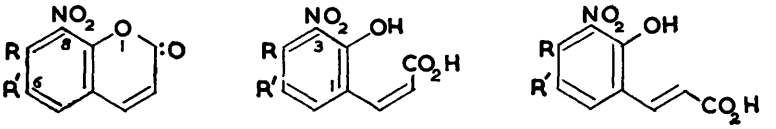
422. *The Stability of Coumarinic Acids. Chelation of the Hydroxyl Group.*

By Malcolm Crawford and J. W. Rasburn.

Examination of a number of new and known substituted coumarins has established that free coumarinic acids can readily be isolated from 8-nitrocoumarins but not from other nitrocoumarins. The stability of these acids is attributed to chelation of the nitro-group with the neighbouring hydroxyl group. The isomeric coumaric acids have also been prepared.

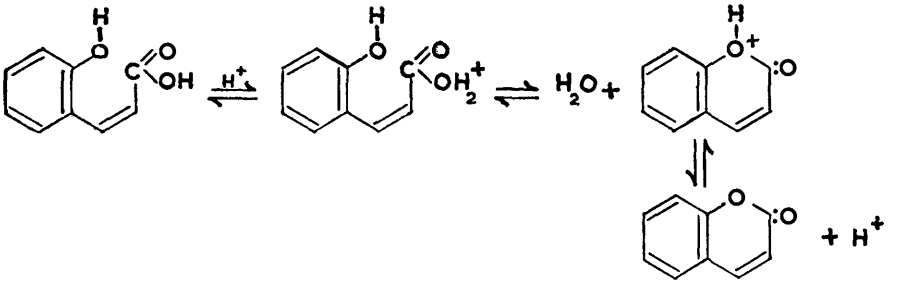
3-Nitrocoumarinic acid (II; R = R′ = H) was obtained by Miller and Kinkelin [1] on acidification of an alkaline solution of 8-nitrocoumarin (I; R = R′ = H). The acid reverts readily in solution, or when heated, to the coumarin. The *trans*-isomer, 3-nitro-



(I) (II) (III)

coumaric acid (III; R = R′ = H), was much more resistant to cyclisation. Since then the isolation of various coumarinic acids has been claimed,[2] but some of these containing β-methyl groups were later shown [3] to be coumaric acids. It is therefore unsafe to assign *cis* (coumarinic) or *trans* (coumaric) structure to these acids unless both isomers are prepared and their tendencies to coumarin formation are compared, as has been done for most of the examples given below.

The present work shows that 8-nitrocoumarins give stable coumarinic acids. The cyclisation of a coumarinic acid to its coumarin probably takes place by stages which will not differ appreciably from those in the annexed formula sequence. Chelation of the



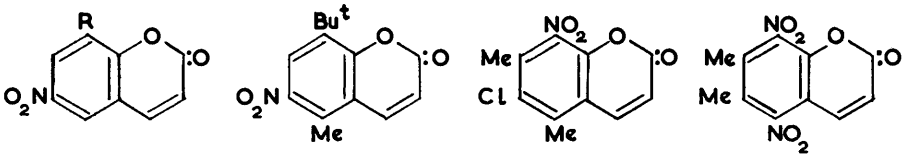
hydroxyl group with an *o*-nitro-group, as in 3-nitrocoumarinic acid (III), known to occur in *o*-nitrophenol, will oppose the loss of a proton in the last stage of the cyclisation, and thus stabilise the coumarinic acid.

The negative character or electron-attractive power of the stabilising group has been held responsible for the stability of some coumarinic acids,[4] yet 6-nitrocoumarin does not yield a stable coumarinic acid, a fact used by Dey and Krishnamurthi [5] in its separation from 8-nitrocoumarin. The 8-nitrocoumarins (I) in which R = H and R′ = Me, Bu^t, Ph, Cl, Br, or OMe, are now shown to give isolable coumarinic acids which are distinct from the coumaric acids, which were also prepared. On the other hand the 6-nitrocoumarins (IV; R = Me, Pr^i, Ph, Br, and OMe) and (V) do not give isolable coumarinic acids. Thus it

[1] Miller and Kinkelin, *Ber.*, 1889, **22**, 1706.
[2] (*a*) Jordan and Thorpe, *J.*, 1915, **107**, 387; Dey, *ibid.*, p. 1606; (*b*) Clayton, *J.*, 1910, **97**, 1388.
[3] Murty, Rao, and Seshadri, *Proc. Indian Acad. Sci.*, 1937, **6**, *A*, 316.
[4] Sethna and Shah, *Chem. Rev.*, 1945, **36**, 23; Whalley, *J.*, 1951, 3235.
[5] Dey and Krishnamurthi, *J. Indian Chem. Soc.*, 1927, **4**, 197.

is clear that the mere bulk of the 8-substituent is not responsible and that the 6-nitro-group is ineffective.

