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EXTRACTIVES OF *DALEA* SPECIES (LEGUMINOSAE)

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Abstract—Coumarin(**4**), 5-methoxycoumarin(**5**) and two deep red pigments have been isolated from the extracts of *Dalea emoryi*. The two pigments, dalrubone and methoxydalrubone differ by a single OMe group and are assigned structures **9** and **10** respectively on the basis of an X-ray crystallographic structure determination as well as their chemical and spectroscopic properties. These pigments appear to be biogenetically derived from a C_6–C_3–C_6 flavonoid system. Extracts of *D. polyadenia* were shown to contain coumarin(**4**), 5-methoxycoumarin(**5**), dalrubone(**9**) and 2S-demethoxymatteucinol(**17**). Dalrubone undergoes a photochemical oxidation leading to a B-ring contracted product (**15**) having an α-hydroxymethyl ketone group.

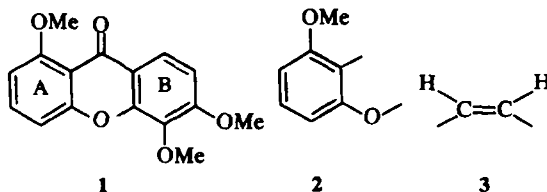
Dalea (Leguminosae) is an American genus of approximately 150 species. It is well represented in the drier regions of the southwestern United States and Mexico.[1,2] Some species of *Dalea* are known for their pigment glands occurring on the stems and leaves and even more pronounced around the base of the fruit. One of the more abundant species among the pigmented *Dalea* is *D. emoryi* A. Gray (Indio bush). This is a small shrub scattered in dry open spaces below 300 M. throughout the Colorado Desert into Arizona and Lower California. This species is covered with yellow–orange glands which stain the skin when crushed in the hands. *D. emoryi* was used by Indians of the desert tribes for coloring deer skins and dyeing reeds used in basket making.[3] The closely related *D. polyadenia* was used by Indians, not only for the dye it produces, but also medicinally in the treatment of numerous ailments.[3]

Extracts of *D. emoryi*, after chromatography on alumina, yielded two red pigments, as well as coumarin and 5-methoxycoumarin. On the basis of their spectroscopic properties, these two pigments appeared to be closely related and differed by a single OMe group. Accordingly, they were named dalrubone and methoxydalrubone.

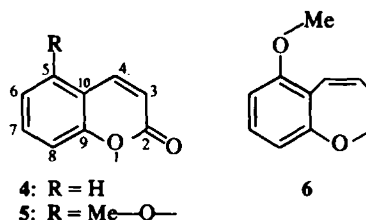
The two pigments were relatively non-polar and easily eluted from alumina. The major pigment in most collections of *D. emoryi* was methoxydalrubone, m.p. 148–149°. It analyzed for $C_{20}H_{20}O_5$ and showed a CO band at 1681 cm^{-1}. Consistent with the non-polar nature of the pigments is the fact that the IR spectrum of each indicated the absence of OH groups. The UV-VIS spectrum of methoxydalrubone consisted of a single band at 432 nm. This spectrum appeared to be consistent with a quinone system[4] and was unlike that of anhydroflavylium systems.[5]

The NMR spectrum of methoxydalrubone showed signals for two identical C-methyls in a relatively saturated environment, a vinyl C-methyl, two OMe groups and five vinyl and/or aromatic protons. The mass spectrum showed a base peak and molecular ion at *m/e* 340, confirming the $C_{20}H_{20}O_5$ analysis. The mass spectrum showed a strong M-15 peak and peaks for the successive loss of two carbonyls. The latter are characteristic of quinone systems.[6] The NMR spectrum of methoxydalrubone showed an AB doublet (δ 8·08 and 7·92, J = 10) in the aromatic region. The large coupling constant argues against assigning these resonances to aromatic protons and is more consistent with the presence of a cis double bond.[7] Such downfield positions for vinyl protons are found in chalcones and related systems.[8]

The aromatic region of the NMR spectrum of methoxydalrubone also showed an AMX system in which protons A and M were not appreciably coupled. Thus, the protons A and M were each a doublet and proton X (downfield) was a triplet. This spin system had J = 8. This AMX system is consistent with three adjacent protons on a benzene ring and was similar to that found in the A-ring of 1,5,6-trimethoxyxanthone (**1**).[9] The above AMX and AB systems were overlapped but resolved at 100 MHz and the relationships were established by spin decoupling. These data suggest the part structures **2** and **3** in methoxydalrubone.

