

## HYDROXYCINNAMIC ACIDS DERIVATIVES ON THE PEEL OF *MALUS ACERBA* MER.

por

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This paper is dedicated to Prof. S.  
Rivas Goday on his 70th birthday.

### PLANT MATERIAL

*Malus acerba* Mer. apples collected in Azpilicueta (Navarra), august 1968, voucher specimens in Herb. of this University; it has astringent properties and is used to graft commertial varieties.

The fresh peel was extracted with EtOH, extract deffated and extracted with EtOAc. TLC on polyamide with 2 % AcOH separated the hydroxycinnamic derivatives from flavonoids. PC (Whatman 3MM) with methylisobutylketone/formic acid/water (14:3:2) (KFW) gave 6 bands: 2-dimensional PC (Whatman 1) with 1, n-butanol/pyridine/water (14:3:3) (BPW), and 2, KFW, revealed (u v + NH<sub>3</sub>, diazonium salts) 19 compounds; 11 were isolated and identified: chlorogenic, iso-chlorogenic, and p-coumaroylquinic acids and others shown on table 1.

### IDENTIFICATION

Chromatographic data (tables 1 and 2), hydrolysis with KOH, —glucosidase (1) or pectinase (2); spectral data (table 3), and further comparation with authentic compounds; the p-coumaroyl-glucoses were synthetized by procedures described elsewhere (3).

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TABLE I  
Paperchromatographic data on hydroxycinnamic acids derivatives

Spot No.	Compound	Rf $\times 100^a$		Color in <sup>b</sup>							
		Rf BPW	Rf KFW	I	II	III	IV	V	VI	VII	VIII
1	—	—	09	07	—	Bl	—	—	—	—	—
2	—	—	40	05	Bl	Y	—	—	—	—	—
3	—	—	06	22	Y	Y	—	—	—	—	—
4	3-feruloylquinic acid	17	25	Bl	Y	Pk	Bl	BrI	Br	V	Bl
5	—	—	33	22	d	Y	—	—	—	—	—
6	—	—	40	19	d	Pk	—	—	—	—	—
7	—	—	40	25	—	Bl	—	—	—	—	—
8	caffeoyleglucose	52	23	Bl	Y	Br	Brd	BrI	Lp	L	—
9	caffeoyleglucose	71	26	Bl	Y	Br	Brd	BrI	Lp	L	—
11	1-feruloylglucose	63	36	Bl	Y	Pk	Bl	BrI	Br	V	—
12	3-p-coumaroylglucose	31	42	dV	BIV	OBr	Bl	BrW	—	R	—
14	1-p-coumaroylglucose	67	42	dV	BIV	OBr	Bl	BrW	—	R	—
16	—	71	80	Bl	BlW	—	—	—	—	—	—
17	6-p-coumaroylglucose	83	76	dV	BIV	OBr	Bl	BrW	—	R	—
18	2-p-coumaroylglucose	83	92	dV	BIV	OBr	Bl	BrW	—	R	—
19	—	—	67	96	Bl	Bl	—	—	—	—	Br

a, see text.

b, I, u v light; II, u v light + ammonia; III, diazotized p-nitro aniline; IV, + sodium carbonate solution; V, tetraazoted benzidine; VI, + sodium carbonate solution; VII, diazotized sulfanilic acid; VIII, Michaud's reagent<sup>4</sup>; IX, aniline/diphenylamine/phosphoric acid (5:5:1). Bl, blue; Br, brown; G, green; L, brick; O, orange; P, purple; Pk, pink; R, red; V, violet; W, white; Y, yellow; d, dark; f, fluorescence; 1, luminous; p, pale.

TABLE 2  
*Rf* × 100 on silicagel TLC of some hydroxycinnamic acids derivatives

Spot No. <sup>a</sup>	I	II	III	IV	V	VI
4	42	18	30	58	76	54
10	38	11	17	55	72	37
11	89	15	19	58	76	31
12	36	—	10	60	73	16
13	42	20	28	55	—	56
14	82	72	64	98	85	93
15	42	19	24	82	92	62
17	91	71	73	98	87	93
18	84	72	55	99	97	90

a. see table 1

I, chloroform/ethyl acetate/formic acid (2:1:1); II, toluene/ethyl acetate/formic acid (5:4:1); III, benzene/methanol/acetic acid (2:2:1) u. ph.; IV, ethyl acetate/formic acid/water/HCl (55:6:8:1); V, ethyl acetate/methylethylketone/formic acid/water (5:3:1:1); VI, benzene/ethyl acetate/formic acid (9:7:4).

TABLE 3  
*Ultraviolet absorption spectral data of hydroxycinnamic acids derivatives*

Compound		CH <sub>3</sub> OH	+NaCH <sub>3</sub> O	+AlCl <sub>3</sub>	+NaCH <sub>3</sub> COO
3-feruloylquinic acid	I	320	360	330	320
	II	235	235	235	235,290 <sup>a</sup>
caffeoyleglucose (both)	I	285	325	310	320
	II	240	240	280 <sup>a</sup>	240,280 <sup>a</sup>
1-feruloylglucose	I	320	370	320	320
	II	235	235,295 <sup>a</sup>	220	240
3-p-coumaroylglucose	I	300	300 <sup>a</sup> ,360	315	270 <sup>a</sup> ,310
1-p-coumaroylglucose	I	315	365	315	315
	II	245	245	245	245
6-p-coumaroylglucose	I	300	360	300	310
	II	240	240	240	240
2-p-coumaroylglucose	I	290	290 <sup>a</sup> ,360	302	310
	II	240	240	250	240
p-coumaric acid	I	305	330 <sup>b</sup>	310	295
	II	230	235	230	230
caffaic acid	I	325	340	310	310
	II	240	240	230	240,290 <sup>a</sup>
ferulic acid	I	320	330	325	310
	II	225	235	240	240,290 <sup>a</sup>

a. shoulder.

## RESUMEN

Han sido detectados en la piel de *Malus acerba* Mer. 19 derivados del ácido hidroxicinámico: ácido 3-feruloilquínico, 1-feruloylglucosa, ácidos clorogénico e isoclorogénico, cafeoilglucosa, ácido 3-p-cumaroilquínico, 1-p-cumaroilglucosa y 3-p-cumaroilglucosa, ya encontrados en las plantas; y la 2- y 6-p-cumaroylglucosa encontradas creemos que por primera vez.

## SUMMARY

Some 19 hydroxycinnamic acids derivatives have been detected on the peel of *Malus acerba* Mer.: 3-feruloylquinic acid, 1-feruloylglucose, chlorogenic and isochlorogenic acids, caffeoylglucose, 3-p-coumaroylquinic acid, and the 1- and 3-p-coumaroylglucose already founded in plants; and 2- and 6-p-coumaroylglucose detected in *Malus* we believe for the first time.

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