

**269.** *The Effect of Molecular Environment on the Absorption Spectra of Organic Compounds in Solution. Part I. Conjugated Dienes.*

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In view of the marked effect of variations in molecular environment on the location of the absorption band due to any particular chromophoric group, an attempt has been made to collect and to classify new and already published absorption-spectra data on conjugated dienes. The location of the band due to the diene chromophore varies between 2170 and 2820 Å. (for alcoholic solutions), whilst the intensity ranges up to  $\epsilon = 35,000$  but most commonly lies between 8,000 and 20,000. The effect of various substituents has been studied and has been found to produce characteristic displacements of the absorption maximum, the location of which thus gives an indication of the type of diene present in any particular compound. The main sub-groups have been found to be acyclic dienes having one, two, or no cyclic substituents, semicyclic dienes, and mono-, di-, and poly-cyclic dienes. In the last case, as has already been discovered in the sterol and the triterpene field, the arrangement of the conjugated system in one or in two rings, respectively, produces a marked difference in the location of the absorption maximum. The data on the various types of dienes have been collected in several tables, and new data are also recorded graphically.

THE use of absorption spectra as an aid to the elucidation of the structure of organic compounds of hitherto unknown constitution is rapidly extending, but progress is considerably handicapped by the fact that, although selective absorption of light of wave-lengths 2000—7700 Å. is always associated with the presence in a molecule of certain specific groupings or chromophores, yet the precise location and intensity of the absorption band are influenced by a number of factors. Of these, the effect of external variables such as the displacement of maxima by change from one solvent to another can usually be foreseen. On the other hand, change of intramolecular environment often has a very marked effect upon the absorption band due to a particular chromophore even when the chromophore

itself remains unchanged. At present, these changes cannot be predicted from fundamental premises, although considerable knowledge of an empirical nature is accumulating. For instance, the typical absorption band of ketones due to the group  $>C=O$  is shown by acetone and the higher homologues of the series, but when the alkyl groups are replaced by certain others, which are themselves normally regarded as non-absorbing groups, a big change in the location of the absorption maximum may be produced. Table I illustrates this point.

TABLE I.

*The effect of substituents on the absorption due to the carbonyl group.*

	$\lambda_{\max.}$	$\log \epsilon.$	Solvent.		$\lambda_{\max.}$	$\log \epsilon.$	Solvent.
Formaldehyde <sup>3</sup>	< 2144	—	H <sub>2</sub> O	Acetone <sup>1</sup>	2725	1.27	EtOH
Acetic acid <sup>4</sup>	ca. 2070	1.47	EtOH	Acetaldehyde <sup>2</sup>	2934	1.072	C <sub>6</sub> H <sub>14</sub>
Acetamide <sup>5</sup>	< 2144	—	H <sub>2</sub> O	Hexamethylacetone <sup>1</sup>	2950	1.326	EtOH
Aminoacetic acid <sup>6</sup>	< 2200	—	H <sub>2</sub> O	Mesityl oxide <sup>4</sup>	3135	1.767	EtOH

<sup>1</sup> Rice, *J. Amer. Chem. Soc.*, 1920, **42**, 727. <sup>2</sup> Schou, *Compt. rend.*, 1926, **182**, 965. <sup>3</sup> Bielecki and Henri, *ibid.*, 1912, **155**, 456. <sup>4</sup> Henri, "Études de Photochimie," Paris, 1919, Gauthier Villars. <sup>5</sup> Bielecki and Henri, *Compt. rend.*, 1912, **156**, 1860. <sup>6</sup> Int. Crit. Tables, **5**, p. 379.

The present paper is the first of a series in which it is planned to collect experimental data on the absorption spectra of compounds containing specific light-absorbing groups of atoms with the object of discovering the effect of various well-defined molecular environments upon the resulting absorption spectra. The data and generalisations so collected could then be used as an argument in support or otherwise of structural formulæ put forward for particular unsaturated compounds.

The first chromophore chosen for such a study has been that characteristic of conjugated dienes typified by butadiene,  $CH_2:CH:CH:CH_2$ . Dimroth and Trautmann (*Ber.*, 1936, **69**, 669) have already directed attention to the fact that the light absorption due to the diene chromophore is influenced by the nature of the molecule in which it occurs, and have shown that absorption-spectra data support the hypothesis that in ergosterol the two double linkages are conjugated and present in one ring (see below).

Mulliken (*J. Chem. Physics*, 1939, **7**, 121), in a theoretical treatment of the light absorption of conjugated dienes, comments on the paucity of quantitative absorption data on pure compounds containing the diene chromophore. This scarcity of data is in part due to the difficulty of obtaining pure specimens of such unsaturated compounds on account of the ease with which they oxidise, polymerise, or isomerise.

Table II shows the new and already-known data on acyclic dienes without cyclic substituents. For strict comparison of absorption spectra, the solvent should be the same in all cases on account of the displacement of the absorption maximum which is often observed when a compound is transferred from one solvent to another. It is fairly well established, however, that for non-polar compounds the location of the absorption maximum is almost

TABLE II.

*Acyclic dienes having only acyclic substituents.*

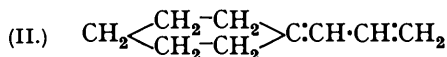
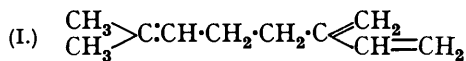
	$\lambda_{\max.}$	$\epsilon_{\max.}$	Solvent.
Butadiene	2170 <sup>1</sup>	20,900	Hexane
Piperylene	2235	23,000	Alcohol
	2235	25,500	Hexane
Isoprene	2200 <sup>1</sup>	23,900	Hexane
	2200 <sup>2</sup>	17,900	Hexahydrotoluene
$\beta\gamma$ -Dimethylbutadiene	2250 <sup>1</sup>	20,400	Hexane
	2260 <sup>3</sup>	21,400	Hexane
	2260 <sup>2</sup>	21,300	Hexahydrotoluene
$\Delta^{2:4}$ -Hexadiene	2270	22,500	Alcohol
	2270	25,500	Hexane
Myrcene (I)	2245	14,600	Alcohol
1 : 6-Diacetoxy- $\Delta^{2:4}$ -hexadiene (IX)	2280	27,300	Alcohol
1 : 6-Diethoxy- $\Delta^{2:4}$ -hexadiene (X)	2280	26,800	Alcohol