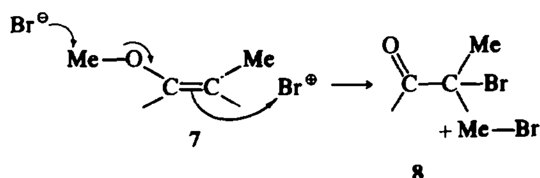


Dalrubone, m.p. 100–101·5°, λ_{max} 425 nm, analyzed for $C_{19}H_{18}O_4$ and appeared on the basis of its NMR spectrum to be similar in structure to methoxydalrubone except that it contained only one OMe group instead of the two present in methoxydalrubone. The mass spectrum showed a strong molecular ion at *m/e* 310 and a cracking pattern containing successive peaks at M-15 and the loss of CO, similar to methoxydalrubone. The NMR spectrum of dalrubone showed resonances for six vinyl or aromatic protons. Again, a downfield AB doublet with a 10 Hz coupling constant could be discerned in the aromatic region and the aromatic resonances of dalrubone and methoxydalrubone differed in the same way that the co-occurring coumarin (**4**) and 5-methoxycoumarin (**5**) differ in their aromatic region. This suggested that methoxydalrubone had part structure **6**. The presence of part structure **6** in methoxydalrubone was confirmed by warming the pigment in a solution of hydrobromic acid in acetic acid. Workup gave a good yield of **5**.



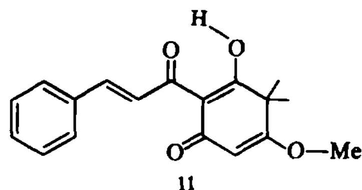
Both dalrubone and methoxydalrubone were thermally stable but were degraded rapidly by hot 5% sodium hydroxide to a multitude of products as determined by TLC. The red color of both pigments was quickly discharged with reducing agents, for example, zinc dust in refluxing acetic acid, sodium borohydride or catalytic reduction conditions. Again many products were formed in each case and it was not possible to isolate any well characterized product. Methoxydalrubone was soluble in CF_3COOH and recovered by dilution with water. The NMR spectrum of methoxydalrubone in CF_3COOH was not readily interpretable.

The bromination of methoxydalrubone was initially studied in an NMR tube. Addition of one mole of bromine in CCl_4 to a solution of methoxydalrubone in deuterio-chloroform resulted in a significant change to the NMR spectrum. One of the OMe resonances showed a striking upfield shift to δ 2·65 and the vinyl C-methyl moved upfield to δ 1·95. After evaporation of solvent, the subsequent NMR spectrum retaken in $CDCl_3$ showed the loss of the upfield "methoxy" signal. Otherwise, the NMR spectrum was the same as that prior to evaporation of the solvent. The 3-proton singlet which disappeared upon removal of solvent from the bromination corresponded in chemical shift to methyl bromide (δ 2·68).[10] Removal of solvent from the bromination mixture and crystallization of the residue gave a yellow monobromo product which analyzed for $C_{19}H_{17}O_5Br$. The bromination results suggest a conversion illustrated by part structures **7** to **8**. The spectral data and course of the reaction indicate that one methoxy group and the vinyl C-methyl group in methoxydalrubone must be located adjacent to one another on a double bond.



