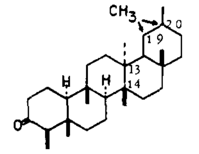
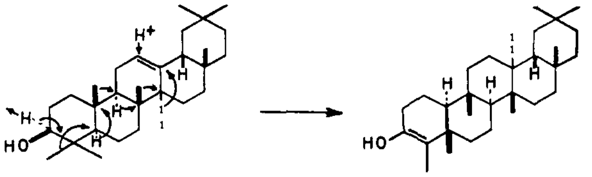


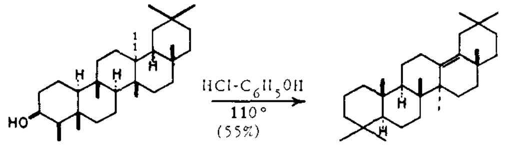
I, CH_3 at C_{19} or C_{20}
V, CH_3 at C_{20}

atoms away from ring A and toward ring E. Consideration of friedelin as a possible rearrangement product of α- or β-amyrin prompted us to undertake the experiments which are outlined in this report and which have led to the direct correlation of friedelin with β-amyrin.



β-amyrin friedelin(enol)

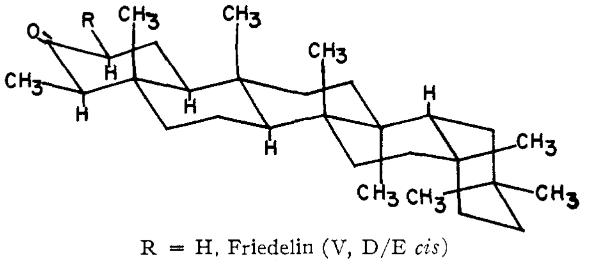
Reduction of friedelin with lithium aluminum hydride produces friedelan-3β-ol (II), m.p. 283.5–285°,[2,3] in which the hydroxyl function is axial. Treatment of II with hydrogen chloride in phenol at 110° causes a remarkable multi-group rearrangement which affords olean-13(18)-ene (III) (55% yield), m.p. 186–187°, $[\alpha]_D$ −12.5° (*C*, 0.80, chloroform), λ_{max} 213 mμ (log ε 3.51), bright yellow coloration with tetranitromethane, *Anal.* Calcd. for $C_{30}H_{50}$: C, 87.73, H, 12.27. Found: C, 87.76, H, 12.37. This material is identical with an authentic sample prepared from β-amyrin by oxidation, Wolff–Kishner reduction and acid-catalyzed isomerization of the 12,13-double bond to the 13,18-position, m.p. 186–187° (undepressed upon admixture with a sample from rearrangement of freidelan-3β-ol), $[\alpha]^{25}D$ −13.9° (*C*, 0.79, chloroform) bright yellow coloration with tetranitromethane. The infrared spectra of the above samples of $\Delta^{13(18)}$-olefin are identical.[4] Further confirmation of identity was obtained by conversion of both products to the same mixture of epimeric oxides with perbenzoic acid, m.p. *ca.* 191–5°, undepressed upon admixture. Both samples of oxide upon treatment with boron trifluoride ethereate yielded olean-11, 13(18)-diene (IV)[4], m.p. 219–220°, $[\alpha]^{25}D$ −72.4° (*C*, 0.95, chloroform), λ_{max} 242, 250, 260 mμ (log ε 4.44, 4.50, 4.31), *Anal.* Calcd. for $C_{30}H_{48}$: C, 88.16, H, 11.84. Found: C, 88.02; H, 11.91, brown coloration with tetranitromethane, mixture m.p. undepressed.



II III

The conversion of II into III proves the location of methyl groups at C_{17} and C_{20} as in β-amyrin and, together with the degradative work, establishes beyond any doubt structure V for friedelin, which is complete except for the orientation of the hydrogen at C_{18}.

The biosynthetic pathway for the conversion of lupeol (VI)[5] into friedelin by a sequence of 1,2-shifts would lead not only to the correct carbon skeleton, but also to the experimentally established stereochemical configuration at all asymmetric centers and to the β-orientation of the hydrogen at C_{18} (D/E *cis*) as in α[6]- and β-amyrin.[7] For this reason we favor the view that the hydrogen at C_{18} in friedelin is β-oriented.[8]



R = H, Friedelin (V, D/E *cis*)
R = OH, cerin

If the above biosynthetic pathway is correct, two sequences for formation of pentacyclic triterpenes follow: (1) lupeol → β-amyrin → friedelin and (2) lupeol → α-amyrin → presently unknown relative of friedelin. We are currently engaged in a search for the missing α-amyrin analog of friedelin as well as for other intermediates in both series.