<sup>1</sup> Smakula, *Angew. Chem.*, 1934, **47**, 657. <sup>2</sup> Scheibe and Pummerer, *Ber.*, 1927, **60**, 2163. <sup>3</sup> Scheibe, *Ber.*, 1926, **59**, 1333.

identical in ethyl alcohol and hexane, a point which has been confirmed in several cases among the dienes examined here. The same generalisation does not, however, apply to the intensity of absorption, which usually tends to be higher in hexane than in ethyl alcohol (cf. piperylene and  $\Delta^{2:4}$ -hexadiene, Table II).

In the six purely hydrocarbon dienes considered, the location of the maximum falls within the limits 2170—2270 Å., and if butadiene is taken as the parent compound, the inclusion of one methyl group displaces the absorption maximum to longer wave-lengths by 20 and 65 Å. severally in two different compounds, whilst the increment of displacement is 90 and 100 Å. in two different dimethyl compounds. When the two terminal methyl groups contain a substituted hydroxyl group (ethoxy- or acetoxy-), the slight extra displacement (10 Å.) is almost within the experimental error in determination of the maximum in bands of this type.

In the carotenoid polyenes, Kuhn and Grundmann (*Ber.*, 1937, 70, 1318) have observed that a methyl group on the polyene chain causes a displacement of the absorption maximum to longer wave-lengths, and that the amount of this displacement is equal to about one-quarter of that usually found for one ethylene linkage. For this particular series, the increment for a conjugated ethylene linkage is of the order of 210 Å., making the increment for one methyl group of the order of 50 Å., which is about the same as that observed with the methylbutadienes. In butadiene with a six-carbon-atom acyclic substituent as in myrcene (I), there is a displacement of 75 Å., *i.e.*, intermediate between the values just noted for the increments due to one and two methyl groups respectively.



Lowry and Allsopp (*Proc. Roy. Soc.*, 1937, 163, A, 356) have pointed out that the simple substituted butadienes are notable for their very high extinction coefficients. The values quoted as due to Smakula (*Angew. Chem.*, 1934, 447, 657) are, however, 2-3 times too high owing to confusion between logarithmic scales. Even when this is corrected, the higher values of some of the acyclic dienes are still notable (Table II). For instance, the values of  $\epsilon$  in the simple butadienes range from 14,000 to

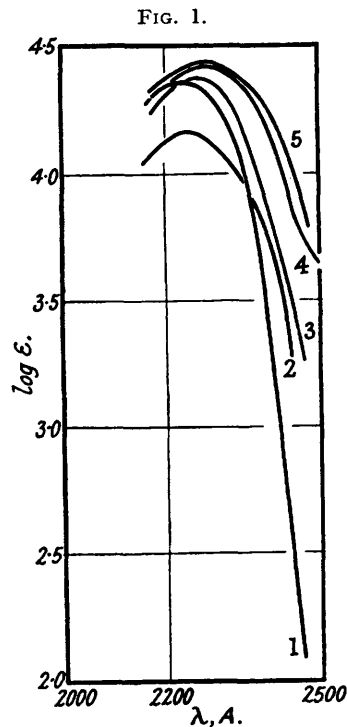


FIG. 1.  
Absorption spectra of alcoholic solutions of: (1) Piperylene. (2) Myrcene. (3)  $\Delta^{2:4}$ -Hexadiene. (4) Diethoxy- $\Delta^{2:4}$ -hexadiene. (5) Diacetoxy- $\Delta^{2:4}$ -hexadiene.

TABLE III.

*Dienes having only One Cyclic Substituent.*

	$\lambda_{\text{max}}$ .	$\epsilon$ .	Solvent.
Allylidencyclohexane (II)	2365	>7,700	EtOH
Zingiberene (III)	2355	5,300	"
$\gamma$ -2-Dimethylaminomethylcyclohexylidene- $\Delta^{\alpha}$ -propene (VIII)	2360 <sup>1</sup>	10,500	"

<sup>1</sup> Milas and Alderson, *J. Amer. Chem. Soc.*, 1939, 61, 2534.

27,000, but the introduction of a single saturated cyclic substituent (Table III) lowers these values considerably. With two such cyclic substituents the values go up again, in one case to 35,000 (Table IV).

When the substituent of the butadiene contains a single cyclohexyl group, as in allylidencyclohexane (II), there is a larger displacement than occurs with either one or two

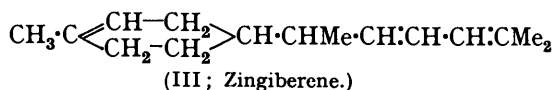
TABLE IV.

*Acyclic Dienes having Two Cyclic Substituents.*

	$\lambda_{\max.}$	$\epsilon.$	Solvent.
	2480 <sup>1</sup>	34,900	Et <sub>2</sub> O
	2450 <sup>3</sup>	16,400	EtOH
	2460 <sup>3</sup>	18,800	„
	2470 <sup>3</sup>	13,700	„

<sup>1</sup> Dimroth and Jonssen, *Ber.*, 1938, **71**, 2658. <sup>2</sup> Aldersley, Burkhardt, Gillam, and Hindley, this vol., p. 10. <sup>3</sup> We are indebted to Drs. Burkhardt and Hindley for the opportunity to examine this compound.

methyl groups, *viz.*, to approximately 2360 Å. Although the three compounds of this type examined (Table III) are chemically very different from each other, it is notable that the absorption maximum in each of the three cases is so close to 2360 Å. (within  $\pm 5$  Å.) as to be virtually identical. The displacement of the maximum from that of butadiene is thus 190 Å.



When two substituents of the butadiene are *cyclohexyl* groups (cf. Table IV) there is a further displacement of about 90 Å. for the second *cyclohexyl* group. Here, again, in four different compounds the maximum falls within the narrow range 2450—2480 Å.

