development of such standards before use of the molecular extinction coefficient for the determination of anything but the relative molecular weights of the amyloses.

The wave lengths of maximum absorption of the amylopectin–iodine solutions are all at much shorter wave lengths than those found for the amylose–iodine solutions. The wave lengths are again a reproducible function of the source of the amylopectin. There is a great deal of similarity in the wave length, molecular extinction coefficient, and general character of the absorption spectra of the amylopectins and the low molecular weight amylodextrin. The latter appears to have all the characteristics of an unbranched, but short chain material. The amylopectin, on the other hand, is of high molecular weight. The similarity in the absorption spectra seems to result from a similarity in the length of the free, unbranched portions of the chains in the amylopectin molecules and the length of the amylodextrin chains. It is believed that the wave length of maximum absorption and the molecular extinction coefficient of the amylopectin–iodine solutions are measures of the average length of the unbranched portions of the amylopectin chains. On this basis it appears that glycogen is most highly branched, and following in order, waxy rice, waxy maize, waxy barley, potato- and corn-amylopectin. Where tetramethyl end-group assay is known it is in agreement with this assignment. This order is also in agreement with the results of the potentiometric titration.[3]

Summary

Study of absorption spectra confirms the great difference in behavior of amylose and amylopectin with iodine found by the potentiometric iodine titration,[3] and provides another means of analyzing for the two components in whole starch. The differences in individual amyloses and amylopectins from different starches make a simple colorimetric analysis for the two components unreliable however.

The amount of iodine bound in complex formation with amylose increases as the concentration of iodide decreases, becoming one iodine molecule for six glucose residues for infinitely dilute iodide solutions.

The wave length of maximum absorption of an amylose solution shifts toward the red as the chain length of the amylose is increased. The shift is in the same direction when the lengths of the unbranched portions of an amylopectin are increased. An increase in the molecular extinction coefficient accompanies an increase in the length of an amylose or an increase in the lengths of the unbranched portions of an amylopectin. Both these properties permit the relative evaluation of molecular weight of an amylose and degree of branching of an amylopectin. The change in the molecular extinction coefficient is the more sensitive.

The relative molecular weights of a few amyloses and the degree of branching of some amylopectins have been examined. Results are in agreement with other determinations.

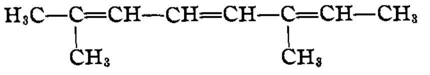
AMES, IOWA RECEIVED SEPTEMBER 28, 1943

[CONTRIBUTION FROM NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

Raman Spectra of Two Forms of *allo*-Ocimene

BY J. J. HOPFIELD,[1] S. A. HALL[2] AND L. A. GOLDBLATT

Among the products obtained in the pyrolysis of α-pinene[3] at about 375°, *allo*-ocimene



$$\mathrm{H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_3}$$

(2,6-dimethyl-2,4,6-octatriene), is of the greatest interest, both from a practical and theoretical viewpoint.

On careful re-fractionation of the portion of α-pinene pyrolysate boiling in the *allo*-ocimene range, two components were obtained, a major component boiling at 89.0° at 20 mm. pressure and a minor component boiling at 91°. Both components yield with maleic anhydride the same adduct (m. p. 83–84°) but the two components exhibit differences in their freezing points, densities and Raman spectra.

It may be reasonably assumed that these are two forms of *allo*-ocimene, of which there are four possible geometric isomers, arising from the double bonds at the 4 and 6 positions. Models (Fisher–Herschfelder) of the four geometrical isomers show that the *cis* form arising from the double bond at the C_4 carbon atom (regardless of whether the configuration at C_6 is *cis* or *trans*) is one of very limited rotation. The probability of its formation and continued existence during the high temperature pyrolysis of α-pinene would appear to be slight.[4] Such a configuration would be more likely to form a stable ring compound, such as one of the pyronenes which are also ob-

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[1] Transferred to National Bureau of Standards, Washington, D. C., 10/18/42.

[2] Transferred to Bureau of Entomology and Plant Quarantine, 5/5/43.