The formulation of cerin as 2β-hydroxy friedelin follows from the location of the hydroxyl at C_2 and from the fact that the hydroxyl is very easily acylated or sulfonated (equatorial orientation).

In connection with the work in this and the preceding paper, we wish to express our thanks to Dr. I. H. Riley for the X-ray measurements, to Dr. R. A. Sneen for the deuterium analyses, to Messrs. H. C. Huang, D. F. Joesting and R. G. Schultz for help in isolation of friedelin and preparation of intermediates, to the Armstrong Cork Company for supplies of cork wax and to the Eli Lilly Company for generous financial support.

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[2] J. J. Lander and W. J. Svirbely, THIS JOURNAL, 66, 235 (1944).

[3] Recently isolated from various natural sources by P. R. Jefferies, *J. Chem. Soc.*, 473 (1954), and by T. Bruun, *Acta Chem. Scand.*, **8**, 71 (1954).

[4] K. Takeda, *J. Pharm. Soc. Japan*, **63**, 197 (1943); *C. A.*, **45** 586 (1951).

[5] See L. Ruzicka, A. Eschenmoser and H. Heusser, *Experientia*, **9**, 357 (1953).

[6] E. J. Corey and J. J. Ursprung, *Chem. and Ind.*, 1387 (1954).

[7] D. H. R. Barton and N. J. Holness, *J. Chem. Soc.*, 78 (1952).

[8] This view is confirmed by a 2-dimensional Fourier X-ray analysis on friedelan-3α-ol chloro and bromoacetates made in these Laboratories by Dr. I. H. Riley, the results of which are completely concordant with structure V (D/E *cis*) for friedelin. These results will be reported later.

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LUMINESCENCE SPECTROSCOPY OF PORPHYRIN-LIKE MOLECULES INCLUDING THE CHLOROPHYLLS[1]

Sir:

The understanding of the participation of the chlorophylls in the primary reaction of photosynthesis demands an exact knowledge of the location and characteristics of the lowest excited states of these molecules.[2]

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[1] Work done under a contract between the Office of Naval Research, U. S. Navy, and the Florida State University.

[2] R. S. Becker and M. Kasha, "Luminescence Spectroscopy of Molecules and the Photosynthetic System," Conference on Luminescence, Pacific Grove, California, March 29, 1954, National Research Council Bulletin, in press.

The low temperature light emission properties of several metallo-derivatives of phthalocyanines, porphyrins and chlorophylls have been studied. The lowest triplet–singlet emissions of the latter two groups of molecules have been located and shown to be in accord with expected behavior based on spin-orbital perturbations introduced by heavy and paramagnetic atoms.[3,4,5] The results are summarized in Table I.

The phosphorescence of chlorophyll-*b* was reported earlier by Calvin and Dorough,[6,7] but could not be duplicated by later work.[8] Our work provides proof that the phosphorescence of chlorophyll-*b* reported earlier is a *bona fide* emission.

We observed a phosphorescence in chlorophyll-*b* with a first strong band at 8650 Å. (0,0-band at 11618 cm.$^{-1}$), using two chromatogrammed samples from different sources. Using pheophorbide-*a* as an analog of chlorophyll, we showed that its strong fluorescence (6701 Å., first band) is converted completely to phosphorescence in Cu^{++}-pheophorbide-*a*. Moreover, the phosphorescence occurs at 8675 A. (first strong band). This complete conversion in the presence of a paramagnetic ion, and the position of the emission, indicate that the phosphorescence observed in the pheophorbide and the chlorophyll are the lowest triplet → singlet emissions in these molecules.[3,5]

TABLE I

LUMINESCENCE DATA ON PORPHYRIN-LIKE MOLECULES, (ALL IN EPA GLASS[a] AT 77°K.)

Molecule	Wave length of first strong band, Å.	
	Fluorescence	Phosphorescence
Etioporphyrin-II	6236	8060
Zn^{++}-Etioporphyrin-II	5730	7000
Cu^{++}-Etioporphyrin-II	None	6812
Ni^{++}-Etioporphyrin-II	None	6812
Phthalocyanine	6918	Not obsd.
Mg^{++}-Phthalocyanine	6705	Not obsd.
Zn^{++}-Phthalocyanine	6731	Not obsd.
Pheophorbide-*a*	6701	None found
Cu^{++}-Pheophorbide-*a*	None	8675
Chlorophyll-*a*	6645[b]	None found
Chlorophyll-*b*	6564	8650
Chlorophyll-*b*	6485[b]	..

