

viewed with reserve in view of the recent refutation by Griffin¹⁴ of analogous claims by the same author.

(14) N. F. Hepfinger and C. E. Griffin, *Tetrahedron Letters*, No. 21, 1361, 1365 (1963).

(15) NATO Postdoctoral Fellow.

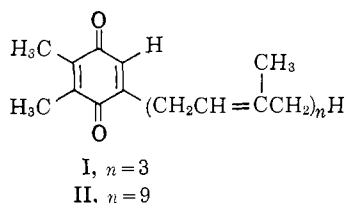
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Identification of Plastoquinone-3 from Chloroplasts¹

Sir:

Plastoquinone-3 (I) has been isolated from chloroplasts and identified for the first time as a natural product. This quinone could be functional in photosynthetic electron transfer.



New quinones of unknown structure, "PQB, PQC, and PQD," have been obtained² from chloroplasts of spinach along with tocopherylquinones, and two general statements were made about their restoration of photo-reductase activities; none of the quinones stimulated all activities and the tocopherylquinones tended to be effective at lower levels than the plastoquinones. We have carried out isolation and structure studies on the plastoquinones from chloroplasts of spinach.

A quinone fraction was eluted with 10% ether-hexane on a decalco column, giving a crystalline product, m.p. 44-46°; ultraviolet, infrared, and n.m.r. absorption spectra revealed this product to be 2,3-dimethyl-solanesyl-1,4-benzoquinone (II, plastoquinone-9). A second quinone fraction was eluted by 20% ether-hexane and was further purified by a decalco column and preparative thin layer chromatography. The chromatograms (silica gel G), developed by chloroform, showed several leucomethylene blue sensitive spots but two major spots with R_f 0.32 and 0.62. The ultraviolet spectra and chromatographic behavior of the quinone R_f 0.32 and of an authentic sample of α -tocopherylquinone showed that these two compounds are identical. The quinone R_f 0.62 was a red-yellow oil which was very unstable, even at 0°; R_f 0.81 on silicon-impregnated paper in reverse phase chromatography. The ultraviolet spectrum of the eluted and still impure quinone showed λ_{\max} at 253 ($E_{1\text{ cm}}^{1\%}$ 115) and 261 μ (shoulder) in ethanol; reduction with sodium borohydride gave a hydroquinone with λ_{\max} 289 μ ($E_{1\text{ cm}}^{1\%}$ 71) in ethanol. The infrared spectrum in carbon tetrachloride differed from that of plastoquinone-9 mainly in the presence of a band at 1730 cm^{-1} and was analogous to the infrared spectrum of a mixture of plastoquinone-4 and the "dimers" of plastoquinone-4 and -9.³ The n.m.r. spectrum showed signals at τ 3.62

(t), 4.44 (b), 4.92 (b), 6.90 (d), 7.34 (b), 8.03 (bs), 8.35, 8.42 (s), 8.75, 8.84 (s), and 9.0-9.3 (m) (s, singlet; d, doublet; t, triplet; m, multiplet; b, broad). This spectrum was very similar to the spectrum of the synthetic "dimer" of plastoquinone-9.³ The mass spectrum at different temperatures showed significant peaks at m/e 340, 271, 203, and 189 (base peak). No peaks were present beyond m/e 340. The peaks can be assigned as follows: m/e 340 (M^+ $\text{C}_{23}\text{H}_{32}\text{O}_2$); m/e 271 ($M^+ - \text{C}_5\text{H}_9$; $\text{C}_{18}\text{H}_{23}\text{O}_2$); m/e 203 [$M^+ - 2(\text{C}_5\text{H}_9)$; $\text{C}_{13}\text{H}_{15}\text{O}_2$]; m/e 189 (base peak = $\text{C}_{12}\text{H}_{13}\text{O}_2$). The spectroscopic and chromatographic data show that this quinone was 2,3-dimethyl-5-farnesyl-1,4-benzoquinone (plastoquinone-3) containing apparently some of the "dimers" of plastoquinone-3 and -9. 2,3-Dimethyl-5-farnesyl-1,4-benzoquinone (plastoquinone-3) was synthesized⁴ and compared with the isolated quinone; in five chromatographic systems there was no difference, but there was a difference in R_f values between synthetic and isolated plastoquinone-3 (0.45 and 0.33, respectively) in ether-*n*-hexane. This difference may be a result of the impurities which are present in the isolated quinone and possibly a difference in side-chain stereochemistry. Dilley⁵ has observed a difference in R_f values of 0.1 when synthetic plastoquinone-9 was compared with the natural compound.

