A Mass Spectrometric Criterion for Determining the B- and E-Ring Hydroxylation Pattern in Dimeric Biflavanoids

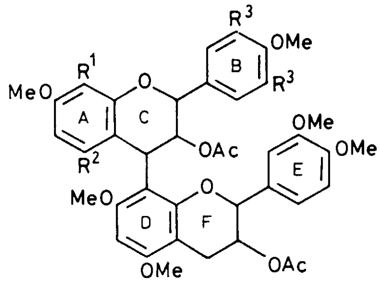
Jan A. Delcour* and Geert M. Tuytens

Laboratorium voor Toegepaste Organische Scheikunde, Katholieke Universiteit te Leuven, Kardinaal Mercierlaan 92, B-3030 Heverlee, Belgium

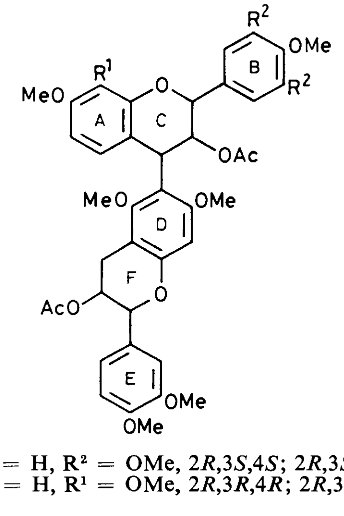
Since only the ions with *m/z* corresponding to retro-Diels–Alder fragmentation products consisting of the original A-, B-, C-, and D-rings can be observed by the low-resolution mass spectra of the methyl ether diacetates of biflavanoids these ions can be used to determine the hydroxylation patterns of the B- and E-rings of unknown dimeric biflavanoids provided ^{1}H n.m.r. data are available as well.

The chemistry of the dimeric procyanidins is well understood.[1–3] In the past few years significant work has also been devoted to other biflavanoids.[4–6] Methyl ether acetates of biflavanoids have in the past proved to be useful derivatives to allow the differentiation between the alternatives of C(4)–C(6″) and C(4)–C(8″) interflavanoid links by ^{1}H n.m.r. spectroscopy,[3,7] to allow good mass spectra to be obtained, and to allow for a purification after each derivatisation step.[5] We here show that these derivatives have the further advantage that by interpretation of their mass and ^{1}H n.m.r. spectra the hydroxylation pattern of the B- and E-rings can be deduced, a feature up to now not possible with ^{1}H n.m.r. spectroscopy, but only possible through degradations of the pure phenolic substances and chromatography of the resultant products.[2]

Thus, in the case of derivatives of prodelphinidin B3 (**1**), a second biflavanoid (**2**) isolated from beer,[8,9] and also the five synthetic biflavanoids[5] (**3**)–(**7**), only the ions with *m/z* values corresponding to retro-Diels–Alder fragmentation products[1] consisting of the original A, B-, C-, and D-rings can be observed. Indeed, if retro-Diels–Alder fragmentation in the 'lower' flavan unit (after a loss of acetic acid in the 'upper' unit) of (**1**) and (**2**) is detectable, an ion with *m/z* 522 is expected. If the opposite breakdown process (loss of acetic acid in the 'lower' unit, retro-Diels–Alder fragmentation in the 'upper' unit) is detectable, an ion with *m/z* 492 will be observed. Since only ions with *m/z* 522 were observed, we concluded that only the retro-Diels–Alder fragmentation products consisting of the original A-, B-, C-, and D-rings are detectable. In the case of the synthetic biflavanoid derivatives[5] (**3**)—(**7**) we found ions at *m/z* 492, 492, 462, 492, and 462, respectively, all indicative of retro-Diels–Alder fragmentation ions as in the case of (**1**) and (**2**). If the alternative breakdown pattern were to be detectable we should have observed peaks at *m/z* 462, 462, 492, 462, and 492, respectively. This fragmentation probably occurs as well since the retro-Diels–Alder fragments consisting of the original B-ring are found in the case of (**3**), *m/z* 252; (**4**), 252; (**5**), 192; (**6**), 252; and (**7**), 192. Since in the spectra of (**1**), (**2**), (**5**), (**7**) the ions with *m/z* 222 (corresponding to the original E-rings) are found, these ions can be of no diagnostic value.



(**1**) R^1 = H, R^2 = R^3 = OMe, 2*R*,3*S*,4*S*; 2*R*,3*S*
(**2**) R^1 = H, R^2 = R^3 = OMe, 2*R*,3*R*,4*S*; 2*R*,3*S*
(**3**) R^1 = R^2 = H, R^3 = OMe, 2*R*,3*S*,4*R*; 2*R*,3*S*
(**4**) R^1 = R^2 = H, R^3 = OMe, 2*R*,3*S*,4*S*; 2*R*,3*S*
(**5**) R^2 = R^3 = H, R^1 = OMe, 2*R*,3*R*,4*R*; 2*R*,3*S*



(**6**) R^1 = H, R^2 = OMe, 2*R*,3*S*,4*S*; 2*R*,3*S*
(**7**) R^2 = H, R^1 = OMe, 2*R*,3*R*,4*R*; 2*R*,3*S*

From the above it is clear that, for example, a biflavanoid such as prodelphinidin B3 can be distinguished from a dimer having (+)-catechin as 'upper' unit and (+)-gallocatechin as the 'terminal' unit by mass spectrometry of the methyl ether diacetate derivative. It is further obvious that ^{1}H n.m.r. spectroscopy is less adequate in this respect.

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