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Natural anthraquinonoid colorants as platform chemicals in the synthesis of sustainable disperse dyes for polyesters

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ABSTRACT

Natural anthraquinonoid dyes (alizarin and purpurin) were used as platform chemicals to synthesise sustainable alternatives to existing synthetic dyes by alkylation of hydroxy groups in the 1- and 2-positions. In comparison with the parent compounds, the derivatised dyes were insensitive to pH change, insoluble in alkali and the λ_{max} for the mono-alkylated derivatives was unchanged and that of the bis-alkylated derivatives was reduced by 53–54 nm. Melting points decreased with derivatisation as the ability of the dyes to form inter-molecular interactions decreased. Dye exhaustion and colour strength values for dyeings on PET were relatively high for the parent and mono-alkylated derivatives and lower for the larger bis-alkylated derivatives. Mono-alkylation with methyl-4-butanoate groups improved the dyeing properties of the dyes on PLA. All dyeings displayed excellent wash fastness and the light fastness was improved in the case of the mono-alkylated derivatives owing to the removal of the photo-sensitive 2-hydroxy group.

1. Introduction

Natural dyes were universally employed in textile dyeing until Perkin's 1856 accidental discovery of the 'coal-tar' dye, Mauveine, [1], which triggered a decline in the dominance of natural dyes in world markets. Indeed, between 1870 and 1880, virtually all natural dyes were replaced on an industrial scale by synthetic examples, with indigo being one of the last to be replaced by its synthetic equivalent in 1883 [2]. Natural dyes suffered the disadvantage that, for application to either cellulosic or proteinaceous fibres, many dyes required the pre- and/or post-application of a mordant (commonly a metal salt of *e.g.* Al^{III}, Fe^{II}, Cu^{II}, Sn^{II}, Cr^{III}) to provide sufficient substantivity between dye and fibre and secure satisfactory fastness. Synthetic dyes were much more acceptable to the dyer due to their ease of production, simplicity of the dyeing process, reproducibility in shade, higher tinctorial strength, wider colour gamut, brighter colours, superior fastness and lower overall cost.

Nowadays, the production of synthetic dyes contributes to the depletion of global supplies of non-renewable fossil fuels, which has recently caused resurgence in research into the potential use of natural dyes as alternatives to existing synthetic compounds [3–5]. Many research projects have evaluated the techno-economic feasibility of plants from which dyes can be extracted and have developed novel methods of cultivation to improve dye harvests [6,7]. Studies in agronomy, biochemistry and the dye production capacity of several species of plants have led to the conclusion that some natural dyes can provide a viable alternative to synthetic dyes on an industrial scale [8,9]. Research being carried out on the development of extraction techniques and analytical methods to separate, identify and quantify the components of the different classes of natural dyes found in plants [10]. However, natural dyes have their own limitations, including limited availability, low colour yield, low stability, complexity of dyeing processes involved, reproducibility of shades, and limited substantivity for textile fibres, particularly synthetic fibres [5,11,12]. Whilst the introduction of natural dyes into modern dyeing procedures can be seen as one step towards increased sustainability by affording at least a partial replacement of synthetic dyes, the technical aspects of dyeing, defined by the demands of the modern dyehouse and the producer of the dye, have to be considered.

One of the oldest dyes used throughout history is the mixture of compounds extracted from the European madder plant (*Rubia tinctorum* L.), which provides an orange-red coloured dye; a red dye

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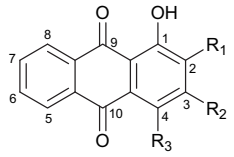
can also be obtained from the Indian madder plant (*Rubia cordifolia* L.). Madder plants contain an impressive number of anthraquinone derivatives; of the thirty-six compounds now identified in madder roots, fifteen play an important role in dyeing and are grouped together in the Colour Index as C. I. Natural Red 8. The main colouring species extracted from *R. tinctorum* and *R. cordifolia* are alizarin (**1**) and purpurin (**2**); other colorants present are xanthopurpurin (**3**), rubiadin (**4**), pseudopurpurin (**5**), munjistin (**6**), and lucidin (**7**) [13,14].



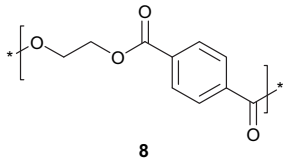
1: R_1 = OH; R_2 = R_3 = H
2: R_1 = R_3 = OH; R_2 = H
3: R_1 = R_3 = H; R_2 = OH
4: R_1 = CH_3; R_2 = OH; R_3 = H
5: R_1 = COOH; R_2 = R_3 = OH
6: R_1 = COOH; R_2 = OH; R_3 = H
7: R_1 = CH_2OH; R_2 = OH; R_3 = H

Alizarin (1,2-dihydroxyanthraquinone; C. I. Mordant Red 11; **1**) is the main dye (orange-red crystals) extracted from *R. tinctorum*, which occurs in the roots of the plant as the glycosylated compound ruberthyric acid, where a 2-*O*-primeverose group is present rather than the 2-hydroxy group in alizarin; the primeverose moiety is hydrolysed to the hydroxy group during extraction and dyeing [15]. Purpurin (1,2,4-trihydroxyanthraquinone; C. I. Natural Red 16; **2**) is a minor component in the roots of *R. tinctorum*, but is the main dye (bright red crystals) extracted from *R. cordifolia* [6,14]. Both alizarin and purpurin are only sparingly soluble in water, but are freely soluble in alcohol, ether, acetone and alkaline solutions. It has been demonstrated that alizarin can be extracted from the roots of *R. tinctorum* with methanol at 25 °C with an extraction yield of 2.9 g kg^{-1} of dried material [7]; this yield can be increased to 4.0 g kg^{-1} by means of Microwave Assisted Extraction (MAE), with purpurin being extracted from *R. tinctorum* at a yield of 2.1 g kg^{-1} by MAE [10]. It has also been demonstrated that extraction of *R. tinctorum* in methanol/water mixtures can be conducted at lower temperatures and in shorter times to obtain similar yields by application of ultrasound assisted extraction [16].

Electron-donating hydroxy groups in the 1- or 4-positions of alizarin and purpurin are able to form intramolecular hydrogen bonds with the keto groups (9- and 10-positions) of the anthraquinone moiety; however, the hydroxy group in the 2-position is unable to form intramolecular hydrogen bonds with the keto groups [13,14,17,18]. Individual dye molecules are also attracted to each other through van der Waals forces and inter-molecular hydrogen bonds, with the result that many dyes exist in solution as aggregates [19]. The large size of these dye aggregates can lead to a significant reduction in the rate of fibre sorption, or in some cases to the precipitation of the dye from solution.

Alizarin and purpurin vary in aqueous solubility and colour under different pH conditions; strong alkali will create a violet–blue colour, dilute alkali a violet–red, whilst a strong acid with produce an orange colour; the compounds are practically insoluble at pH 4–6. This change in colour and increase in solubility with increasing pH is due to the ability of the hydroxy groups to ionise, forming salts with greater water solubility. Alkali also reduces inter-molecular hydrogen bonding, decreasing the extent of aggregation, further enhancing the solubility of the dye [20]. Absorbance at longer wavelengths (bathochromic shift) at higher pH arises from the formation of more electron-rich conjugated π-systems, such as those shown in Scheme 1.

In 1998, poly(ethyleneterephthalate) (PET; **8**), overtook cotton as having the highest consumption of any fibre in the world. PET is a highly crystalline linear aromatic polymer with a small number of amorphous regions available for sorption and diffusion and can only be dyed practically with hydrophobic disperse dyes [21]. Poly(lactic acid) (PLA; **9**) is a linear aliphatic polymer made from renewable raw materials which are fermented to produce lactic acid, which is then polymerised to make the polymer *via* a dimeric lactide intermediate. It has been demonstrated that PLA can be dyed with disperse dyes designed for use on PET [22]. Disperse dyes are generally non-ionic and are typically only sparingly soluble in water. It is not possible to dye hydrophobic fibres with a mixture of the dye and water alone because the dye particles would not be distributed uniformly and would precipitate from solution, therefore, disperse dyeing requires incorporation of a surface-active (dispersing) agents. Since ester fibres and disperse dyes do not typically contain any ionic groups, dye–fibre attraction clearly originates in hydrogen bonding, dipole–dipole interaction, hydrophobic effects and dispersion forces [23]. Studies have demonstrated that all the polar groups in a disperse dye molecule can contribute to its substantivity for an ester fibre, in addition, provided the dye molecule is planar and can lie flat against the cyclic nuclei in the ester polymer segments, all polar substituents on the fringes of the rings in the dye have the potential to contribute to the overall strength of the dye–fibre multiple bonding [23].