[3] Goldblatt and Palkin, THIS JOURNAL, **63**, 3517 (1941).

[4] In the case of pentadiene-1,3 (piperylene), however, Robey, *Science*, **96**, 470 (1942), reports that the *cis* isomer, which is similarly more hindered than the *trans* isomer, is much more prominent in mixtures from high temperature processes.

tained in the pyrolysis of α-pinene, or be "cracked" at the high temperature (375°) prevailing, thus accounting for the small percentage of very low-boiling substances always obtained during pyrolysis. On the other hand, the model of the *trans* form at C_4 shows relative freedom of rotation for all groups. Of the *cis* and *trans* configurations at the C_6 carbon atom, the model of the *cis* form appears to be slightly more compact, which should, of course, be reflected in a slightly greater density.

Although methods for the assignment of the *cis* or *trans* configuration to isomers of an olefin on the basis of their physical properties are admittedly of doubtful use,[5a] nevertheless, it is usually true that the *cis* isomer of an olefin has the lower melting point[5b] and the higher boiling point and higher density.[6]

If the two forms of *allo*-ocimene obtained are indeed the *trans*-(C_4)–*cis*-(C_6) and the *trans*-(C_4)–*trans*-(C_6) isomers, then we might expect from their physical properties to find as the *cis* isomer the hydrocarbon of higher boiling point, higher density, and lower melting point. The Raman spectra of these isomers tend to support this interpretation.

Materials.—125 grams of a fraction of *allo*-ocimene boiling at 89.0° at 20 mm. and melting at −24.3 to −22.6° was recrystallized twice from absolute alcohol; 125-cc. portions of the alcohol were used and crystallization was effected by cooling the solution in a bath of dry-ice in acetone. Filtration was accomplished in the usual manner, but in a refrigerated room (0°) using a Buchner funnel previously chilled in dry-ice. The occluded alcoholic mother liquor was readily removed by distillation and as a final purification the material was vacuum distilled. During and after distillation a blanket of nitrogen gas was used to avoid exposure to air for the *allo*-ocimene, after an induction period of about two hours, absorbs oxygen quite rapidly.

Approximately 50 g. of the isomer boiling at 91° at 20.0 mm. pressure and melting at −35.9 to −33.4° was subjected to the same procedure except that only one crystallization from alcohol was made.

The fractions thus purified have the following physical properties:

	B. p. at 20 mm.	M. p., °C.	d^{20}_4	n^{20}_D
"A" form	89.0°	−21.0 to −20.6°	0.8060	1.5446
"B" form	91°	−35.4 to −34.0°	0.8118	1.5446

Procedure.—The Raman spectrograms were obtained with a Gaertner L-256 spectrograph having a dispersion of 39.5 A./mm. at 4500 Å. The Raman cell was specially constructed of a 12 mm. o. d. Pyrex tube enclosed by an outer tube to give a 30 mm. thickness of filter. A Hanovia fused quartz mercury arc lamp (Model 2444, 110 volt d. c., 4.5 amp.) was used for excitation. The filter solution for isolating the Hg 4358 A. line was the one recommended by Edsall and Wilson.[7] The slit opening was 100 μ and effective aperture F:4.5. Eastman II-J plates, developed at 20° for six minutes with developer DK-50, were used. The respective spectrograms of the "A" and "B" forms of *allo*-ocimene were taken on the same plate to obviate any differences in line densities arising from differences in plate gamma or in development time. Three different exposure times were used, namely, four, sixteen and thirty-two minutes. The spectrograms of the shorter exposures were used for the measurement of the strongest lines; but such measurements were checked with measurements of longer exposures. Also, doublets which were not well resolved were checked by examination of the spectra excited by the Hg 3650 Å. triplet. Because of the greater dispersion of the spectrograph at the lower wave lengths, a much better resolution of such doublets was effected. The lines were measured with a Gaertner comparator. The wave length shifts were calculated from these data by a three-constant quadratic equation[8] based on the measured positions and

Table 1[a]

