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ON THE STEREOCHEMISTRY OF OCCIDENTALOL

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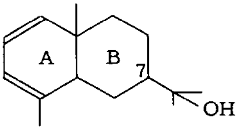
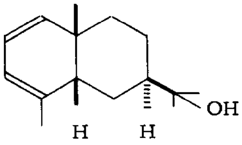
VON RUDLOFF and Erdtman have recently concluded that (+)-occidentalol has the constitution I and that the two rings are cis-fused.[2] If this assignment is correct, a choice still remains from among four stereoisomers: diastereoisomers II and III, and their mirror images IV and V. We now wish to present arguments which restrict the alternatives to II and V, and which therefore indicate that the absolute configuration at C-7 is (R).



I



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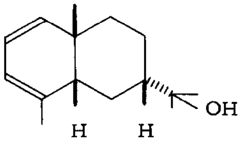

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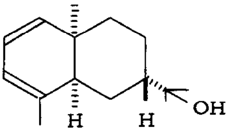

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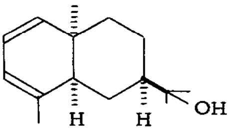

V

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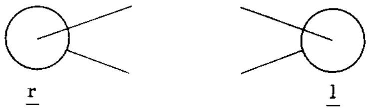
[2] E. von Rudloff and H. Erdtman, Tetrahedron 18, 1315 (1962).

On the assumption that ring B exists mainly in the chair form, two conformers are possible for each of the isomers II-V; in one the isopropyl alcohol group at C-7 is equatorial (*e*) while in the other it is axial (*a*). Furthermore, each conformer contains a skewed *cisoid* butadiene moiety, incorporated in ring A, which may take the form of a right- or a left-handed helix (denoted *r* and *l* for the purpose of the present discussion). Models disclose that a unique relationship exists between the conformation at C-7 and the sense of skew of the butadiene helix which is summarized in Table I.

Table I

Stereoformula	Conformation at C-7 in ring B	Chirality of butadiene moiety in ring A
II	*e*	*r*
	a	*l*
III	*e*	*l*
	a	*r*
IV	*e*	*l*
	a	*r*
V	*e*	*r*
	a	*l*



A decision among these alternatives is facilitated by considering the optical rotation of (+)-occidentalol[2] ($[\alpha]_D$ + 363.2°). The magnitude of this rotation, contrasted to those of the di- and tetrahydro derivatives ($[\alpha]_D$ + 65.5° and 42.5°), may be regarded as *prima facie* evidence for the presence of a high amplitude positive Cotton effect centered at the lowest diene absorption band. According to the helicity rule,[3] (+)-occidentalol therefore contains a skewed r-butadiene moiety. If we allow with von Rudloff and Erdtman that the isopropyl alcohol group is equatorial,[2] it follows from Table I that only configurations II and V meet the given requirements, and hence that the absolute configuration at C-7 is (R).

It has been reported[4, 5] that (+)-occidol has the (R) configuration at C-7. Hence, the present findings support the suggestion[5] that (+)-occidentalol and (+)-occidol are biogenetically related.

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[3] A. Moscowitz, E. Charney, U. Weiss and H. Ziffer, J. Am. Chem. Soc. **83**, 4661 (1961).

[4] M. Nakazaki, Chem. and Ind. 413 (1962).

[5] M. Nakazaki, Bull. Chem. Soc. Japan **35**, 1387 (1962).