

TABLE I  
 CHEMICAL SHIFTS AND COUPLING CONSTANTS OF CERTAIN AMINOHEXOSE DERIVATIVES<sup>a</sup>

Compd. <sup>b</sup>	H-1	H-2	H-3	H-4	H-5	H-6	NH	OAc	NAc <sup>c</sup>	OMe
2	4.45 <sup>d</sup> axial	4.95	5.22	4.20	3.78	4.28	6.10 (d, 8.5) <sup>e</sup>	2.05 2.10	1.95	3.53 equat.
3	4.17 equat.	4.9			4.00	4.22	5.60 (d, 7.5)	2.05 2.08	1.90	3.45 axial
4	4.75 (d, 3.5) equat.	4.30	5.25	5.08	3.93	4.20	5.82 (d, 9.5)	2.02 2.08	1.95	3.40 axial
5	4.65 (d, 8.0) axial	3.92	5.33	5.08	3.75	4.25	6.12 (d, 8.5)	2.05 2.10	1.97	3.53 equat.
6 <sup>f</sup>	5.02 equat.	5.20	5.37	~4.27	3.96	4.27	6.13 (d, 8.5)	2.07 2.08	1.97	3.43 axial
7 <sup>g</sup>	4.65 equat.	4.95	4.67— broad	4.83	3.96		5.80 (d, 8.0)	2.05 2.15, axial	1.93	3.38 axial
8	4.77 equat.	5.08	4.42	4.92	3.93	4.22	5.80 (d, 9.0)	2.08 2.05	1.93	3.42 axial
9	~5.00 equat.	~5.00	5.30	~4.18	3.90	4.22	5.80 (d, 8)	2.08 2.10	1.95	3.62 axial
10	5.73 axial	~5.23	~5.23	~4.25	3.77	4.23	6.25 (d, 9.0)	2.05 2.10 2.08	1.95	

<sup>a</sup> Measured in p.p.m. from internal TMS in CDCl<sub>3</sub> solution at 60 Mc. <sup>b</sup> Numbered as in Chart I. <sup>c</sup> Methyl resonances. <sup>d</sup> Mid-point of doublet. <sup>e</sup> Coupling constant for doublet (d). <sup>f</sup> Spectrum is identical with the  $\alpha$ -D anomer: Dr. E. J. Reist. <sup>g</sup> The C-5 methyl is a doublet at 1.18 p.p.m.

### Experimental

The H<sup>1</sup> n.m.r. spectra were obtained by means of the Varian HR-60 spectrometer at 60 Mc. (14.092 kgauss) and the Varian A-60 spectrometer. The decoupling experiments were done with the NMR Specialties PD-60 homonuclear decoupler. The 100-Mc. spectra were obtained by means of the Varian Associates HA-100 spectrometer. The chemical shifts are measured in cycles per second from internal tetramethylsilane. Decoupled spectra were obtained at first by irradiating at higher field than the observed peak, between -25 and -115 c.p.s. in 3-c.p.s.

increments, and then by irradiating the low-field peak while observing the high-field peak. Where decoupling was noted, the system was optimized, and more accurate data were obtained.

Since the amide proton exchanges only slowly in water, the exchange was accelerated by the addition of a base. The spectrum was obtained of 0.4 ml. of a deuteriochloroform solution of the sample. Then 50  $\mu$ l. of deuterium oxide and 5  $\mu$ l. of triethylamine were added to the tube and the mixture was shaken several times. The exchange was quantitative, as evidenced by the absence of the amide proton signal.

## Osage Orange Pigments. XVI. The Structure of Alvaxanthone<sup>1a</sup>

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Alvaxanthone, a pigment obtained from the root bark of the osage orange (*Maclura pomifera* Raf.), is shown to be 2-(1,1-dimethylallyl)-1,3,5,6-tetrahydroxy-8-(3-methyl-2-butenyl)xanthen-9-one (1).