In the previous cases considered the butadienes have all been acyclic even if in some cases the substituents have been cyclic. The next class to be considered is one where one of the two ethylene linkages is in a hydroaromatic ring, the other one being *exocyclic*. In eight compounds in this class the absorption falls within the limits 2300—2420 Å. (cf. Table V). In pulegone-enol and *isopulegone-enol* the locations of the maxima

TABLE V.

*Semicyclic Dienes.*

	$\lambda_{\max.}$	$\epsilon.$	Solvent.
$\beta$ -Phellandrene (VI)	2312 <sup>1</sup>	9,120	C <sub>6</sub> H <sub>14</sub>
	2320	9,200	EtOH
$\Delta^1$ - <i>cyclo</i> Hexenylethylene	2300 <sup>4</sup>	8,500	„
2-Methyl- $\Delta^3$ - <i>cyclo</i> hexenylethylene	2330 <sup>4</sup>	7,200	„
Pulegone-enol (XIV)	2380 <sup>3</sup>	3,844	C <sub>6</sub> H <sub>14</sub>
<i>iso</i> Pulegone-enol (XV)	2364 <sup>3</sup>	1,320	„
Menthadiene (XVIII)	2350	10,700	EtOH
$\Delta^3$ : <sup>8(9)</sup> -Normenthadiene (XIX)	2420	9,950	„
7-Methylencholesterol (XI)	2360 <sup>2</sup>	20,000	„

<sup>1</sup> Macbeth, Smith, and West, J., 1938, 119.

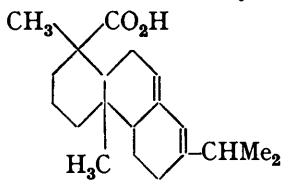
<sup>2</sup> Bann, Heilbron, and Spring, J., 1936, 1274.

<sup>3</sup> Savard, *Bull. Soc. chim.*, 1928, **43**, 524, 978.

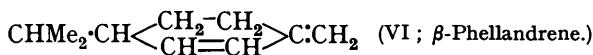
<sup>4</sup> We are indebted to Dr. G. N. Burkhardt and Dr. W. N. Hindley for specimens of these two compounds.

are close to the means of those found for other members of this group, which suggests that the hydroxyl group on the conjugated system has very little effect on the absorption due to the diene. The low intensity of the absorption recorded for these compounds indicates

that they contain considerable quantities of the unconjugated isomers, a conclusion which has also been reached by Savard (*Bull. Soc. chim.*, 1928, 43, 524, 978).

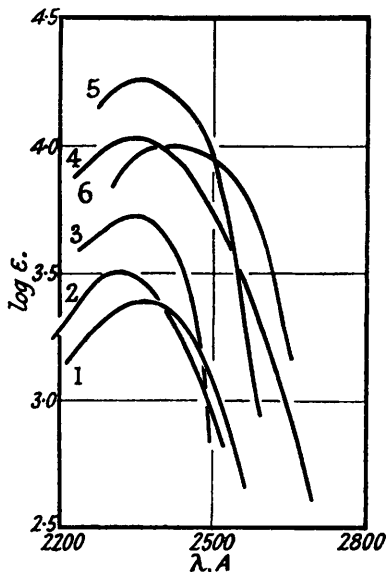


(IV; Abietic acid.)



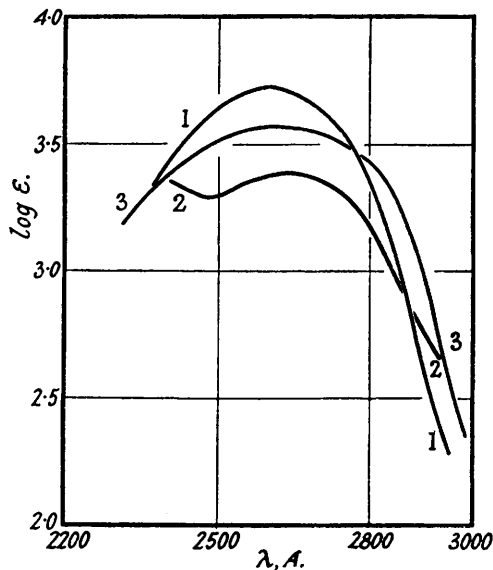
The close similarity in the locations of the maxima for this group of dienes and that of acyclic dienes having a single cyclic substituent (see above) should be noted, and it follows

FIG. 2.



Absorption spectra of alcoholic solutions of: (1) Allylidencyclohexane. (2)  $\beta$ -Phellandrene. (3) Zingiberene. (4) Menthadiene. (5) Di- $\Delta^{1:1}$ -cyclohexene. (6)  $\Delta^{3:8(9)}$ -Normenthadiene.

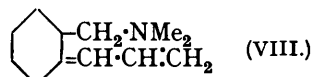
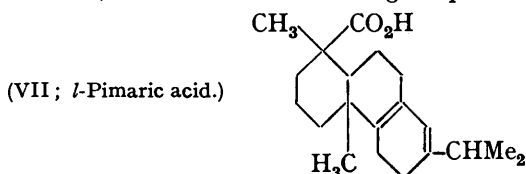
FIG. 3.



Absorption spectra of alcoholic solutions of: (1) 1-Methyl- $\Delta^{2:4}$ -cyclohexadiene. (2)  $\alpha$ -Phellandrene. (3)  $\alpha$ -Terpinene.

that in the presence of a single cyclic group absorption spectra alone will not differentiate between purely acyclic and semicyclic dienes. Methylenecholesterol, one of this class of diene, exhibits a maximum at exactly the same wave-length as the other members of the class, despite the polycyclic environment which exerts such a large effect on the absorptions of the cyclic dienes (see below).