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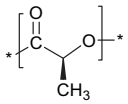

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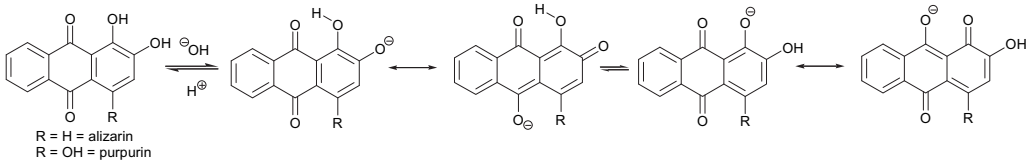
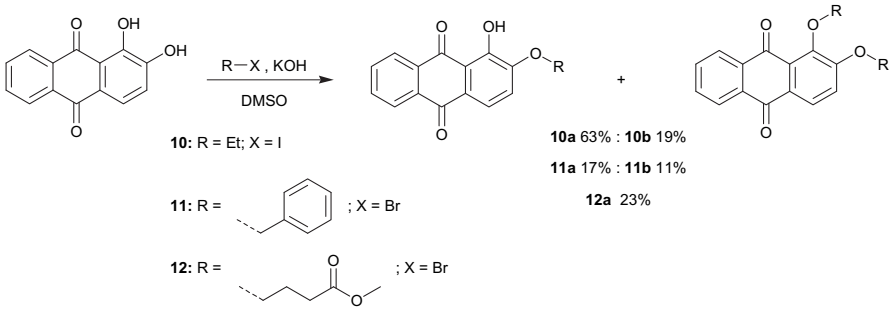
Synthetic fibres are generally not dyeable with natural dyes, yet synthetic anthraquinonoid compounds constitute 32% of all commercial disperse dyes designed for use on polyester and other hydrophobic fibres, hence, there is potential for utilising natural anthraquinonoid dyes based on alizarin and purpurin as disperse dyes for such fibres [13,20,24]. The research herein is aimed at chemically modifying the natural dyes alizarin and purpurin to increase their substantivity for polyester fibres, specifically PET and PLA, in order to promote the utilisation of natural dyes as platform chemicals for the sustainable production of alternatives to existing synthetic dyes, but which maintain technical performance. The second goal is to achieve a better understanding of the sorption properties of disperse dyes on PLA fibres and to encourage the utilisation of this sustainable fibre.

2. Results and discussion

The aim of the synthesis work was to chemically modify the alizarin and purpurin structures to produce dyes with greater



Scheme 1. Solubilisation of alizarin and purpurin in alkali.



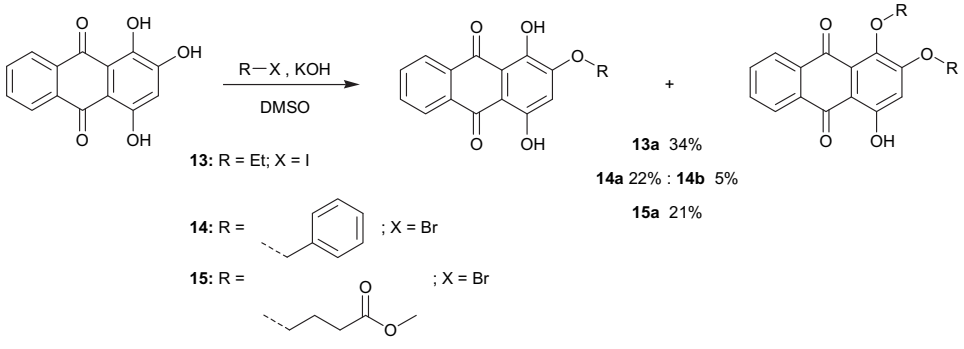
Scheme 2. Alkylation reactions of alizarin to produce derivatised dyes.

substantivity for synthetic polyester fibres, in comparison with the parent compound. Natural dyes tend to be hydrophilic and have limited substantivity for hydrophobic substrates, therefore, the most important objective was to design compounds with greater hydrophobicity than alizarin and purpurin. A possible route for derivatisation of the natural compounds was through alkylation of the phenolic compounds. Reactions were based on a rapid, mild, one-step procedure developed by Johnstone and Rose for the alkylation of phenols, utilising a base (KOH) and a suitable alkyl halide in DMSO [25]. Ethyl iodide, benzylbromide, and methyl-4-bromobutyrate were selected as reagents for the proposed reactions to derivatise the hydroxy groups in alizarin (Scheme 2) and purpurin (Scheme 3). It was envisaged that these reactions would allow the preparation of derivatives containing simple alkyl, aryl and ester groups, to help determine the relative importance of structural characteristics in the dye adsorption process for the two polymers investigated.

The derivatives shown in Table 1 were successfully synthesised, as detailed in the experimental section. Although yields were modest, these were usually of analytically pure products, and were unoptimised. It was also envisaged that if promising dyeing results were obtained, then a more environmentally acceptable alkylation procedure could be adopted. In all cases the predominant product resulted from alkylation of the 2-hydroxy position, rather than the 1-hydroxy. Although the precise reason for this is unclear, it is consistent with literature precedent [26,27]. Substantial amounts of the bis-alkylated products were also isolated in some cases, and provided further insight into the influence of structure on the dyeing process.

Physical properties of the derivatised dyes and their parent compounds are shown in Table 1. As discussed earlier, alizarin and purpurin are soluble in alkali, and are subject to colour changes under different pH conditions, this could cause problems during dyeing processes in industry, where aqueous solutions in different pH ranges are used. Although both parent compounds were soluble in 1M NaOH solution, none of the derivatised dyes were soluble in this medium, probably due to their significantly greater hydrophobicity. Additionally, in anthraquinonoid compounds a hydroxy group β (positions 1, 4, 5, 8) to the carbonyl has a much higher pK_a value than a hydroxy group γ to the carbonyl group due to an internal hydrogen bond between the β-OH and the carbonyl group; in the case of alizarin the pK_a values are 12.0 and 8.2 for the β and γ hydroxy group, respectively [15]. Hence, the pK_a of the remaining 1-hydroxy group in the derivatised compounds would be expected to be significantly higher than that of the 2-hydroxy group in the parent compound, and solubility in 1M NaOH solution would be significantly reduced. Neither the parent dyes nor the derivatives were soluble in distilled water or 1M HCl solution. These results demonstrate that the derivatised compounds are more suitable for disperse dye application under a variety of different pH conditions and are more hydrophobic and less acidic than the parent compounds.

When considering the light absorption properties of each compound, it was observed that the wavelength of maximum absorption (λ_{max}) in acetone for the mono-alkylated derivatives (where only the 2-position was derivatised) was almost the same as the respective parent compound, demonstrating that the alkylated phenolic compounds have similar electronic properties to the original phenol. However, when the 1-position was also derivatised the λ_{max} of all the bis-alkylated derivatives was reduced by 53–54 nm (hypsochromic shift) for both alizarin and purpurin. Alizarin and purpurin both possess low-lying LUMOs, hence they are good electron acceptors; the electron-donating hydroxy groups increase molecular conjugation, in comparison with anthraquinone, lowering the energies of the LUMOs. Consequently, $\pi \rightarrow \pi^*$ transitions can occur in the visible region, resulting in intense visible absorptions and the molecules being coloured [28]. In anthraquinonoid dyes, an enhanced bathochromic effect (absorption at longer wavelengths) is observed when a protic group in the 1-position (*e.g.* –OH or –NHR) is able to hydrogen bond with the



Scheme 3. Alkylation reactions of purpurin to produce derivatised dyes.