In a previous paper<sup>2</sup> in this series, we have described the isolation and partial characterization of three new yellow pigments from the root bark of the osage orange (*Maclura pomifera* Raf.). These were tentatively assigned substituted polyhydroxyxanthone structures on the basis of their ultraviolet spectra and various diagnostic tests and were accordingly designated macluraxanthone, osajaxanthone, and alvaxanthone. Subsequently, macluraxanthone and osajaxanthone were shown to be 12-(1,1-dimethylallyl)-5,9,10-trihydroxy-2,2-dimethyl-2H,6H-pyrano[3,2-b]xanthen-6-one<sup>3</sup> and

5,8-dihydroxy-2,2-dimethyl-2H,6H-pyrano[3,2-b]xanthen-6-one,<sup>1a</sup> respectively.

We wish to report herein the elucidation of the structure of the third osage orange root bark pigment, alvaxanthone.

As reported previously,<sup>2</sup> alvaxanthone, C<sub>23</sub>H<sub>24</sub>O<sub>6</sub>, can be obtained in 0.15% average yield from the dry root bark of the osage orange. Further, acetylation and methylation under mild or severe conditions yielded a bright yellow triacetate and trimethyl ether, respectively. The presence of a fourth hydroxyl, severely hindered and also possibly hydrogen bonded, was indicated by a faint, but definite, alcoholic ferric chloride test on the triacetate.

Although this fourth hydroxyl could not be methylated under the most severe conditions and could not be acetylated under conditions which normally would

(1) (a) Preceding paper in this series: M. L. Wolfrom, F. Komitsky, Jr., and J. H. Looker, *J. Org. Chem.*, **30**, 144 (1965). (b) National Science Foundation Cooperative Graduate Fellow, 1961-1964.

(2) M. L. Wolfrom, E. E. Dickey, P. McWain, A. Thompson, J. H. Looker, O. M. Windrath, and F. Komitsky, Jr., *ibid.*, **29**, 689 (1964).

(3) M. L. Wolfrom, F. Komitsky, Jr., G. Fraenkel, J. H. Looker, E. E. Dickey, P. McWain, A. Thompson, P. M. Mundell, and O. M. Windrath, *ibid.*, **29**, 692 (1964).

TABLE I  
 ULTRAVIOLET SPECTRA<sup>a</sup> OF ALVAXANTHONE DERIVATIVES AND KNOWN XANTHONES

Compd.	$\lambda_{\text{max}}^{\text{EtOH}}, m\mu (\log \epsilon)$				
Alvaxanthone	257 (4.88)	280 (3.94)	332 (4.38)		
Tetrahydromacluraxanthone	254 (4.60)	287 (4.07)	332 (4.31)		
Dihydrojacareubin <sup>b</sup>	251 (4.55)	284 (4.05)	330 (4.24)		
1,3,5,6-Tetrahydroxyxanthone	251 (4.42)	283 (3.81)	324 (4.21)		
Alvaxanthone trimethyl ether	249 (4.65)	260 (4.41) <sup>c</sup>	276 (3.93) <sup>c</sup>	323 (4.39)	357 (3.64) <sup>c</sup>
Tetrahydroalvaxanthone trimethyl ether	249 (4.65)	261 (4.41) <sup>c</sup>	277 (4.02) <sup>c</sup>	323 (4.40)	357 (3.68) <sup>c</sup>
Tetrahydromacluraxanthone trimethyl ether	248 (4.57)	262 (4.28)	289 (3.91)	327 (4.30)	355 (3.79)
Dihydrojacareubin dimethyl ether	246 (4.63)	255 (4.33) <sup>c</sup>	285 (3.85)	322 (4.40)	346 (3.79) <sup>c</sup>
1-Hydroxy-3,5,6-trimethoxyxanthone	245 (4.67)		282 (4.03)	314 (4.37)	338 (3.79) <sup>c</sup>
Alvaxanthone triacetate	240 (4.56)	260 (4.50)		309 (4.17)	367 (3.66)
Tetrahydroalvaxanthone triacetate	238 (4.53)	259 (4.49)		308 (4.16)	367 (3.66)
Tetrahydromacluraxanthone diacetate	243 (4.43)	266 (4.30)		324 (4.17)	366 (3.62)
1-Hydroxy-3,5,6-triacetoxoxanthone	237 (4.32)	254 (4.40)	292 (4.11) <sup>c</sup>	297 (4.16)	351 (3.74)

<sup>a</sup> Cary Model 14 recording spectrometer. <sup>b</sup> See ref. 3. <sup>c</sup> Infection.

be expected to acetylate a hydrogen-bonded xanthone C-1 hydroxyl, even if hindered,<sup>3</sup> alvaxanthone trimethyl ether could be converted to its monoacetate by refluxing overnight in pyridine-acetic anhydride.

