Dyes and Pigments **6** (1985) 27–30

A New *C*-Glycosylanthraquinone from Madder Root

A. Vaidyanathan

Department of Chemistry, The Open University,
Milton Keynes MK7 6AA, Great Britain

(Received: 1 September, 1983)

SUMMARY

The compound rubianine isolated from the roots of Rubia tinctorum Linn *by Schunck (1845–1855) is identified with the help of* ^{1}H *and* ^{13}C *NMR spectra as 1,3-dihydroxy-2-C-glycosylanthraquinone.*

Madder, the ground root of *Rubia tinctorum Linn*, is one of the earliest known important natural dyestuffs. Its principal constituent is alizarin, 1,2-dihydroxyanthraquinone, which occurs in the fresh root as its primveroside, ruberythric acid. Several minor components have also been isolated and identified including rubiadin, 1,3-dihydroxy-2-methylanthraquinone,[1] which is present as its 3-glucoside[2] or possibly its primveroside,[3] and xanthopurpurin, 1,3-dihydroxyanthraquinone.[4]

Seven of the anthraquinone compounds[5] isolated from the roots of *Rubia tinctorum Linn* by Schunck—rubiretene, rubiagine, rubiacine, rubianine, chlorubian, chlorubiadine, perchlororubian—still exist in the Schunck collection of the North-Western Museum of Science and Industry, Manchester, Great Britain. Farrar[6] has recently re-examined some of these compounds and suggested that rubianine is a *C*-glycosylanthraquinone, a class of compound[7] of which only a handful are known, none of them in madder. In order to ascertain the correct structure of the compound, a small sample (85·0 mg) of rubianine was obtained from the Director of the Museum (Dr R. L. Hills).

Dyes and Pigments 0143-7208/85/$03·30

Rubianine is a bright yellow compound, m.p. 223–224 °C with decomposition. The analysis of the compound gave the molecular formula $C_{20}H_{18}O_9$. A Molisch test showed the presence of glycoside and on boiling with an acid solution no presence of free sugar was found; this showed that the compound has a *C*-glycosydic link. The compound on treatment with dilute alkali gave a red colour, which on addition of sodium dithionate and on reoxidation gave the original colour and thereby confirmed the presence of an anthraquinone molecule. The infrared spectrum of rubianine showed a strong carbonyl absorption at 1660 cm^{-1} and the UV and visible spectra of the compound exhibited strong absorptions at 244, 264 and 408 nm, very similar to 1,3-dihydroxyanthraquinone.

The ^1H and ^{13}C NMR spectra of rubianine were recorded in DMSO-d_6 on a Bruker 400 MHz instrument at the University of Warwick. The proton

TABLE 1
^{13}C Chemical Shifts (ppm)

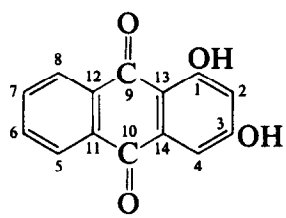
Carbon	*1,3-Dihydroxy-anthraquinone*[a] (1)	*β-D-Glucopyranosyl-benzene* (2)	*Rubianine* (3)
1	164·79		161·94
2	107·74		101·09
3	165·32		162·19
4	108·34		111·41
5	126·74		126·98
6	134·64b[b]		134·80a[b]
7	134·47b[b]		134·65a[b]
8	126·30		126·49
9	185·88		187·04
10	181·79		181·35
11	132·98		132·88
12	132·98		132·77
13	108·40		106·51
14	134·93		133·75
1′		81·26	77·44
2′		74·55	69·58
3′		78·34	73·42
4′		70·25	65·16
5′		81·05	76·16
6′		61·33	60·65

[a] Values from Ref. 9.