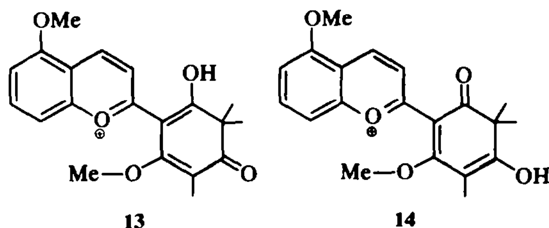
Since much of the chemical and spectroscopic evidence for the pigments suggested a quinone system, an attempt was made to prepare a phenazine derivative with *o*-phenylenediamine. Refluxing methoxydalrubone with *o*-phenylenediamine in glacial acetic acid resulted in a host of products as indicated by TLC. In refluxing alcohol, a yellow product was obtained. However, it did not correspond to a phenazine derivative either in its C and H analysis or in its spectroscopic properties.

At this juncture, the results of the X-ray studies became available which indicated structure **10** for methoxydalrubone.[11] From the spectroscopic data it follows that dalrubone must have structure **9**. Of special interest is the close structural similarity of the dalrubones with the chalcone ceroptene (**11**).[12]



The dalrubones appear to be closely related to the $C_6C_3C_6$ flavonoid systems (**12**) in which the acetate derived A-ring of the flavonoid system, marked by the *meta* oxygen functions, and the high degree of C-methylation along with the adjacent oxygen function at C-2 has ended up as the B-ring in the dalrubones (Scheme 1). The dalrubones do not have any close structural similarities to other extractives of the Leguminosae.[13]

With the structure of **10** available it was now apparent that the NMR spectrum in CF_3COOH was due to the presence of a mixture of the anthocyanins **13** and **14**.

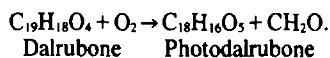


During the course of the structure determination, it was noted that some pigment fractions which had stood on the bench top for extended periods of time decomposed forming a yellow product. When placed in a window and monitored by TLC, the conversion of a methanolic solution of dalrubone took about a month. The photocon-

Scheme 1. Possible biosynthetic relationship between dalrubones (**9** and **10**) and demethoxymatteucinol (**17**).

version took only a few days when a dioxane solution was saturated with oxygen and irradiated with a sun lamp. Formaldehyde could be detected by the chromotropic acid test[14] as a volatile product of the photolysis. In a similar manner, methoxydalrubone could be converted to a yellow photoproduct which proved to be more difficult to isolate and purify than that from dalrubone. As a result, it was not completely characterized.

The carbon–hydrogen analysis and molecular weight by MS of photodalrubone suggested the conversion:

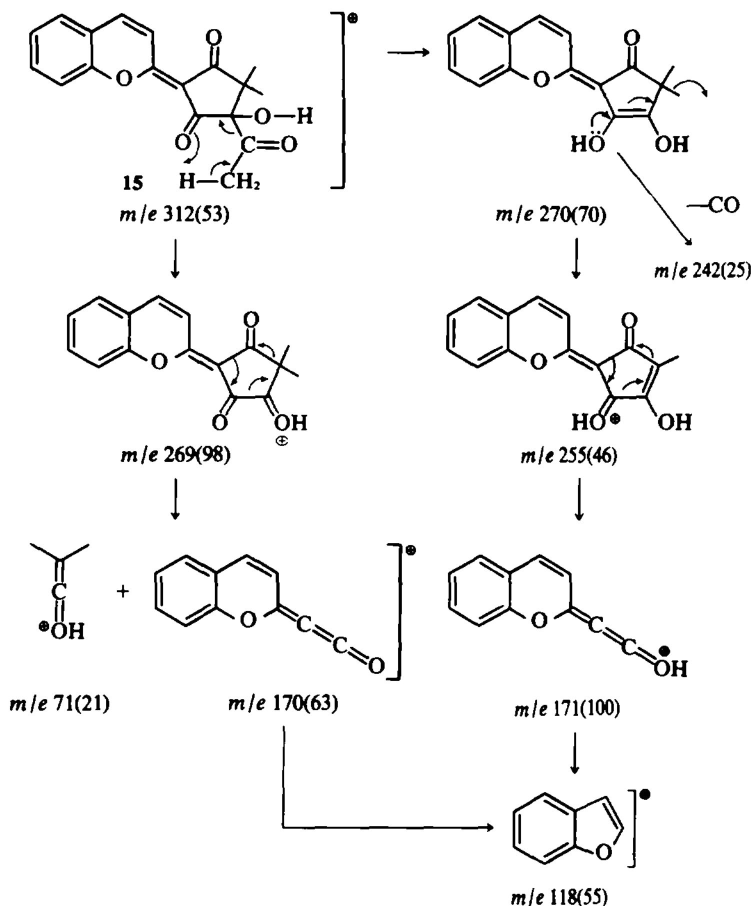


$$C_{19}H_{18}O_4 + O_2 \rightarrow C_{18}H_{16}O_5 + CH_2O.$$

Dalrubone Photodalrubone

The IR spectrum of photodalrubone indicated the presence of a hydroxy group and showed carbonyl bands at 1695 and 1642 cm^{-1}. The UV-VIS spectrum showed λ_{max} at 440, 422 and 448 nm indicating the presence of a conjugated system possibly similar to that in dalrubone.

The NMR spectrum of photodalrubone showed a six proton singlet at δ 1·14 assigned to the gem dimethyl group and a three proton singlet at δ 2·18 assigned to the vinyl C-methyl group. The methoxy resonance of dalrubone was absent in the photoproduct. The aromatic region which integrated for six protons was complex and not easily interpreted. Even though dalrubone and photodalrubone had several prominent MS peaks in common, for example, *m/e* 118, 115 and 69, the overall MS fragmentation pattern was somewhat different. The vinyl C-methyl resonance of dalrubone (**9**) underwent a striking upfield shift in the photoproduct. Its position at δ 2·18 suggested the presence of an aromatic methyl group or a methyl ketone. Since the former was impossible, methyl ketone structures were indicated. The UV spectrum changed with added base, but the photoproduct failed to give a positive $FeCl_3$ test. The UV data suggested that the hydroxy group was enolic, but inconsistently, the



Scheme 2. Major MS fragmentation routes for photodalrubone (15).

negative $FeCl_3$ test suggested that the OH group indicated by the IR spectrum must be alcoholic. The presence of a methyl ketone group was supported by strong M–$COCH_3$ and M–$COCH_2$ peaks in the MS, the latter apparently arising by hydrogen transfer as shown in Scheme 2. These data are best interpreted in terms of structure **15**.

In an effort to test this structural proposal, the ^{13}C NMR spectra of dalrubone (**9**), ceroptene (**12**) and photodalrubone were compared with one another (Table 1). The interpretation of the spectrum of ceroptene (**12**) was complicated by the fact that it exists as a mixture of tautomeric forms as previously pointed out by Nilsson.[11] Partial decoupling helped assign some of the signals for carbons which had hydrogens attached. On the other hand, the ^{13}C resonances of **9** and **15** could be assigned with a fair degree of certainty on the basis of their chemical shifts.

As the data in Table 1 illustrates, the pattern of aromatic and C-ring vinyl resonances for dalrubone (**9**) and photodalrubone (**15**) compare closely with the corresponding resonances of coumarin (**4**).[15] A number of features of the ^{13}C NMR of 15 were revealing. Firstly, the two C-methyl carbons of the gem dimethyl group were non-equivalent. Secondly, a band at 90·4 ppm was present in the photoproduct which had no equivalent in dalrubone (Table 1). The chemical shift of this resonance was

