Tetrahedron Letters,Vol.28,No.11,pp 1199-1202,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

THE CHEMICAL NATURE OF FLAVOKERMESIC ACID

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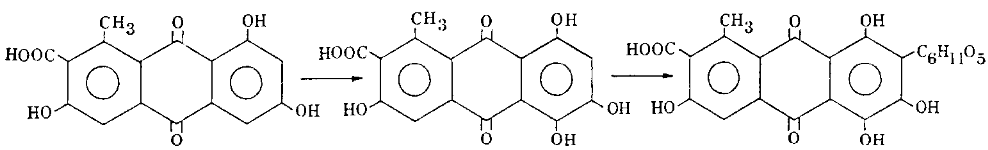
Summary. Flavokermesic acid, a minor dye constituent isolated from Kermes insects, was identified as 1-methyl-3,6,8-trihydroxy-9,10-anthracene dione-2-carboxylic acid (synonym for laccaic acid D or xanthokermesic acid).

In earlier reviews, flavokermesic acid was mentioned as a dyestuff accompanying kermesic acid in extracts of insects referred to as *Kermes ilicis*. This shield-louse species belongs to the family of the Kermesidae (1,2); it lives on the *Ilex* tree in Mediterranean countries. Always, reference was made to the same article that describes the isolation of both kermesic acid and flavokermesic acid (3). The composition of flavokermesic acid was proposed to be $C_{13}H_8O_6$, but no structural formula was put forward; it would occur for approximately 0.06% in the Kermes material studied by Dimroth. In a more recent review on natural anthraquinone dyestuffs, flavokermesic acid was no longer mentioned, probably because of its doubtful characterization and unknown significance for identification purposes (4).

Recent investigations at our laboratory in the rapidly expanding field of natural dyestuff analysis and involving HPLC of extracts from various shield- louse species, known for their production of valuable red dyes, revealed that minor constituents might be conclusive for the determination of the exact species that was used in the past for dyeing wool and silk (5). Such an increased analytical refinement concerning natural dyestuffs detected on pieces of art, could add important historical and geographical data to cultural- historical points of view.

Apart from a possible role for flavokermesic acid in these determinations, it seemed very reasonable to us that this product might have its place, perhaps still unknown, in biosynthetic pathways of insect anthraquinone dyes, together with a.o. laccaic acid D (structure I), identical to xanthokermesic acid (6), kermesic acid (structure II) and carminic acid (structure III) (7).



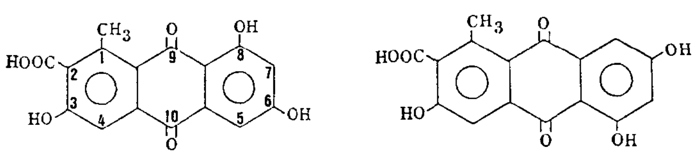
(I) (II) (III)

We received a sample of flavokermesic acid from the collection of Professor O. Dimroth, which must have been prepared prior to 1913 (3). This sample and reference products were analyzed by HPLC: Spherisorb ODS2, 4.1mm x 15cm; gradient elution from 20 to 75% (v/v) methanol in the presence of 0.5% (w/v) phosphoric acid; flowrate 1.8ml/min; column temperature 21°C; detection wavelength 275nm; scanning wavelength range 230 to 380nm. Reference products were laccaic acid D and kermesic acid, both synthetic (8), carminic acid (Fluka A.G., Switzerland), laccaic acid A and B (Dr. R. White, National Gallery, London). Comparison of the standard chromatogram with that of flavokermesic acid showed the major peak of the latter to coincide with laccaic acid D. Expressed as laccaic acid D, the purity of the old preparation would be 80%; 13% kermesic acid and minor unidentified peaks for a total of 7% were also present.

