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SYNTHESIS OF OPTICALLY ACTIVE OCHOTENSANES

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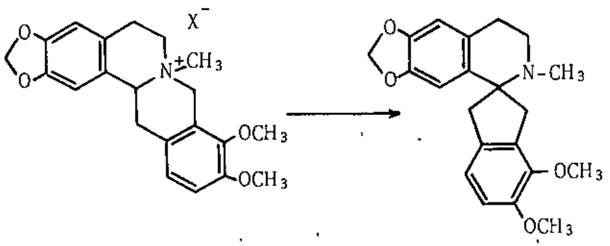
Treatment of *l*-(14 S)-β- (Ia) and *d*-(14 R)-β-canadine methochlorides (Ib) with organolithiums, lithium aluminium hydride, or sodium methylsulfinyl carbanion in tetrahydrofuran gave *d*- (IIa) and *l*-2,3-methylenedioxy-9,10-dimethoxyochotensanes (IIb), respectively. The structures of those have been proved by the results of the Hofmann degradation and spectral means. The cd spectra of IIa and IIb showed Davydov split extrema centered at 284 nm whose first Cotton effects corresponded to the absolute configurations.

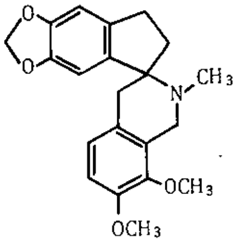
In the preliminary publication[1] a base-induced rearrangement of the nonphenolic protoberberinium salts was described. During duplicate experiments it was found that the product should be assigned to the structure II rather than the originally proposed structure III. We would like to revise our previous proposal and now report the synthesis of optically active ochotensanes[2].

When *l*-(14 S)-β-canadine methochloride (Ia, X=Cl, mp 262°, $[\alpha]_D^{16}$ -161°) and *d*-(14 R)-β-canadine methochloride (Ib, X=Cl, mp 262°, $[\alpha]_D^{16}$ +161°) were treated with butyllithium in tetrahydrofuran, *d*-2,3-methylenedioxy-9,10-dime-



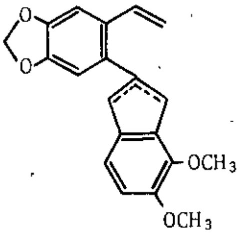
Ia: *l*-Form (14 S)
Ib: *d*-Form (14 R)

IIa: *d*-Form
IIb: *l*-Form

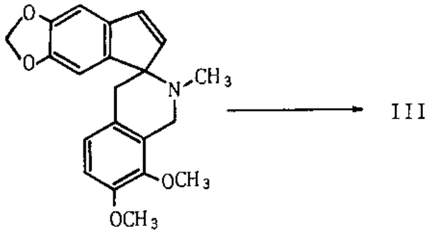


III

thoxyochotensane (IIa, mp 104-105°, $[\alpha]_D^{16}$ +60°) and *l*-2,3-methylenedioxy-9,10-dimethoxyochotensane (IIb, mp 104-105°, $[\alpha]_D^{16}$ -60°) were formed, respectively. The ochotensane derivative was also obtained on treatment of *N*-methyltetrahydroberberinium salts with phenyllithium, lithium aluminium hydride, sodium methylsulfinyl carbanion, or 3% sodium amalgam instead of butyllithium. The structures of IIa and IIb were unequivocally confirmed by the following manner; II provided, after the Hofmann degradations in twice, the nitrogen-free substance (IV), $C_{20}H_{18}O_4$ (M^+ 322), mp 155-156°. The uv spectrum of IV showed absorption maxima at 224 (log ε 4.25), 265 (3.88), 301 (4.02), and 313 nm (3.99). In the nmr spectrum of IV, signals which newly appeared at 5.15 ppm



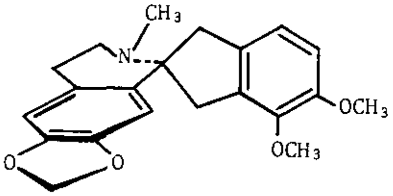
IV



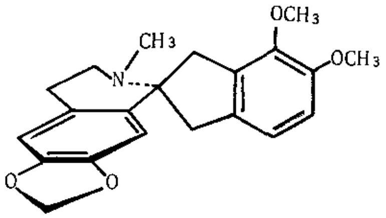
V

(1H, dd, J_1=11 Hz, $J_2 \simeq$1 Hz) and 5.53 ppm (1H, dd, J_1=17 Hz, $J_2 \simeq$1 Hz) were indicative of the formation of the vinyl group. Moreover, the alternative structure (III) could be ruled out by the fact that III derived from *N*-methyl-7,8-dimethoxy-1,2,3,4-tetrahydroisoquinoline-3-spiro-1′-5′,6′-methylenedioxyindene (V)[3] did not agree with the rearrangement product (in the ir and nmr spectra in solutions).