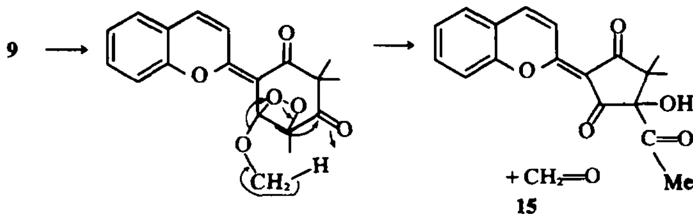


Table 1. ^{13}C resonances

Compound		5	6	7	8	2	3	4	9	10	1′	3′	7′	8′ & 9′	Methoxy
Coumarin[a]	(4)	116·5	124·3	127·9	131·7	160·4	116·4	143·4	153·8	118·7	—	—	—	—	—
Dalrubone	(9)	119·1	124·7	127·2	131·4	166·4	116·0	133·7	152·5	117·8	120·6	57·4	9·0	22·9	59·4
Photodalrubone	(15)	119·2	124·3	126·7	131·7	162·2 162·7	115·3	140·9	150·1	115·3	102·2	50·6 51·1	15·1	22·3 26·2	—
Ceroptene	(11)	123·0	128·3	128·3	—	187·2	130·0	144·9	—	134·8	105·2	48·9	—	24·3	56·2

Other Assignments

Compound		Assignments
Dalrubone	(9)	201·7, 199·4, C-2′ and C-4′; 105·2, C-5′; 156·6, C-6′.
Photodalrubone	(15)	200·7, 198·2, 196·3, 195·4, 193·4, C-2′ and C-6′; 209·0, C-5′; 90·4, C-4′.
Ceroptene	(11)	206·4, 196·9, 190·3, 187·2, 179·6, C-2′, C-4′ and C-6′; 95·0, C-5′.

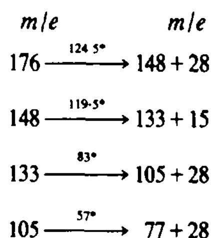
[a] Data taken from Ref. 15.

consistent with a carbon having a OH group attached. Thirdly, there was a doubling of a number of resonances associated with groups in the B-ring (Table 1).

The doubling of some of the ^{13}C resonances indicates that 15 exists as a mixture of stereoisomers about the 2–1′ double bond. The change in the UV spectrum with added base can be rationalized in terms of a reverse aldol reaction of the B-ring β-hydroxyketo system. The formation of **15** can probably best be rationalized by direct 1,2-addition of oxygen to the 5′,6′ double bond of the dalrubone and subsequent ring contraction-fragmention with hydrogen transfer to the 4′-carbonyl group.

Workup of the mother liquors remaining from the isolation of the bulk of the pigments from *D. emoryi* extracts by chromatography on silicic acid gave two further colorless compounds in very small amounts. One of these proved to be coumarin itself. The second compound, m.p. 80–81°, showed a typical coumarin CO band in the IR, but its UV spectrum and its properties did not correspond in detail with any of the common types found in nature.[16] The NMR spectrum showed a OMe resonance, a typical coumarin AB doublet ($J = 10$ Hz) and finally an AMX aromatic system similar in detail to that described for methoxydalrubone. These data suggested the second colorless metabolite was 5-methoxycoumarin (**5**). 5-Methoxycoumarin (**5**) has been reported as a synthetic material[17] but has not yet been reported as occurring in nature.

The mass spectrum of 5 showed an intense molecular ion at m/e 176. Metastable peaks indicated the following fragmentation pattern:



The UV spectrum of **5** matched the curve published by Böhme and Severin.[18]

The co-occurrence of coumarin and 5-methoxycoumarin with the dalrubones and their obvious structural relationships suggests that the coumarins, **4** and **5**, are degradation products of the dalrubones in the plant. It may be that some coumarins, especially those of the limettin type, found in plant sources have their origin in the A-ring of anthocyanin pigments.[19] Anthocyanins are probably responsible for the characteristic blue color of *Dalea* flowers.

Initial isolation studies on *D. polyadenia* failed to demonstrate the presence of dalrubones in plant material collected early in the spring. However, plant material collected in July, which was in fruit, contained a non-polar red pigment. Fractions were obtained by repeated chromatography in which the pigment was concentrated. In spite of this concentration the pigment could not be induced to crystallize. 2S-demethoxymatteucinol (**17**) was also obtained from the chromatography fractions.

In spite of the relatively high molecular weights of the dalrubones it was possible to gas chromatograph the compounds on SE-30 at 200° using a short column. By this method it was demonstrated that the red pigment in *D. polyadenia* was **9** and that **4** and **5** were also present. Methoxydalrubone (**10**) could not be detected. It seems probable that the dalrubones and demethoxymatteucinol arise by a common flavonoid ($C_6C_3C_6$) intermediate (**18**) (Scheme 1).