Hydrogenation of alvaxanthone trimethyl ether or triacetate led to tetrahydro derivatives. The lack of a concomitant change in the ultraviolet spectra of these compounds (Table I) revealed both double bonds to be nonconjugated with the xanthone nucleus.<sup>4,5</sup>

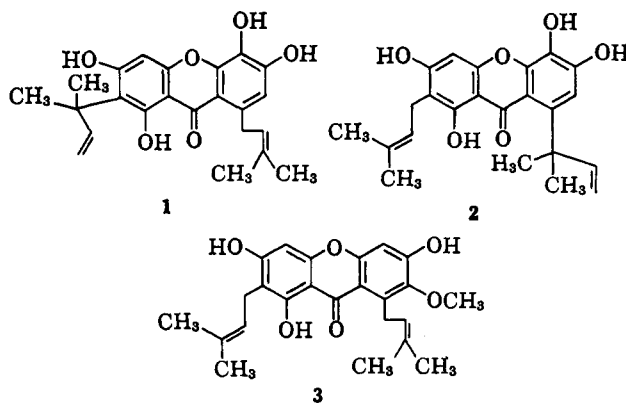
Since the previous work on macluraxanthone<sup>3</sup> and osajaxanthone<sup>1a</sup> had demonstrated the utility of ultraviolet spectral studies in assigning the oxygenation pattern of a xanthone, the spectra of alvaxanthone derivatives were compared with those of various known tetraoxygenated xanthones.<sup>3,5,6</sup> A close resemblance (Table I) was noted between the spectra of alvaxanthone derivatives and those of 1,3,5,6-tetraoxygenated xanthone<sup>3</sup> derivatives such as macluraxanthone<sup>3</sup> and jacareubin.<sup>7</sup> A visual comparison (Figure 1) of the spectra of tetrahydroalvaxanthone trimethyl ether and dihydrojacareubin dimethyl ether demonstrates especially convincingly that alvaxanthone has a 1,3,5,6-oxygenation pattern.

With the placement of the four hydroxyl groups on the xanthone nucleus, it remained to determine the nature of the remaining ten carbon atoms, which were presumed to be incorporated in two isoprenoid groups.<sup>2</sup>

To be sure, the n.m.r. spectrum of alvaxanthone triacetate (Figure 2) revealed the presence of a 1,1-dimethylallyl group,<sup>3</sup> which gives the sharp singlet at  $\tau$  8.41 due to the geminal methyl groups and an ABX system [ $\tau$  5.09, 5.13, and 3.72 ( $J_{a,x} = 10.8$ ,  $J_{b,x} = 18.0$ , and  $J_{a,b} = 1.2$  c.p.s.)] due to the vinyl group. The second was clearly a 3-methyl-3-butenyl group.<sup>8</sup> The geminal methyls give the line at  $\tau$  8.25, which is broadened because the methyls are nonequivalent. This nonequivalence induces a shift between them and the coupling between the two species of protons coalesces the two signals into one broad one. The single olefinic proton and the allylic methylene protons are coupled ( $J = 6.6$  c.p.s.) and give a broad triplet and a broad doublet at  $\tau$  4.62 and 5.96, respectively. The acetate

methyl protons give three sharp singlets at  $\tau$  7.62, 7.67, and 7.78. This leaves three signals to be accounted for, all sharp singlets. Two of these, at  $\tau$  3.53 and 2.97, are due to aromatic protons. A careful consideration of these signals proves to be quite informative. The high shift of the former places it on the phloroglucinol ring. Further, since this proton is not split, one of the terpenoid groups must be substituted on this ring. This information, coupled with the knowledge that alvaxanthone has a 1,3,5,6-oxygenation pattern, leaves only two positions possible for the remaining aromatic proton, C-7 or C-8 of the xanthone nucleus. The intermediate shift of the signal due to this proton places it at C-7 since if it were at C-8, adjacent to the xanthone carbonyl, its shift would be about 1 p.p.m. lower. For example, the C-7 proton of macluraxanthone trimethyl ether gives a signal at  $\tau$  3.04, while the signal due to the C-8 proton occurs at  $\tau$  1.99.<sup>3</sup> Thus it is concluded that alvaxanthone has a proton at C-7 and therefore an isoprenoid group must be at C-8.