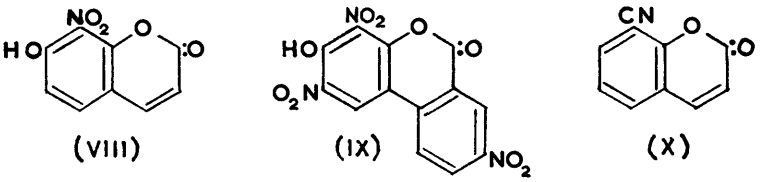
That chelation of the nitro- and the hydroxy-group stabilises coumarinic acids is supported by the low stability of the acid from 7-methyl-8-nitrocoumarin (I; R = Me, R′ = H), where the 7-substituent interferes with the coplanarity of the 8-nitro-group and the ring, which is necessary for maximum chelation with the *o*-hydroxy-group. When a further substituent is introduced into the 6-position, as in (I; R = R′ = Me), (VI), and (VII), the resulting buttressing action pushes the 7-methyl group in the direction of the



(IV) (V) (VI) (VII)

8-nitro-group, thus moving the latter further from coplanarity and further reducing chelation and the stability of the coumarinic acid, as now observed. Lower stability was reported by Clayton [2b] for the acid from (VII).

The introduction of a 7-hydroxyl group has a very different effect. 7-Hydroxy-8-nitrocoumarin (VIII) gives a remarkably stable coumarinic acid, in which the nitro-group appears to be doubly chelated by a hydroxyl group on each side. Thus held from both sides in the plane of the ring, the nitro-group is less subject to the twisting effect of thermal



(VIII) (IX) (X)

agitation and hence proton loss is opposed all the more. 7-Hydroxy-6 : 8 : 2′-trinitro-3 : 4-benzocoumarin (IX) also gives a stable acid of coumarinic type; in it the *cis*-configuration is necessitated (there can be no *trans*-isomer).

Examination of 8-cyanocoumarin (X) gives further evidence in favour of chelation. The nitrile group, although electron-attractive, cannot, however, owing to its linearity, form a chelate linkage with an *o*-hydroxy-group; as expected, no stable coumarinic acid was obtained from this coumarin.

Experimental

2 : 4-*Dihydroxy*-3 : 5-*dinitro*allo*cinnamic Acid.*—A solution of 7-hydroxy-6 : 8-dinitrocoumarin (0·5 g.), prepared according to Clayton,[2b] in a mixture of 10% sodium hydroxide solution (3 ml.) and water (10 ml.) was boiled for 5 min., cooled in ice, filtered, and added to an ice-cooled mixture of 2N-hydrochloric acid (8 ml.) and water (not more than 10 ml.). The precipitate of *acid* was washed with a little ice-water and crystallised from 30% aqueous alcohol as yellow needles, m. p. 160—161° (Found: C, 40·3; H, 2·4; N, 10·0. $C_9H_6O_8N_2$ requires C, 40·0; H, 2·2; N, 10·4%).

6-*Methyl*-8-*nitrocoumarin.*—A mixture of 2-hydroxy-5-methyl-3-nitrobenzaldehyde [6] (9 g.), sodium acetate (13·5 g.), and acetic anhydride (20 ml.) was refluxed for 3½ hr. The resulting dark brown solid was extracted with 50% acetic acid (200 ml.). The extract was treated with charcoal and cooled, affording the *coumarin* (6·85 g.), m. p. 174° after three crystallisations with charcoal from acetic acid (Found: C, 58·7; H, 3·4. $C_{10}H_7O_4N$ requires C, 58·5; H, 3·4%).

5-*Methyl*-3-*nitrocoumaric Acid.*—The first mother-liquor in the foregoing preparation was concentrated to 50 ml. and diluted with water (400 ml.). The precipitate was extracted with cold 5% sodium carbonate solution, and the filtrate boiled for 15 min. for deacetylation, cooled, and acidified. The precipitate was extracted with sodium hydrogen carbonate solution and

reprecipitated. Recrystallisation from 50% alcohol gave yellow needles of the *acid* (0·75 g.), m. p. 234—236° (decomp.) (Found : C, 53·5; H, 4·2. $C_{10}H_9O_5N$ requires C, 53·8; H 4·1%).

