

Fig. 2.—N.m.r. spectrum of heptalene.

absorption of hydrogen (PtO<sub>2</sub>, cyclohexane-ethanol, 10–12 min.) to yield *cis*(?)-bicyclo[5.5.0]dodecane (mol. wt. (mass spec.), 166), as indicated by identity of its v.p.c. retention time, infrared spectrum, and mass spectral cracking pattern with one of the *cis*, *trans* pair of products obtained from bicyclo[5.5.0]-dodeca-11-ene-1-one<sup>6</sup> on catalytic hydrogenation, tosylation, lithium aluminum hydride reduction, and (iv) especially by the n.m.r. spectrum that contains proton absorptions only in the "vinylic" region (none in the lower field "aromatic" nor in the higher field "aliphatic" regions) and exhibits the uniquely characteristic spin-spin splitting pattern (Fig. 2) of an AB<sub>2</sub>X<sub>2</sub> system (integrated intensities: A = 1.82, AB<sub>2</sub> = 5.86, X<sub>2</sub> = 4.14 protons) as expected for heptalene. In dilute carbon tetrachloride solution heptalene reacts instantaneously with bromine to give a yellow hygroscopic precipitate that is largely water-soluble; the similarity of these properties to those of tropenium bromide suggests that the major product is bromoheptalenium bromide.

The limited data available allow only tentative conclusions to be made about the nature of the heptalene system. Its facile reactions with catalytic hydrogen, oxygen, acids and bromine, and the greater stability of 1-heptalenium ion than 1-azulenium ion,<sup>5</sup> indicate that heptalene is a very reactive compound, and both more reactive and more basic than azulene. Preferential protonation at the 1-position<sup>5</sup> shows that nucleophilic localization energy is lowest at this position, and the higher field positions of the n.m.r. absorptions of X<sub>2</sub> protons that of A or B<sub>2</sub> protons suggests that electron densities are highest at the 1, 5, 6, and 10 positions. The location of all proton absorptions at the high field end of the "vinylic" region probably is attributable to the lack of appreciable aromatic ring current.<sup>7</sup> Its ultraviolet absorption maxima occur at much shorter wave lengths (256, 352 mμ) than those predicted by the simple molecular orbital method for a fully conjugated system, but are in good agreement with those approximated by the weakly-interacting independent-systems method of Simpson<sup>8</sup> (245, allowed; 387 mμ, allowed and forbidden); the long tail through the visible region may arise from a forbidden transition becoming partially allowed by molecular vibrations or twisting, from transitions according to the Franck-Con-

(6) G. Bichi and O. Jeger, *Helv. Chim. Acta*, **32**, 538 (1949); we are grateful to Professor A. G. Anderson, Jr., for the 5-(1'-cycloheptenyl)-pentanoic acid used in this synthesis.

(7) G. Berthier, B. Pullman and J. Baudet, *J. Chim. Phys.*, **49**, 641 (1952), predicted a pronounced diminution of diamagnetic susceptibility in heptalene (and pentalene), in contrast to the exaltations found in azulene and benzenoid aromatic compounds.

(8) W. T. Simpson, *J. Am. Chem. Soc.*, **77**, 6164 (1955); we are indebted to Professor Simpson for this suggestion and for the calculation of these values.

don principle from a ground state with a single or double potential energy minimum, or from limited resonance splitting of N and/or E states.<sup>8</sup> Provided these initial deductions are correct, heptalene more resembles a weakly-interacting cyclic polyene than a strongly-interacting aromatic system, presumably because of theoretical reasons or non-planarity.

(9) Acknowledgment is gratefully made to the U. S. Army Research Office for partial support of this work, and to the Standard Oil Company of California for a fellowship held by D. J. B. during a portion of this research.

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#### THE CONFIGURATIONS OF LEVOPIMARIC ACID AND $\alpha$ -PHELLANDRENE; INTERPRETATION OF THEIR ROTATORY DISPERSIONS

Sir:

Levopimaric ( $\Delta^{6,8(14)}$ -abietadienoic) acid (I) has been assigned the  $\beta$ -configuration at C-13 (steroid numbering, C-9) by Klyne<sup>1</sup> from a comparison of its [M]<sub>D</sub> with that of 2,4-cholestadiene (II) (*cf.* 589 mμ region of Fig. 1). Recently, however, Schuller and Lawrence<sup>2</sup> have presented strong chemical