Table 1
Physical properties of anthraquinonoid dyes.

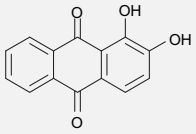
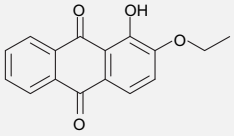
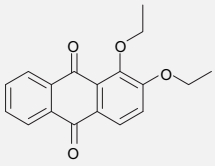
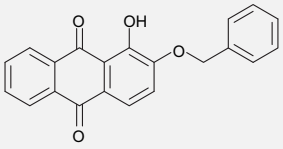
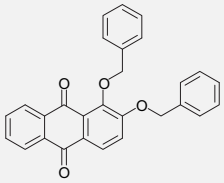
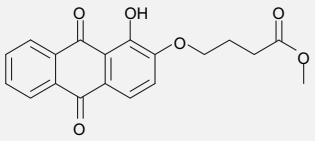
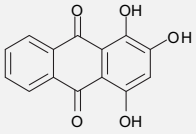
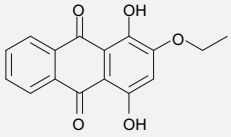
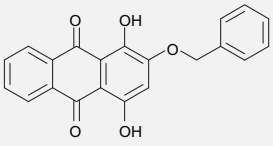
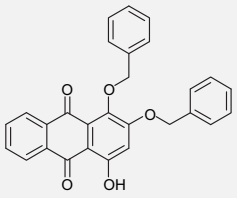
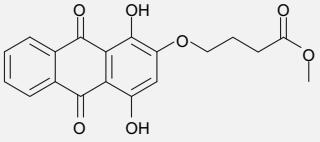
Compound	Name	Structure	Solubility (1M NaOH)	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} cm^{-1})	Melting point (°C)
1	alizarin (1,2-dihydroxyanthracene-9,10-dione)		Soluble (purple-red colour)	429	4300	278–280
10a	2-ethoxy-1-hydroxyanthracene-9,10-dione		Insoluble	425	6800	182–185
10b	1,2-diethoxyanthracene-9,10-dione		Insoluble	375	4600	129–132
11a	2-(benzyloxy)-1-hydroxyanthracene-9,10-dione		Insoluble	423	3600	170–174
11b	1,2-bis(benzyloxy)anthracene-9,10-dione		Insoluble	375	3700	144–147
12a	methyl-4-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)butanoate		Insoluble	424	5900	145–148
2	purpurin (1,2,4-trihydroxyanthracene-9,10-dione)		Soluble (purple-red colour)	482	6200	265–270
13a	2-ethoxy-1,4-dihydroxyanthracene-9,10-dione		Insoluble	480	6500	199–201
14a	2-(benzyloxy)-1,4-dihydroxyanthracene-9,10-dione		Insoluble	480	2200	202–205

Table 1 (*continued*)

Compound	Name	Structure	Solubility (1M NaOH)	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} cm^{-1})	Melting point (°C)
14b	1,2-bis(benzyloxy)-4-hydroxyanthracene-9,10-dione		Insoluble	429	3600	174–176
15a	methyl-4-(9,10-dihydro-1,4-dihydroxy-9,10-dioxoanthracen-3-yloxy)butanoate		Insoluble	480	8100	149–152

adjacent carbonyl group, which assists conjugation of the donor lone pair electrons with the anthraquinone ring [29,30]. Hence, derivatisation at the 1-position with substituents that were unable to hydrogen bond with the 9-ketone group caused a reduction in conjugation in the chromophore, resulting in absorption at shorter wavelengths.

In terms of extinction coefficient (ε_{max}), it is known that a 2-methoxy group gives a slightly higher ε_{max} in comparison with a 2-hydroxy group in substituted anthraquinonoid dyes [30]; accordingly, it is observed that derivatisation of the 2-hydroxy group in both alizarin and purpurin with 2-ethoxy or methyl-4-butanoate results in an increase in ε_{max}, which can be explained in terms of PPP-MO calculations [29]. It is noted that the 1,2-diethoxy alizarin derivative only gave a slight increase in ε_{max}, in comparison with alizarin, but a significantly lower ε_{max}, in comparison with its 2-hydroxy counterpart; this is probably because the 1-ethoxy group is unable to fully conjugate due to steric affects and its inability to hydrogen bond to the 9-ketone group, which is known to decrease tinctorial strength [30]. However, derivatisation with a 2-benzyloxy group caused a decrease in ε_{max}, it is not clear why this occurred, but is certainly worthy of further investigation. The λ_{max} at longer wavelengths observed for purpurin and its derivatives, in comparison with alizarin and its derivatives, is as a result of the presence of two electron-donating groups in the 1,4-positions, which gives rise to a bathochromic shift (increased λ_{max}) [30].

All derivatives have significantly lower melting points in comparison with their respective parent compound; it is also evident that the bis-alkylated derivatives have lower melting points than their respective mono-alkylated derivative. In the case of alizarin, Guilhem demonstrated [31] that relatively strong inter-molecular hydrogen bonds (O–H···O; 21 kJ mol^{-1} [32]) cause the formation of aggregates comprising a 'triple molecule complex' of three alizarin molecules (Fig. 1), wherein the individual triple molecule complexes are linked together by weaker van der Waals forces.

Distinct needle-like crystals are formed as a result of the short length of the **b**-axis as compared to the other crystal axes of the monoclinic unit cell [33]. From Fig. 1 it can be seen that the 2-hydroxy group plays an important role in the formation of this triple molecule complex (through inter-molecular hydrogen bonds) and in van der Waals interactions between separate complexes; the role of the 2-hydroxy group is important in relation to the crystallinity of solid alizarin. Hence, when this position is derivatised, and is no longer able to bond with adjacent molecules, it would be expected that lower crystallinity of the solids would result, which explains the observed reduction in melting temperatures. Additional derivatisation of the 1-hydroxy group to form the bis-alkylated derivatives reduces the potential for molecular bonding even further, and even lower melting temperatures are observed.

Table 2 shows the results of the dyeing and fastness properties of the parent and derivatised anthraquinonoid dyes on PET and PLA; it is observed that, as expected, % exhaustion figures relate directly to *K*/*S* values, insofar as when exhaustion is high, *K*/*S* values are also relatively high. It is apparent that, in the case of PET, exhaustion >84% and high *K*/*S* values were observed for both

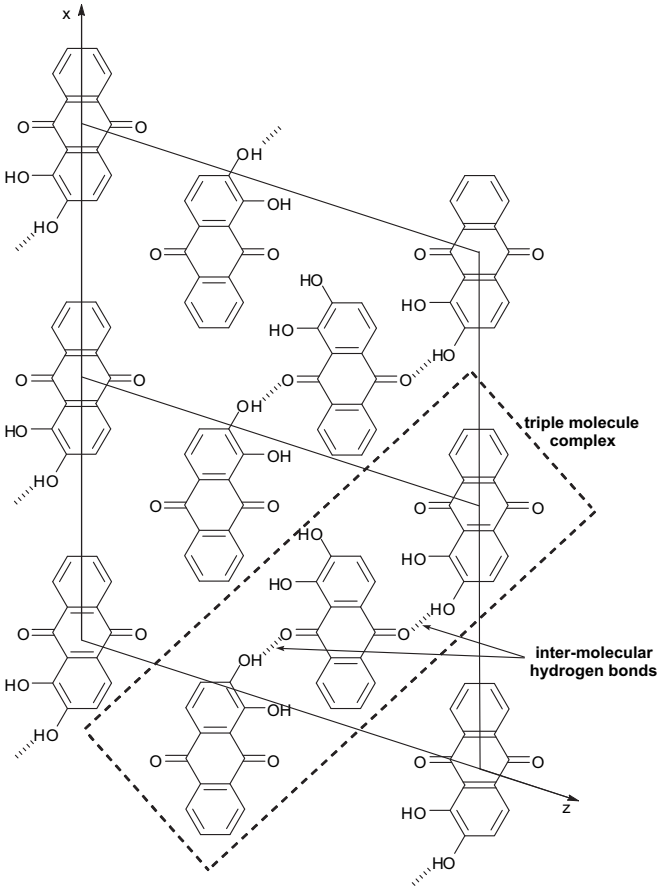


Fig. 1. Molecular bonding in alizarin [15].

parent compounds (**1** and **2**) and the mono-alkylated derivatives (**10a**–**15a**), we propose that this is due to interactions between aromatic residues in the dyes and the polymer having the greatest contribution to dye–fibre substantivity, rather than other forces of attraction such as hydrophobic interactions, dipolar interactions and hydrogen bonding. Derivatisation of both alizarin and purpurin at the 2-hydroxy position with one $-OCH_2CH_3$ group (**10a**, **13a**) did afford a slight increase in % exhaustion values with respect to their parent compounds, most likely as a result of the a greater hydrophobicity of upon derivatisation. However, derivatisation 2-hydroxy position with one $-OCH_2C_6H_5$ group (**11a**, **14a**) did not afford any change in % exhaustion values.

