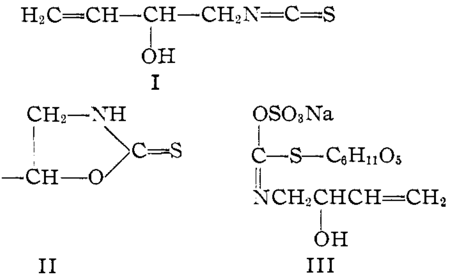
Seeds of the genus *Brassica* contain a higher concentration of goitrin than do the edible portions of rutabaga and turnip. In studies of these seeds, it was found that goitrin was not formed when the enzyme was destroyed by suspending the seeds in boiling water. Subsequent treatment of the filtrate with a purified myrosin preparation liberated goitrin. The precursor was found to have a specific absorption at 225–227 mμ compared to 240 mμ for goitrin, greatly facilitating its fractionation. Since the precursor was heat stable, water soluble, and ether insoluble and the goitrin could be delivered by enzymatic hydrolysis, it was suggested that the compound might be similar to known mustard oil precursors.[4] It has now been possible to isolate, crystallize and identify this precursor, henceforth called progoitrin.

Rutabaga seed was ground in a coffee mill, extracted three times with ether and dried. Approximately 300 g. of the ether-extracted ground seed was poured slowly into approximately 2 liters of boiling water and boiled for 30 minutes. The suspension was cooled and filtered and the residue resuspended in 1 liter of cold water overnight. This was again filtered; the filtrates were combined and evaporated *in vacuo* at a temperature of 38°. The concentrated extract was made up to 80% ethanol by volume to precipitate the protein and was again filtered and concentrated. The concentrate was dissolved in a small volume of 80% ethanol and placed on an 80% ethanol washed alumina column. After developing with two column volumes of 80% ethanol the column was eluted with 60% ethanol and approximately 70% of the progoitrin in greatly purified form was obtained. This purified progoitrin was then rechromatographed in a similar manner three times. The material from the last chromatogram was evaporated to dryness and dissolved in a small volume of hot 95% ethanol. After standing several months in the cold, crystals eventually formed. Subsequent seeding of chromatographically purified material allowed crystallization of relatively large quantities of fine needle-like white crystals. After several recrystallizations from 80 to 95% ethanol, the material gave a constant decomposition point. After thorough desiccation, the crystals began to turn brown at 128–130° and melted at 135–140°. Optical rotation was $[\alpha]_D$ −22.3° (water). Elemental analysis was consistent with the empirical formula listed below. The pure compound could easily be split by a purified myrosin preparation yielding stoichiometric amounts of goitrin, glucose, sulfate and sodium.

The structure of the compound has tentatively been assigned as a glucoside related to L-2-hydroxy-3-butenyl isothiocyanate (I). Progoitrin has a specific absorption at 227 mμ very similar to sinigrin[5]; the spectral shift to 240 mμ during enzymatic hydrolysis indicates that cyclization to goitrin (II) occurs. It seems probable that progoitrin is analogous in structure to sinigrin but contains an extra CHOH group. If Gadamer's structure for sinigrin[6] is accepted, progoitrin may then be written as III. The molar extinction of progoitrin at 227 mμ is 7700; its infrared spectrum is consistent with the structure advanced above.



$H_2C{=}CH{-}\underset{OH}{CH}{-}CH_2N{=}C{=}S$

I

II

III

Fig. 1.—(I) 2-Hydroxy-3-butenyl isothiocyanate; (II) 5-vinyl-2-thioöxazolidone; (III) possible structure of progoitrin.

	Elemental Analysis for ($C_{11}H_{18}O_{10}NS_2Na$) C	H	N	S	Na
Found	32.44	4.59	3.39	15.27	5.52
Calcd.	32.11	4.38	3.41	15.56	5.59

---

(3) E. B. Astwood, M. A. Greer and M. G. Ettlinger, *J. Biol. Chem.*, **181**, 121 (1949).

(4) M. A. Greer, M. G. Ettlinger and E. B. Astwood, *J. Clin. Endocrinology*, **9**, 1069 (1949).

(5) Obtained through the courtesy of Drs. M. G. Ettlinger and A. J. Lundeen.