Conjugated dienes exhibit the kind of absorption typical of all compounds containing conjugated systems, *i.e.*, the so called *K*-bands. These bands usually have intensities ranging from about 10,000 to approximately 500,000 for the molecular extinction coefficient  $\epsilon$ , depending upon the length of the conjugated system present, and are notably different in intensity and in the effects produced by certain substituents from the so-called *R*-bands of which the ketone band is typical (*cf.* Burawoy, J., 1939, 1177). In the dienes already considered, the values of  $\epsilon$  have ranged up to 35,000, 10,000—15,000 being most usual.



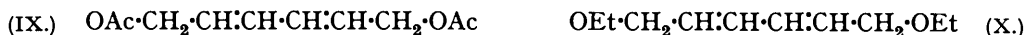
When we compare the monocyclic dienes with the acyclic members of the series, the first notable point is the considerable displacement of the maximum to longer wave-lengths in the cyclic series (cf. Table VI). The second point is the comparative lowness of the extinction coefficient; *e.g.*, an apparently pure specimen of  $\alpha$ -phellandrene gave a value

TABLE VI.  
*Monocyclic dienes.*

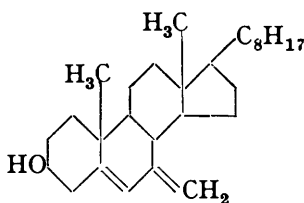
	$\lambda_{\max.}$	$\epsilon$ .	Solvent.
<i>cyclo</i> Pentadiene	2385 <sup>1</sup>	3400	Hexane
$\Delta^{1:3}$ - <i>cyclo</i> Hexadiene	2560 <sup>2</sup>	9900	<i>cyclo</i> Hexane
	2560 <sup>3</sup>	7940	Hexane
$\alpha$ -Phellandrene (V)	2630	2500	Alcohol
	2650—2700 <sup>4</sup>	—	—
2-Methylcarvenene (XII)	2650—2700 <sup>4</sup>	—	—
1-Methyl- $\Delta^{2:4}$ - <i>cyclo</i> hexadiene	2600	4910	Alcohol
$\alpha$ -Terpinene (XIII)	2620	>3620	„

<sup>1</sup> Scheibe, *Ber.*, 1926, **59**, 1333.    <sup>2</sup> Allsopp, *Proc. Roy. Soc.*, 1934, **143**, A, 618.    <sup>3</sup> Henri and Pickett, *J. Chem. Physics*, 1939, **7**, 439.    <sup>4</sup> Dimroth and Trautmann, *Ber.*, 1936, **69**, 669.

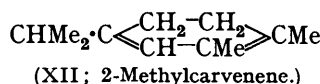
for  $\epsilon$  of only 1600, and even after rigorous purification this was only raised to 2500. It is perhaps significant that, in recording the absorption spectra of  $\alpha$ -phellandrene and 1-methylcarvenene, Dimroth and Trautmann (*loc. cit.*) recorded only the location of the maximum in each case, but not the intensity.



In 1-methyl- $\Delta^{2:4}$ -*cyclo*hexadiene and  $\alpha$ -terpinene also, only low values have been observed for  $\epsilon$ , and it would seem either that these cyclic dienes exhibit intrinsically low intensities of absorption or more probably that there is a tendency for one of the ethylene linkages to move out of conjugation to produce an equilibrium mixture of conjugated and unconjugated isomers, in which case the intensity of absorption would fall in proportion to the amount of unconjugated isomer present. All the cyclic dienes for which data are available give low values of  $\epsilon$  except  $\Delta^{1:3}$ -*cyclo*hexadiene, the values for which can be regarded as approximately normal. In the case of *cyclopentadiene*, which exhibits a low value comparable with the other members of the group, a displacement of either of the ethylene linkages would still leave a conjugated system, so that in this compound, where isomerisation into an unconjugated form is not possible, the question is only whether the low value of  $\epsilon$  is due to the difficulty of obtaining the compound sufficiently pure.



(XI; 7-Methylenecholesterol.)



*Polycyclic Dienes.*—No discussion on the absorption spectra of cyclic dienes would be complete without the inclusion of compounds in the sterol and the triterpene series where, not only are important dienes known, but their absorption spectra have been determined in many cases and the data used to indicate or confirm parts of their molecular structure. No new data on these compounds are now recorded, but the existing data are collected and reviewed for the sake of completing the diene survey. At the same time, it has to be borne in mind that, although the absorption spectra of the polycyclic dienes fall into line with generalisations obtained from a study of simpler compounds as well as certain polycyclic compounds of known composition (*e.g.*, ergosterol), yet the constitutions of all the sterol and triterpene compounds listed in Tables VII and VIII are not rigidly proved independently of spectroscopic considerations.

TABLE VII.

Polycyclic dienes (having two double bonds in one ring).

	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$	Solvent.
Ergosterol	2800 <sup>1</sup>	11,800	Et <sub>2</sub> O
	2800 <sup>2</sup>	13,500	"
	2815 <sup>3</sup>	10,200	EtOH
	2815 <sup>4</sup>	12,000	"
Lumisterol	2790 <sup>4</sup>	8,500	"
7-Dehydrocholesterol	2800 <sup>1</sup>	11,400	Et <sub>2</sub> O
22-Dihydroergosterol	2800 <sup>1</sup>	11,800	"
Ergostatriene	2800 <sup>2</sup>	12,200	"
7-Dehydrocholestene	2800 <sup>2</sup>	12,700	"
isoDehydrocholesterol	2700—2800 <sup>5</sup>	5,340	"
Dehydro- $\beta$ -amyrenyl acetate	2820 <sup>6</sup>	9,550	EtOH
Dehydro- $\alpha$ -amyrenyl acetate	2800 <sup>6</sup>	11,400	"
$\Delta^2:4$ .Cholestadiene	2600 <sup>7</sup>	—	—
l-Pimaric acid	2725	7,080	"

<sup>1</sup> Windaus, Lettré, and Schenck, *Annalen*, 1935, **520**, 98. <sup>2</sup> Dimroth and Trautmann, *Ber.*, 1936, **69**, 669. <sup>3</sup> Morton, Heilbron, and Kamm, *J.*, 1927, 2000. <sup>4</sup> Heilbron, Moffatt, and Spring, *J.*, 1937, 411. <sup>5</sup> Windaus, Linsert, and Eckhart, *Annalen*, 1938, **534**, 22. <sup>6</sup> Beynon, Sharples, and Spring, *J.*, 1938, 1233; Picard and Spring, this vol., p. 1198. <sup>7</sup> Staveley and Bergmann, *J. Org. Chem.*, 1937, **1**, 577. <sup>8</sup> Kraft, *Annalen*, 1935, **520**, 133.