The identity of laccaic acid D with flavokermesic acid was also suggested by their UV spectrum, taken by stopped- flow analysis: laccaic acid D reference: max. at 289nm, shoulder at 345nm, absorbance ratio 6.9; flavokermesic acid: max. at 288nm, shoulder at 347nm, absorbance ratio 7.8.

The identity was further evidenced by n.m.r. spectroscopy: ppm $(CD_3)_2SO$:

laccaic acid D: 2.67, s, $ArCH_3$; 6.55, d, J 2.5Hz, H7; 7.04, d, J 2.5Hz, H5; 7.58, s, H4; (8); flavokermesic acid: 2.68, s, $ArCH_3$; 6.59, d, J 2.3Hz, H7; 7.07, d, J 2.3Hz, H5; 7.58, s, H4. However, these proton n.m.r. data did not allow a distinction between the 6,8- and the 5,7-di(OH) isomers of the same basic structure (structures IV and V resp.). For the laccaic acid D reference the 6,8- di(OH) isomer was evident following the synthetic pathway used (8), but for the unknown natural product, this was unraveled further by ^{13}C- ^{1}H two- dimensional long- range correlation spectroscopy: in structure IV, C10 (carbonyl) must give a long- range correlation with both H4 and H5 (d, downfield); in structure V, it can give long- range correlation only with H4. Apart from other long- range correlations, the two- dimensional spectrum indeed shows a ^{n}J correlation of this C10 at 181.62 with both H4 and H5. The following shift values could be attributed unequivocally: ppm, 80mg flavokermesic acid in 0.7ml $(CD_3)_2SO$: 139.86, C1; 122.39, or 131.24, C2; 111.94, C4; 107.5, C5; 108.14, C7; 164.27, C8; 187.75, C9; 181.62, C10; 131.24 or 122.39, C11; 110.08, C14; 19.77, C16.



(IV) (V)

Also mass spectrometry indicated total identity of laccaic acid D and flavokermesic acid: laccaic acid D: m/e 314 (M, 35), 296 (56), 270 (100); (8); flavokermesic acid: m/e 314 (M, 68), 296 (100), 270 (18).

It is now clear that for one and the same product, 1-methyl-3,6,8-trihydroxy-9,10-anthracenedione-2-carboxylic acid (structure IV), three trivial names exist: laccaic acid D, flavokermesic acid and xanthokermesic acid. We propose the general acceptance and use of the term flavokermesic acid. Not only it refers both to the yellow color of the dye in neutral aqueous solution and to its presence in the Kermes insect extract and -dyeings, but also this name honours Professor O. Dimroth, who was the first to detect and purify this product.

Acknowledgement

We are greatly indebted to Professor K. Dimroth for his generous gift of flavokermesic acid, and to eng. M. Mannens (Analytical department of Agfa-Gevaert n.v., Mortsel, Belgium) for the recording and interpretation of n.m.r. and mass spectral analyses. We also thank Dr. R. White and Professor D. Cameron for providing us with samples of laccaic acids A, B and D, and kermesic acid.

References

1. F. Mayer and A.H. Cook, The Chemistry of Natural Coloring Matters, p. 144, (1943).
2. R.H. Thomson, Naturally Occurring Quinones, p. 227, (1957).
3. O. Dimroth and W. Scheurer, Ann. 399, 43-59, (1913).
4. R.H. Thomson, Naturally Occurring Quinones, 2 ed., (1971).
5. J. Wouters, Studies in Conservation 30, 119-128, (1985).
6. A.R. Mehandale, A.V. Rama Rao, I.N. Shaikh and K. Venkataraman, Tetrahedron Letters 18, 2231-2234, (1968).
7. D.D. Gadgil, A.V. Rama Rao and K. Venkataraman, Tetrahedron Letters 18, 2223-2227, (1968).
8. D.W. Cameron, D. Deutscher, G.I. Fentrill and P.G. Griffiths, Aust. J. Chem. 34, 2401-2421, (1981).

(Received in UK 24 November 1986)