Some plant material used in this study was infested with *Pilostyles thurberi* Gray, a rare parasitic plant, whose sole host is *D. emoryi* and *D. schotti.*[20] *P. thurberi* was manually picked off the *Dalea* and extracted with acetone. TLC of the extracts did not show the presence of fluoresent compounds. Sucrose was the only product isolated upon workup of the extracts.

EXPERIMENTAL

NMR data are given in δ. The areas of the peaks were consistent with their assignments. TLC using silicic acid and 1:1 chloroform:ethyl acetate was used as a monitoring system. ^{13}C NMR were taken on a JEOL C-60 HL equipped with a pulsed FT system operating at 15·09 MHz. The samples were locked on the $CDCl_3$ solvent and all signals were referenced to internal TMS.

Isolation. D. emoryi was collected just east of Telegraph Pass on Highway 80 east of Yuma, Arizona. On other occasions plant material was obtained on the east shore of the Salton Sea and the

upper part of Borrego Valley, San Diego County, California. Collections were made in June and July except that in Borrego Valley which was made early in April.

The dried and ground plant material was extracted with benzene. Solvent was removed from the benzene extracts and the residue chromatographed on alumina. Large amounts of waxes were eluted with hexane. Octacosane, m.p. 59–61°, was identified in the wax fraction. Continued elution of the column with hexane–benzene solvent combinations brought down more polar fractions. Finally, the red pigment bands were eluted with dichloroethylene. It was often necessary to rechromatograph the red fraction a second time before the pigment fraction could be induced to crystallize. Methoxydalrubone (**10**) was the major red pigment obtained except for one collection of plant material from the Borrego Valley in April. Dalrubone was the major pigment in this case. Methoxydalrubone (**10**) gave m.p. 148–149°, from ethyl acetate–hexane; ν 1681 cm^{-1} (Nujol); λ_{max}^{EtOH} 432 (log ϵ 4·33) nm; $\lambda_{max}^{HClO_4}$ 473 nm; NMR δ 7·71 (d, J = 10) H-10, 7·65 (d, J = 10) H-3 and H-4, 7·38 (t, J = 8) H-7, 6·87 (d, J = 8), 6·69 (d, J = 8) H-6 and H-8, 3·94, 3·83 methoxys, 1·96 vinyl C-methyl, 1·38 C-methyls ($CDCl_3$); δ 3·60, 3·50 methoxys, 2·20 vinyl C-methyl, 1·47 C-methyls (benzene). The C-methyl resonances and the downfield half of the AB doublet showed the greatest downfield shift with added Eu(fod)$_3$. MS m/e (rel. intensity) 340 (100), 325 (24), 310 (13), 297 (42), 282 (6), 281 (5), 270 (19), 269 (15), 253 (12), 241 (7), 239 (12), 211 (7), 201 (5), 199 (13), 184 (7), 161 (5), 156 (9), 149 (10), 141 (7), 69 (5), 57 (7), 55 (7), 43 (20), 41 (15). (Found: C, 70·5; H, 5·92. $C_{20}H_{20}O_5$ requires: C, 70·5; H, 5·92%).

The mother liquors from the isolation of methoxydalrubone were rechromatographed and repeated crops of methoxydalrubone removed by crystallization. A point was then reached where substantial amounts of red oil remained which could not be induced to crystallize. The oil appeared to be homogeneous by TLC. This oil was chromatographed on a 40 cm column of silicic acid and 10 ml fractions collected. The composition of the fractions was monitored by removal of solvent and running the NMR spectrum of the residue in CCl_4. It was apparent by this means that the first red fractions from the column differed from the later red fractions in composition. After much manipulation, the non-polar fractions were induced to crystallize to give a second red pigment, dalrubone (**9**), identical in color with **10**.