The last signal occurs far downfield at  $\tau$  -2.45 and can only be due, in this case, to the strongly hydrogen-bonded C-1 hydroxyl. It will be recalled that this hydroxyl could not be characterized under conditions which usually methylate or acetylate chelated hydroxyls even if hindered. Thus the second terpenoid group must be positioned at C-2. This was confirmed when alvaxanthone trimethyl ether gave a positive Gibbs test<sup>7</sup> proving the position *para* to the free C-1 hydroxyl (at C-4) to be unsubstituted, bearing only the lone phloroglucinol ring proton which gave the signal at  $\tau$  3.53 in the n.m.r. spectrum of the triacetate. The above leads to only two possible structures for alvaxanthone, 1 and 2.



(4) Cf., for example, M. L. Wolfrom, W. D. Harris, G. F. Johnson, J. E. Mahan, S. M. Moffett, and B. S. Wildi, *J. Am. Chem. Soc.*, **68**, 406 (1946).

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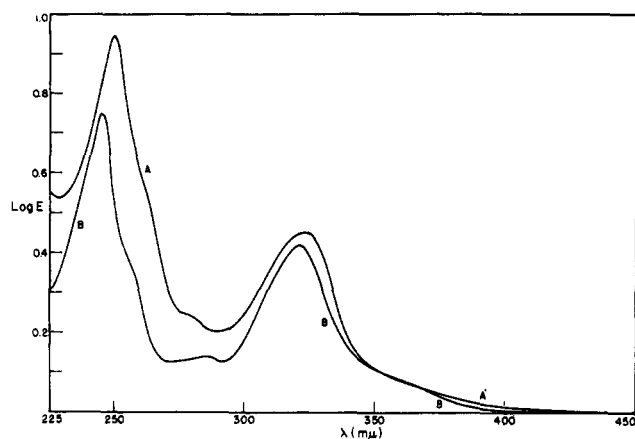


Figure 1.—Ultraviolet spectra ( $m\mu$ ) of tetrahydroalvaxanthone trimethyl ether (curve A) and dihydrojacareubin dimethyl ether (curve B); see Table I.

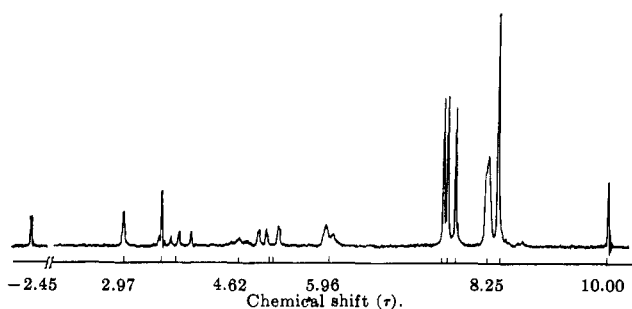


Figure 2.—N.m.r. spectrum of alvaxanthone triacetate ( $\tau$ ) in saturated deuteriochloroform solution with tetramethylsilane as internal reference standard (Varian A60 spectrometer).

A choice between these structures is immediately apparent on further examination of the n.m.r. spectrum of the triacetate. The chemical shift of the allylic methylene group of the 3-methyl-2-butenyl substituent,  $\tau$  5.96, definitely places this substituent on an electron-poor ring atom, *ortho* or *para* to the xanthone carbonyl. Of the two choices possible, the C-2 position is electron rich since it is part of the phloroglucinol ring and *meta* to the xanthone carbonyl, while the C-8 position is *ortho* to the carbonyl and thus electron poor. Therefore the 3-methyl-2-butenyl group must be the terpenoid substituent at C-8 and alvaxanthone must possess structure 1. The allylic methylene protons of 3-methyl-2-butenyl groups substituted at C-8 of the xanthenes mangostin<sup>5</sup> (3) and celebixanthone<sup>9</sup> give shifts of  $\tau$  5.92 and 6.03, respectively,<sup>9</sup> which compare favorably with the shift of the same protons in alvaxanthone,  $\tau$  5.96. Furthermore, the allylic methylene protons of the C-2 3,3-dimethylallyl group of mangostin give a signal at  $\tau$  6.68.<sup>9</sup> If 2 were the structure of alvaxanthone, the shift of these same protons would be expected to be very similar since 2 and 3, mangostin, do not differ in structure in the phloroglucinol ring.