5-*Methyl*-3-*nitrocoumarinic Acid*.—6-Methyl-8-nitrocoumarin (0·5 g.) was dissolved in hot sodium hydroxide solution, filtered cold, cooled further to 0°, and added to chilled hydrochloric acid. The yellow *acid* precipitated was washed with ice-water and recrystallised from aqueous alcohol as yellow needles, m. p. (sealed tube) 166—167° (decomp. to a solid of m. p. 173—174°) (Found : C, 53·9; H, 3·9; N, 6·0. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·1; N, 6·3%).

5-tert.-*Butyl*-2-*hydroxybenzaldehyde*.—*p-tert.*-Butylphenol (100 g.), hexamethylenetetramine (100 g.), glycerol (600 g.), and boric acid (140 g.) were treated, according to the conditions of the Duff reaction, to give a pale yellow oil (32 g.), yielding on distillation the aldehyde (21·4 g.), b. p. 80—86°/1 mm., and a fraction (7 g.), b. p. 86—98°/1 mm. The phenylhydrazone of the aldehyde had m. p. 184° as reported by Henry and Sharp.[7]

3 : 5-*Di*-tert.-*butyl*-2-*hydroxybenzaldehyde*.—The foregoing higher-boiling fraction, which partly solidified on cooling, gave on recrystallisation from alcohol the new *aldehyde* (1·5 g.), m. p. 61·5—63° (Found : C, 76·4; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). Its *phenylhydrazone*, plates from aqueous alcohol, had m. p. 140·5—141·5° (Found : C, 77·7; H, 8·7; N, 8·75. $C_{21}H_{28}ON_2$ requires C, 77·7; H, 8·7; N, 8·6%). This aldehyde probably arises from 2 : 4-di-*tert.*-butylphenol present in the sample of *p-tert.*-butylphenol used. Its resistance to bromination and nitration indicates that it is not an octyl compound.

5-tert.-*Butyl*-2-*hydroxy*-3-*nitrobenzaldehyde*.—5-*tert.*-Butyl-2-hydroxybenzaldehyde (5·35 g.) was treated at room temperature with fuming nitric acid (1·3 ml.) in acetic acid (47 ml.). Three crystallisations of the product from alcohol gave the *nitro-aldehyde* (4 g.) as pale lemon-yellow plates, m. p. 91—92° (Found : C, 59·4; H, 5·6; N, 6·1. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·9; N, 6·3%).

6-tert.-*Butyl*-8-*nitrocoumarin*.—The foregoing nitro-aldehyde (4·46 g.) was subjected to the Perkin reaction. The product was boiled with acetic acid (100 ml.) and filtered, the filtrate boiled with charcoal and filtered hot. Dilution of this filtrate with water (500 ml.) gave a precipitate, which was extracted with cold 5% sodium carbonate solution. The residue on two crystallisations (charcoal) from 80% acetic acid gave the *nitrocoumarin* (1·93 g.) as colourless plates, m. p. 175—176° (Found : C, 63·2; H, 5·3; N, 5·6. $C_{13}H_{13}O_4N$ requires C, 63·2; H, 5·3; N, 5·7%).

5-tert.-*Butyl*-3-*nitrocoumaric acid*.—Acidification of the sodium carbonate extract from the last preparation gave this *acid* (0·33 g.), yellow plates, m. p. 222—223° (decomp.) (from aqueous alcohol) (Found : C, 59·2; H, 5·6; N, 5·2. $C_{13}H_{15}O_5N$ requires C, 58·9; H, 5·7; N, 5·3%).

5-tert.-*Butyl*-3-*nitrocoumarinic Acid*.—A filtered and chilled solution of 6-*tert.*-butyl-8-nitrocoumarin (0·5 g.) in dilute sodium hydroxide solution was added to chilled dilute hydrochloric acid. The precipitate, washed with cold water and recrystallised from aqueous alcohol, gave yellow needles of the *acid*, m. p. 133—134° (decomp.), second m. p. 174—175° (Found : C, 58·6; H, 5·7%).

