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The Phytoalexins of Oat Leaves: 4H-3,1-Benzoxazin-4-ones or Amides?

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SUMMARY: Synthetic evidence is presented that the major phytoalexin of oat leaves is not the 4-H-3,1-benzoxazin-4-one previously reported, but the corresponding amide. Other oat and carnation phytoalexins are prepared.

The phytoalexins of oat leaves produced on infection with an incompatible race of oat crown rust (Puccinia coronata f. sp. avenae) have been isolated.[1,2] The major phytoalexin is reported to be (1), avenalumin I, which occurs with related minor components avenalumins II (2) and III (11). In connection with our earlier interests in the defence compounds of oat roots against fungal attack[3] we have made specimens of avenalumins I and II, together with the open hydrated forms, the avenanthramides A (6) and B (7) which are reported to occur in oat groats and hulls.[4] Other simlar avenanthramides e.g (8), (9) and (10) are found in the latter source whilst a 4-H-3,1-benzoxazin-4-one (12)[5] and related amides (13)and (14)[6,7] are reported as phytoalexins in the carnation plant.

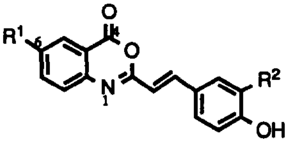
Corresponding compounds of the synthetic avenalumin and aventhramide series can be distinguished in terms of infra-red carbonyl stretching frequencies, v_{max}~1755 and 1650 cm^{-1} for (1) and (6) respectively, but these data were not reported for natural avenalumin I and much of the structural work was done on on the diacetate (17). However, ^1H and ^{13}C nmr data are reported for the natural material[1] and critical data for this and our synthetic avenalumin I (1) and its avenanthramide A (6) are compared in Table 1. The data indicate that the natural phytoalexin is in fact the open amide and not the benzoxazinone.

TABLE I. Comparative Data for Natural Oat-Leaf Phytoalexin with Synthetic Avenalumin I and Aveanthramide A .

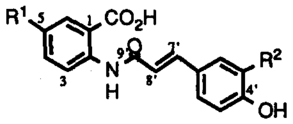
Nucleus	Synthetic Avenanthramide A	Natural (Reassigned) [a,b]	Synthetic Avenalumin 1 [b]	Natural (Lit.) [1,b]
3-^1H	8.37(1H,d,J9.0Hz)	8.40(1H,d,J9.0Hz)	7.84(1H,d,J8.7Hz)	8.40(1H,d,J9.0Hz)
2-^{13}C	132.9	133.0	139.5	133.0
3-^{13}CH	122.3	119.4	128.2	117.4,118.5 or119.4
5-^{13}C	152.4	151.6	151.6	162.9
7-^{13}C	163.6	162.9	159.5	170.7
8'-^{13}CH	118.9	118.5	111.4	116.7
9'-^{13}C	169.2	170.7	158.9	151.6

[a] Reassigned by aromatic shift calculation and other considerations.
[b] Avenanthramide numbering is used for the comparison.

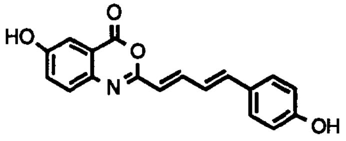
Both (1) and (6) give (17) under suitable acetylation conditions. The latter acetate was made by condensing 2-methyl-6-acetoxybenzoxazin-4-one with 4-acetoxybenzaldehyde. This was deacetylated using sodium borohydride in dimethoxyethane[1] but chemical comparison with the natural phytoalexin is not reported, though it is said to have the same antifungal activity as the natural product.[1] In our hands this procedure was inefficient so (17) was hydrolysed to the amide (6) and then recyclised using trifluoroacetic anhydride (TFAA) in tetrahydrofuran: the readily hydrolysed O-trifluoroacetyl groups are removed during work-up. Avenalumin II and avenanthramide B were made by a similar procedure.



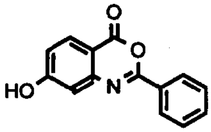
(1) $R^1 = OH, R^2 = H$ (4) $R^1 = H, R^2 = H$
(2) $R^1 = OH, R^2 = OMe$ (5) $R^1 = H, R^2 = OMe$
(3) $R^1 = OH, R^2 = OH$



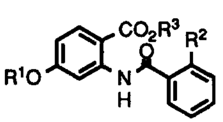
(6) $R^1 = OH, R^2 = H$ (9) $R^1 = H, R^2 = H$
(7) $R^1 = OH, R^2 = OMe$ (10) $R^1 = H, R^2 = OMe$
(8) $R^1 = OH, R^2 = OH$



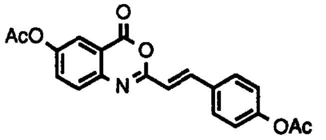
(11)



(12)



(13) $R^1 = Me, R^2 = OH, R^3 = H$
(14) $R^1 = H, R^2 = OH, R^3 = Me$
(15) $R^1 = H, R^2 = OH, R^3 = H$
(16) $R^1 = H, R^2 = H, R^3 = H$



(17)

Avenanthramides C (8), D (9), and E (10) were all conveniently prepared by base hydrolysis of the corresponding benzoxazinones (3) - (5) which are easily accessible by Bain and Smalley's method.[8] The reported carnation phytoalexin (12) was made by acylation of 2-amino-4-hydroxybenzoic acid with benzoyl chloride in the presence of aqeous sodium carbonate which gave (16) cyclised to the benzoxazinone (12) by TFAA. The carnation phytoalexin (15) was made by hydrolysis of the acetate derived from the reaction of 2-amino-4-hydroxybenzoic acid with acetylsalicoyl chloride. There seems no direct evidence on the question of whether benzoxazinones are phytoalexins in addition to amides but their ease of hydrolysis in some cases, along with the above evidence regarding avenalumin I, makes it questionable.

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