A consideration of the chemistry of the C-1 hydroxyl rules out any further consideration of 2 as the structure of alvaxanthone. The C-1 hydroxyl of alvaxanthone is not methylated by methyl sulfate in refluxing acetone solution with a potassium carbonate base.<sup>2</sup> These conditions will usually methylate a chelated hydroxyl which is hindered by a 3,3-dimethylallyl group, such as

that of osajin and pomiferin.<sup>4</sup> Refluxing acetic anhydride with a sodium acetate base will normally acetylate such a hindered and chelated hydroxyl,<sup>4</sup> but these conditions gave only a triacetate with alvaxanthone. In the present work, all attempts to methylate the C-1 hydroxyl of alvaxanthone, its trimethyl ether, and tetrahydrotrimethyl ether met with failure. As mentioned, the trimethyl ether could be acetylated by refluxing under nitrogen in pyridine-acetic anhydride for a minimum of 8 hr. The severity of the conditions required for this acetylation can only be explained by concluding that the C-1 hydroxyl of alvaxanthone is very severely hindered by the 1,1-dimethylallyl group which must be at C-2 and therefore the structure 1 for alvaxanthone is confirmed. If 2 was the structure, the C-1 hydroxyl would also be hindered but not to such an extent that it could not be methylated or acetylated by comparatively mild conditions. Moreover, the trimethyl ether and triacetate of 2 would be expected to give strong ferric chloride tests, which they do not.<sup>2</sup>

The chemistry of 3, mangostin,<sup>5</sup> a xanthone closely analogous to 2, confirms the above conclusions. The C-1 hydroxyl of mangostin, which is *ortho* to a 3-methyl-2-butenyl group, is methylated by refluxing the dimethyl ether with methyl sulfate and sodium in benzene or toluene.<sup>10</sup> When alvaxanthone trimethyl ether was subjected to these conditions, it was recovered unchanged. Mangostin itself is completely acetylated by heating in sodium acetate-acetic anhydride for 3 days<sup>11</sup> or by pyridine-acetic anhydride at room temperature for 20 days.<sup>10</sup> These conditions returned unchanged the triacetate of alvaxanthone. The C-1 hydroxyl of the dimethyl ether of mangostin could be acetylated by heating in sodium acetate-acetic anhydride for 2 hr.<sup>11</sup> or pyridine-acetic anhydride at 100° overnight.<sup>5</sup> These conditions yielded only starting material when applied to alvaxanthone trimethyl ether. It is considered doubtful that alvaxanthone would behave so differently from mangostin if the structure were 2.

Structure 1, with the hindered C-1 and C-3 hydroxyl, also explains the instability of alvaxanthone to air. Phenols which are hindered by *ortho* tertiary alkyl groups are known to be unstable to air and readily undergo oxidation<sup>12</sup> thus serving admirably as commercial antioxidants. Air oxidations are free-radical reactions, the first step probably being removal of the phenolic proton.<sup>12</sup> The radical obtained is a resonance hybrid of many quinoid forms, giving the aromatic ring great flexibility,<sup>12</sup> thus allowing the tertiary group to move out of the plane of the ring to a less strained position and providing a driving force for the reaction. In the case of alvaxanthone, the unsubstituted position at C-4 allows a peroxide to be formed which can decompose to a 1,4-quinone. The red color of alvaxanthone which has been allowed to decompose is similar to the color of other hydroxyquinones. When the C-3 hydroxyl of alvaxanthone is methylated or acetylated, the resulting compounds are stable to air.<sup>2</sup> This is probably because a radical electron at the C-4 position can no longer be stabilized by the C-3 hydroxyl and, as a result, molecular oxygen cannot attack the ring.