2-*Hydroxy*-3-*nitro*-5-*phenylbenzaldehyde*.—2-Hydroxy-5-phenylbenzaldehyde (5·85 g.), obtained from *p*-hydroxydiphenyl by the Duff reaction, was nitrated in acetic acid at 20—30°, giving the *nitro-aldehyde* (6·7 g.) as orange-yellow needles (from alcohol), m. p. 115—116° (Found : C, 63·6; H, 3·7; N, 5·7. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7; N, 5·8%).

8-*Nitro*-6-*phenylcoumarin*.—The foregoing aldehyde (6·07 g.), subjected to the Perkin reaction for 8 hr., gave the *coumarin* (4·07 g.). On repeated recrystallisation with charcoal from aqueous acetic acid it formed pale yellow needles, m. p. 178—178·5° (Found : C, 67·5; H, 3·2; N, 5·3. $C_{15}H_9O_4N$ requires C, 67·4; H, 3·4; N, 5·2%).

3-*Nitro*-5-*phenylcoumaric Acid*.—The sodium carbonate extract of the crude initial product of the foregoing Perkin reaction yielded the *acid* (0·27 g.), yellow needles (from alcohol), m. p. 225—226° (decomp.) (Found : C, 63·3; H, 3·9; N, 4·8. $C_{15}H_{11}O_5N$ requires C, 63·2; H, 3·9; N, 4·9%).

3-*Nitro*-5-*phenylcoumarinic acid*.—Prepared from 8-nitro-6-phenylcoumarin (0·5 g.), this *acid*, orange-yellow needles from alcohol, had m. p. 180—181° (decomp.) in a sealed tube (after cooling, m. p. 177—178°) (Found : C, 62·8; H, 3·9; N, 4·6%).

6-*Chloro*-8-*nitrocoumarin*.—5-Chloro-2-hydroxy-3-nitrobenzaldehyde (10·08 g.), m. p. 108—109°, obtained from 5-chloro-2-hydroxybenzaldehyde (lit.,[8] m. p. 105—107°), gave the *coumarin* (6·65 g.) by the Perkin reaction, as colourless needles (from 80% acetic acid),

[6] Borsche, *Ber.*, 1917, **50**, 1345.
[7] Henry and Sharp, *J.*, 1926, 2437.
[8] Lovett and Roberts, *J.*, 1928, 1978.

m. p. 153—154° (Found : C, 48·1; H, 1·6; N, 6·2. $C_9H_4O_4NCl$ requires C, 47·9; H, 1·8; N, 6·2%).

5-*Chloro*-3-*nitrocoumaric Acid*.—Acidification of the sodium carbonate extract of the initial product from the preceding Perkin reaction gave the *acid*, yellow needles (0·31 g.), m. p. 221—222° (decomp.) (from aqueous alcohol) (Found : C, 44·9; H, 2·4; N, 5·9. $C_9H_6O_5NCl$ requires C, 44·4; H, 2·5; N, 5·8%).

5-*Chloro*-3-*nitrocoumarinic Acid*.—Prepared from 6-chloro-8-nitrocoumarin as yellow plates from aqueous alcohol, this *acid* had m. p. 146—147° (decomp.), second m. p. 151—152° (Found : C, 44·5; H, 2·6; N, 5·8%).

6-*Bromo*-8-*nitrocoumarin*.—5-Bromo-2-hydroxy-3-nitrobenzaldehyde (12·3 g.), obtained by bromination of salicylaldehyde and nitration of the product, was submitted to the Perkin reaction for 3 hr. Repeated recrystallisation of the product from aqueous acetic acid with charcoal gave the *nitrocoumarin* (8·8 g.) as pale yellow needles, m. p. 180—180·5 (Found : C, 40·3; H, 1·6; N, 5·0. $C_9H_4O_4NBr$ requires C, 40·0; H, 1·5; N, 5·2%).

5-*Bromo*-3-*nitrocoumaric Acid*.—Acidification of the sodium carbonate extract of the initial product from the preceding Perkin reaction gave the *acid* (0·23 g.), yellow needles, m. p. 237—238° (decomp.) (from aqueous alcohol) (Found : C, 37·5; H, 2·1; N, 5·0. $C_9H_6O_5NBr$ requires C, 37·5; H, 2·1; N, 4·9%).

