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AN ISOPENTENYLFLAVANONE FROM *EVODIA RUTAECARPA*

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The isolation of a flavanone glucoside-B, mp 245–248°, from the leaves of *Evodia rutaecarpa* Hook has previously been reported [1]. The glucoside yielded *p*-coumaric acid and phloroglucinol on heating with alkali. We now present evidence for the structure of this glucoside showing that the flavanone A-ring carries an isopentenyl substituent which is lost during the degradation with alkali. A few other isopentenyl flavones are known and a summary of their occurrence has been given [2, 3].

Compound-B analyses for a diglucoside. The elemental analysis and mass spectral data indicate the aglucone to have a molecular formula $C_{20}H_{20}O_5$. The glucoside shows the UV spectrum (MeOH) expected for a flavanone derivative [4] with λ_{max} 288 nm (log ϵ 4·10) and 340 nm (log ϵ 3·46). The UV spectrum was unchanged on addition of NaOAc + H_3BO_3, addition of NaOMe caused no change in absorbance but a shift of the long wavelength band only to 365 nm. $AlCl_3$ caused a small increase in intensity and a shift of both absorption bands to λ_{max} 312 and 400 nm, unchanged after the further addition of HCl. This indicates the presence of a free 5-hydroxyl and the absence of a free 7-hydroxyl group [4].

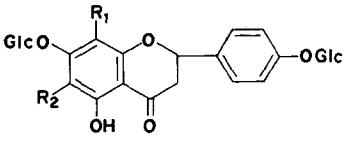
Glucoside-B gave a mass spectrum containing a strong ion, *m/e* 340, due to the aglucone and a weak ion, *m/e* 502 corresponding to monoglucoside. The molecular ion was not seen. Further fragmentation to ions with *m/e* 340 (100%), 325 (16), 297 (23), 285 (46), 220 (20), 192 (33), 177 (33), 165 (100), 120 (33) can be rationalised as follows. The fragment *m/e* 120 is assigned to the product from the usual reverse Diels–Alder cleavage of the aglucone heterocyclic ring since alkali degradation is known to yield *p*-coumaric acid. The second Diels–Alder fragment must then have *m/e* 220 which corresponds to the ring-A fragment from a flavanone with the addition of a C_5H_9 moiety. Phloroglucinol is another product from alkali degradation of the glucoside so ring-A must be derived from a pentyl substituted phloroglucinol.

The NMR spectrum (DMSO-d_6) of glucoside-B showed one phenolic hydroxyl proton at τ −2·1 which, because it is so far downfield, must be from a 5-OH group. There is a single resonance at τ 8·42 due to two methyl groups. From this and biogenetic considerations, the C_5H_9 moiety must be either an isopentenyl group or form part of a 2,2-dimethyl chroman ring by cyclisation on an adjacent phenolic group. The following positions for methyl proton resonances were recorded (DMSO-d_6) for comparison: 2-methylbutan-2-ol τ 8·94, 7-hydroxy-2,2-dimethylchroman τ 8·75, 7-hydroxy-8-(3-methylbut-2-enyl)coumarin τ 8·20 and 8·32. From the position of its methyl resonance, the C_5H_9 chain in glucoside-B appears to be a 3-methylbut-2-enyl group. The spectrum lacks a triplet around τ 8·3 which can be attributed to a non-benzylic CH_2 group and this supports our deduction on the nature of the C_5H_9 chain. This region of the spectrum is not obscured by lines attributed to the solvent. The two methyl groups in a 3-methylbut-2-enyl substituent are expected to give rise to separate NMR signals but in some derivatives the signals are coincident [2].

Fragmentation of the C_5-chain in the mass spectrometer with loss of Me · and C_4H_7 · radicals is characteristic both of substances where the chain is present as a 3-methylbut-2-enyl substituent or cyclised in the corresponding 2,2-dimethylchroman. Recent work on prenylated flavanones and chalcones from *Cordoa piaca* [2] and a prenylated flavone from *Phebalium dentatum* [3] illustrates this. In our example, the open chain may cyclise onto an adjacent phenolic group to give a 2,2-dimethylchroman in the inlet system of the mass spectrometer.

The aromatic proton region of the NMR spectrum of glucoside-B shows an A_2B_2 quartet with τ 2·56 and 2·92, J 9Hz, attributable to the protons on ring-B. The signal at τ 2·92 is attributed to the 3′,5′-protons, it is moved downfield relative to the position (τ 3·20) for other 4′-hydroxyl flavanones indicating that the 4′-hydroxyl group is glucosylated [5]. There is also a one proton singlet at τ 3·73 due to the proton on ring-A. Its position is consistent with the proton being adjacent to an etherefied 7-OH group (compare hesperitin, 6,8-protons at τ 4·05 with its 7-methyl ether, τ 3·81 and 3·87) [5] but it is not possible to decide whether this is a 6- or an 8-proton.

Thus glucoside-B is considered to be the 4′,7-diglucoside of 6- or 8-(3-methylbut-2-enyl)-4′,5,7-trihydroxyflavanone (**1**). It shows a strong Cotton effect in its ORD-curve and a comparison with the ORD-curves of naringin and hesperidin [6] indicates a high degree of optical purity and the 2S-configuration for glucoside-B.



(1) $R_1 = CH_2CH = CMe_2$, $R_2 = H$
or *vice versa*

Extraction of the leaves of *Evodia rutaecarpa* as previously described [1] gave glucoside B, m.p. 245–248°, (Found: C, 56·3; H, 6·1; glucose, 43·5. $C_{32}H_{40}O_{15} \cdot H_2O$ requires C, 56·3; H, 6·7; 2 glucose, 48·8; 1 glucose 32·3%) $[\alpha]_D$ −47° (c 0·7 in MeOH pyridine), ORD-curve (c 0·098 in EtOH) $[\phi]_{297}$ −41000 (tr), $[\phi]_{284}$ O, $[\phi]_{270}$ + 28000 (pk), $[\phi]_{250}$ + 15000.

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