The cd spectrum of IIa showed Davydov split extrema centered at 284 nm with a positive first Cotton effect[4], while IIb showed the antipodal curve of IIa (Fig. 1). Therefore, the absolute configurations of IIa and IIb should be the 14 R (VI) and 14 S (VII), respectively.



VI (14 R)



VII (14 S)

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2. Nomenclature and numbering in this system followed in the literature, M. Shamma and J. F. Nugent, *Tetrahedron*, **29**, *1265 (1973).*

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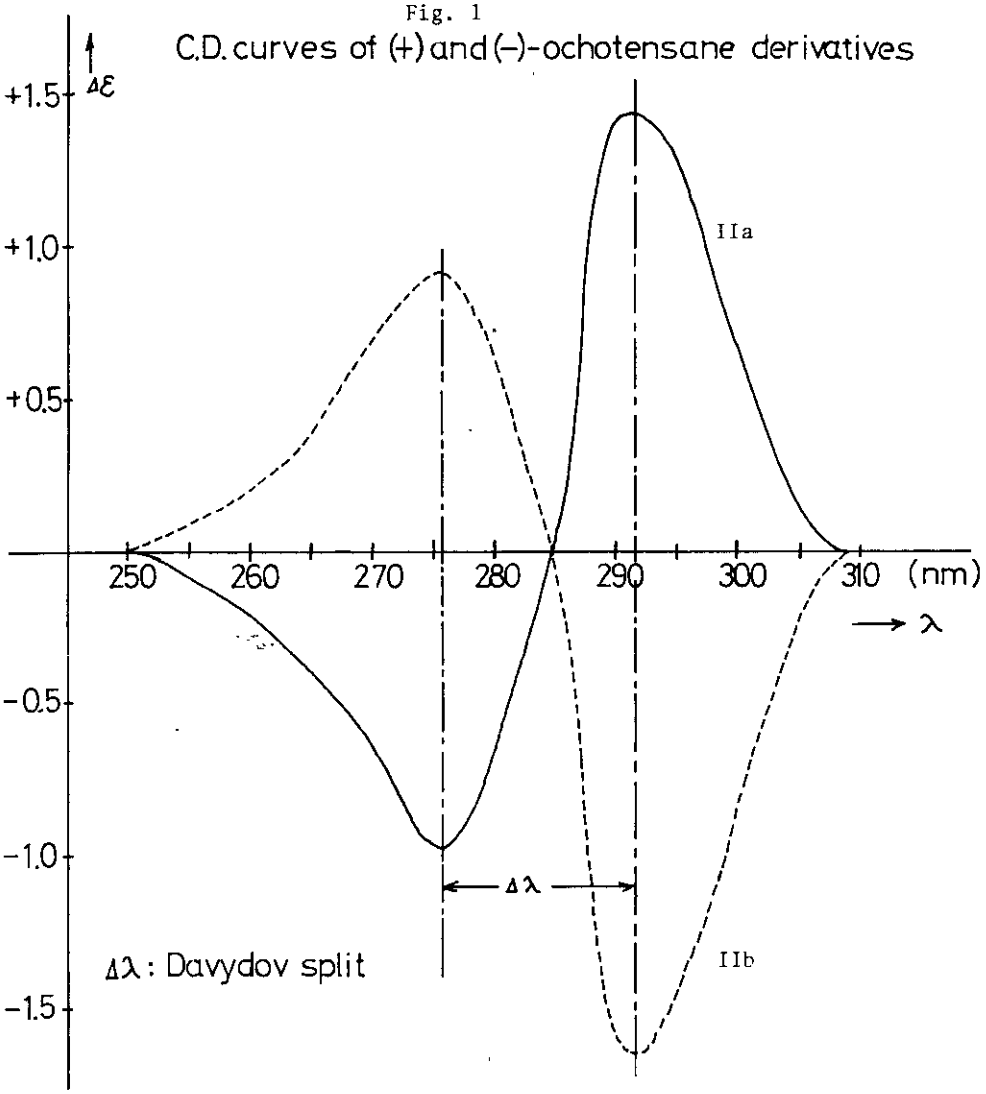
Fig. 1

C.D. curves of (+) and (−)-ochotensane derivatives



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