5-*Bromo*-3-*nitrocoumarinic Acid*.—Prepared from 6-bromo-8-nitrocoumarin as golden-yellow platelets (from aqueous alcohol), this *isomer* had m. p. 148—149° (decomp.), second m. p. 178—180° (Found : C, 37·8; H, 2·0; N, 4·8%).

6-*Methoxy*-8-*nitrocoumarin*.—2-Hydroxy-5-methoxy-3-nitrobenzaldehyde [9] (2 g.) gave in a Perkin reaction (3½ hr.) the *coumarin* (1·35 g.) as pale yellow needles (from acetic acid), m. p. 219—219·5° (Found : C, 54·0; H, 3·5; N, 6·3. $C_{10}H_7O_5N$ requires C, 54·3; H, 3·2; 6·3%).

5-*Methoxy*-3-*nitrocoumaric acid*.—This *acid* was obtained from the products of the preceding Perkin reaction in two forms (orange needles and red prisms), both of which (from alcohol) had m. p. 226—227° (decomp.) (Found : C, 50·0; H, 4·0; N, 6·0. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·8; N, 5·9%).

5-*Methoxy*-3-*nitrocoumarinic acid* was obtained from 6-methoxy-8-nitrocoumarin as orange needles (from alcohol), m. p. (sealed tube) 167° (decomp.), second m. p. 215—217° (Found : C, 50·6; H, 4·0; N, 5·7%).

8-*Methyl*-6-*nitrocoumarin*.—2-Hydroxy-3-methyl-5-nitrobenzaldehyde (6·03 g.), prepared by nitration of 2-hydroxy-3-methylbenzaldehyde, gave by the Perkin reaction, after several recrystallisations from dilute acetic acid (charcoal), the *nitrocoumarin* (4·8 g.), colourless needles, m. p. 197—198° (Found : C, 58·4; H, 3·4. $C_{10}H_7O_4N$ requires C, 58·5; H, 3·4%). On careful acidification at 0° of its solution in alkali only the nitrocoumarin and no coumarinic acid was obtained.

3-*Methyl*-5-*nitrocoumaric Acid*.—This *acid* (0·13 g.) was obtained from the carbonate extract of the initial product of the foregoing Perkin reaction as almost colourless needles, m. p. 233—234° (decomp.) (from aqueous alcohol) (Found : C, 54·0; H, 4·1; N, 6·2. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·1; N, 6·3%).

2-*Hydroxy*-3-iso*propylbenzaldehyde*.—*o-iso*Propylphenol (100 g.), by the Duff reaction, gave, in the final steam-distillation, first a pale yellow oil (16·5 g.), and then colourless needles (1·3 g.). Distillation of the oil afforded the *aldehyde* (15·5 g.), b. p. 88—94°/6 mm. (Found : C, 72·9; H, 7·1. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%). The colourless needles on recrystallisation had m. p. 80—81° and consisted almost certainly of 2 : 4-*diformyl*-6-iso*propylphenol* (Found : C, 69·0; H, 6·4. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

2-*Hydroxy*-5-*nitro*-3-iso*propylbenzaldehyde*.—Treatment of 2-hydroxy-3-*iso*propylbenzaldehyde (10·5 g.) with fuming nitric acid in acetic acid at room temperature gave the *nitro-aldehyde* (11 g.) as pale yellow plates (from acetic acid), m. p. 105—106° (Found : C, 57·7; H, 5·5; N, 6·7. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3; N, 6·7%).

6-*Nitro*-8-iso*propylcoumarin*.—The foregoing nitro-aldehyde (5·23 g.) on 10 hours' submission to the Perkin reaction gave the *coumarin* (3·5 g.) as colourless plates (from 80% acetic acid), m. p. 152—153° (Found : C, 61·8; H, 4·8; N, 5·9. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·8; N, 6·0%). No coumarinic acid could be isolated, nor did a coumaric acid appear to be formed during the Perkin reaction.

3-tert.-*Butyl*-2-*hydroxy*-6-*methylbenzaldehyde*.—The Duff reaction on 2-*tert.*-butyl-5-methylphenol (100 g.) gave the almost colourless *aldehyde* (14 g.), m. p. 23—23·5°, b. p. 104—106°/3 mm. (Found : C, 74·6; H, 8·2. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%).

[9] Rubenstein, *J.*, 1925, **127**, 1998.

