shown by the easy oxidation (dehydrogenation) of (**2**) and the formation of a methylene-dioxy derivative on treatment with CH_2Br_2/CsF.[4]

Compound (**3**) is obtained by degradation of the monomethyl derivative of (**1**) with, successively, $NaBH_4$,



(**1**) R = β-glucosyl
(**2**) R = H

(**3**)

† By chromatography of the methanolic or dichloromethane extract of the endosperm.

$NaIO_4$, and H^+/H_2O, and it contains as the only free hydroxy-group the one which was involved in the glucosidic linkage. Acetylation of (**3**) causes shifts to low field of the ^{13}C resonances of C-1 (δ 110.6 to 118.2), C-3 (δ 144.0 to 148.2), and C-5 (δ 126.3 to 133.0). Therefore, this hydroxy-group, and in consequence the glucosidic linkage in (**1**) must be at C-2.

The relative configuration depicted in (**1**) and (**2**) is derived from the ^{13}C n.m.r. data[3] and from nuclear Overhauser enhancement studies of 2,3-di-*O*-methyl-(**2**) and of cucurbitacin I (= elatericin B).[3,5]

Compounds (**1**) and (**2**) are the first members of the hitherto unknown group of norcucurbitacins, which structurally differ from the known cucurbitacins by loss of one of the geminal methyl groups at C-4 and an aromatized ring A.

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