(10) M. Murakami, *Ann.*, **496**, 122 (1932).

(11) S. Yamashiro, *Bull. Chem. Soc. Japan*, **7**, 1 (1932).

(12) C. D. Cook, N. G. Nash, and H. R. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783 (1955).

(9) G. H. Stout, V. F. Stout, and M. J. Welsh, *Tetrahedron*, **19**, 667 (1963).

Considering the evidence for **1** as the structure of alvaxanthone in retrospect, the weakest point is the assignment of the oxygenation pattern as 1,3,5,6 out of a multitude of possibilities on the sole basis of ultraviolet spectra. However, n.m.r. undeniably places a hydroxyl at C-1 and the 3-methyl-2-butenyl group at C-8. The chemical behavior of the C-1 hydroxyl places the 1,1-dimethylallyl group at C-2, and the positive Gibbs test on the trimethyl ether, a proton at C-4. Since the C-4 proton is a sharp singlet in the n.m.r. spectrum of alvaxanthone triacetate, no other protons may be placed in this ring and the only available substituent for C-3 is a hydroxyl function. This leaves two hydroxyl groups and a proton to be placed at C-5, C-6, and C-7. These hydroxyls are *ortho*<sup>2</sup> and thus only the 1,3,5,6 and 1,3,6,7 oxygenation patterns are possible. The great difference between the ultraviolet spectra of alvaxanthone derivatives (Table I) and those of the 1,3,6,7 oxygenated xanthenes mangostin<sup>5</sup> and mangiferin<sup>13</sup> shows that alvaxanthone cannot have a 1,3,6,7 oxygenation pattern. Thus again, one must conclude that the oxygenation pattern of alvaxanthone is 1,3,5,6 and it possesses structure **1**.

### Experimental

**Isolation of Alvaxanthone.**—It was found that alvaxanthone could be isolated in higher yield, as its trimethyl ether, than previously recorded, by the following procedure. The root bark was extracted in a Soxhlet apparatus using 5 l. of ether/kg. of bark. The 5 l. of extract was reduced to 1 l. and processed according to the previous procedure.<sup>2</sup> However, after removal of the crude mixture of macluraxanthone and osajaxanthone, the ether filtrate containing the alvaxanthone was evaporated to dryness, the residue was weighed and then methylated as pure alvaxanthone. In this way, 1 kg. of root bark yielded 1.42% of the trimethyl ether, as compared with the previous average yields of 0.15%<sup>2</sup> of the free pigment.

**Tetrahydroalvaxanthone Trimethyl Ether.**—An amount of 400 mg. of alvaxanthone trimethyl ether<sup>2</sup> was dissolved in the minimum of hot benzene and the resulting solution was diluted to 250 ml. with absolute ethanol. After hydrogenation overnight with a 5% palladium-on-charcoal catalyst at 3 atm., the solution was filtered to remove the catalyst and evaporated to dryness. The residue was recrystallized from ethanol-water, giving yellow needles of tetrahydroalvaxanthone trimethyl ether: yield 379 mg., m.p. 158–160°.

*Anal.* Calcd. for C<sub>28</sub>H<sub>34</sub>O<sub>6</sub>: C, 70.56; H, 7.74. Found: C, 70.41; H, 7.57.

**Tetrahydroalvaxanthone Triacetate.**—An amount of 100 mg. of alvaxanthone triacetate was hydrogenated in ethyl acetate solution as described above for the preparation of tetrahydroalvaxanthone trimethyl ether. Recrystallization from benzene-ethanol gave feathery yellow needles: yield 75 mg., m.p. 170–171°.

*Anal.* Calcd. for C<sub>28</sub>H<sub>34</sub>O<sub>9</sub>: C, 66.14; H, 6.51. Found: C, 66.44; H, 6.68.

**Alvaxanthone Trimethyl Ether Acetate.**—An amount of 300 mg. of alvaxanthone trimethyl ether<sup>2</sup> was dissolved in about 1 ml. of pyridine and 7 ml. of acetic anhydride was added. The solution was refluxed under nitrogen for 8 hr., then poured into 50 ml. of ice and water. Recrystallization of the residue from acetic acid gave very light yellow needles: yield 180 mg., m.p. 158–160°.

