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SHORT COMMUNICATION

HYDROXYCINNAMIC ACID DERIVATIVES OF *RHEUM RHAPONTICUM**

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Abstract—Further work on the polyphenols of *Rheum rhaponticum* has led to the isolation of a range of hydroxycinnamic acid derivatives. Compounds identified were the 1-glucose esters of ferulic, sinapic and *p*-coumaric acids. Several other feruloyl derivatives were found, some of which must have complex structures.

INTRODUCTION

ANALYSIS of rhubarb, *Rheum rhaponticum*, has led to the identification of two anthocyanins[1] and a number of flavanols.[2] This paper reports the isolation of a number of hydroxycinnamic acid derivatives from the petiole of this species.

Bate-Smith[3] observed hydroxycinnamic acids in the acid hydrolysates of plant extracts which must have been present in the living tissues in some combined form. Harborne and Corner[4] isolated a large range of simple sugar esters of these acids, and provided evidence that they were of wide occurrence in plants. Corner *et al.*[5] showed that complex derivatives of ferulic and sinapic acids occurred in *Polygala senega.*

RESULTS AND DISCUSSION

The compounds were identified on the basis of their chromatographic and spectrophotometric properties. All the compounds were hydrolysed to the aglycone and sugar or other residue, and where sufficient material was available the ratio of hydrolysis products was determined. The chromatographic properties of the compounds isolated is shown in Table 1, and the spectrophotometric and hydrolysis data in Table 2.

All the compounds were hydrolysed by alkali in the cold and must contain an ester linkage. Four compounds FE1, FE2, SN1 and PC1 gave equimolecular amounts of the respective hydroxycinnamic acid and glucose and comparison of R_fs with those published by other workers[4] has led to identification as follows: FE2—1-feruloylglucose; SN1—1-sinaoylglucose; PC1—1-*p*-coumaroylglucose. The further compound, FE1, which also gave ferulic acid and glucose in a 1:1 ratio must be an isomer of feruloylglucose. It is not possible to ascertain positively which carbon atom of the sugar is linked to the ferulic acid, but comparison

* Part II in the series "Polyphenols of *Rheum rhaponticum*;" for Part I, see Ref. 2.

[1] R. A. GALLOP, *Sci. Bull. No.* 5, *Fruit and Veg. Canning Quick Freez. Res. Assoc.* (1965).
[2] H. A. W. BLUNDSTONE, *Phytochem.* 6, 1449 (1967).
[3] E. C. BATE-SMITH, *Chem. & Ind.* 1457 (1954).
[4] J. B. HARBORNE and J. J. CORNER, *Biochem. J.* 81, 242 (1961).
[5] J. J. CORNER, J. B. HARBORNE, S. G. HUMPHRIES and W. D. OLLIS, *Phytochem.* 1, 73 (1962).

with the data of Birkofer[6] suggests 6-feruloylglucose as the most likely identity. This isomer is the only one with R_fs appreciably lower than all the other isomers in alcoholic solvents.

Compound FEQ gave a 2:1 ratio of ferulic acid to glucose and was complex in its chromatographic behaviour; two other derivatives of ferulic acid, FE3 and FE5 both gave a greater proportion of ferulic acid to glucose on hydrolysis, but the small amounts of these compounds isolated prevented further structural investigation.

A second derivative of *p*-coumaric acid, PC2, was isolated. This gave no sugar on hydrolysis and a possible quinic acid spot was observed amongst the hydrolysis products. When PC2

TABLE 1. R_fS AND COLOURS OF THE HYDROXYCINNAMIC ACID DERIVATIVES IN RHUBARB

Compound	R_f (× 100) Whatman No. 1 paper in BN	BEW	BAW	R_f (× 100) cellulose TLC 6% HOAc	Colour u.v.	u.v. + NH_3
FE1	11	43	44	72/84	blue	blue-green
FE2	22	60	59	68/76		
FE3	23	52	58	55/76		
FE5	72	84		38/58		
FEQ	13	65	69	25/37/51		
SN1	18	54	53	60/70		green
PC1	27	61	65	61/80	—	blue
PC2	10	42	70	56/78	—	

For solvent key, see Experimental.

TABLE 2. SPECTROPHOTOMETRIC AND HYDROLYSIS DATA ON HYDROXYCINNAMIC ACID DERIVATIVES FROM RHUBARB

Compound	Spectral maxima (nm) EtOH	EtOH + NaOEt	Hydrolysis products and ratios
FE1	323 (301)	380	Ferulic acid (1·0), glucose (0·9)
FE2	328 (302)	382	Ferulic acid (1·0), glucose (1·0)
FE3	329 (302)	388	Ferulic acid (5·0), glucose (1·0)
FE5	326 (300)	380	Ferulic acid, glucose (trace)
FEQ	329 (300)	387	Ferulic acid (2·0), glucose (1·0)
SN1	330	400	Sinapic acid (1·0), glucose (1·0)
PC1	313	370	*p*-Coumaric acid (1·0), glucose (1·3)
PC2	312	368	*p*-Coumaric acid, quinic acid (?)

was chromatographed with 3-*O*-*p*-coumaroylquinic acid, it separated from it although the R_fs were very close. It is possible that this compound is a *p*-coumaroylquinic acid with a linkage through a carbon atom other than number 3. This would be quite feasible as caffeic acid derivatives have been observed where the linkage is through the 4 and 5 hydroxyl groups of quinic acid.[7]

Rhubarb is interesting in the large range of ferulic acid derivatives which it contains, and these range from simple glucosides to more complex molecules. It is also interesting that no

[6] L. BIRKOFER, C. KAISER, M. DONIKE and W. KOCH, *Z. Naturforsch.* **20b**, 424 (1965).
[7] M. L. SCARPATI, and P. ESPOSITO, *Tetrahedron Letters* 1147 (1963).

caffeic acid derivatives were isolated, in spite of the fact that the anthocyanins and flavonols in rhubarb have the orthodihydroxyl grouping in the B ring.

EXPERIMENTAL

Extraction and Purification

Fresh rhubarb petiole was cut into small pieces and extracted three times in boiling 80% methanol containing 1% acetic acid. The extract was concentrated and extracted with petroleum spirit (60–80° B.R.) to remove chlorophyll. The concentrated extract was applied to a column of polyvinyl pyrrolidone (PVP) and washed with water. The hydroxycinnamic acid derivatives were eluted with 80% methanol and the bands were separated on a fraction collector. The compounds were detected by TLC in u.v. light and purified by streaking on 3 MM paper and running in the solvents used for identification.

Identification

The purified compounds were identified by chromatography in BN (*n*-BuOH–2 N-NH_4OH, 1:1 BEW (*n*-BuOH–EtOH–H_2O, 4:1:2·2) and BAW (*n*-BuOH–HOAc–H_2O, 4:1:5) on Whatman No. 1 paper (ascending) and in 6% HOAc by cellulose TLC. Spectra were measured in absolute ethanol. Hydrolysis was carried out in 2 N NaOH at 20° followed by neutralization with Zeo Karb 225 resin. An aliquot of the neutral hydrolysate was spotted on Whatman No. 1 paper with standard glucose (four concentrations). The sheet was run in EtOAc–HOAc–H_2O (9:2:2) and sprayed with aniline phthalate followed by heating at 110° for 5 min. The spots were cut out and eluted in HOAc for 12 hr. The absorbance was measured at 400 nm.

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