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Absolute Conformation of Methyl 3-(1,4-Dimethoxy- and 1,4-dimethyl-9-triptycyl)-3-methylbutanoate Rotamers[1)]

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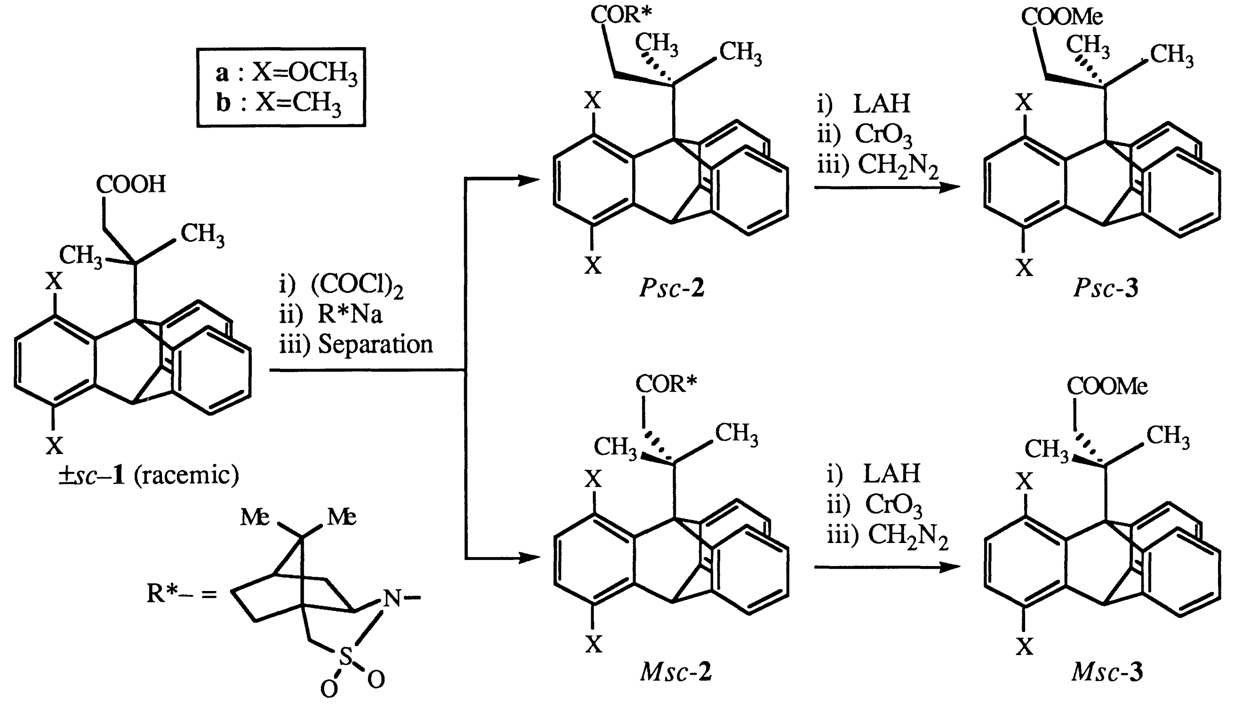
The racemates of the rotational isomers of the mother acids of the title compounds were resolved via their camphor sultam amides and their absolute conformation was determined by X-ray crystallography. The chiroptical properties of the methyl esters are correlated with the absolute conformations. Both of these compounds are shown to possess dextrorotatory property at Na D line, if their stereochemistry is *Psc*.

Recently we, in collaboration with Swedish chemists, have reported resolution of methyl 3-(1,4-dimethoxy- and 1,4-dimethyl-9-triptycyl)-3-methylbutanoates by column chromatography with use of cellulose triacetate. Our attempt to elucidate their absolute conformation by fitting the calculated spectra with the observed CD was unsuccessful[2)] because the methodology was premature. It was felt necessary to establish absolute conformation before any meaningful calculation be made but resolution of the enantiomers of the methyl esters on a preparative scale by the column chromatography was tedious. Thus it was necessary to resolve them via a diastereomer method with use of a chiral auxiliary.