*Anal.* Calcd. for C<sub>28</sub>H<sub>32</sub>O<sub>7</sub>: C, 69.98; H, 6.71. Found: C, 70.08; H, 6.46.

**Attempted Methylations of the C-1 Hydroxyl of Alvaxanthone Derivatives.**—An amount of 200 mg. of alvaxanthone<sup>2</sup> was dissolved in 20 ml. of acetone, and 5.0 g. of potassium carbonate was added. The solution was brought to reflux and 1.5 ml. of dimethyl sulfate was added over a period of 1 hr. After a 24-hr. reflux period, a further amount of 1.0 ml. of dimethyl sulfate was added. The solution was refluxed 48 hr. more, filtered, and evaporated. Recrystallization of the residue from benzene-ethanol gave alvaxanthone trimethyl ether, identified by its infrared spectrum as compared with that obtained from the product of diazomethane methylation<sup>2</sup>: yield 91 mg., m.p. 150–152°.

Amounts of 200 mg. each of alvaxanthone trimethyl ether and its tetrahydro derivative were subjected to identical methylation conditions as described above for alvaxanthone. In both cases the starting material was recovered in good yield: the former, 77%; the latter, 86%.

A solution of 206 mg. of alvaxanthone trimethyl ether under nitrogen in 100 ml. of xylene was stirred over about 100 mg. of 3:1 sodium-potassium alloy. After 12 hr. a reddish precipitate formed. An amount of 1.5 ml. of dimethyl sulfate was added and the solution was refluxed overnight. About 10 ml. of ethanol was added, followed by 50 ml. of water, and 5 ml. of acetic acid. The organic layer was separated, dried, and evaporated. Recrystallization of the residue from benzene-ethanol gave 64 mg. of starting material, identified by its infrared spectrum.

**Attempted Acetylations of the C-1 Hydroxyl of Alvaxanthone Derivatives.**—An amount of 300 mg. of alvaxanthone trimethyl ether<sup>2</sup> was dissolved in 1 ml. of pyridine and 7 ml. of acetic anhydride. The solution was maintained at 100° for 12 hr., then poured into water. Recrystallization of the resulting precipitate from benzene-ethanol gave 280 mg. of starting material, identified by its infrared spectrum.

A solution of 200 mg. of alvaxanthone trimethyl ether in 10 ml. of acetic anhydride was refluxed with 1.0 g. of sodium acetate for 2 hr. Processing and recrystallization gave 157 mg. of starting material, identified by its infrared spectrum.

An amount of 300 mg. of alvaxanthone trimethyl ether was dissolved in 1 ml. of pyridine and 7 ml. of acetic anhydride was added. The solution was refluxed 3 hr. and poured into water. Recrystallization from benzene-ethanol gave 270 mg. of starting material, identified by its infrared spectrum. When the mother liquors were allowed to evaporate for 2 weeks, more starting material was obtained along with 7 mg. of the acetate, identified by its infrared spectrum.

A solution of 100 mg. of alvaxanthone triacetate in 1 ml. of pyridine and 5 ml. of acetic anhydride was allowed to stand at room temperature for 21 days. Processing and recrystallization gave 78 mg. of starting material, identified by its infrared spectrum.

A solution of 250 mg. of alvaxanthone triacetate in 10 ml. of acetic anhydride under nitrogen was refluxed with 1 g. of sodium acetate for 39 hr. Processing and recrystallization yielded 191 mg. of starting material, identified by its infrared spectrum.

An amount of 78 mg. of alvaxanthone triacetate was placed in a 5-ml. round-bottomed flask followed by a spatula of magnesium powder. About 1 ml. of acetyl chloride was added, and the mixture was refluxed 1 hr. The solution was poured over ice and solid sodium bicarbonate was added. The mixture was extracted with benzene, and the extract was dried and evaporated. Recrystallization of the residue from benzene-ethanol gave a good yield of starting material, identified by its infrared spectrum.

**Acknowledgment.**—We wish to thank W. D. Ollis of the University of Bristol and Gideon Fraenkel of this department for enlightening discussions. Analyses were performed by W. N. Rond.

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