TABLE VIII.

Polycyclic dienes (double bonds not in the same ring).

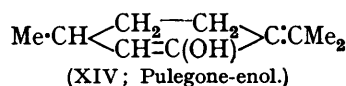
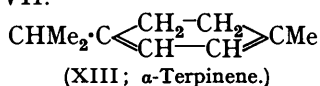
	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$	Solvent.
3 : 5-Cholestadiene	2350 <sup>1, 2</sup>	23,000	EtOH
Cholestadienol-C	2480 <sup>3</sup>	17,820	Et <sub>2</sub> O
Cholestadienol-D acetate	2450 <sup>3</sup>	11,700	"
Cholestadienol-B <sub>3</sub> acetate	2460 <sup>3</sup>	14,000	"
Ergosterol-D	2420 <sup>4</sup>	21,400	EtOH
Ergosterol-B <sub>3</sub>	2420 <sup>4</sup>	10,100	"
$\alpha$ -Dihydroxycholadienic acid	2400—2480 <sup>4</sup>	9,300	"
$\beta$ -Dihydroxycholadienic acid	2480 <sup>4</sup>	16,700	"
Dehydroergosterol	2480 <sup>5</sup>	19,900	Et <sub>2</sub> O
Abietic acid	2375 <sup>6</sup>	16,100	EtOH

Bicyclic diene (double bonds not in the same ring).

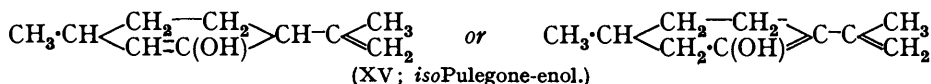
Di- $\Delta^{1:1}$ -cyclohexene (XVI)	2360	18,100	EtOH
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<sup>1</sup> Staveley and Bergmann, *J. Org. Chem.*, 1937, **1**, 567. <sup>2</sup> Schoenheimer and Evans, *J. Biol. Chem.*, 1936, **114**, 567. <sup>3</sup> Windaus, Linsert, and Eckhart, *Annalen*, 1938, **534**, 22. <sup>4</sup> Callow, *J.*, 1936, 462. <sup>5</sup> Windaus and Lüttringhaus, *Annalen*, 1930, **481**, 119. <sup>6</sup> Kraft, *Annalen*, 1935, **520**, 133.

Dimroth and Trautmann (*loc. cit.*) have shown that two conjugated double bonds in one ring in a polycyclic compound are alone sufficient to displace the location of the absorption band due to the diene chromophore to approximately 2800 Å., *i.e.*, the location of the band of ergosterol. Typical compounds of otherwise known constitution exhibiting this type of absorption are lumisterol, ergostatriene ( $\Delta^5:7:22$ ), 7-dehydrocholestene, and 22-dihydroergosterol. Absorption spectra data on these and other compounds of this type are given in Table VII.



Callow (*J.*, 1936, 462) has suggested, from combined chemical and more particularly spectrographic evidence, that the structure of ergosterol-D, dehydroergosterol, ergosterol-B<sub>3</sub>, and the  $\alpha$ - and  $\beta$ -dihydroxycholadienic acids are best explained by assuming that the light absorption, situated in all these cases between 2400 and 2480 Å. (log  $\epsilon$  of order 4.0), is due to a system of two conjugated double bonds having one bond in each of two rings.



In considering the structure of the polycyclic diene, abietic acid, Fieser and Campbell (*J. Amer. Chem. Soc.*, 1938, **60**, 159) have reviewed in detail the absorption spectra of related compounds in this class and agree with the generalisation which has been slowly emerging that the polycyclic dienes fall into two classes of compound absorbing maximally at 2400—2500 and 2600—2820 Å., severally. They have concluded that the chemical evidence, where it is available, supports the suggestion that compounds in the first group have their two double bonds conjugated but situated in adjacent rings, whereas in the second group the conjugated system is present in one ring. Table VIII shows the collected data on the dienes where the conjugated system extends into two rings. In the case of abietic acid, absorption data alone would leave open the possibility of a semicyclic diene structure such as occurs in methylenecholesterol, but the chemical evidence excludes this possibility, leaving the most probable formula as (IV) (cf. Fieser and Campbell, *loc. cit.*). The structure of *l*-pimaric acid has also been discussed by these authors who, after giving full weight to spectroscopic and chemical evidence, put the most probable formula as (VII), thus placing it in the class of polycyclic compounds having two double bonds in one ring.

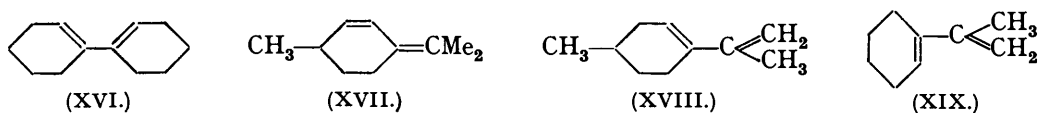
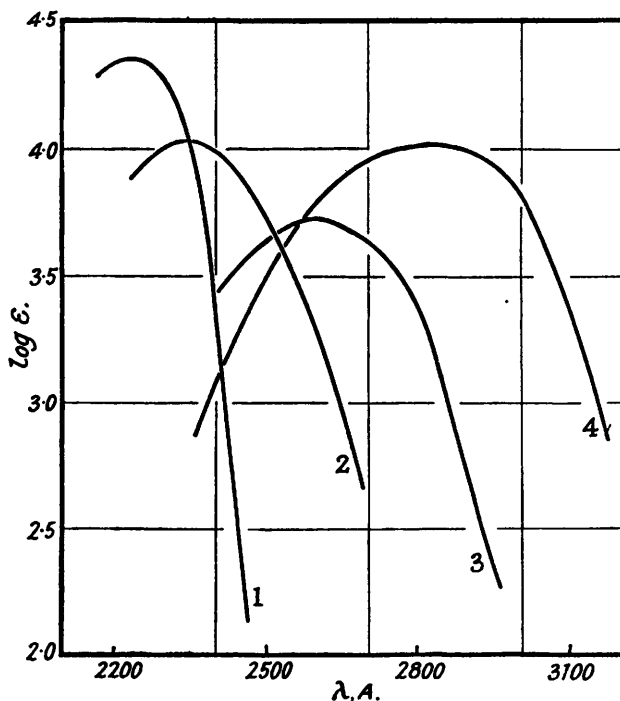