Since we were successful in resolving one of the rotational isomer pair via menthyl esters,[3)] we first tried to use menthyl esters of the carboxylic acids. The diastereomeric menthyl esters were barely separated by HPLC but resisted crystallization. During these processes, Harada et al. reported a successful use of camphor sultam amides of carboxylic acids for resolution.[4)] We used the same resolving reagent for the present case and were able to separate them by HPLC. In addition, they gave suitable crystals for crystallography. This letter is to report the results together with their absolute conformations and chiroptical properties.

The conformational isomers of 3-(1,4-dimethoxy- or 1,4-dimethyl-9-triptycyl)-3-methylbutanoic acid (**1**), *ap* and ±*sc*, were separated by chromatography as was reported earlier.[5)] The *ap*-form should be achiral but the ±*sc* chiral. For optical resolution of the ±*sc* form, ±*sc*-**1** was converted to its acid chloride with oxalyl dichloride and then to camphor sultam amides (**2**) by treating the resulted chloride with a sodium salt of camphor sultam.[6)] The diastereomers of the sultam amide could be separated by recrystallization from dichloromethane for the dimethoxy compound (**2a**) and the better soluble isomer was submitted to the X-ray analysis.[7)] For the dimethyl compound (**2b**), the sultam amides were separated by HPLC (Chemcosorb 5Si, $10\phi \times 300$, dichloromethane eluent) with baseline separation, and the easily eluted isomer crystallized from hexane-THF was submitted to X-ray crystallography.[8)]

ORTEP drawings of these isomers are given in Fig. 1, in which stereochemistry of camphor sultam is consistent with the known absolute stereochemistry. Torsion angles of C(9a)–C(9)–C(17)–C(20) are +62.3° and +61.6° for the dimethoxy compound and the dimethyl compound, respectively, indicating that both of these



triptycenes possess *Psc* absolute conformations around the C(9)—C(17) bonds. These results assure that another isomer has *Msc* conformation in both compounds.

Camphor sultam was removed from **2** by reduction with lithium aluminium hydride and the resulted primary alcohols were oxidized with chromium(VI) oxide to afford the optically active carboxylic acids,[9,10] which were converted to the methyl esters with diazomethane. Specific rotations ($[\alpha]^{25}_{D}$) of the methyl esters, *Psc*-**3a** and *Psc*-**3b**, as measured for chloroform solutions were +20° and +32°, respectively. Thus the *Psc* forms of these esters are both dextrorotatory. The enantiomers of the esters, *Msc*-**3a** and *Msc*-**3b**, show levorotatory properties and the absolute values of their rotational angles were identical with those for the *Psc* forms.

The CD spectra of the *Psc* methyl esters recorded as methanol solutions are shown in Fig. 2. Their peaks and troughs[11] well correspond to UV absorptions measured as hexane solutions.[12] Generally speaking, the CD properties of both compounds are very similar if the conformations are *Psc*, although heights of peaks and depths of troughs are different for the corresponding absorptions of respective compounds. It is also interesting to note that the CD spectrum of the methoxy compound (*Psc*-**3a**) is a mirror image of that reported earlier, whereas that of *Psc*-**3b** is identical with that reported earlier.[2] This means that the enantiomer eluted first in chromatography on the triacetylcellulose column was *Psc* for the 1,4-dimethyl compound, whereas that for the 1,4-dimethoxy compound was *Msc*.

Although several empirical and nonempirical rules for correlation between CD spectra and absolute configuration are proposed,[13] a series of experimental data as well as theoretical studies are necessary for understanding the chiroptical properties of triptycene derivatives. Optical resolution of other triptycene derivatives toward this end is underway in our laboratory.