In the case of the bis-alkylated derivatives (**10b**, **11b**, **14b**), exhaustion on PET was between 55 and 65%, and *K*/*S* values were less than half the value of their respective mono-alkylated derivative. It might be expected that the introduction of a second substituent into the anthraquinonoid structure with increased substantivity for the polyesters should improve exhaustion, however, the bis-alkylated derivatives have a larger, more bulky, less planar molecules in comparison with their mono-alkylated derivative counterparts, which is disadvantageous in disperse dyeing of crystalline polyesters [34], resulting in the lower sorption observed. Greater differences in sorption and *K*/*S* values are observed between parent dyes and the various derivatives in the case of PLA dyeings; the polymer does not have any aromatic moieties, so hydrophobic interactions, dipolar interactions, and hydrogen bonding involving other moieties is more important in dye–fibre substantivity. Karst and Yang demonstrated that the sorption of substituted anthraquinonoid dyes onto PLA was highest when the substituents present were $-NHR$, $-NR_2$, $-NHCOR$, $-COR$, $-OR$, $-COOR$, or a phenyl, wherein the R group was $-CH_3$, $-(CH_2)_nCH_3$, or a phenyl, and when the groups $-NO_2$, $-NH_2$, $-OH$, $-CN$, or a halide were absent [35]. They also demonstrated in later work that the substituents in dye molecules that form the strongest interactions with PLA included $-N(C_2H_4OCOCH_3)_2$, $-(CO)_2N-C_3H_6OCH_3$, and $-CH(CO)_2C_6H_4$ [21]. As such, it is understandable that derivatisation of alizarin to form **10a** and **11a** caused and improvement in sorption properties by addition of $-OCH_2CH_3$ and $-OCH_2C_6H_5$ groups, respectively, and removal of one $-OH$ group in both cases; however, this was not reflected in the respective mono-alkylated derivatives of purpurin (**13a** and **14a**), and this requires further investigation to understand the possible reasons. In addition, the same observations were made with the bis-alkylated derivatives on PLA as for PET, insofar as no improvement in sorption was noted due to the increase in molecular size of these derivatised dyes. Highest sorption on PLA was observed with the two compounds derivatised with one methyl-4-butanoate group (**12a** and **15a**) where a significant increase in exhaustion and *K*/*S* was noted for both alizarin and purpurin derivatives. In agreement with Karst and Yang's work the presence of a $-O(CH_2)_3COOCH_3$ group provides greatest dye–fibre affinity, which is logical as the considering the interactions with the similar $-COCH(CH_3)O-$ repeat units of the polymer.

CIELab data is provided in Table 2, and from calculated saturation (chroma; C^*) values it can be seen that alizarin and purpurin provided dull shades (relatively low C^* values), whereas their mono-alkylated counterparts provided bright shades (relatively high C^* values). This was probably due to reduced hydrogen-bonding, resulting from derivatisation of the 2-hydroxy, which decreased the ability of the dyes to form aggregates; aggregation of dyes can cause interactions between conjugated systems, resulting in a broadening of the absorption peak, as observed herein; this is in keeping with the reduction in melting point upon derivatisation as discussed above. The λ_{max} values at longer wavelengths observed for purpurin and its derivatives, in comparison with alizarin and its derivatives, is as a result of the presence of two electron-donating groups in the 1,4-positions, which increases λ_{max} [30]; the higher *K*/*S* values observed for purpurin and its derivatives could also be due to the presence of two electron-donating groups in the 1,4-positions, which can increase ε_{max} [30], although this is not always as straightforward as it has been observed that it is not always possible to directly relate solution spectral parameters such as molar extinction coefficient to colorimetric data from dyed fibre [36].

Table 2 shows that, in terms of wash fastness, dyeings on PET with derivatised dyes display slightly improved wash fastness in comparison with the parent structures (the level of wash fastness being excellent) probably as a result of greater dye–fibre interaction. All dyeings on PLA display excellent wash fastness; and no staining

Table 2
Dyeing and fastness properties of anthraquinonoid dyes on PET and PLA.

Fibre	Compound	Exhaustion (%)	L^*	a^*	b^*	C^*	h°	*K*/*S* at λ_{max}	Wash fastness (colour loss) (1–5)	Light fastness (1-8)
PET	**1**	91.0	63.2	12.2	66.6	67.8	79.6	15.1	4	5
	10a	97.5	75.2	15.7	90.5	91.9	80.2	18.1	5	7
	10b	65.4	77.4	9.6	60.6	61.4	81.0	6.8	5	4
	11a	90.0	74.7	14.6	87.5	88.7	80.5	17.4	5	6
	11b	57.1	81.3	4.4	46.4	46.6	84.6	5.4	5	4
	12a	95.3	75.3	14.4	87.7	88.9	80.7	16.4	5	7
	2	85.6	52.8	41.4	51.6	66.1	51.3	17.1	4/5	4
	13a	96.6	62.8	50.3	76.5	91.6	56.7	24.8	5	7
	14a	84.2	66.8	49.2	79.1	93.2	58.1	19.9	5	5
	14b	55.0	72.2	23.7	71.2	75.1	71.6	8.6	5	3
	15a	97.3	50.8	39.1	53.3	66.1	53.8	21.9	4/5	5
PLA	**1**	29.9	82.6	2.0	47.6	47.6	87.7	2.3	5	4
	10a	41.1	86.4	1.2	69.4	69.4	89.0	3.9	5	7
	10b	17.6	84.5	2.0	59.1	59.2	88.0	2.6	5	3
	11a	40.1	82.2	2.8	61.6	61.6	87.4	3.9	5	4
	11b	15.3	84.8	2.7	43.7	43.8	86.4	2.4	5	1
	12a	82.4	80.6	5.8	75.4	75.6	85.6	8.4	5	7
	2	39.8	63.8	31.3	43.7	53.8	54.4	5.7	5	3
	13a	6.5	78.1	23.3	49.9	55.1	65.0	2.4	5	4
	14a	7.5	77.2	25.4	55.7	61.2	65.5	2.8	5	3
	14b	6.1	79.3	22.6	57.4	61.6	68.5	2.7	5	2
	15a	60.1	65.1	35.7	56.5	66.8	57.7	8.6	5	4

was observed on any of the adjacent multifibre strip materials for any dyeing after washing (all grade 5).