Synthetic plastoquinone-3 and the isolated quinone were reduced and acetylated with acetic anhydride in the presence of zinc powder. The hydroquinone diacetate from synthetic plastoquinone-3 and the material obtained from the isolated quinone were chromatographically compared. The material from the isolated quinone showed three spots when detected by 2% aqueous potassium permanganate. One of these spots (R_f 0.21, 20% ether-hexane, and 0.29, chloroform) showed the same R_f value (0.22, 20% ether-hexane, and 0.30, chloroform) observed for the hydroquinone diacetate of synthetic plastoquinone-3. The peak at m/e 340 might have resulted from the loss of water from a " γ -hydroxyquinone derivative" of plastoquinone-3, 2,3-dimethyl-5-(3'-hydroxy-3',7',11'-trimethyl-6',10'-dienedodecyl)-1,4-benzoquinone (mol. wt. 358). This possibility was eliminated by synthesis of the " γ -hydroxyquinone derivative" through the steps: plastoquinone-3, chromenol, chromanol, and γ -hydroxyquinone. As expected, the R_f value (0.23 on silica gel G thin layer plates in chloroform) was different from that of plastoquinone-3 (0.62).

It is difficult to evaluate plastoquinone-3 in terms of quinones of unknown structure² from spinach chloroplasts; "PQB" ($\lambda_{\max}^{\text{EtOH}}$ 255 μ ($E_{1\text{ cm}}^{1\%}$ 202); R_f 0.13 on silicon-impregnated paper); "PQC" (data from three publications: $\lambda_{\max}^{\text{EtOH}}$ 255 μ ($E_{1\text{ cm}}^{1\%}$ 66), 255, 262, ($E_{1\text{ cm}}^{1\%}$ 96); 262 ($E_{1\text{ cm}}^{1\%}$ 75), shoulder at 255; R_f values of 0.75 on silicon-impregnated paper, 0.0 on silica gel G thin layer plates in 15% trichloroethyl-acetate in benzene, and 0.49 on silica gel G plates in 1% ether in chloroform); and "PQD" ($\lambda_{\max}^{\text{EtOH}}$ 262 μ ($E_{1\text{ cm}}^{1\%}$ 75), shoulder at 255; R_f values at 0.0 on silica gel G thin layer plates in 15% trichloroethyl acetate in benzene and 0.40 on silica gel G thin layer plates in 1% ether in chloroform). A product corresponding to PQB was

(1) Coenzyme Q. LXIII.

(2) (a) L. P. Kegel, M. D. Henninger, and F. L. Crane, *Biochem. Biophys. Res. Commun.*, **8**, 294 (1962); (b) M. D. Henninger and F. L. Crane, *Plant Physiol.*, **39**, 598 (1964).

(3) N. Eck and A. Trebst, *Z. Naturforsch.*, **18B**, 446 (1963).

(4) N. R. Trenner, B. H. Arison, R. E. Erickson, C. H. Shunk, D. E. Wolf, and K. Folkers, *J. Am. Chem. Soc.*, **81**, 2026 (1959).

(5) R. A. Dilley, *Anal. Biochem.*, **7**, 240 (1964).

not observed. The spectral and chromatographic data of isolated plastoquinone-3 do not agree in every detail with PQC or PQD. However, a compound called "R 253" ($\lambda_{\text{max}}^{\text{EtOH}}$ 253 ($E_{1\text{cm}}^{1\%}$ 15); R_f values of 0.69 on silica gel G in 1% ether in chloroform, and 0.53 on silica gel G thin layer plates in 15% trichloroethyl acetate in benzene), also reported by Crane² from spinach chloroplasts, does compare favorably with plastoquinone-3 in ultraviolet absorption data and chromatographic behavior. Also, a quinone isolated by Eck and Trebst³ from chestnut tree leaves and tentatively identified as plastoquinone-4 shows properties quite similar to those of plastoquinone-3; plastoquinone-4, kindly provided by Professor Trebst, and plastoquinone-3 are not identical.

Plastoquinone-3 is surprisingly unstable. During isolation, the elution time from the decalso column was very critical. Plastoquinone-3 largely decomposed within 1 hr. upon exposure to sunlight to give a number of leucomethylene blue sensitive compounds and changes in room light; chromatography was performed under a red safety lamp.

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Bis(2,4-pentanediono)diacetatosilicon(IV)

Sir:

We wish to report the preparation of bis(2,4-pentanediono)diacetatosilicon(IV) which is representative of a new class of hexacoordinate silicon chelate compounds having β -diketone ligands.