Raman Spectra of Two Forms of *allo*-Ocimene

Form "A"		Form "B"	
$\Delta\mu$	I	$\Delta\mu$	I
		151	$^1/_4$
196	2vb		
		227	$^1/_2$d
258	$^1/_4$		
		277	$^1/_4$
296	$^1/_4$		
		335	$^1/_4$d
361	$^1/_4$		
440	$^1/_2$		
		446	$^1/_2$d
518	$^1/_8$d	518	$^1/_8$d
790	$^1/_2$b		
		800	$^1/_4$bd
844	$^1/_4$b	844	$^1/_2$b
871	1	871	1
		961	3b
964	5		
1026	$^1/_4$	1026	2
		1054	$^1/_2$d
		1082	1
1091	$^1/_2$d		
1151	7	1151	7
1184	5	1184	7
		1231	3
1236	6		
		1272	4
1307	6	1308	1b
		1347	3
1365	3		
1383	3	1383	3
1448	2b	1448	2b
1532	$^1/_2$d	1532	$^1/_2$d
1590	6		
		1597	3d
		1627	10b
1631	10vb		
		1648	4
		2860	1d
2878	1vbd		
		2911	3b
2914	3b		
2971	$^1/_2$d		
		2977	$^1/_4$vbd
3012	$^1/_4$d		

[a] $\Delta\mu$ = Raman shift in cm.$^{-1}$; I = estimated intensity; v, b, d = very, broad, diffuse.

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(5)(a) Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, New York, N. Y., 1938, p. 370; (b) *ibid.*, p. 372.

(6) Egloff, "Physical Constants of Hydrocarbons," Vol. I, A. C. S. Monograph No. 78, 1939, pp. 186, 200, 214, 216.

(7) Edsall and Wilson, *J. Chem. Phys.*, **6**, 124 (1938).

(8) Russel and Shenstone, *J. Opt. Soc.*, **16**, 298 (1928).

wave numbers of three selected lines of the iron spectrum. Thus, instead of interpolating to the nearest iron line (which might not be well defined or, in some cases, might be an appreciable distance from a Raman line) the wave numbers were obtained from this equation and a correction curve based on some of the other iron lines in the region. For well-defined Raman lines an accuracy to 1 cm.$^{-1}$ was obtainable; but for broad or diffuse lines the accuracy was limited to about 3 cm.$^{-1}$.

Results

The results obtained for the two isomers are listed in Table I and shown graphically in Fig. 1. A photograph of the three exposures for each isomer is shown in Fig. 2. *allo*-Ocimene gives a very strong Raman spectrum in an unusually short exposure time.