(6) J. Gadamer, *Arch. Pharm.*, **235**, 44 (1897).

RADIOISOTOPE SERVICE, VETERANS ADMINISTRATION
HOSPITAL, LONG BEACH, CALIFORNIA AND
DEPARTMENT OF MEDICINE
UNIVERSITY OF CALIFORNIA MONTE A. GREER
LOS ANGELES, CALIFORNIA

RECEIVED FEBRUARY 6, 1956

THE ELECTRONIC SPECTRA AND STRUCTURE OF THE PLEIADIENES

Sir:

The unusual peri-condensed aromatic hydrocarbons, acepleiadiene, pleiadiene, and acepleiadylene, have been synthesized recently by Boekelheide and co-workers.[1,2] The study of such aromatic systems provides an excellent opportunity to test the various theories of electronic structure of complex molecules.

The study of the electronic spectra of aromatic hydrocarbons in dilute mixed crystals at low temperatures has led to a detailed analysis of the vibrational structure and polarization properties of the electronic transitions of numerous cata-condensed aromatic hydrocarbons.[3–6] Accordingly, the spectra of acepleiadiene and acepleiadylene have been measured in dilute solid solutions in pyrene, using single crystals and polarized light. The polarization properties which are observed for the lowest transition in each of these molecules conclusively demonstrate that the transition at 17 kk.[7] ($\log \epsilon = 2.3$) in acepleiadiene is polarized along the transverse direction ($^1B_1 \leftarrow$

---

(1) V. Boekelheide, W. E. Langeland and C. T. Liu, THIS JOURNAL, **73**, 2432 (1951).

(2) V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956).

(3) Naphthalene: D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954); **24**, 1 (1956).

(4) Azulene: J. W. Sidman and D. S. McClure, *ibid.*, **24**, in press.

(5) Anthracene and tetracene: J. W. Sidman, *ibid.*, **24**, in press.

(6) Stilbene: R. H. Dyck and D. S. McClure, to be published.

(7) 1 kk. = 1 kilokayser = 1000 cm.$^{-1}$.

$^1A_1$), whereas the transition at 18 kk. ($\log \epsilon = 3.5$) in acepleiadylene is polarized along the symmetry axis ($^1A_1 \leftarrow {}^1A_1$), as is shown in Fig. 1.

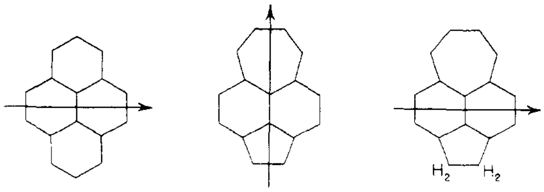


Fig. 1.—Polarization properties of the lowest electronic transitions in pyrene and in the pleiadienes.

The low intensity of the 17 kk. transition in acepleiadiene suggests a $^1L_b \leftarrow$ 'A assignment. Elementary considerations based on the method of the polarization diagram[8] predict that the $^1L_b \leftarrow {}^1A$ transition is polarized along the transverse direction, in agreement with observation.

The predictions based on the polarization diagram indicate that the $^1L_b \leftarrow {}^1A$ transition in acepleiadylene is polarized along the symmetry axis. The intensity appears somewhat high for a $^1L_b \leftarrow {}^1A$ transition, but the polarization properties are not consistent with a $^1L_a \leftarrow {}^1A$ assignment. The lowest transition in acepleiadylene is therefore assigned as $^1L_b \leftarrow A^1$. The rather high intensity for this transition is ascribed to the long-field nature of the molecule.[9]

By treating the cata-condensed hydrocarbon as a perturbed cyclic polyene, Moffitt[10] has given an elegant account of the large energy decrease of the $^1L_b \leftarrow A^1$ transition in azulene relative to its π-isomer, naphthalene. FEMO calculations lead to a $^1L_b \leftarrow {}^1A$ assignment for the lowest absorption transition in pyrene at 27 kk.[11] The 9 kk. decrease in the transition in acepleiadylene relative to its π-isomer, pyrene, is in agreement with Moffitt's perturbation theory. It therefore appears that Moffitt's description of a cata-condensed system may also be useful for a peri-condensed system, which may be thought of as a perturbed bicyclic polyene in which the inner atoms lie on a perimeter which is coaxial with the perimeter of the outer atoms. Both the inner and outer perimeters separately satisfy the Hückel ($4n + 2$) rule in pyrene[12] and in acepleiadylene.