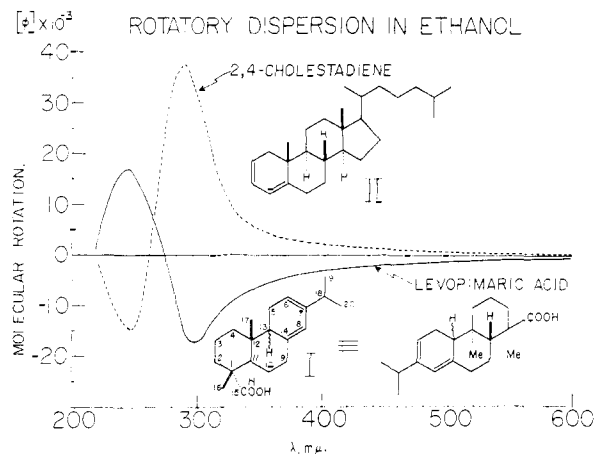


Fig. 1.

evidence for the  $\alpha$ -orientation at this center. In addition, other facts, such as formation of a common hydrogenation product<sup>3</sup> from both I and neoabietic ( $\Delta^{7(18),8(14)}$ -13 $\alpha$ -abietadienoic) acid<sup>4</sup> can be viewed as favoring the  $\alpha$ -configuration at C-13 in I.<sup>5</sup>

We have measured the complete Cotton-effect curves of I, II, and several related compounds, and have observed an antipodal relationship between those of I and II (Fig. 1). Although at first sight this result would seem to confirm the 13 $\beta$ -assignment, we wish to suggest an alternative interpreta-

(1) W. Klyne, *J. Chem. Soc.*, 3072 (1953).

(2) W. H. Schuller and R. V. Lawrence, *Chemistry & Industry*, 105 (1961); *J. Am. Chem. Soc.*, **83**, 2563 (1961); *cf.* also W. D. Lloyd and G. W. Hedrick, *J. Org. Chem.*, **26**, 2029 (1961).

(3) *Cf.* J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4762 (1960).

(4) Proof of configuration: C. Djerassi, R. Riniker and B. Riniker, *ibid.*, **78**, 6365 (1956).

(5) Epimerization of an unstable  $\beta$ -configuration at C-13 during hydrogenation would, of course, invalidate this particular argument.

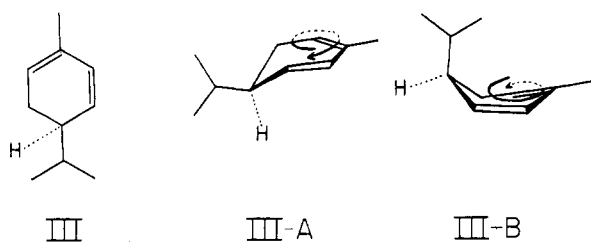


Fig. 2.

tion which is compatible with the chemical evidence for the  $13\alpha$ -configuration.

A fundamental analysis<sup>6</sup> of the rotatory dispersion of optically active 1,3-cyclohexadienes has revealed that the skewness imposed on such diene systems by structural factors constitutes the major element of asymmetry responsible for the Cotton effect, its contribution to optical activity far outweighing that of adjacent asymmetric centers. In addition, it has been derived theoretically and demonstrated experimentally<sup>6</sup> that the direction of the Cotton effect so produced depends upon the sense of helicity of the diene, a left-handed helix producing a negative effect. On the basis of this rule, the negative Cotton effect of I requires that its dienic system form a left-handed helix. It is apparent from Dreiding models that this requirement is met not only by the  $13\beta$ -configuration of I, but also by one (I-A)<sup>7</sup> of two possible conformations with  $13\alpha$  (the other one, I-B, predicts a positive Cotton effect). Since the first of these possibilities is contrary to the available chemical evidence, we feel that the second one with its  $13\alpha$ -configuration is likely to be correct.

An analogous situation obtains in (-)- $\alpha$ -phellandrene (III), our only other case (out of eleven compounds studied so far) of a seemingly wrong prediction of the sign of a Cotton effect from the helicity rule.<sup>8</sup> Here, a positive Cotton effect is expected if the isopropyl group has the quasi-equatorial conformation III-A usually assumed to be the preferred one. The observed negative effect suggests that the alternative conformation III-B with a quasi-axial isopropyl group is in fact correct; in this case the diene system assumes the required left-handed helicity.