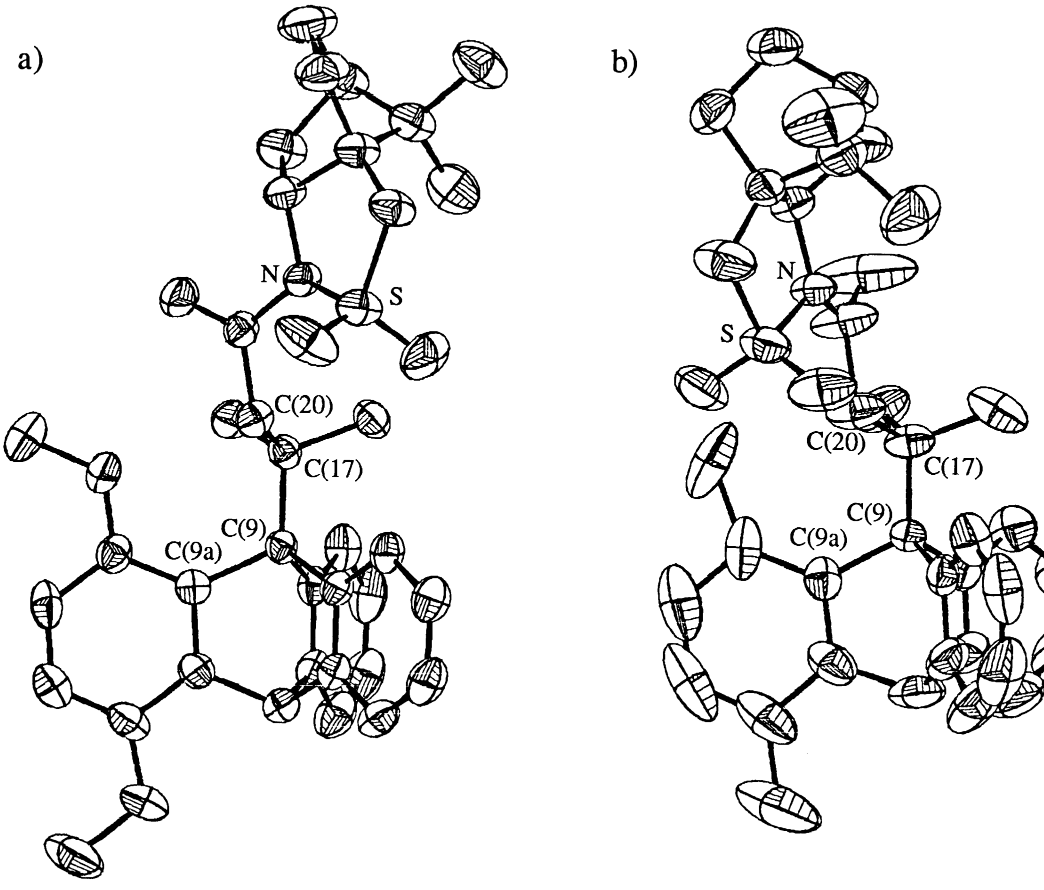


Fig. 1 ORTEP drawings of compounds **2**: a) *Psc*-**2a**, b) *Psc*-**2b** (All hydrogen atoms are omitted).