In terms of fastness to light, a noticeable improvement is observed for all mono-alkylated derivatives on PET and most mono-alkylated derivatives on PLA in comparison with the parent structure (no decrease being observed); in some cases very high light fastness ratings (7) are observed. In the parent structures of alizarin and purpurin, the presence of an electron-donating group in the 2-position (the 2-hydroxy group) is undesirable because, unlike similar groups in the 1- and 4-positions, the group is unable to form intramolecular hydrogen bonds with the keto groups of anthraquinone and hence is highly susceptible to photo-oxidation [37]. With the mono-alkylated derivatives this group has been replaced with groups with lower electron-donating capacity and so the dye has higher light fastness. Conversely, when the hydroxy groups in the 1-position are removed it appears that light fastness is reduced, in comparison with the parent structure, as observed herein in the case of the bis-alkylated derivatives. There are two explanations as to why this is observed: the presence of a 1-hydroxy group in anthraquinonoid dyes stabilises the compound against photo-oxidation as a result of the intramolecular hydrogen bond with the 9-ketone group, which is not possible with the bis-alkylated derivatives; alternatively, light fastness is also related to differences in the concentration of dye in fibre, and the apparent reduction in photostability between those of dyes **10a** and **11a** compared to **10b** and **11b**, could be attributable to a significantly lower concentration of colorant in the substrate in the case of the bis-alkylated dyes.

The research has demonstrated the possibility of using alizarin and purpurin as platform chemicals for the production of sustainable alternatives to existing synthetic dyes, which have very good technical performance, superior to the dyeing properties of the parent compounds. The research has also provided additional understanding of the sorption properties of disperse dyes on of PLA fibres in terms of insight into which chemical groups provide greatest substantivity for PLA.

3. Conclusions

The research herein has demonstrated that disperse dyes which yield high colour strength and high fastness properties on PET and PLA can be synthesized from natural anthraquinonoid colorants by derivatisation of the 2-hydroxy position in alizarin and purpurin. It was also possible to produce derivatives of alizarin and purpurin where both the 1- and 2-positions were alkylated. In comparison with parent compounds, the following observations were made for derivatised dyes: insensitive to pH change; insoluble in alkali; λ_{max} for mono-alkylated derivatives was the same; λ_{max} for bis-alkylated derivatives was reduced by 53–54 nm, as a result of reduction in conjugation in the chromophore; melting points decreased as the ability of the dyes to form inter-molecular interactions decreased with derivatisation, yielding less crystalline solids.

Exhaustion and *K*/*S* values for dyeings on PET were high for parent and mono-alkylated derivatives, and lower for bis-alkylated derivatives, due to formation of larger, more bulky molecules in comparison with their mono-alkylated counterparts. Mono-alkylation with ethoxy, benzyloxy, and, particularly, methyl-4-butanoate groups improved dyeing properties on PLA. Dyeings on PET with derivatised dyes displayed slightly improved wash fastness in comparison with the parent structures; all dyeings on PLA displayed excellent wash fastness. Light fastness was improved in the case of the mono-alkylated derivatives due to the removal of the 2-hydroxy group, which is highly susceptible to photo-oxidation; conversely, light fastness was reduced in the case of the bis-alkylated derivatives either due to removal of the 1-hydroxy group (which helps to stabilises the dye against photo-oxidation), or by virtue of the lower colour strength of the dyeings, which can often cause a reduction in light fastness in comparison with dyeings of higher *K*/*S* values.

4. Experimental section

4.1. Materials

Spun jersey knitted fabric samples of 100% PLA fibre and 100% PET fibre of the same fabric construction and weight (155 g m^{-2}) were kindly supplied by NatureWorks LLC. A sample of the dispersing agent *Borresperse NA* (sodium lignosulfonate) was supplied by Borregaard Lignotech. Sample of the surfactant *Kieralon MFB* (mixture of non-ionic and anionic surfactants) and the anti-oxidant *Ludigol AR* were supplied by BASF. A sample of the levelling agent *Levagal DLP* was supplied by Lanxess. All other chemicals for synthesis and dyeing were obtained from Sigma–Aldrich. Alizarin (supplied as 97%) and purpurin (supplied as 90%) were purified before use by recrystallisation from ethanol (CAUTION: Highly flammable. Irritating to eyes).

4.2. Analytical procedures

^{1}H and ^{13}C NMR spectra were recorded respectively at 300 MHz and 75 MHz on a *Bruker B-ALS 60* spectrometer using deuterated DMSO and chloroform (CAUTION: Harmful if swallowed. Irritating to skin. Limited evidence of a carcinogenic effect), respectively, as the solvent and residual proton signals of respective solvents as an internal standard. FT-IR absorbance/transmission spectra were recorded on a *Perkin Elmer Spectrum One* spectrometer with the sample compressed into NaCl discs, and held in a specimen holder. UV/visible spectrophotometry was conducted using a *Jasco V-530* spectrophotometer using 50:50 (v/v) acetone (CAUTION: Highly flammable. Irritating to eyes): water as solvent. Concentrations were calculated from calibration graphs at the wavelength of maximum absorption (λ_{max}); concentration of residual dye in solution was calculated from calibration plots, and dye adsorbed by the fibre calculated from the difference before and after exhaustion. No difference in the shape of the absorption spectrum before and after dyeing was noted. Mass spectra were recorded on a *VG Autospec* mass spectrometer for electron impact (EI) and fast atom bombardment (FAB) spectra. Molecular ions are reported as mass with percentage abundance quoted in brackets. Melting points were determined on a *Reichert Hot Stage* apparatus and are uncorrected. Microanalyses were carried out at the University of Leeds Microanalytical laboratory; all C and H analytical figures are expressed in percentage values of total molecular weight. All solvents used in analytical procedures were purified before use using established procedures [38].

4.3. Synthesis

2-Ethoxy-1-hydroxyanthracene-9,10-dione (10a) and 1,2-diethoxyanthracene-9,10-dione 10). Powdered potassium hydroxide (CAUTION: Harmful if swallowed. Causes severe burns) (164 mmol) was added to DMSO (41 cm^3) at 37 °C. After stirring for 5 min, alizarin (20.5 mmol) was added, followed immediately by the ethyl iodide (CAUTION: Harmful by inhalation. Irritating to eyes, respiratory system and skin) (82 mmol). Stirring was continued for 24 h, after which the mixture was poured into aqueous hydrochloric acid solution (1M, 400 cm^3) and extracted with dichloromethane (CAUTION: Limited evidence of a carcinogenic effect) (3 × 400 cm^3). The combined organic extracts were washed with distilled water (5 × 500 cm^3), dried ($MgSO_4$) and evaporated in a rotary evaporator. The residue was dried further under high vacuum (24 h). The solid

contained a mixture of **10a** and **10b** and was dissolved in dichloromethane (100 cm^3). Compound **10a** was extracted into sodium hydroxide (1M, 2 × 20 cm^3) which was then neutralised to give the product: **10a** (3.53 g, 13.2 mmol, yield: 63%). m.p. 182–185 °C; (Found: C, 70.4; H, 4.5; $C_{16}H_{12}O_4$ requires C, 71.6; H, 4.5%); ν_{max} (solid)/cm^{-1} (C–H) 3094–2891, (–OH) 3000–2600, (C=O) 1660, (C–O) 1272; ^{1}H nmr, δ_H (300 MHz, $(CD_3)_2SO$); 12.71 (1H, s, C–OH), 8.22–8.11 (2H, m, H-5,8), 7.92 (2H, m, H-6,7), 7.69 (1H, d, *J* 7.5, H-4), 7.40 (1H, d, *J* 8.4, H-3), 4.19 (2H, q, *J* 6.6, H-15), 1.40 (3H, t, *J* 6.6, H-16); ^{13}C {^{1}H} nmr, δ_C (75 MHz, $CDCl_3$); 189.6 (C=O, C-9), 181.9 (C=O, C-10), 153.9 (quat. Ar.C, C-2), 153.3 (quat. Ar.C, C-1), 135.1 (Ar.C, C-6), 134.5 (quat. Ar.C, C-12), 134.2 (Ar.C, C-7), 133.8 (quat. Ar.C, C-11), 127.8 (Ar.C, C-5), 127.3 (Ar.C, C-8), 125.5 (quat. Ar.C, C-14), 121.5 (Ar.C, C-3), 117.0 (Ar.C, C-4), 116.5 (quat. Ar.C, C-13), 65.3 (O–CH_2–CH_3, C-15), 15.0 (O–CH_2–CH_3, C-16); *m*/*z* (ESI) 291 (100%, MNa^+); UV/vis λ_{max} (CH_3COCH_3) 425 nm.

