

STRUCTURE OF THE THREE DICAFFEYOYL-QUINIC ACIDS
OF COFFEE (ISOCHLOROGENIC ACID)

M.L.Scarpati e M.Guiso

Istituto di Chimica Organica dell'Università - Roma

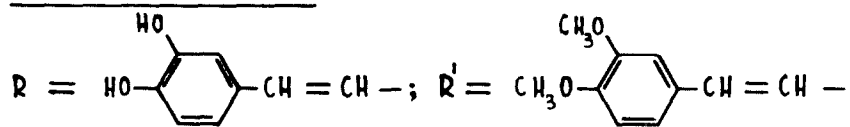
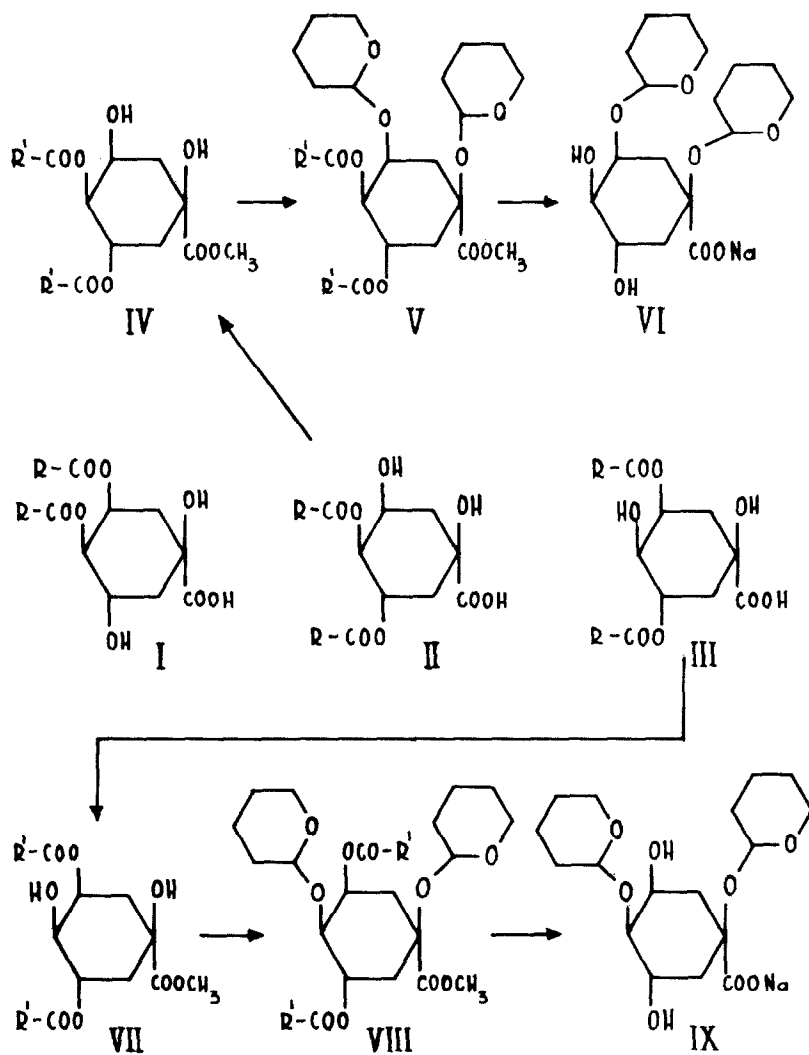
(Received 30 July 1964)

We have recently reported (1) that the so-called isochlorogenic acid (2) of coffee and mate is actually a mixture of three dicaffeoyl-quinic acids (named compound A, compound B and compound C).

We have now been able to show that A is identical with 4,5-dicaffeoyl-quinic acid (I), synthesized (3) some years ago in this Institute, and that B and C are respectively 3,4-(II) and 3,5-dicaffeoyl-quinic acids (III).

Structure (II) was assigned to B on the basis of the following evidence. Methylation of B with diazomethane gave pentamethyl-derivative (IV), which, by addition to dihydropyran, was transformed into bis-tetrahydropyranylether (V). The salt (VI), obtained by alkali hydrolysis of (V), when submitted, without isolation, to periodic acid oxidation at pH 7-7.2 consumed 1 molecule of periodic acid.

The structure of C was demonstrated in the same way: alkali hydrolysis of (VIII), obtained from C, via pentamethyl-derivative (VII), gave salt (IX), which, when submitted to



periodic acid oxidation did not consume periodic acid¹.

In addition it was found that these acids, (I), (II) and (III), show the same ease of isomerization, by migration of the caffeoyl residues, previously observed in the case of 3-, 4- and 5-monocaffeoyl-quinic acids (4), (5).

On boiling a sample of (I) or (II) or (III) in phosphate buffer at pH 7-7.2, the formation of a mixture of the three isomers, in approximately equivalent amounts, could be chromatographically detected.

When a more consistent sample of 4,5-dicaffeoyl-quinic acid (I) was submitted to isomerization in these conditions, it was possible to isolate, in addition to some unchanged (I), the two pure acids (II) and (III)².

¹ In a recent paper of E.Haslam, G.K.Makinson, M.O.Naumann and Jill Cunningham (J.Chem.Soc., 2137 (1964)), which appeared in June 1964, it was suggested to give substance C the structure (III), on the basis of the results of the acid hydrolysis of this compound.

² As 4,5-dicaffeoyl-quinic acid (I) is easily obtained by synthesis, isomers (II) and (III) may be prepared by this procedure.

REFERENCES

- (1) M.L.Scarpati and M.Guiso, Annali di Chimica, 53, 1315 (1963)
- (2) H.M.Barnes, J.R.Feldmann and W.V.White, J.Am.Chem.Soc., 72, 4178, (1950)
- (3) M.L.Scarpati, G.Oriente and I.Panizzi, Annali di Chimica, 48, 997,(1958)
- (4) M.L.Scarpati and P.Esposito, Tetrahedron Letters, 1147, (1963)
- (5) M.L.Scarpati and P.Esposito, Annali di Chimica, 54, 51, (1964)