Fig. 4 illustrates graphically the important fact emerging from Table IX, *i.e.*, that the diene chromophore is responsible for an absorption band located somewhere within the

FIG. 4.



Displacement of the diene absorption band by change in molecular environment. Alcoholic solutions of: (1) Piperylene. (2) Menthadiene. (3) 1-Methyl- $\Delta^{2:4}$ -cyclohexadiene. (4)  $\beta$ -Amyradienyl acetate.

range 2170—2820 Å., the particular location depending solely on molecular environment. The choice of  $\beta$ -amyradienyl acetate as a representative of the polycyclic dienes rather than a simpler one of more certain constitution, such as ergosterol, was determined by the fact that the former gives a smooth curve with a single maximum such as is shown by the



TABLE IX.  
Classified Summary of Absorption Spectra of Dienes.

	$\lambda_{\max.}$	$\epsilon_{\max.}$ , range.	Average $\epsilon$ , approx.
1. <i>Acyclic dienes.</i>			
(a) Having only acyclic substituents	2170—2280	14,600—25,500	22,000
(b) Having one cyclic substituent	2355—2365	5,300—10,500	7,800
(c) Having two cyclic substituents	2460—2480	13,700—34,900	20,900
2. <i>Semicyclic dienes.</i>	2300—2420	1,320—20,000	8,800
3. <i>cycloHexadienes.</i>	2560—2650	2,500—9,900	5,470
4. <i>Bicyclic diene.</i>			
(a) Having two double bonds in different rings	2360	18,100	18,100
5. <i>Polycyclic dienes.</i>			
(a) With two double bonds in the same ring	2600—2820	5,300—13,500	10,500
(b) With two double bonds in different rings	2350—2480	9,300—23,000	16,000

simpler dienes, whereas the latter gives a curve exhibiting a main maximum and two sub-maxima which, while being irrelevant to the main issue here, might appear to confuse it.

#### EXPERIMENTAL.

*Determination of Absorption Spectra.*—All the determinations were carried out photographically with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, the light source being a high-tension spark between tungsten-steel electrodes. The resulting spectrum is such that the range 2200—7000 Å. is spread over 18 cm. The solvent most generally used was ethyl alcohol, previously freed from polymerisable materials by refluxing with metallic sodium followed by distillation. Some compounds have also been examined in solution in hexane, which was freed from aromatic compounds by shaking with concentrated sulphuric acid, the product being finally washed with water, dried, and distilled. This process was repeated until absorbing impurities could not be detected in a 4-cm. layer. The molecular extinction coefficient,  $\epsilon$ , has the usual significance,  $\epsilon = (\log I_0/I)/cd$ , where  $I_0$  = intensity of incident light,  $I$  = intensity of transmitted light,  $c$  = concentration (g.-mols./l.), and  $d$  = the thickness of the layer of solution (in cm.).

*Piperylene*,  $\text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_3$ .—Crotonaldehyde (1 mol.) was allowed to react with methylmagnesium iodide, and the product decomposed with dilute hydrochloric acid. The ether extract yielded 52 g. of the alcohol,  $\text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , b. p. 60—63°/55 mm. This was dehydrated by the method of Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 986), the vapour being passed over previously ignited kaolin in a silica tube 100 cm. long, the temperature being kept at 450—470° (thermocouple in the kaolin) and the pressure at ca. 12 mm. The issuing vapours were cooled by solid carbon dioxide, and the oily piperylene was quickly poured off the ice. The yields were calculated from the observed volume of water obtained after dehydration; the best yield was 65—70%. The piperylene so obtained was distilled at atmospheric pressure, the main fraction being collected at 40—80°. This was refractionated into seven fractions of 0.5—2.0 ml. each. The fractions of b. p. 42—43° showed the greatest intensity of absorption, *i.e.*,  $\epsilon = 23,000$  at 2235 Å. (alcohol).

$\Delta^2$ :4-*Hexadiene*,  $\text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_3$ .—Dried and distilled crotonaldehyde (70 g.) in pure dry ether (80 ml.) was added dropwise to ethylmagnesium bromide (1 mol.) in ether (200 ml.) cooled in ice. When the vigorous reaction was complete, the mixture was acidified with ice-cold dilute hydrochloric acid, and the ethereal layer removed, dried, and freed from solvent, after which the hexenol was distilled in a vacuum (b. p. 53—57°/22 mm.; yield 41 g.). Dehydration was effected as in the preceding case; as calculated from the water produced in the dehydration the yield was over 70%. The product was distilled, and a number of fractions collected between 85° and 90°, those at 85—87° and 87—89° having the highest intensities of absorption, *i.e.*, 22,100 and 23,000 respectively, in alcohol. The compound decomposes readily, for the intensity of absorption falls rapidly even during 24 hours' storage at 0°.

*Myrcene* (I).—100 ml. of a commercial sample of oil of bay were distilled under reduced pressure and gave a main fraction, b. p. 74°/14.8 mm. This colourless liquid was redistilled over metallic sodium, and the main fraction collected at 67°/2.4 mm. Its refractive index,  $n_D^{18}$  1.4703, agreed well with the value given by Einklaar (*Rec. Trav. chim.*, 1907, **26**, 166) for the pure liquid, *i.e.*,  $n_D^{18}$  1.4700. The absorption spectrum showed a maximum at 2250 Å. with  $\epsilon = 12,400$ . A second sample of myrcene prepared by Dr. T. F. West from oil of bay had  $d_4^{20}$  0.8010,  $n_D^{20}$  1.4714, b. p. 71—73°/23 mm. It exhibited an absorption maximum at 2245 Å. with  $\epsilon = 14,600$ , which indicates it to be a purer sample than the first.