Evaporation of the remaining dichloromethane solution *in vacuo* gave a solid, which was further dried in a high vacuum to give **10b**: (1.18 g, 3.98 mmol, yield: 19%). m.p. 129–132 °C; (Found: C, 73.1; H, 5.2; $C_{18}H_{16}O_4$ requires C, 73.0; H, 5.4%); ν_{max} (solid)/cm^{-1} (C–H) 3084–2893, (C=O) 1669, (C–O) 1264; ^{1}H nmr, δ_H (300 MHz, $(CD_3)_2SO$); 8.27–8.17 (2H, m, H-5,8), 8.04–7.92 (3H, m, H-4,6,7), 7.57 (1H, d, *J* 6.0, H-4), 4.24 (2H, q, *J* 6.6, H-15), 4.15 (2H, q, *J* 6.9, H-17), 1.45 (6H, m, H-16,18); δ_C (75 MHz, $CDCl_3$); 182.7 (C=O, C-9), 182.5 (C=O, C-10), 158.8 (quat. Ar.C, C-2), 149.1 (quat. Ar.C, C-1), 135.3 (quat. Ar.C, C-12), 134.1 (Ar.C, C-6), 133.8 (Ar.C, C-7), 133.1 (quat. Ar.C, C-11), 127.3 (Ar.C, C-5), 126.6 (Ar.C, C-8), 125.0 (Ar.C, C-3), 121.1 (quat. Ar.C, C-14), 116.9 (Ar.C, C-4), 116.8 (quat. Ar.C, C-13), 69.8 (O–CH_2–CH_3, C-17), 64.9 (O–CH_2–CH_3, C-15), 15.7 (O–CH_2–CH_3, C-18), 14.7 (O–CH_2–CH_3, C-16); *m*/*z* (ESI) 319 (100%, MNa^+); UV/vis λ_{max} (CH_3COCH_3) 375 nm.

2-(Benzyloxy)-1-hydroxyanthracene-9,10-dione (11a). Powdered potassium hydroxide (82 mmol) was added to DMSO (82 cm^3) at 37 °C. After stirring for 5 min, alizarin (41 mmol) was added, followed immediately by the benzylbromide (CAUTION: Irritating to eyes, respiratory system and skin) (37.5 mmol). Stirring was continued for 24 h, after which time the mixture was poured into aqueous hydrochloric acid (1M, 400 cm^3) and extracted with dichloromethane (3 × 400 cm^3). The combined organic extracts were washed with water (5 × 500 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dried further under high vacuum (24 h). The solid contained a mixture of **11a**, **11b** and alizarin (**1**). The mixture was recrystallised repeatedly from ethylacetate (CAUTION: Highly flammable. Irritating to eyes) to give the product **11a** (2.3 g, 6.96 mmol, yield: 17%). m.p. 170–174 °C; (Found: C, 75.5; H, 4.2; $C_{21}H_{14}O_4$ requires C, 76.4; H, 4.3%); ν_{max} (solid)/cm^{-1} (C–H) 3057–2900, (–OH) 2900–2600, (C=O) 1667, (C–O) 1262; ^{1}H nmr, δ_H (300 MHz, $(CD_3)_2SO$); 12.75 (1H, s, C–OH), 8.23–8.18 (2H, m, H-5,8), 7.93 (2H, m, H-6,7), 7.73 (1H, d, *J* 9.0, H-4), 7.56–7.40 (6H, m, H-3,16-21), 5.29 (2H, s, H-15); ^{13}C {^{1}H} nmr, δ_C (75 MHz, $CDCl_3$); 189.2 (C=O, C-9), 181.5 (C=O, C-10), 153.3 (quat. ArC, C-2), 153.1 (quat. ArC, C-1), 135.7 (quat. ArC, C-16), 134.8 (ArC, C-6), 134.1 (quat. ArC, C-12), 133.8 (ArC, C-7), 133.4 (quat. ArC, C-11), 128.8 (2 ArC, C-18,20), 128.4 (ArC, C-19), 127.4 (2 ArC, C-17,21), 127.4 (ArC, C-5), 126.9 (ArC, C-8), 125.7 (quat. ArC, C-14), 120.8 (ArC, C-3), 118.1 (ArC, C-4), 116.4 (quat. ArC, C-13), 71.2 (–O–CH_2–Ph, C-15); *m*/*z* (ESI) 353 (100%, MNa^+); UV/vis λ_{max} (CH_3COCH_3) 423 nm.

1,2-Bis(benzyloxy)anthracene-9,10-dione (11b). Powdered potassium hydroxide (164 mmol) was added to DMSO (82 cm^3) at 37 °C. After stirring for 5 min, alizarin (41 mmol) was added, followed immediately by the benzylbromide (102.5 mmol). Stirring was continued for 24 h, after which the mixture was poured into aqueous hydrochloric acid (1M, 400 cm^3) and extracted with dichloromethane (3 × 400 cm^3). The combined organic extracts were washed with distilled water (5 × 500 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dried further under high vacuum (24 h). The solid contained a mixture of **11a**, **11b** and alizarin (**1**) and was dissolved in dichloromethane (100 cm^3). The compound **11a** and alizarin were removed by extraction with sodium hydroxide (1M, 2 × 20 cm^3). Concentration of the dichloromethane solution *in vacuo* gave a solid, which was further dried in a high vacuum and was proven to be **11b** (1.92 g, 4.52 mmol, yield: 11%). m.p. 144-147 °C; (Found: C, 78.4; H, 4.6; $C_{28}H_{20}O_4$ requires C, 80.0; H, 4.8%); ν_{max} (solid)/cm^{-1}) (C–H) 3067–2873, (C=O) 1668, (C–O) 1260; ^{1}H nmr, δ_H (300 MHz, $(CD_3)_2SO$); 8.21–8.15 (2H, m, H-5,8), 8.06 (1H, d, *J* 9.0, H-4), 7.95–7.88 (2H, m, H-6,7), 7.69 (1H, d, *J* 9.0, H-3), 7.50–7.32 (10H, m, H-17-21,24-28), 5.32 (2H, s, H-22), 5.04 (2H, s, H-15); ^{13}C {^{1}H} nmr, δ_C (75 MHz, $CDCl_3$); 181.6 (C=O, C-9), 181.4 (C=O, C-10), 157.4 (quat. ArC, C-2), 147.6 (quat. ArC, C-1), 136.1 (quat. ArC, C-23), 134.6 (quat. ArC, C-16), 134.2 (quat. ArC, C-12), 132.8 (ArC, C-6), 132.4 (ArC, C-7), 132.0 (quat. ArC, C-11), 128.0–125.6 (10 ArC), 124.5 (quat. ArC, C-14), 124.2 (ArC, C-3), 116.8 (ArC, C-4), 116.8 (quat. ArC, C-13), 74.2 (–O–CH_2–Ph, C-22), 70.2 (–O–CH_2-Ph, C-15); *m*/*z* (ESI) 443 (100%, MNa^+); UV/vis λ_{max} (CH_3COCH_3) 375 nm.