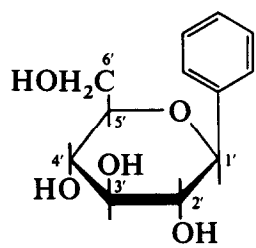
[b] a, b: assignments might be reversed.

chemical shifts are expressed on a δ-scale downfield from internal tetramethylsilane (TMS). The proton spectrum showed the presence of five aromatic protons and six hydroxyl groups. Two of the aromatic protons appeared as multiplets in the region 8·24–8·27 and 8·17–8·20 respectively, corresponding to two β-protons and two other protons appeared as multiplets in the region 7·92–7·96 corresponding to two α-protons in an anthraquinone ring. A singlet at 7·48 showed the presence of an aromatic proton which is not coupled at any other proton. These assignments agree with the assignments for 1,2,3-trisubstituted anthraquinone. For the glucose moiety, only the hydroxyl and anomeric proton signals are not hidden by the DMSO solvent signals. One hydroxyl group in the glucose molecule appeared as a doublet at 5·17 and two more hydroxyls as a triplet at 5·09. The positions of these hydroxyl groups are in accordance with the position of hydroxyl groups found in β-D-xylopyranosylbenzene in DMSO-d_6.[8] Hence, chemical shifts at 5·17 and 5·09 were assigned to O(2′)H, O(3′)H and O(4′)H. The doublet at 5·50 corresponded to the free hydroxyl group in the anthraquinone molecule and the broad peak around 4·70 showed the presence of one chelated hydroxyl group. The anomeric proton (H-1′) and O(6′)H appeared in the region 4·56–4·68 corresponding to two protons.

The ^{13}C chemical shifts of 1,3-dihydroxyanthraquinone (**1**), β-D-glucopyranosylbenzene (**2**) and rubianine (**3**) are given in Table 1.

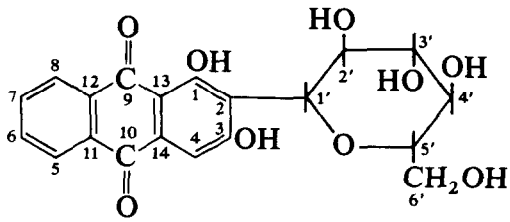


(1)



(2)

The ^{13}C NMR spectrum of rubianine (**3**) showed the presence of glucose and 1,3-dihydroxyanthraquinone in the molecule. The carbon at the anomeric centre (C-1) appeared at 77·44 ppm. This is in accordance with the value obtained for C-1′ in β-D-glucopyranosylbenzene.[8] This indicates that the sugar moiety is attached to the anthraquinone by C—C linkage at the 2-position. If the glucose is linked through an oxygen bond (O—C—), C-2 should appear at low field due to the carbonyl group and



(3)

C-1′ in the glucose moiety should appear in the region 100 ppm. The high values for carbon chemical shifts observed for glucose in rubianine (**3**) is due to the presence of hydroxyl groups in *ortho*-positions as indicated in the structure (**3**). Based on this evidence, rubianine has been assigned as 1,3-dihydroxy-2-*C*-glycosylanthraquinone (**3**).

ACKNOWLEDGEMENTS

Thanks are due to Dr D. Randall for recording the ^{1}H and ^{13}C spectra at the University of Warwick, Dr R. L. Hills for supplying a sample of rubianine, Professor C. A. Russell for sending a reprint of Dr Farrar's paper and Dr J. D. Coyle for useful suggestions.

REFERENCES

1. E. Schunck, *Trans. Roy. Soc.*, **143**, 67 (1833); E. Schunck and L. Marchlewski, *J. Chem. Soc.*, **63**, 969 (1893); *J. Chem. Soc.*, **65**, 182 (1894).
2. E. T. Jones and A. Robertson, *J. Chem. Soc.*, 1699 (1930).
3. R. Hill and D. Richter, *J. Chem. Soc.*, 1714 (1936).
4. P. Schutzenberger, *Bull. Soc. Chem. France*, **4**, 12 (1865).
5. R. H. Thomson, *Naturally occurring quinones*, Academic Press, New York (1971).
6. W. V. Farrar, *AMBIX*, **22**, 151 (1975).
7. L. J. Haynes, *Adv. Carbohydrate Chem.*, **18**, 227 (1963); *Adv. Carbohydrate Chem.*, **20** 357 (1965).
8. A. Vaidyanathan, unpublished work.
9. Y. Berger and A. Castonguay, *Org. Magn. Resonance*, **7**, 375 (1978).