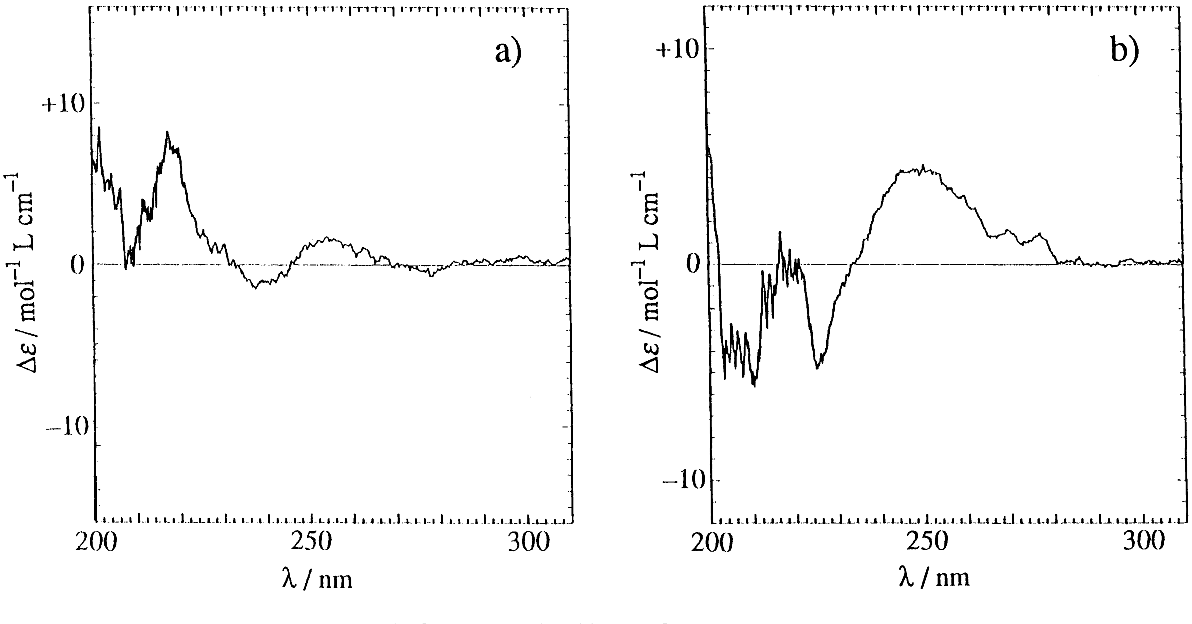


Fig. 2 CD spectra of compounds **3**: a) *Psc*-**3a**, b) *Psc*-**3b**.

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References

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7) X-Ray data were collected with a MAC Science MXC diffractometer with Mo $K\alpha$ radiation (λ = 0.71073 Å). *Psc*-**2a**: $C_{37}H_{41}NO_5S$, FW=611.80, Orthorhombic, Space group $P2_12_12_1$, a=10.846(2), b=10.858(2), c=27.577(7) Å, V=3248(2) Å^3, Z=4, D_c=1.25 g cm^{-3}, μ=1.05 cm^{-1}. Among 5282 unique reflections, 3860 reflections within $|F_o|>3\sigma(F_o)$ were used. R 0.064, R_w 0.060.
8) X-Ray data of *Psc*-**2b**: $C_{37}H_{41}NO_3S$, FW=579.80, Orthorhombic, Space group $P2_12_12_1$, a=16.529(6), b=18.346(6), c=10.316(4) Å, V=3128(2) Å^3, Z=4, D_c=1.23 g cm^{-3}, μ=1.03 cm^{-1}. Among 4510 unique reflections, 3551 reflections within $|F_o|>2\sigma(F_o)$ were used. R 0.053, R_w 0.041.
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11) CD: λ_{max}/nm($\Delta\varepsilon_{max}$). *Psc*-**3a**: 201.0 (+8.1), 207.0 (−0.3), 217.0 (+8.3), 237.0 (−1.5), 254.0 (+1.7), 278.5 (−0.7), 296.5 (+0.5), 300.0 (+0.3), 308.0 (+0.5). *Psc*-**3b**: 211.0 (−0.53), 217.0 (+1.0), 225.0 (−4.7), 249.0 (−4.4), 270.0 (+1.5), 277.0 (+1.5), 291.0 (−0.1).
12) UV: λ_{max}/nm(logε_{max}). **3a**: 214 (4.79), 262.5 (3.28), 271.5 (3.34), 278 (3.48), 296 (3.60). **3b**: 216.0 (4.77), 261.2 (3.28), 271.0 (3.28), 278.2 (3.28).
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