Methyl-4-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)butanoate (12a). Powdered potassium hydroxide (160 mmol) was added to DMSO (80 cm^3) at 37 °C. After stirring for 5 min, alizarin (40 mmol) was added, followed immediately by the methyl-4-bromobutyrate (CAUTION: Harmful if swallowed. Irritating to skin) (100 mmol). Stirring was continued for 72 h, after which time an additional amount of methyl-4-bromobutyrate was added (100 mmol). The mixture was stirred for another 24 h and then it was poured into aqueous hydrochloric acid solution (1M, 400 cm^3) and extracted with dichloromethane (3 × 400 cm^3). The combined organic extracts were washed with water (5 × 500 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dried further under high vacuum (24 h). The solid contained a mixture of **12a**, traces of di-derivative (**12b**) and alizarin (**1**). The mixture and was recrystallised twice from ethylacetate to give the product **12a:** (3.2 g, 9.4 mmol, yield: 23%). m.p. 145–148 °C; (Found: C, 66.9; H, 4.7; $C_{19}H_{16}O_6$ requires C, 67.1; H, 4.7%); ν_{max} (solid)/cm^{-1} (C–H) 3100–2885, (–OH) 3000–2600, (C=O) 1730–1667, (C–O) 1278; ^{1}H nmr, δ_H (300 MHz, $CDCl_3$); 13.1 (1H, s, C–OH), 8.32–8.30 (2H, m, H-5,8), 7.85 (1H, d, *J* 8.4, H-4), 7.82–7.79 (2H, m, H-6,7), 7.18 (1H, d, *J* 8.4, H-3), 4.22 (2H, t, *J* 6.3, H-15), 3.71 (3H, s, H-19), 2.61 (2H, t, *J* 6.9, H-17), 2.25 (2H, qu, *J* 6.6, H-16); ^{13}C {^{1}H} nmr, δ_C (75 MHz, $CDCl_3$); 189.2 (C=O, C-9), 181.5 (C=O, C-10), 173.4 (quat. –CH_2–$COOCH_3$, C-18), 153.4 (quat. ArC, C-2), 153.1 (quat. ArC, C-1), 134.8 (ArC, C-6), 134.2 (quat. ArC, C-12), 133.8 (ArC., C-7), 133.4 (quat. ArC, C-11), 127.4 (ArC, C-5), 126.9 (ArC, C-8), 125.5 (quat. ArC, C-14), 121.0 (ArC, C-3), 117.2 (ArC, C-4), 116.3 (quat. ArC, C-13), 68.2 (–O–CH_2–CH_2–CH_2-, C-15), 51.8 (–CH_2–$COOCH_3$, C-19), 30.3 (–CH_2–$COOCH_3$, C-17), 24.3 (–CH_2–CH_2–CH_2-, C-16); *m*/*z* (ESI) 363 (100%, MNa^+); UV/vis λ_{max} (CH_3COCH_3) 424 nm. Through the work conducted herein, it was not possible to synthesise significant quantities of the di-derivative product (**12b**).

2-Ethoxy-1,4-dihydroxyanthracene-9,10-dione (13a). Powdered potassium hydroxide (77.6 mmol) was added to DMSO (50 cm^3) at 37 °C. After stirring for 5 min, purpurin (19.5 mmol) was added, followed immediately by the ethyl iodide (23.4 mmol). Stirring was continued for 72 h, after which the mixture was poured into hydrochloric acid (1M, 400 cm^3) and extracted with dichloromethane (3 × 400 cm^3). The combined organic extracts were washed with distilled water (5 × 500 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dried further under high vacuum (24 h). The solid contained **13a** as well as impurities. Column chromatography, using DCM as eluent gave **13a** (1.90 g, 6.68 mmol, yield: 34%). m.p. 199–201 °C; (Found: C, 67.6; H, 4.2; $C_{16}H_{12}O_5$ requires C, 67.6; H, 4.2%); ν_{max} (solid)/cm^{-1} (C–H) 2987, (–OH) 3000–2600, (C=O) 1619, (C–O) 1281; ^{1}H nmr, δ_H (300 MHz, $(CD_3)_2SO$); 13.49 (1H, s, C(-4)–OH), 13.22

(1H, s, C(-1)–OH), 8.28–8.25 (2H, m, H-5,8), 8.00–7.95 (2H, m, H-6,7), 6.97 (1H, s, H-3), 4.23 (2H, q, *J* 8.7, H-15), 1.41 (3H, t, *J* 8.7, H-16); $^{13}C\{^1H\}$ nmr, δ_C (75 MHz, $CDCl_3$); 186.2 (C=O, C-9), 183.3 (C=O, C-10), 160.0 (quat. Ar.C, C-4), 156.1 (quat. Ar.C, C-2), 149.5 (quat. Ar.C, C-1), 133.5 (Ar.C, C-6), 133.1 (quat. Ar.C, C-12), 132.8 (Ar.C, C-7), 132.3 (quat. Ar.C, C-11), 126.0 (Ar.C, C-5), 125.8 (Ar.C, C-8), 111.4 (quat. Ar.C, C-13), 106.3 (Ar.C, C-3), 105.0 (quat. Ar.C, C-14); *m/z* (ESI) 285 (100%, MH^+); UV/vis λ_{max} (CH_3COCH_3) 480 nm. Through the work conducted herein, it was not possible to synthesise significant quantities of the di-derivative product (**13b**).

2-(Benzyloxy)-1,4-dihydroxyanthracene-9,10-dione (14a) and 1,2-bis(benzyloxy)-4-hydroxyanthracene-9,10-dione (14b). Powdered potassium hydroxide (156 mmol) was added to DMSO (80 cm^3) at 37 °C. After stirring for 5 min, purpurin (39 mmol) was added, followed immediately by the benzylbromide (195 mmol). Stirring was continued for 24 h, after which the mixture was poured into hydrochloric acid (1M, 400 cm^3) and extracted with dichloromethane (3 × 400 cm^3). The combined organic extracts were washed with distilled water (5 × 500 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was a viscous mixture of **14a**, **14b** and impurities. The mixture was purified using column chromatography (DCM as eluent) to give two major fractions. The first fraction was a viscous oil which solidified on trituration with diethylether (CAUTION: Extremely flammable. May form explosive peroxides. Harmful if swallowed). Recrystallisation twice from ethylacetate to give **14a**. (2.9 g, 8.37 mmol, yield: 22%). m.p. 202–205 °C; (Found: C, 73.0; H, 4.1; $C_{21}H_{14}O_5$ requires C, 72.8; H, 4.1%); ν_{max} (solid)/cm^{-1} (C–H) 3065–2954, (–OH) 3000–2600, (C=O) 1674, (C–O) 1274; ^1H nmr, δ_H (300 MHz, $(CD_3)_2SO$); 13.45 (1H, s, C(-4)–OH), 13.21 (1H, s, C(-1)–OH), 8.27 (2H, m, H-5,8), 7.97 (2H, m, H-6,7), 7.52–7.39 (5H, m, H-16-21), 7.12 (1H, s, H-3), 5.34 (2H, s, H-15); $^{13}C\{^1H\}$ nmr, δ_C (75 MHz, $CDCl_3$); 186.3 (C=O, C-9), 183.5 (C=O, C-10), 159.7 (quat. Ar.C, C-4), 155.7 (quat. Ar.C, C-2), 149.7 (quat. Ar.C, C-1), 133.9 (quat. Ar.C, C-16), 133.6 (Ar.C, C-6), 133.1 (quat. Ar.C, C-12), 132.8 (Ar.C, C-7), 132.3 (quat. Ar.C, C-11), 127.9 (2 ArC), 127.6 (2 ArC), 126.5 (2 ArC), 126.0 (Ar.C, C-5), 125.9 (Ar.C, C-8), 111.7 (quat. Ar.C, C-13), 107.4 (Ar.C, C-3), 105.4 (quat. Ar.C, C-14), 70.3 (–O–CH$_2$–Ph, C-15); *m/z* (ESI) 369 (100%, MNa^+); UV/vis λ_{max} (CH_3COCH_3) 480 nm.

A second fraction was obtained from the column, and was dissolved in dichloromethane (100 cm^3) and washed with sodium hydroxide (1M, 20 cm^3). Evaporation of the dichloromethane solution gave a solid, which was further dried in a high vacuum to give **14b:** (0.9 g, 2.06 mmol, yield: 5%). m.p. 174–176 °C; (Found: C, 77.0; H, 4.5; $C_{28}H_{20}O_5$ requires C, 77.1; H, 4.6%); ν_{max} (solid)/cm^{-1} (C–H) 3061–2959, (–OH) 3000–2600, (C=O) 1671, (C–O) 1270; ^1H nmr, δ_H (300 MHz, $(CD_3)_2SO$); 13.57 (1H, s, C(-1)–OH), 8.25 (2H, m, H-5,8), 7.95 (2H, m, H-6,7), 7.51–7.29 (10H, m, H-17-21,24-28) 7.13 (1H, s, H-3), 5.32 (2H, s, H-15), 4.98 (2H, s, H-22); $^{13}C\{^1H\}$ nmr, δ_C (75 MHz, $CDCl_3$); 187.0 (C=O, C-9), 182.0 (C=O, C-10), 162.6 (quat. Ar.C, C-4), 161.1 (quat. Ar.C, C-2), 143.8 (quat. Ar.C, C-1), 137.1 (quat. Ar.C, C-16), 135.1 (quat. Ar.C, C-22), 135.0 (quat. Ar.C, C-12), 134.2 (Ar.C, C-6), 133.6 (Ar.C, C-7), 132.9 (quat. Ar.C, C-11), 128.9–126.4 (10 ArC, C-17-21,24-28), 106.9 (ArC, C-3), 75.2 (–O–CH$_2$–Ph, C-15), 71.3 (–O–CH$_2$–Ph, C-15); *m/z* (ESI) 459 (100%, MNa^+); UV/vis λ_{max} (CH_3COCH_3) 429 nm.