The more polar fractions from the column consisted largely of methoxydalurbone. Dalrubone, m.p. 100·5–101·5°, from ethyl acetate–hexane, showed ν 1695, 1640 cm^{-1} (Nujol); λ_{max}^{EtOH} 425 (log ϵ 4·31) nm; NMR δ 7·57 (d, J = 10), 7·00 (d, J = 10) H-3 and H-4, 7·20 (m) aromatic, 3·73 methoxy, 1·85 vinyl C-methyl, 1·25 C-methyls (CCl_4); δ 3·36 methoxy, 2·20 vinyl C-methyl, 1·48 C-methyls (benzene); MS m/e (rel. intensity) 310 (100), 295 (58), 267 (82), 240 (30), 181 (33), 169 (30), 146 (46), 118 (51), 115 (18), 89 (20), 83 (25), 70 (26), 69 (26), 63 (21), 57 (20), 56 (20), 55 (22). (Found: C, 73·4; H, 5·84. $C_{19}H_{18}O_4$ requires: C, 70·31; H, 4·69%).

The mother liquors from the above isolation operations were rechromatographed over silicic acid. Elution with increasing amounts of benzene in hexane gave colorless fractions which showed fluorescent non-polar spots on TLC. Workup of these fractions gave **5**, m.p. 80–81°, from hexane; ν 1729, 1609 cm^{-1} (Nujol); λ_{max}^{EtOH} 298 nm; NMR δ 8·09 (d, J = 10) H-4, 7·44 (t, J = 8) H-7, 6·92 (d, J = 8), 6·72 (d, J = 8) H-6 and H-8, 6·33 (d, J = 10) H-3, 3·95 methoxy ($CDCl_3$); MS m/e (rel. intensity) 176 (69), 148 (100), 133 (66), 118 (20), 105 (23), 91 (10), 77 (10). Metastable peaks occurred at m/e 124·5, 119·5, 83 and 57.

Other colorless fractions eluted ahead of the pigment fractions gave small amounts of coumarin, m.p. 68–69°, from hexane; ν 1754, 1712, 1609 cm^{-1} (Nujol); λ_{max}^{EtOH} 310, 274 nm. The mass spectrum was identical with literature values.[21] The IR spectrum proved to be identical with that of an authentic sample of coumarin.

D. polyadenia was obtained in two locations in the Owens Valley, California. Material collected in March, 10 miles north of Bishop, did not contain any extractable pigment. Material collected in June, 8 miles north of Independence along Highway 395, contained a red pigment. Chromatography of the benzene extracts over silicic acid gave initially waxes and fats which were discarded. Further elution with benzene gave material showing a positive ferric chloride test as well as a red pigment fraction. Workup of these fractions gave 2S-demethoxymatteucinol, m.p. 209–211°; green $FeCl_3$ test; NMR δ 7·48 (s) aromatic, 5·45 (m) H-2, 2·98 (m) H-3, 2·10, 2·10 C-methyls ($CDCl_3$); MS m/e (rel. intensity) 284 (84), 266 (5), 241 (4), 207 (41), 186 (7), 180 (89), 152 (100). A metastable peak occurred at m/e 128·3 corresponding to fragmentation of species m/e 180 → 128. GLC of the red fractions indicated the presence of compounds **4**, **5** and **9**.

The CD curve of **17** compared well with the data reported by Gaffield[22] indicating the 2S configuration.

Acetylation of demethoxymatteucinol with acetic anhydride–pyridine gave the diacetate, m.p. 180–181·5°, from MeOH; ν 1760, 1695, 1620 (Nujol); NMR δ 7·43 (s) aromatic, 5·50 (m) H-2, 2·93 (m) H-3, 2·42, 2·37 acetoxys, 2·07, 1·97 C-methyls ($CDCl_3$).

Ceroptene (**11**) was isolated largely according to the procedure of Nilsson;[12] m.p. 135·5–136·5°; λ_{max} 326, ~310, 365 nm; $\lambda_{max}^{EtOH-NaOH}$ 290, 344 nm.