Silicon acetylacetonates were first reported by Dilthey,¹ who prepared a number of derivatives of the tris(2,4-pentanediono)siliconium ion, $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Si}^+$, formed by treating silicon tetrachloride with acetylacetone. Salts such as $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Si}^+\cdot\text{HCl}_2^-$ and $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Si}^+\cdot\text{FeCl}_4^-$ were isolated and characterized. The assigned octahedral structure for this class of chelates was later confirmed by infrared analysis,² partial resolution,³ and more recently by nuclear magnetic resonance data.⁴

We have found that use of organocarboxysilanes in place of the previously employed tetrachlorosilane leads to the formation of a new class of hexacoordinate acetylacetonate silicon derivatives. Tetraacetoxysilane was treated with acetylacetone in a 1:2.1 mole ratio in chloroform solvent under a nitrogen atmosphere. A temperature rise of approximately 30–60° was noted on mixing the reagents. Subsequent heating of the reaction mixture at 70° for 2 hr. produced a light yellow solid. Collection of the solid by filtration under suction followed by recrystallization from a chloroform-petroleum ether mixture gave white, crystalline bis(2,4-pentanediono)diacetatosilicon(IV) (I), m.p. 178–180° dec. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_8\text{Si}$: C, 48.82; H,

5.85; Si, 8.16; equiv. wt., 86.1; mol. wt., 344.39. Found: C, 48.52; H, 5.98; Si, 8.19; equiv. wt., 88.0; mol. wt., 346. The recrystallized material is stable for an indefinite period when stored in a sealed container, but turns yellow in color when exposed to the atmosphere for several hours.

The nonionic nature of the chelate I was demonstrated by treatment of the material with ferric chloride in chloroform under conditions similar to those employed by Dilthey¹ for the preparation of the salts mentioned above. No reaction was detected, either by a rise in temperature or by the precipitation of an iron salt.

The infrared spectra of metal acetylacetonates have been studied extensively by many investigators. Nakamoto⁵ has compiled much of these data. The key assignments in Table I are made based on the infrared spectrum of I.

Table I. Infrared Absorption Bands

Frequency, cm^{-1}	Assignment
1705	Normal $>\text{C}=\text{O}$ absorption in the $\text{CH}_3\text{COO}-$ group
1575	$\text{C}=\text{C}$ stretch
1550	$\text{C}=\text{O}$ stretch
1050	$\equiv\text{Si}-\text{O}-\text{C}\equiv$
830	$\pi(\text{C}=\text{H})$
693	Ring deformation + (Si—O)
665	$\text{C}-\text{CH}_3$ bonding + (Si—O)

All but the band at 1705 cm^{-1} are observed, in general, for the metal acetylacetonates. The assignments are made based on the conclusions of Nakamoto.⁵ The intensification and very large shift of the $\text{C}=\text{O}$ absorption band from 1625, observed in acetylacetone, to 1550 cm^{-1} in compound I is typical of metal chelates formed with acetylacetonate ligands.

Holm and Cotton⁶ have reported that the feature of the ultraviolet spectra of metal acetylacetonate compounds is the very strong absorption band occurring usually from about 270 to 300 $\text{m}\mu$ with ϵ_{max} generally greater than $20,000\text{ l. mole}^{-1}\text{ cm}^{-1}$. The spectrum of I in chloroform solvent shows λ_{max} 279 $\text{m}\mu$, ϵ 20,041 $\text{l. mole}^{-1}\text{ cm}^{-1}$. This increase in the extinction coefficient over that of acetylacetone (ϵ_{max} 10,600 $\text{l. mole}^{-1}\text{ cm}^{-1}$) is typical of the chelates investigated previously.⁶

Further evidence to support the chelate structure of I was obtained by carrying out the above-described reaction at a relatively low temperature. The reaction temperature was not allowed to exceed 5° by addition of the acetylacetone in a dropwise manner. After the addition was complete, the reaction mixture was stirred for an additional 15 min. at 0–5°. A white, chalky precipitate was obtained. A portion of this material was isolated by filtration and dried under reduced pressure (10 mm.) at room temperature, m.p. 150° dec. The infrared spectrum showed *no absorption* in the 1500–1600 or 650–700 cm^{-1} regions which are indicative of bidentate chelation of the acetylacetone group to a metal atom. This material (II) may be the diacetoxysilyl ester of the normal enolate of acetylacetone. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_8\text{Si}$: Si, 8.16; equiv. wt.,

(5) See K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 216, and references therein.

(6) R. N. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

(1) W. Dilthey, *Ber.*, **36**, 926 (1903).

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(3) S. K. Dahr, V. Doron, and S. Kirschner, *ibid.*, **80**, 753 (1958).

(4) R. E. Herter, *Chem. Ind.* (London), 1397 (1963).