Methyl-4-(9,10-dihydro-1,4-dihydroxy-9,10-dioxoanthracen-3-yloxy)butanoate (15a). Powdered potassium hydroxide (160 mmol) was added to DMSO (80 cm^3) at 37 °C. After stirring for 5 min, purpurin (40 mmol) was added, followed immediately by methyl-4-bromobutyrate (100 mmol). Stirring was continued for 72 h, after which time more methyl-4-bromobutyrate (100 mmol) and potassium hydroxide (160 mmol) was added. After 4 days the mixture was poured into hydrochloric acid (1M, 400 cm^3) and extracted with dichloromethane (3 × 400 cm^3). The combined organic extracts were washed with distilled water (5 × 500 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dried further under high vacuum (24 h). The viscous product was triturated with diethylether and was recrystallised twice from ethylacetate to give **15a** (2.9 g, 8.13 mmol, yield: 21%). m.p. 149–152 °C; (Found: C, 63.8; H, 4.4; $C_{19}H_{16}O_7$ requires C, 64.0; H, 4.4%); ν_{max} (solid)/cm^{-1} (C–H) 2954–2887, (–OH) 2900–2600, (C=O) 1730, (C–O) 1278; ^1H nmr, δ_H (300 MHz, $CDCl_3$); 13.52 (1H, s, C(-4)–OH), 13.45 (1H, s, C(-1)–OH), 8.33–8.30 (2H, m, H-5,8), 7.82–7.78 (2H, m, H-6,7), 6.67 (1H, s, H-3), 4.18 (2H, t, *J* 6.0, H-15), 3.71 (3H, s, H-19), 2.60 (2H, t, *J* 6.0, H-17), 2.25 (2H, q, *J* 6.0, H-16); $^{13}C\{^1H\}$ nmr, δ_C (75 MHz, $CDCl_3$); 186.2 (C=O, C-9), 183.5 (C=O, C-10), 172.2 (quat. –CH$_2$COOCH$_3$, C-18), 159.8 (quat. ArC, C-4), 155.9 (quat. ArC, C-2), 149.6 (quat. ArC, C-1), 133.5 (ArC, C-6), 133.1 (quat. ArC, C-12), 132.8 (ArC., C-7), 132.3 (quat. ArC, C-11), 126.0 (ArC, C-5), 125.9 (ArC, C-8), 111.5 (quat. ArC, C-13), 106.7 (ArC, C-3), 105.2 (quat. ArC, C-14), 67.4 (–OCH$_2$CH$_2$CH$_2$-, C-15), 50.7 (–CH$_2$COOCH$_3$, C-19), 29.2 (–CH$_2$COOCH$_3$, C-17), 23.0 (–CH$_2$CH$_2$CH$_2$-, C-16); *m/z* (ESI) 379 (100%, MNa^+); UV/vis λ_{max} (CH_3COCH_3) 480 nm. Through the work conducted herein, it was not possible to synthesise significant quantities of the di-derivative product (**15b**).

4.4. Preparation of dye dispersions

Both the parent dyes (alizarin and purpurin) and derivatives were insoluble in water under the pH required for the dyeing of these fibres (pH 4.5–5.0). Consequently, the addition of a dispersing agent (surfactant; *Borresperse NA*) was required to produce a dispersion of the dye in water for dyeing. Each dye compound was ground into a fine powder by hand using a mortar and pestle. A 100 cm^3 jar was filled with 6 mm diameter steel ball bearings to one third of its height and 1 g of *Borresperse NA* and 1 g of dye were added. Distilled water was added until the balls were just below the surface. The jar was placed in a milling apparatus for three days, where the jar was rolled; at the end of the milling process the dispersed colorant was washed from the jar with 50 cm^3 of distilled water into a 100 cm^3 volumetric flask which was then filled to 100 cm^3.

4.5. Pre-treatment of fabrics

Prior to dyeing fabric samples (5 g) were scoured using 2 g dm^{-3} sodium carbonate (CAUTION: Irritating to eyes) and 1 g dm^{-3} *Kieralon MFB* using a 20:1 liquor ratio at 60 °C for 15 min. Samples were scoured in stainless steel, sealed dye tubes in a laboratory-scale *Roaches Pyrotec 2000* dyeing machine. At the end of the treatment, the samples were rinsed with water and dried in air.

4.6. Dyeing

Scoured fabric samples (5 g) were dyed at a concentration of 2% on mass of fibre (omf) using a liquor:fibre ratio (LR) of 10:1 liquor ratio. Dyeing assistants added were 1 g dm^{-3} *Levagal DLP* and 2 g dm^{-3} *Ludigol AR*. The pH was adjusted to 4.5–5.0 using acetic acid/sodium acetate buffer. Samples were dyed in stainless steel, sealed dye tubes in a laboratory-scale *Roaches Pyrotec 2000* dyeing machine. The dyebath was heated steadily (2 °C min^{-1}) until the dyeing temperature was achieved (PET, 130 °C; PLA 115 °C), then held at that temperature for 45 min. After dyeing, the dyebaths were cooled and the residues retained for analysis; dyed samples were rinsed with water and left to dry in air under ambient conditions.

4.7. Post-dyeing treatment of fabrics

Reduction clearing was conducted to remove any dye that had not diffused into the fibres and was deposited on the surface. Dyed fabric samples were treated with 1.5 g dm^{-3} sodium carbonate and 2.0 g dm^{-3} sodium hydrosulfite using a LR of 20:1 in stainless steel, sealed dye tubes in a laboratory-scale *Roaches Pyrotec 2000* dyeing machine. The dyebath was heated rapidly to 60 °C then held at that temperature for 15 min. After treatment, the samples were rinsed with water and left to dry in air under ambient conditions.

4.8. Colour measurement

Spectral reflectance factors (taken between 400 and 700 nm wavelengths in 20-nm increments) of the samples were measured using a Datacolor Spectraflash SF600 reflectance spectrophotometer (Datacolor International Ltd, UK) interfaced to a computer. Each fabric sample was folded twice to give a total of four layers. Four different areas of each sample were measured and the average colour value was automatically calculated and saved by the computer. CIELAB values (under illuminant D65 using the 10° standard observer) and *K*/*S* values (representing absorption) were automatically calculated from reflectance factors *R* at the desired wavelength (usually λ_{max}) by the software using the Kubelka–Munk equation (1).

$$\frac{K}{S} = \frac{(1 - R_\lambda)^2}{2R_\lambda} \quad (1)$$

4.9. Wash fastness testing

Dyed samples were subjected to ISO 105:C06/C2S wash fastness test [39] using SDC Multifibre as adjacent fabric in a laboratory-scale *Roaches Washtec-P* wash fastness testing machine. Dyed samples were assessed using grey scales according to the ISO 105:A02 [39] for assessing change in colour. Rating was given using a grey scale ranging between 1(worst) and 5 (best) with half-points in between.

4.10. Light fastness testing

Dyed samples were subjected to ISO 105:B02 [39] light fastness test (Method 2) using a *Xenotest Alpha LM* apparatus using blue wool standards as reference. Blue wool standards fade on a scale of 1 (worst) to 8 (best) and dyed samples were assessed against these references.

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