Bromination of methoxydalrubone. Equal molar amounts of methoxydalrubone and bromine in chloroform were allowed to stand overnight. Solvent was removed. The residue was recrystallized from CCl_4 and then ethyl acetate–hexane, m.p. 162°, λ_{max}^{EtOH} 480 (log ϵ 4·13); NMR δ 8·10 broadened singlet, 7·55 (t, J = 7), 7·10 (d, J = 7) H-8, 6·80 (d, J = 7) H-6, 3·95 methoxy, 1·95, 1·65, 1·35 C-methyls ($CDCl_3$); MS m/e (rel. intensity) 407 (5), 406 (20), 405 (5), 404 (20), 327 (12), 326 (80), 325 (12), 324 (50), 311 (5), 298 (30), 297 (100), 296 (10), 283 (60), 270 (30), 245 (50), 201 (80), 200 (90), 148 (50). (Found: C, 56·3; H, 4·24. $C_{19}H_{17}O_5Br$ requires: C, 56·3; H, 4·22%). The bromination could also be followed by running the reaction in an NMR tube using CCl_4 as the solvent.

Hydrolysis of methoxydalrubone. To a soln of 50 mg of methoxydalrubone in 6 ml glacial AcOH was added 6 ml HBr bromic acid. The soln was heated on a steam bath for 1 hr until the red color was largely destroyed. Water was added to the soln and it was extracted 5X with ether. The ether extracts were dried with K_2CO_3, solvent removed and the residue sublimed to give 28 mg of 5-methoxycoumarin.

Photodalrubone. A dilute methanol soln of dalrubone was allowed to stand in a window for 30 days. During this period chemical changes were monitored by TLC. A polar yellow spot grew in intensity while the amount of red pigment decreased. When most of the red pigment had been converted, the solvent was removed and the residue chromatographed on alumina. Dalrubone and other impurities were eluted followed by the yellow photoproduct. The content of the fractions were monitored by TLC. Solvent was removed from those fractions containing mostly the polar photoproduct and the residue crystallized from EtOAc–hexane. Recrystallization from EtOAc gave an anal. sample, m.p. 188–191°; negative $FeCl_3$ test; ν 3480, 1695, 1645 cm^{-1} (Nujol); λ_{max}^{EtOH} ~383, 400, 422, 448 nm; the spectrum decayed with added 5% NaOH; NMR δ 8·16–7·00 (complex system, aromatic), 4·16, 4·12 (hydroxy), 2·18 methyl ketone, 1·14 C-methyls ($CDCl_3$); MS m/e (rel. intensity), 312 (53), 270 (70), 269 (98), 255 (46), 253 (19), 242 (25), 171 (100), 170 (63), 169 (17), 118 (55), 115 (43), 114 (24), 83 (17), 71 (21), 69 (25), 57 (14), 55 (15). (Found: C, 68·9; H, 5·20. $C_{18}H_{16}O_5$ requires: C, 69·22; H, 5·16%).

The photoproduct was also produced by saturating a dioxane solution of dalrubone with oxygen and irradiation for two days with a sun lamp. The oxygen effluent was trapped in a dilute ammonia soln. The ammonia solution gave a positive test for formaldehyde with chromotropic acid.[14]

Reaction of methoxydalrubone with o-phenylenediamine. Equal amounts of methoxydalrubone and o-phenylenediamine were refluxed on a steam bath for 8 hr. The mixture was cooled, dil. HCl added and extracted with benzene. The benzene extracts were washed and dried. The concentrated benzene extracts were chromatographed through a short column of alumina. The fractions were monitored by TLC. Those fractions showing a yellow non-polar component were combined, solvent removed and the residue crystallized several times from EtOAc–hexane, m.p. 191–194°; ν 2985 (N–H); 1625 (carbonyl) cm^{-1} (Nujol); λ_{max}^{EtOH} 392 nm; MS *m/e* (rel. intensity) 448 (23), 340 (52), 325 (17), 310 (10), 297 (28), 241 (23), 240 (37), 119 (29), 108 (63), 69 (100). (Found: C, 69·3; H, 6·32. $C_{26}H_{28}N_2O_5$ requires: C, 69·6; H, 6·29%).

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