It seems significant that both in III-B and in I-A the protons of an alkyl group (17-methyl in I, isopropyl in III) are spatially close to the center of the unsaturated system. This suggests some type of interaction which stabilizes an otherwise unfavorable conformation.<sup>9,10</sup> A special condition of the protons on C-17 of I is actually suggested by n.m.r.

(6) A. Moscovitz, E. Charney, U. Weiss and H. Ziffer, *J. Am. Chem. Soc.*, **83**, 4661 (1961).

(7) Models of I-A actually show an almost planar diene; it is plausible to assume, however, that in reality this system is more strongly twisted to avoid serious crowding of the hydrogen atoms at C-4 and C-5.

(8) The absolute configuration of III appears well established; cf., *inter alia*, the discussion by K. Freudenberg and W. Lwowski, *Ann.*, **587**, 213 (1954), and literature quoted there.

(9) Cf. also the case of isomenthone: (a) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960, pp. 106, 107; (b) C. Djerassi, *et al.*, *J. Am. Chem. Soc.*, **83**, 3334 (1961).

(10) The positive Cotton effect observed for II clearly eliminates a possible "folded" conformation resembling I-A (left-handed helix). In II the absence of an alkyl group at C-9 precludes the stabilizing interaction assumed for I-A and III-B, and hence the extended conformation (cf. I-B) with a right-handed helix prevails.

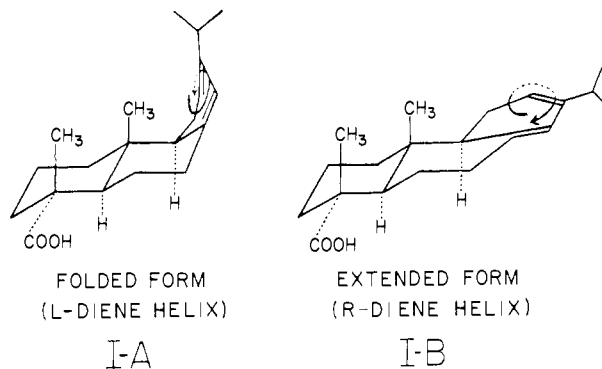


Fig. 3.

data.<sup>3</sup> The signal caused by them is shifted  $\sim 0.17$  p.p.m. downfield from its position in thirteen related compounds, including, e.g., neoabietic acid ( $\Delta^{7(18),8(14)}$ ) and pimaric acid ( $\Delta^{8(14)}$ ). Hence, this shift appears to be due to a specific interaction, possible only in I, between the methyl protons and the entire diene, rather than to the presence of the  $\Delta^{8(14)}$  bond, isolated or conjugated.<sup>11</sup>

While this interpretation is permissive rather than decisive, it removes the otherwise unresolved discrepancy between chemical evidence and rotational data. It also emphasizes the importance of making due allowance for conformational influences not immediately obvious.

We wish to thank Dr. R. V. Lawrence, Naval Stores Research Laboratory, Olustee, Florida, for samples of resin acids, and several colleagues for helpful discussions.

(11) The downfield shift<sup>3</sup> in compounds with a  $\Delta^{13}$  bond (e.g., palustric acid) is normal for a double bond at this distance and hence not relevant (cf. J. N. Shoolery and M. T. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958)).

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#### OPTICAL ACTIVITY IN SKEWED DIENES

Sir:

In connection with our interest in dissymmetric chromophores,<sup>1,2</sup> we have considered the optical activity associated with skewed dienes.<sup>3</sup> It will be recognized that butadiene would be optically active in any of its nonplanar forms and that comparable dissymmetric diene conformations may be achieved permanently when the conjugated moiety is part of a rigidly fixed ring system, e.g., in lumisterol (I).

(1) K. Mislow, M. A. W. Glass, A. Moscovitz and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 2771 (1961).

(2) A. Moscovitz, *Tetrahedron*, **13**, 48 (1961).

(3) While this manuscript was in preparation, the publication of R. Deen and H. J. C. Jacobs, *Koninkl. Nederl. Akademie Van Wetenschappen Amsterdam*, **64**, 313 (1961), came to our attention. From both theoretical and experimental considerations (see also R. Deen, Thesis, Leiden, September, 1961), these authors conclude that "an asymmetrically situated butadiene system will either in itself or due to its environment bring about optical activity correlated with its longest wavelength transition." The present work is in agreement with and supports this conclusion.