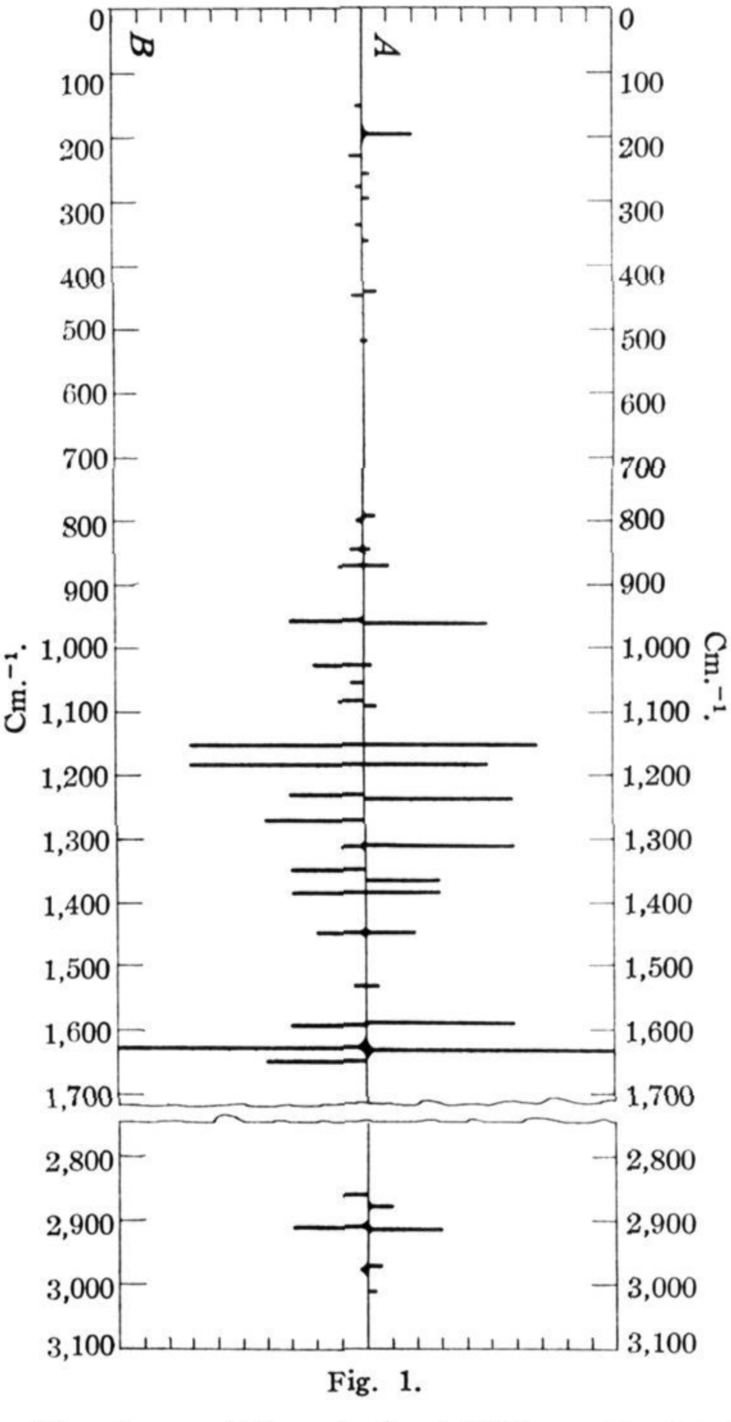

Fig. 1.