I am grateful to Prof. V. Boekelheide and to Prof. M. Szwarc for gifts of the hydrocarbons.

(8) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

(9) J. R. Platt, *ibid.*, **18**, 1168 (1950).

(10) W. Moffitt, *ibid.*, **22**, 320 (1954).

(11) N. S. Ham and K. Ruedenberg, *ibid.*, **24**, in press.

(12) F. O. Rice and E. Teller, "The Structure of Matter," J. Wiley and Sons, New York, N. Y., 1949, p. 107.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK
JEROME W. SIDMAN

RECEIVED FEBRUARY 23, 1956

TERPENES V. THE STRUCTURE OF PATCHOULY ALCOHOL

Sir:

Patchouly oil is one of the most important raw materials for the composition of fancy perfumes. The mysterious scent of the essence is partly due to patchouly alcohol ($C_{15}H_{26}O$), a tricyclic sesquiterpene first isolated by Gal in 1869. The early structural investigations of Gadamer, Semmler and Wallach[1] have been continued by Treibs[2] who proposed I as a structural expression for this natural product.

We would like to discuss evidence which shows that patchouly alcohol is represented by II. Acetylation of II with ketene produced the acetate (VIII), m.p. ~24°, (*Anal.* Calcd. for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.05; H, 10.64) which was reduced to II with lithium aluminum hydride. Pyrolysis of VIII at 300° led to a mixture of liquid patchoulenes (IX and X), b.p. 141–142° (17 mm.), $[\alpha]^{30}D$ −43°, (*Anal.* Calcd. for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.34; H, 11.82) which on oxidation with osmium tetraoxide was converted to two isomeric, saturated diols (XI and XII). Diol XI, m.p. 95–96°, (*Anal.* Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.75; H, 11.06) on cleavage with lead tetraacetate gave formaldehyde and a norketone (XIII), (*Anal.* Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 80.94; H, 10.45) infrared max. 5.86 μ; 2,4-DNP, m.p. 144–145°, (*Anal.* Calcd. for $C_{20}H_{26}N_4O_4$: C, 62.16; H, 6.78. Found: C, 61.88; H, 6.85). Oxidation of diol XII, m.p. 107–108°, (*Anal.* Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.61; H, 10.84) with lead tetraacetate produced a ketocarboxylic acid (XIV), m.p. 82.5–83.5° (*Anal.* Calcd. for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.30; H, 9.60), infrared max. 3.1–4.0; 5.90; 8.25 μ; oxime m.p. 164–165° (*Anal.* Calcd. for $C_{15}H_{25}NO_3$: C, 67.38; H, 9.43. Found: C, 67.39; H, 9.44). Condensation of XIII with isoamyl nitrite in the presence of sodium ethoxide gave the oximinoketone (XV), m.p. 131–132°, (*Anal.* Calcd. for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00. Found: C, 71.65; H, 9.04), $\lambda_{max.}$ 234 mμ (ϵ 8400) rather than an oximinoester. Examination of the infrared spectrum of XIII indicates the presence of a substituted cyclohexanone or a cycloheptanone. Convincing evidence for the size of ring A was obtained in the following way: Oxidation of a mixture of IX and X consecutively with potassium permanganate and with nitric acid led to a dicarboxylic acid (XVI), m.p. 225–227° (*Anal.* Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.92; H, 8.33). The corresponding anhydride (III), m.p. 109–110°, (*Anal.* Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.21; H, 8.04) with infrared peaks at 5.60 and 5.73 μ is clearly a glutaric anhydride and ring A therefore six-membered.

Information as to the size of ring B was adduced by further degradation of XVI. The action of phenylmagnesium bromide on the dimethyl ester (*Anal.* Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 67.45; H, 8.90) of XVI followed by

---

(1) An outline of previous investigations on the structure of patchouly alcohol is given in J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, London, 1952. For a complete and authoritative discussion on patchouly oil see E. Guenther, "The Essential Oils," Vol. III, Van Nostrand Co., Inc., New York, N. Y., 1949.

(2) W. Treibs, *Ann.*, **564**, 141 (1949).