*Zingiberene* (III).—Oil of ginger (500 ml.) was fractionated under reduced pressure, a long column being used. The main fraction (100 ml.) distilled over a narrow range of temperature and was refractionated three times. The best fraction exhibited a single absorption band in alcohol,  $\epsilon_{\max.} = 5,300$  at 2355  $\text{\AA}$ ., which was not increased in intensity by three further fractionations. This observed intensity of absorption is rather lower than might have been expected for this compound by comparison with similar ones in the same class, but as repeated distillation does not yield fractions of higher absorption, and further, as the observed refractive index,  $n_D^{20} = 1.4956$ , is identical with the value reported for apparently pure material, it must be assumed that the best fraction was substantially pure and that this diene exhibits an intrinsically low intensity of absorption. Nevertheless, natural zingiberene always contains small quantities of the unconjugated terpene bisabolene which would act as a non-absorbing diluent (cf. Simonsen, "The Terpenes," Vol. II, p. 494).

*l*- $\alpha$ -*Phellandrene* (V).—We are indebted to Dr. T. F. West for a sample of this terpene prepared from commercial phellandrene derived from the oil of *Eucalyptus dives*. This specimen had b. p. 77—78°/25 mm.,  $[\alpha]_D -58.5^\circ$ ,  $n_D^{20} 1.4765$ ;  $d_{15}^{20} 0.8523$ . The absorption curve exhibited a maximum at 2630  $\text{\AA}$ .,  $\epsilon = 1610$ . In view of the low intensity of absorption, a second sample was kindly prepared by Dr. West and was even more rigorously purified and freshly distilled before being examined (cf. Goodway and West, *J. Soc. Chem. Ind.*, 1937, 56, 472  $\tau$ ). The physical constants of this sample were: b. p. 87—88°/42 mm.,  $d_{15}^{20} 0.8401$ ,  $[\alpha]_D -95.37^\circ$ ,  $n_D^{20} 1.4750$ , and it can be taken as an especially pure specimen of *l*- $\alpha$ -phellandrene. The absorption curve gave  $\lambda_{\max.}$  2630  $\text{\AA}$ .,  $\epsilon = 2,300$ , indicating that considerable further purification had been achieved. No higher values for  $\epsilon$  have been obtained.

$\beta$ -*Phellandrene* (VI).—The sample was freshly distilled by Dr. T. F. West and had  $d_{15}^{20} 0.8496$ ,  $n_D^{20} 1.4800$ ,  $[\alpha]_D -46.58^\circ$ , b. p. 74—75°/22 mm. The solution in alcohol exhibited a single absorption maximum at 2320  $\text{\AA}$ . with  $\epsilon = 9,200$ , which is comparable with the value of 2312  $\text{\AA}$ . ( $\epsilon = 9,120$ ) for hexane solution given by Macbeth, Smith, and West (J., 1938, 119).

*s*-*Divinyglycol*,  $\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2$ .—This was prepared by reduction of distilled acraldehyde by Griner's method (*Ann. Chim. Phys.*, 1892, 26, 368). The main fraction distilled at 95—130°/18 mm., and on refractionation at 104—106°/18 mm. It was brominated by means of phosphorus tribromide (Farmer, Laroia, Switz, and Thorpe, J., 1927, 2946); the recrystallised 1:6-dibromohexadiene, after separation from the liquid 3:4-dibromide, had m. p. 84—86° and  $\lambda_{\max.}$  2580  $\text{\AA}$ .,  $\epsilon = 27,700$ .

1:6-*Diethoxy- $\Delta^2$ :4-hexadiene*.—This was prepared from the foregoing dibromide by the method of Farmer *et al.* (*loc. cit.*). After fractionation, it distilled at 104—106°/12 mm., and had  $\lambda_{\max.}$  2280  $\text{\AA}$ .,  $\epsilon = 26,800$ .

The corresponding 1:6-diacetoxy-compound was also prepared from the 1:6-dibromide by the same authors' method. It had b. p. 156—159°/14 mm.,  $\lambda_{\max.}$  2280  $\text{\AA}$ .,  $\epsilon_{\max.}$  27,300 (alcohol).

*Allylidene*cyclohexane (II).—1-Allylcyclohexanol was prepared from cyclohexanone and allylmagnesium bromide (Jaworski, *Ber.*, 1909, 42, 436; Mazurewitsch, *Zentr.*, 1911, ii, 1922; Aldersley, Burkhardt, Gillam, and Hindley, this vol., p. 10). After removal of excess cyclohexanone with sodium bisulphite, the product was distilled and collected at 74—85°/12 mm., and on refractionation the main portion boiled at 76—80°/12 mm. The product was acetylated with acetic anhydride and sodium acetate, and on distillation the main fraction of the acetyl derivative boiled at 91—94°/12 mm. The acetate was heated with copper-bronze powder (2 hours at 220°) and finally extracted with ether. The dried product was vacuum-distilled, and the fraction, b. p. <75°/12 mm., collected and redistilled at 760 mm.; b. p. 160—163°. Saizew (*Zentr.*, 1913, i, 23) prepared the diene by heating  $\text{C}_6\text{H}_{10}\text{Cl}\cdot\text{CH}_2\text{CH}:\text{CH}_2$  with silver carbonate, and the main portion boiled at 161—163°. He suggested that the product may consist of a mixture of conjugated and unconjugated isomers. Our product boiled at the same temperature as that of Saizew and exhibited a single absorption maximum at 2365  $\text{\AA}$ .,  $\epsilon = 7700$ , which indicates that it was very largely the conjugated form although the precise percentage of non-absorbing, unconjugated form present is unknown.