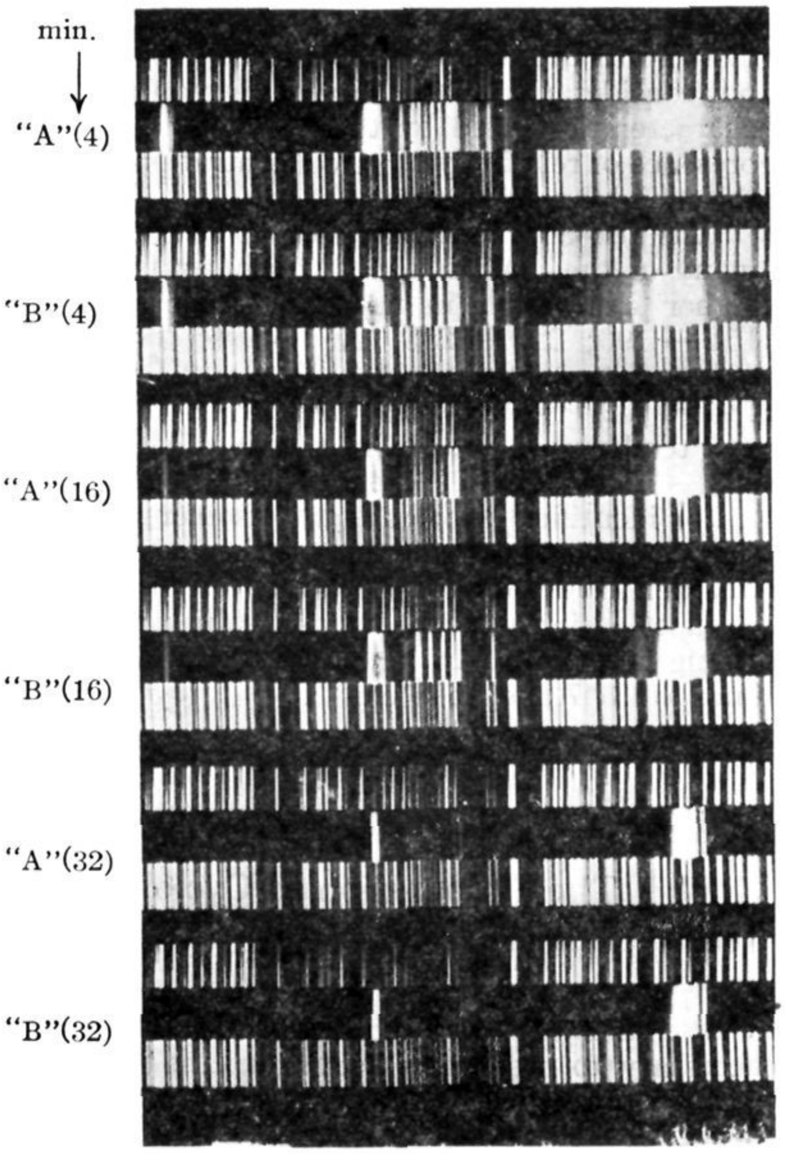

Fig. 2.

The strongest line at about 1631 cm.$^{-1}$, due to the double-bond vibration, is easily discernible after an exposure time of only twenty seconds. The isomeric triolefin, myrcene (2-methyl-6-methylene-2,7-octadiene), requires at least eight minutes exposure time under the same conditions to make visible its corresponding strong line at about 1636 cm.$^{-1}$. With *allo*-ocimene, four minutes exposure brings out 11 Raman lines; sixteen minutes brings out 26 lines; and thirty-two minutes brings out 28 lines. Longer exposures appear to be unprofitable, for the increasingly prominent background tends to obscure any additional weak lines.

Discussion

The line at 1307 cm.$^{-1}$, which is much more intense in the "A" than in the "B" isomer, is interpreted as due to a *trans* configuration.[9] The rather strong lines at 1272 cm.$^{-1}$ and at 1648 cm.$^{-1}$ in the "B" form, which have no counter parts in the "A" form, are attributed to a *cis* configuration.[10] A *trans* configuration should be reflected in a Raman line[11] at about 1673 cm.$^{-1}$, lowered somewhat by the influence of conjugation. Curiously this line is absent in both the "A" and the "B" isomers. Nor has it been reported by Dupont and co-workers in their work[12] on the Raman

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(9) Gredy, *Compt. rend.*, **202**, 322 (1936); *Bull. soc. chim.*, **3**, 1101 (1936); **4**, 415 (1937).

(10) Bourgel, Gredy and Piaux, *Compt. rend.*, **195**, 129 (1933); Van Risseghem, Gredy and Piaux, *ibid.*, **196**, 938 (1933).

(11) Hibben, "The Raman Effect and its Chemical Applications," A. C. S. Monograph No. 80, 1939, pp. 170–171.

(12) Dupont, Dulou, Desreux and Picoux, *Bull. soc. chim.*, **5**, 322 (1938); Dupont and Dulou, *ibid.*, **3**, 1639 (1936).

spectrum of *allo*-ocimene. These authors did not distinguish between the two forms of *allo*-ocimene but consideration of the Raman data and physical characteristics cited by them would indicate the presence of relatively large concentrations of both the A and B components.

It is also apparent that there is a tendency for many of the lines in the "A" isomer to shift to higher frequencies in the "B" isomer, namely, 151 → 196; 227 → 258; 277 → 296; 335 → 361; 961 → 964; 1082 → 1091; 1231 → 1236; 1347 → 1365; 1627 → 1631; 2911 → 2914. The opposite tendency is shown by the lines 446 → 440; 800 → 790 and 1597 → 1590.

For identification of the "A" isomer in a mixture, one could conveniently use the rather strong, well-defined 1365 line, while the "B" form could be most easily detected by its unique and rather strong line at 1272 cm.$^{-1}$, or alternatively by its lines at 1347 and 1648 cm.$^{-1}$.

