

Structure of Xanthomegnin and Related Pigments: Reinvestigation by ^{13}C Nuclear Magnetic Resonance Spectroscopy

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Summary The correct structures of xanthomegnin, rubrosulphin, and viopurpurin have been established as naphtho[2,3-*c*]pyran-8-yl dimers from ^{13}C n.m.r. data.

TABLE
 ^{13}C N.m.r. chemical shifts of xanthomegnin (2) and xanthomegnin diacetate (3) and ^{13}C -H coupling constants of (3) (δ in p.p.m. from external Me_4Si , J_{CH} in Hz).^a

XANTHOMEGNIN, first isolated from the mycelium of various *Trichophyton* spp., was assigned structure (1) from degradation studies and spectroscopic and chemical evidence.¹ Recently ^{13}C n.m.r. data were obtained for xanthomegnin produced by *Aspergillus melleus*^{2,3} which seemed to provide additional support for the proposed structure.

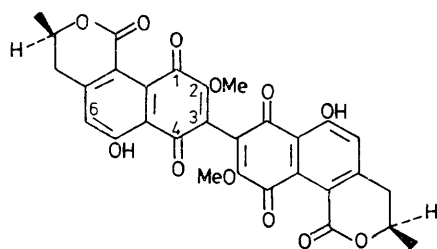
According to our investigation of different naphtho- and anthra-quinones⁴ the long-range coupling of the aromatic proton (*e.g.*, J_{CH} 5 Hz, to C-1) is in contradiction to structure (1). However, it is in good agreement with the isomeric structure (2) which also fits the chemical shift data since substituent-induced shifts are of the same order for *ortho*- and *para*-substituents. To prove the identity of the pigments obtained from different sources and the proposed structure (2) we have measured the proton-coupled and -decoupled ^{13}C n.m.r. spectra of authentic samples of xanthomegnin and its diacetate supplied by Professor G. Just.

The results given in the Table are identical with those reported by Simpson² thus confirming the existence of only one type of xanthomegnin with structure (2).† The minor

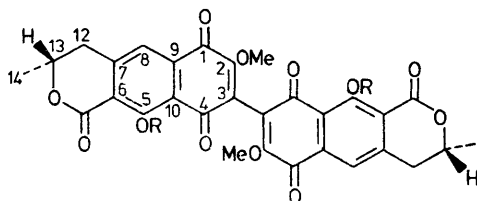
Carbon	Compound		J_{CH}
	(2)	(3)	
	δ	δ	
1	179.7	179.7	d, 4
2	157.9	157.7	q, 3.5
3	122.7	124.0	s
4	186.1	180.5	s
5	162.0	150.9	s
6	117.2	125.2	s
7	148.2	147.7	s
8	116.8	124.0	d, 168
9	134.6	135.8	s
10	114.5	123.0	d, 6
11	161.9	160.0	s
12	35.8	34.3	t, 130
13	74.4	74.1	d, 152
14	20.4	19.6	q, 128
2-OMe	61.2	60.2	q, 147
5-Ac		{ 168.3	q, 3.5
		{ 20.2	q, 130

^a Bruker WH 270 spectrometer operating at 67.88 MHz was used; the spectrum of (2) was measured in $(\text{CD}_3)_2\text{SO}-\text{CDCl}_3$ (1:4) at 60 °C and that of (3) in $(\text{CD}_3)_2\text{SO}$ at 100 °C. At 30 °C broad or doubled signals are observed as in the ^1H n.m.r. spectra (ref. 3).

† An independent proof of structure (2) could be obtained by oxidative dimerisation of semi-vioxanthin as originally suggested by us (A. Zeeck, personal communication).

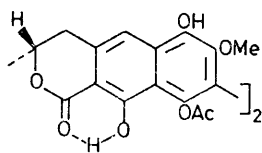


(1)



(2); R = H

(3); R = Ac



(4)

differences observed for the corresponding acetate (± 1 p.p.m.) may be caused by the different conditions of the measurements.† As expected for (3), the C-1 and C-10 signals show long-range coupling to the proton at C-8 ($^3J_{\text{CH}}$ 4 and 6 Hz, respectively) while the acetoxy-bearing C-5, now separated by four bonds from this proton, gives a singlet. Broad signals are observed for C-6, C-7, and C-8 owing to multiple long-range coupling with the protons at C-12 and C-13.

Catalytic hydrogenation of (3) to the quinol was accompanied by rapid migration of the acetyl group to form (4) which is stabilized by a strong hydrogen bond to the lactonic carbonyl group. In the original work on xanthomegnin and related compounds^{1,3} the lowering of the lactonic carbonyl frequency on reduction of the corresponding acetates was thought to be a characteristic feature of the angular orientation of the δ -lactone ring.

Since the related pigments viomellein,³ rubrosulphin,³ and viopurpurin^{3,5} show the same ¹³C chemical shifts as the corresponding xanthomegnin derivative for the naphthoquinone part as well as the characteristic long-range coupling of the aromatic proton,² their structures have to be changed in the same way. As a consequence the biosynthesis of all members of the xanthomegnin family§ can now be derived from a single intermediate, the dimeric naphthalene vioxanthin.⁵

We thank Professor G. Just for a generous gift of xanthomegnin derivatives and for references.

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† The correct signal of C-6 (125.2 p.p.m.; in ref. 2, 132.7 p.p.m.) might have been overlooked because it is very broad at 30 °C.

§ This includes floccosin whose structure has been determined recently by X-ray analysis (F. Brisse, G. Just, and F. Blank, *Acta Cryst.*, 1978, **B34**, 557).

¹ G. Just, W. C. Day, and F. Blank, *Canad. J. Chem.*, 1963, **41**, 74; A. S. Ng, G. Just, and F. Blank, *ibid.*, 1969, **47**, 1223.

² T. J. Simpson, *J.C.S. Perkin I*, 1977, 592.

³ R. C. Durley, J. MacMillan, T. J. Simpson, A. T. Glen, and W. B. Turner, *J.C.S. Perkin I*, 1975, 163.

⁴ G. Höfle, *Tetrahedron*, 1977, **33**, 1963.

⁵ F. Blank, A. S. Ng, and G. Just, *Canad. J. Chem.*, 1966, **44**, 2873.