[a] G. N. Lewis and D. Lipkin, THIS JOURNAL, **64**, 2801 (1942). [b] Room temp. in ether solution, F. Zscheile and P. Harris, *J. Phys. Chem.*, **47**, 623 (1943).

Phosphorescence was not found in chlorophyll-*a*, and that observed in chlorophyll-*b* was relatively weak, indicating a quantum efficiency of the order of magnitude of 0.1 or less under the conditions studied. However, in Cu^{++}-pheophorbide-*a* the quantum yield of phosphorescence is probably close to unity, as the emission was relatively intense. A detailed consideration of the role of chlorophyll in photosynthesis must include the possibility of strong *inter-molecular* spin-orbital perturbations. Thus, the low yield of phosphorescence in chlorophyll-*a* (*i.e.*, 0) and in chlorophyll-*b* (≤ 0.1) observed in dilute rigid glass solution at low temperatures does not rule out the lowest triplet state from participation in the photosynthetic reaction.

All observations were made using a Steinheil Universal Spectrograph GH, with f/3 coated glass optics, using three large coated glass prisms. The exciting light was the AH-6 high-pressure 1 kw. water-cooled mercury arc, monochromatized by suitable filters. Both steady excitation with filtered light, and intermittent excitation with a phosphoroscope of 10^{-4} sec. resolving time was used. In the case of Ni^{++} and Cu^{++} derivatives, only steady excitation yielded emission, indicating the shortening of T → S emission lifetime by the strong spin-orbital coupling in those compounds.

In the case of phthalocyanines, no phosphorescence was observed in the photographic infrared up to 9000 Å., it appears that the lowest triplet states of these molecules lie at longer wave lengths.

In the case of the metal derivatives of etioporphyrin-II, the strong fluorescence of the parent compound was partially quenched with consequent enhancement of phosphorescence[3,5] in the Zn^{++} derivative, while in the Ni^{++} and Cu^{++} complexes only (strong) phosphorescence was observed, as expected for strong spin-orbital coupling.

A complete discussion of the above results and the publication of the spectra obtained will be presented in a forthcoming paper.

The recent observations by Livingston, *et al.*,[9] on the transient absorption originating in excited chlorophyll molecules is thus most probably the triplet–triplet absorption, in accordance with similar observations made on other molecules.[10]

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(4) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(5) P. Yuster and S. I. Weissman, *ibid.*, **17**, 1182 (1949).

(6) M. Calvin and G. Dorough, *Science*, **105**, 433 (1947).

(7) M. Calvin and G. Dorough, THIS JOURNAL, **70**, 699 (1948).

(8) R. Livingston, "The Photochemistry of Chlorophyll," p. 179–196, in "Photosynthesis in Plants," edited by J. Franck and W. E. Loomis, Iowa State College Press, Ames, Iowa, 1949.

(9) R. Livingston and V. A. Ryan, THIS JOURNAL, **75**, 2176 (1953); R. Livingston, G. Porter and M. W. Windsor, *Nature*, **173**, 485 (1954); R. Livingston, THIS JOURNAL, **77**, 2179 (1955).

(10) G. Porter and M. W. Windsor, *J. Chem. Phys.*, **21**, 2088 (1953).

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A WATER SOLUBLE SYSTEMIC INSECTICIDE O,O-DIETHYL *S*-2-ETHYLMERCAPTOETHYL PHOSPHOROTHIOLATE METHOSULFATE

Sir:

In connection with studies concerning the chemistry and toxicology of the thiono- and thiol-isomers of Systox,[1] we have prepared and measured the insecticidal activity of O,O-diethyl S-2-ethylmercaptoethyl phosphorothiolate methosulfate (methosulfate of the thiol isomer). The product was obtained by heating equimolar amounts of O,O-diethyl S-2-ethylmercaptoethyl phosphorothiolate,[2] b.p. 106–108° (0.3 mm.), n^{26}D 1.4926, and freshly distilled methyl sulfate on the steam-bath for one hour.[3] The phosphorothiolate

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(1) Systox is the trade name given by the Chemagro Corp., New York, N. Y., for a technical mixture of O,O-diethyl O-2-ethylmercaptoethyl phosphorothionate and O,O-diethyl S-2-ethylmercaptoethyl phosphorothiolate.

(2) G. Schrader, "Die Entwicklung neure Insektizide auf Grundlage organischer Fluor und Phosphor-Verbindungen," Monograph No. 62, *Angewandte Chemie*, 1952.

(3) I. A. Usov, M. Z. Finkelshtein and V. N. Belov, *J. Gen. Chem. (U.S.S.R.)*, **17**, 2253 (1947).