Acknowledgment.—The continued interest and advice of the late Dr. S. Palkin, Chief of the Naval Stores Research Division, who originally proposed the project, is gratefully acknowledged.

Summary

Two forms of *allo*-ocimene, designated as A- and B- have been isolated.

Both forms yield with maleic anhydride the same adduct but they exhibit differences in boiling point, freezing point, density and Raman spectra.

Both forms give strong Raman spectra in an exceptionally short exposure time. Each may be detected in a mixture by the characteristic Raman lines at 1365 cm.$^{-1}$ (A-form) and 1272 cm.$^{-1}$ (B-form).

The Raman spectra tend to support the interpretation that these forms are two of the four possible geometric stereoisomers of *allo*-ocimene.

NEW ORLEANS, LA. RECEIVED JULY 30, 1943

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MISSOURI]

The Preparation of Cyclohexanols by Catalytic Reduction of Phenols

BY HERBERT E. UNGNADE AND A. DOUGLAS MCLAREN[1,2]

In connection with another problem it became necessary to prepare alkylcyclohexanols in moderately large quantities. This has been accomplished by the catalytic reduction of alkyl-, alkenyl- and acylphenols with Raney nickel.

Since alkylphenols could be hydrogenated readily to the corresponding cyclohexanols, the chief limitation was the availability of the phenols. The ease of reduction was not greatly affected by substituents in the ring unless two ethyl or *n*-propyl groups occupied the ortho positions (Table I). In the latter cases no cyclohexanols were formed at temperatures above 300°. 2,6-Di-*n*-propylphenol was recovered unchanged but 2,6-diethyl-4-methylphenol underwent hydrogenolysis and reduction of the ring to give 1-methyl-3,5-diethylcyclohexane. The corresponding cyclohexanols could be obtained from the two phenols when the hydrogenation was carried out in the presence of a small amount of a 40% aqueous solution of sodium hydroxide. When the other phenols were reduced in the presence of alkali a slight promoting effect was evidenced in some cases by lower initial reduction temperatures. The promoting effect was lost when the phenolic hydroxyl was methylated (Table II). The formed cyclohexanols consisted predominantly of one of the possible geometric isomers. The same isomer was usually obtained regardless of whether the hydrogenation was carried out in the presence of base or not. An exception was 2-*t*-butyl-4-methylphenol. Higher temperatures were required for reduction in the presence of base, and the product was a mixture of *cis*, *trans* isomers differing only in the position of the hydroxyl group since they could be oxidized to the same cyclohexanone.[3] Only one of the isomers was obtained in the absence of base. The effect of the base in this case may be similar to the inversion observed by Vavon, *et al.*, when the sodium salts of alkylcyclohexanols were heated.[4]

It is interesting to note in this connection that the 2,6-di-*n*-propylcyclohexanol obtained by reduction in presence of alkali was the $1^t,2^c,6^c$-isomer which was prepared by Vavon and Anziani by rearrangement of the $1^c,2^c,6^c$-isomer by heating of the sodium salt.[5]

The effect of alkali was striking in the reduction of *p*-phenylphenol (Table III). The time required for absorption of the same amount of hydrogen in the presence of alkali was one half of that required for the same amount of substance in the absence of alkali. Moreover the ratio of the products was not the same. The percentage of *p*-cyclohexylphenol and *p*-cyclohexylcyclohexanol was smaller and the amount of *p*-phenylcyclohexanol larger when alkali was used as a promoter. It is therefore possible by means of

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(1) An abstract of a dissertation submitted by A. Douglas McLaren in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1943.

(2) Presented before the Division of Organic Chemistry at the 105th meeting of the American Chemical Society, Detroit, Michigan, April 13, 1943.

(3) Unpublished data by the authors.

(4) Vavon, *et al.*, *Bull. soc. chim.*, (4) **39**, 1142 (1926); (4) **41**, 357 (1927); (4) **45**, 961 (1929).

(5) Vavon and Anziani, *ibid.*, (5) **4**, 1080 (1937).