3-tert.-*Butyl*-2-*hydroxy*-6-*methyl*-5-*nitrobenzaldehyde*.—Nitration of the foregoing aldehyde (5·6 g.) in acetic acid at 35° gave the *nitro-aldehyde* (4 g.) as pale yellow needles or plates (from alcohol), m. p. 114—114·5° (Found: C, 61·1; H, 6·6; N, 5·9. $C_{12}H_{15}O_4N$ requires C, 60·8; H, 6·4; N, 5·9%).

8-tert.-*Butyl*-5-*methyl*-6-*nitrocoumarin*.—When the foregoing nitro-aldehyde (1·19 g.) was submitted to the Perkin reaction for 14 hr. the *nitrocoumarin* (0·88 g.) resulted, forming pale yellow needles, m. p. 141·5—142·5°, after successive recrystallisations from 50% acetic acid and from alcohol (Found: C, 64·0; H, 5·8. $C_{14}H_{15}O_4N$ requires C, 64·4; H, 5·8%). No coumaric acid appeared to be formed nor could a coumarinic acid be isolated.

2-*Hydroxy*-5-*nitro*-3-*phenylbenzaldehyde*.—Nitration of 2-hydroxy-3-phenylbenzaldehyde (7 g.) in acetic acid at room temperature gave the *nitro-aldehyde* (6·5 g.) as light brown needles (from alcohol), m. p. 143—144° (Found: C, 64·2; H, 3·7; N, 5·9. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7; N, 5·8%).

6-*Nitro*-8-*phenylcoumarin*.—Submitting the foregoing nitro-aldehyde (4·05 g.) to the Perkin reaction for 7 hr. gave the *nitro-coumarin* (1·95 g.) as colourless needles, m. p. 210—211°, from 80% acetic acid (charcoal) (Found: C, 67·4; H, 3·5; N, 5·2. $C_{15}H_9O_4N$ requires C, 67·4; H, 3·4; N, 5·2%). A very small amount of an acid, presumably crude 5-nitro-3-phenylcoumaric acid, m. p. 185—190° (decomp.), was isolated from the mother-liquors.

8-*Bromo*-6-*nitrocoumarin*.—This compound was prepared from 6-nitrocoumarin in 83% yield by Dey and Row's method,[10] considerably improved by using concentrated sulphuric acid in place of acetic anhydride. No coumaric could be obtained.

3-*Methoxy*-5-*nitrocoumaric acid*.—By Dey and Kutti's method [11] 8-methoxy-6-nitrocoumarin, m. p. 206—207°, was obtained in 42% yield in 8 hr. instead of 17 hr., from 2-hydroxy-3-methoxy-5-nitrobenzaldehyde (9·85 g.). The *nitrocoumaric acid* (0·22 g.), m. p. 252—253° (decomp.), cream-coloured needles from aqueous alcohol, was also isolated (Found: C, 50·7; H, 4·2; N, 5·8. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·8; N, 5·9%). The coumarin could not be converted into a stable coumarinic acid.

Nitration of 2-*Hydroxy*-4-*methylbenzaldehyde*.—The aldehyde (13·4 g.) was nitrated in acetic acid at room temperature to give a mixture of nitro-compounds separated by fractional crystallisation of their sodium salts from water and further crystallisation of the free nitro-aldehydes from alcohol into the 3-nitro- (2·9 g.), m. p. 106—107°, and 5-nitro-compound (6·2 g.), m. p. 146—147°. Clayton [2b] gives m. p. 126—127° for the former and does not mention the latter, which he prepared by a different method. It is considered that Clayton's m. p. is in error.

7-*Methyl*-8-*nitrocoumarin*.—Submission of 2-hydroxy-4-methyl-3-nitrobenzaldehyde (1·45 g.) to the Perkin reaction for 4½ hr. gave the coumarin (0·85 g.), m. p. 166—167°. Clayton [2b] reported m. p. 165—166°. A coumarinic acid was obtained by acidifying its alkaline solution at 0°. This acid is obviously of very low stability as it could not be obtained at room temperature. The dry solid could be kept at room temperature but reverted to the coumarin below its m. p.

6 : 7-*Dimethyl*-8-*nitrocoumarin*.—3 : 4-Dimethylphenol was converted by the Duff reaction in 29% yield into 2-hydroxy-4 : 5-dimethylbenzaldehyde, which was nitrated in 78% yield to 2-hydroxy-4 : 5-dimethyl-3-nitrobenzaldehyde, which (5·6 g.) in the Perkin reaction (3 hr.) gave the nitrocoumarin (3·5 g.), m. p. 202—203°, as pale yellow plates from 80% acetic acid. Clayton [2b] obtained this compound, but records m. p. 190—194°.