*Di- $\Delta^{1:1}$ -cyclohexene* (XVI).—This was prepared from cyclohexanone by first converting this into the pinacol by means of aluminium amalgam (Barnett and Lawrence, J., 1935, 1104). The product, recrystallised from petrol-benzene, had m. p. 127—129°. The pinacol was dehydrated by heating with 10% sulphuric acid (Wallach and Pauly, *Annalen*, 1911, 381, 112; Gruber and Adams, *J. Amer. Chem. Soc.*, 1935, 57, 2555) and steam-distilled; the diene then separated as an oil. On addition of light petroleum and cooling, the oil solidified, and the crude material exhibited an absorption band at 2390  $\text{\AA}$ .,  $\epsilon = 13,500$ , but after two crystallisations the absorption spectrum gave  $\lambda_{\max.} = 2360 \text{\AA}$ .,  $\epsilon = 18,100$ . This intensity could not be increased by further recrystallisations.

*Menthadiene* (XVIII).—Pulegone was reduced by Ponndorf's method (*Z. angew. Chem.*, 1926, **39**, 138) as described by Doeuve and Perret (*Bull. Soc. chim.*, 1935, **2**, 298). After reduction, the residue was steam-distilled and yielded a distillate which was extracted with ether and the product heated with fused potassium bisulphate (15 mins.) to dehydrate any pulegol present. This product was shaken with aqueous sodium bisulphite for several days to remove unchanged pulegone, and after extraction and drying was distilled; the fraction, b. p. 75—82°/20 mm., exhibited a single absorption band at 2350 Å.,  $\epsilon = 10,700$ , not increased by a further fractionation. Doeuve and Perret (*loc. cit.*) have shown that the terpene obtained by this method is a mixture of the two menthadienes (XVII) and (XVIII) in the ratio 27 : 73. As both of these isomers are semicyclic dienes, and as there is no evidence or probability of any difference in absorption spectra in the two isomers, they can be classed without qualification with the semicyclic dienes and the absorption provisionally attributed to the major constituent (XVIII).

1-Methyl- $\Delta^{2:4}$ -cyclohexadiene.—The method of preparation was that of Harries (*Annalen*, 1913, **395**, 253): 1-methylcyclohexan-4-ol was dehydrated with zinc chloride to give 1-methylcyclo- $\Delta^3$ -hexene, which was collected at 102—105°/760 mm. The product was brominated in acetic acid to give the dibromide, which was distilled and collected at 92—100°/12 mm. On heating in a sealed tube with alcoholic trimethylamine (63—70°; 24 hours), the unsaturated quaternary ammonium bromide was obtained after separation of trimethylammonium bromide. The concentrated oily mother-liquor was shaken with silver oxide suspended in water, and the filtered liquid concentrated under reduced pressure and then distilled at normal pressure. The aqueous distillate was ether-extracted, and the extracted material redistilled (b. p. 94—106°), the product being finally distilled over metallic sodium. The absorption spectra of the fractions in alcoholic solution all showed a single absorption band at 2580—2600 Å., the fraction having the highest intensity giving  $\epsilon_{\text{max.}} = 4,910$ .

$\alpha$ -Terpinene (XIII).—The material was prepared by dehydration of terpineol with aqueous oxalic acid (Wallach, *Annalen*, 1893, **275**, 107; Goodway and West, this vol., p. 702), the terpene being separated by steam-distillation followed by fractional distillation at atmospheric pressure. The absorption spectra of the fractions indicate that they are qualitatively different:

	B. p.	Wt., g.	$\lambda_{\text{max.}}$ Å.	$\epsilon$ .		B. p.	Wt., g.	$\lambda_{\text{max.}}$ Å.	$\epsilon$ .
Crude product	—	108	2500	3010	Fraction 4	178—179°	20.0	2535	3230
Fraction 1	171—176°	2.5	2620	3630	„ 5	179—180	10.5	2490	3160
„ 2	176—177	20	2600	3300	Residue	—	24.5	2440	3520
„ 3	177—178	25.5	2560	3480					

The most intensely absorbing fraction had  $\lambda_{\text{max.}}$  2620 Å.,  $\epsilon = 3630$ , but in view of the results obtained by Dupont, Levy, and Marot (*Bull. Soc. chim.*, 1933, **53**, 393), as well as from the relatively low intensity of absorption, it seems clear that this sample was far from pure. These workers thoroughly investigated the composition of the  $\alpha$ -terpinene obtained by dehydration of terpineol, commencing with 6 l. of the starting material and fractionating through a 2-m. column. They concluded that the crude  $\alpha$ -terpinene contains some 40% of 1 : 4-cineole, together with appreciable quantities of dipentene,  $\gamma$ -terpinene, and terpinolene, as well as minor constituents which were not completely separable even under such good conditions. It is noteworthy that  $\alpha$ -terpinene appears to be the only important constituent of the mixture exhibiting intense light absorption at wave-lengths longer than about 2200 Å., so the absorption spectrum gives a measure of the relative amount of this terpene present in various fractions. In view of the technical difficulties in obtaining purer material we did not proceed further and the maximum intensity recorded here is therefore only a minimal value.

$\Delta^{3:8(9)}$ -Normenthadiene (XIX).—This was prepared from hexahydrobenzoic acid (cf. Matsubara and Perkin, *J.*, 1905, **87**, 661). The acid was converted into the acid chloride with phosphorus pentachloride and this was brominated to give the 2-bromo-compound, which was then converted into the ethyl ester by treatment with absolute alcohol. The bromo-ester (b. p. 98—103°/16 mm.) was heated with diethylaniline to remove hydrogen bromide, and the distilled product treated with methylmagnesium iodide (4 mols.). After treatment with dilute sulphuric acid and ether extraction, the crude diene exhibited selective absorption at 2360 Å.,  $\epsilon = 3000$  approx. Five fractionations (the last three over sodium) yielded a product having b. p. 162—162.5°/770 mm. This specimen of the diene gave a single absorption band of good persistence, with a maximum at 2420 Å.,  $\epsilon = 9,550$ .

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