Phytochemistry, 1965, Vol. 4, pp. 977 to 979. Pergamon Press Ltd. Printed in England

SHORT COMMUNICATION

IDENTIFICATION OF NEOCHLOROGENIC AND 3-*O*-FERULOYLQUINIC ACIDS IN TOMATO PLANTS

J. VAN BRAGT,* L. M. ROHRBAUGH and S. H. WENDER

Chemistry and Botany–Microbiology Departments, University of Oklahoma, Norman, Oklahoma, U.S.A.

(*Received* 9 *February* 1965)

Abstract—Neochlorogenic and 3-*O*-feruloylquinic acids have been identified for the first time in the leaves, stems, and roots of tomato plants.

INTRODUCTION

NEOCHLOROGENIC acid, originally isolated from peaches by Corse,[1] has recently been proven to be 5-*O*-caffeoyl-D-quinic acid.[2–4] The depside 3-*O*-feruloylquinic acid has been obtained as a crystalline material from unroasted coffee beans.[5] Neither of these compounds, however, has been found previously in tomato plants. The well-known chlorogenic acid (3-*O*-caffeoylquinic acid), however, has been reported[6] in tomato plants. Pictet and Brandenberger[7] have found three feruloylquinic acids in coffee, but the position of attachment of ferulic acid to quinic acid was not established for any of these three.

RESULTS AND DISCUSSION

Using a procedure described in the Experimental, we have identified three depsides (A, B, and C) from the leaves, stems, and roots of tomato plants as chlorogenic, neochlorogenic, and 3-feruloylquinic acids respectively. Hydrolysis of A and B yielded two compounds which were identified as quinic acid and caffeic acid; hydrolysis of C produced ferulic acid and quinic acid. Two unidentified compounds (D and E) were also isolated from tomato plants; D contains caffeic acid; E contains ferulic acid.

After purification by paper chromatography in several different solvent systems, the individual compounds, as well as their hydrolysis products, were compared with authentic reference compounds by spectrophotometry, paper chromatography, and color tests. R_f values for the purified compounds and reference standards in the various solvents used are recorded in Table 1; spectral results are given in Table 2.

* Present address: Lab. voor Tuinbouwplantenteelt, Landbouwhogeschool, P.O. Box 30, Wageningen, The Netherlands.

[1] J. W. CORSE, *Nature* **172**, 771 (1953).
[2] M. L. SCARPATI and P. ESPOSITO, *Tetrahedron Letters* **18**, 1147 (1963).
[3] E. HASLAM, G. K. MAKINSON, M. O. NAUMANN and J. CUNNINGHAM, *J. Chem. Soc.* 2137 (1964).
[4] J. W. CORSE, a symposium *Phenolics in Normal and Diseased Fruits and Vegetables*, held at Norwood, Mass., July 24 (1964).
[5] J. W. CORSE, E. SONDHEIMER and R. E. LUNDIN, *Tetrahedron* **18**, 1207 (1962).
[6] S. ARONOFF and H. J. PERKINS, *Arch. Biochem. Biophys.* **64**, 506 (1956).
[7] G. PICTET and H. BRANDENBERGER, *J. Chromatog.* **4**, 396 (1960).

TABLE 1. R_f VALUES OF ISOLATED AND REFERENCE COMPOUNDS

Compound	R_f in solvent system*				
	1	2	3	4	5
A	0·69	0·66/0·82	0·58	0·36	0·53
Chlorogenic acid	0·69	0·65/0·81	0·59	0·35	0·53
B	0·56	0·78/0·84	0·35	0·33	0·48
Neochlorogenic acid	0·56	0·78/0·83	0·35	0·33	0·48
C	0·79	0·67/0·79	0·70	0·39	0·62
3-*O*-Feruloylquinic acid	0·79	0·65/0·78	0·70	0·41	0·62
D	0·59	0·65/0·78	0·38	0·75	0·72
E	0·69	0·72/0·78	0·47	0·79	0·79

* The solvent systems used were (1) *n*-butyl alcohol: acetic acid: water (6:1:2); (2) 2 per cent acetic acid in water; (3) methyl isobutyl ketone: formic acid: water (14:3:2); (4) *n*-butyl alcohol: benzene: pyridine: water (5:1:3:3); and (5) *n*-butyl alcohol: ethanol: water (20:5:11).

TABLE 2. SPECTROPHOTOMETRIC ABSORPTION DATA OF ISOLATED AND REFERENCE COMPOUNDS

Compound	Absorption maxima and Minima in aqueous 50% methanol	
	λ_{max} (mμ)	λ_{min} (mμ)
A	242, 323	265
Chlorogenic acid	242, 326	264
B	242, 325	265
Neochlorogenic acid	242, 326	265
C*	248, 324	270
3-*O*-Feruloylquinic acid	235, 325	263
E	328	265

* In aqueous 50% ethanol.

MATERIALS AND METHODS

Leaves, stems, and roots of 28–40 day old, greenhouse-grown tomato plants, *Lycopersicon esculentum* Mill., variety Marglobe, were harvested and separately extracted with methanol. The extracts from roots, leaves, and stems were handled as individual samples in the following procedure. Each extract was concentrated *in vacuo*. Using solvent 1 (Table 1), the concentrates of each sample were developed by paper chromatography. The appropriate zones in each case were cut out and eluted with aqueous 50% methanol. The eluates of each different zone were separately purified further by paper chromatography. For A (chlorogenic acid) and B (neochlorogenic acid), solvent 2 was used. The desired compounds were then eluted with aqueous 50% methanol, streaked on papers, and developed with solvent 3. This procedure was repeated until both depsides appeared to be chromatographically pure.

For purification of compounds C (3-*O*-feruloylquinic acid), D, and E, the second chromatographic development was made with solvent 3. Each desired compound was eluted, streaked on separate papers, and developed with solvent 4, and on repetition, with solvent 5.

The R_f values for each purified compound were compared with reference standards in the various solvents shown in Table 1. Spectral observations were made on solutions of each compound in aqueous 50 per cent methanol, using a Beckman DU spectrophotometer. Similar elutions of blank chromatograms were used as spectral blanks.

For hydrolysis of each isolated compound, the compound was mixed with 1 N sodium hydroxide solution and allowed to stand for 20 min at room temperature. The sodium ions were then removed with Amberlite IR-120(H) resin, and each resulting mixture was extracted with ethyl acetate. Both the ethyl acetate extract and the extracted aqueous solution were co-chromatographed with authentic caffeic acid and ferulic acid in the solvent systems of Table 1. After development, the chromatograms were sprayed with FRS-GG, stabilized diazo salt of *p*-nitroaniline (Antara Chemicals Division of General Aniline and Film Corp.), and the color reactions (caffeic acid—yellow; ferulic acid—blue) were observed. The aqueous solutions, after extraction by ethyl acetate, were co-chromatographed with authentic quinic acid, using solvent systems 1, 2, and 4. The location of quinic acid on the chromatograms was revealed by its positive reaction with the Cartwright–Roberts reagent.[8]

Acknowledgements—We acknowledge with thanks the support by a National Science Foundation grant (GB–181). Dr. J. W. Corse, U.S.D.A., Albany, Calif., supplied the authentic sample of neochlorogenic acid, and Dr. E. Sondheimer, State College of Forestry, Syracuse, N.Y., supplied the reference sample of 3-*O*-feruloylquinic acid.

[8] R. A. Cartwright and E. A. H. Roberts, *Chem. & Ind.* 230 (1955).