4 : 5-*Dimethyl*-3-*nitrocoumaric Acid*.—Extraction of the crude product from the foregoing Perkin reaction with sodium carbonate solution afforded the *nitrocoumaric acid* (0·46 g.) as yellow plates (from alcohol), m. p. 215—216° (decomp.) (Found: C, 55·5; H, 4·8; N, 5·9. $C_{11}H_{11}O_5N$ requires C, 55·7; H, 4·7; N, 5·9%).

4 : 5-Dimethyl-3-nitrocoumarinic acid was precipitated on acidification of an alkaline solution of the coumarin at 0°. Even after drying, the acid was not very stable. Its m. p. could not be determined. It reverted in a few hours to the coumarin.

3-*Chloro*-6-*hydroxy*-2 : 4-*dimethyl*-5-*nitrobenzaldehyde*.—3-Chloro-6-hydroxy-2 : 4-dimethylbenzaldehyde (9·23 g.), prepared by the Duff reaction from 4-chloro-3 : 5-dimethylphenol, was nitrated in acetic acid at 20—30° to give the *nitro-aldehyde* (10·7 g.), pale yellow needles (from alcohol), m. p. 139—140° (Found: C, 47·4; H, 3·5; N, 5·9; Cl, 15·2. $C_9H_8O_4NCl$ requires C, 47·1; H, 3·5; N, 6·1; Cl, 15·4%).

6-*Chloro*-5 : 7-*dimethyl*-8-*nitrocoumarin*.—On submission of the foregoing aldehyde (5·74 g.) to the Perkin reaction for 8 hr. the *coumarin* (4·4 g.) was obtained as light brown needles (from

[10] Dey and Row, *J.*, 1924, **125**, 554.
[11] Dey and Kutti, *Proc. Nat. Inst. Sci. India.*, 1940, **6**, 641.

80% acetic acid; charcoal), m. p. 205—206° (Found: C, 52·2; H, 3·0; N, 5·7; Cl, 13·5. $C_{11}H_8O_4NCl$ requires C, 52·1; H, 3·2; N, 5·5; Cl, 14·0%). None of the corresponding coumaric acid was isolated. The coumaric acid was obtained at 0°. The dry acid reverted to the coumarin within 24 hr.

7-Hydroxy-6 : 8 : 2′-trinitro-3 : 4-benzocoumarin.—7-Hydroxy-3 : 4-benzocoumarin (5 g.), prepared in 29% yield from *o*-bromobenzoic acid and resorcinol according to Hurtley,[12] was nitrated with mixed acid. Repeated crystallisation of the product from 60% acetic acid gave the *trinitrocoumarin* (1·5 g.) as yellow needles, m. p. 253° (decomp.) (Found: C, 45·4; H, 1·5; N, 12·6. $C_{13}H_5O_9N$ requires C, 45·0; H, 1·5; N, 12·1%). There seems little doubt as to the positions taken up by the nitro-groups.

2′ : 4′-Dihydroxy-3′ : 4 : 5′-trinitrodiphenyl-2-carboxylic Acid.—The foregoing coumarin (0·5 g.) was converted into the *coumarinic acid* with the minimum of alkali and water on account of the ready solubility of the acid; the product formed yellow crystals, m. p. 135—136° (decomp.), from aqueous alcohol (Found: C, 43·1; H, 2·1; N, 11·3. $C_{13}H_7O_{10}N_3$ requires C, 42·8; H, 1·9; N, 11·5%).

8-Cyanocoumarin.—Powdered 8-aminocoumarin (4·03 g.) was diazotised in hydrochloric acid, the product added to potassium cuprocyanide solution at 85—90°, and the mixture stirred for 1 hr., cooled, and filtered. The alcoholic extract of the residue, on concentration, deposited the dark solid *cyanocoumarin*, yielding almost white needles (2 g.), m. p. 221·5—222·5°, on several recrystallisations from alcohol (charcoal) (Found: C, 70·6; H, 2·9; N, 8·35. $C_{10}H_5O_2N$ requires C, 70·2; H, 2·9; N, 8·2%). No coumarinic acid could be isolated.

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[12] Hurtley, *J.*, 1929, 1870.