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NEOCHLOROGENIC ACID AND "BAND 510" STRUCTURE

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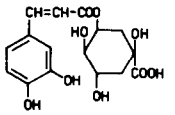
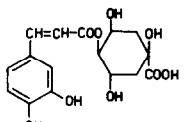
Neochlorogenic acid (I) (1) and a compound designed "Band 510" (II) (2) are known to be monocaffeyl-quinic acids[1], isomers of undetermined structure of chlorogenic acid (III) (caffeyl-3-quinic acid).

The present note reports evidence that (I) is caffeyl--5-quinic acid and (II) is caffeyl-4-quinic acid.



I



II

We have isolated (I) and (II) either from artichoke leaves or - with better results - from coffee beans (3).

After boiling the leaves or beans in water, the decotion is precipitated by lead acetate. The precipitate is decomposed

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[1] We are publishing a paper in which it is shown that isochlorogenic acid [(H.M.Barnes, J.R.Feldman, W.V.White, J.Am.Chem.Soc. 72, 4178 (1950)], which is believed to be caffeyl-5-quinic acid in equilibrium with its lactone, is instead, a mixture of three dicaffeyl-quinic acids.

in water by H_2S and the solution extracted with ethyl acetate. Acid (I) and (II) are isolated from extracts by silica gel column chromatography.

Acid (I) [1], $C_{16}H_{18}O_9$ (m.p. 204-206° dec., $[\alpha]_D^{18}$ = = + 3,1°), is obtained from coffee either pure, or as a caffeine complex (m.p. 128-130°), formed by one molecule of (I) and one of caffeine.

Acid (I) differs in chromatographic behaviour from caffeyl-1-quinic acid (4) and from (III) (see Table II).

(I), treated with HCl in dry acetone, gives lactone (IV), $C_{16}H_{16}O_8$ (m.p. 222-225° dec.; IR γ-lactone band: 1790 cm^{-1}). Lactone (IV), heated in acetone with CH_3I and K_2CO_3, gives lactone dimethyl-ether (V), $C_{18}H_{20}O_8$ (m.p. 178-180°; IR γ-lactone band: 1790 cm^{-1}), that is hidrolized to acid (VI), $C_{18}H_{22}O_9$ (m.p. 183-185°), by warming with diluted acetic acid.

The trimethylether (VII) [2], $C_{19}H_{24}O_9$ (m.p. 83-85°), is obtained, when a methanol solution of (I) is treated with an ether solution of CH_2N_2.

(VII), in diluted acetic acid (5), consumes 1 molecule of periodic acid (see Table I).

Acid (II), $C_{16}H_{18}O_9$ ($[\alpha]_D^{15}$ = - 69°), is a noncry=

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[1] This has been submitted to a direct comparison with an authentic sample of neochlorogenic acid, that Dr. Corse has kindly given to us.

[2] It has been noticed that, by washing an ethyl acetate solution of (VII) with NaOH 1N at 0°, in order to remove traces of nonmethylated products, a mixture of (VII), (IX) and (X) is formed. The same thing is true for (IX) and (X). The tendency to the transesterification, shown by caffeyl in these compounds, has been checked by boiling buffered solutions (at pH 7) of (I), (II) and (III) for 30 minutes. A mixture of (I), (II) and (III), in about equal amounts, is formed by all of them.

stalline substance, with properties which correspond with those described for "Band 510" (2,3). For chromatographic behaviour see Table II.

Acid (II) gives, in the experimental conditions adopted for (I), a trimethylether (VIII), $C_{19}H_{24}O_9$.

Compound (VIII) doesn't consume periodic acid, when submitted to oxidation, in the same conditions adopted for (VII) (see Table I).

Periodic acid oxidation has been extended, at the same time, to chlorogenic acid trimethylether (IX) (6) and the results are in perfect agreement with the theoretical value (see Table I).

TABLE I

Time in Minutes	Moles of HIO_4 / Mole of Substrate		
	(VII)	(VIII)	(IX)
45'	0,84	0,04	1,00
90'	0,88	0,04	1,00
160'	0,94	0,04	1,00

The tabulated results clearly show that neochlorogenic acid is a caffeyl-5-quinic acid and "Band 510" a caffeyl-4-quinic acid.

$[\alpha]_D$ and Rf [either on paper (Schleicher e Schüll 2043 mgl) in 2% acetic acid or on silica gel G thin layer (acidified with $KHSO_4$) in ethyl acetate-acetone 8 : 2] of all the possible monocaffeyl-quinic acids are tabulated below (see Table II).

TABLE II

	(I)	(II)	(III)	caffeyl-1--quinic ac.
$[\alpha]_D$	+ 3,1°	- 69°	- 31,5°	- 8,3°
Rf (Paper)	0,62	0,53	0,56	0,65
Rf (Silica gel G thin layer)	0,32	0,44	0,40	0,27

REFERENCES

(1) J.W. Corse, Nature 172, 771 (1953)

(2) E.Sondheimer, Arch.Biochem.Biophys. 74, 131 (1958)

(3) E.Sondheimer, C.D.Szymanski and J.W.Corse, J.Agric.Fd. Chem. 9, 146 (1961)

(4) M.L.Scarpati, G.Oriente, L.Panizzi, Annali di Chimica 48, 997 (1958)

(5) S.Siggia, Quantitative Organic Analysis via Functional Groups, J.Wiley, New York, 8 (1949)

(6) O.L.Fischer and G.Dangshadt, Berichte 65, 2, 1037 (1932).