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Optical Rotatory Dispersion and Circular Dichroism of the Osmate Esters of Cyclic Mono-olefins[1,2]

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The osmate esters (as the di-pyridine adducts) of optically active mono-, di- and tricyclic mono-unsaturated terpenes were prepared for measurements of optical rotatory dispersion (ORD) and circular dichroism (CD). All the osmate esters of the cyclic olefins examined exhibited a strong Cotton effect in 470 mμ regions and a weak Cotton effect near 600 mμ regions, which were similar to those of the osmate esters of the open chained olefins reported in our previous paper. The sign of CD maximum in 470 mμ regions was found to be correlated to the chirality of gauche structure of the chelate ring containing an osmium chromophore. Furthermore, their absolute configurations were deduced from the data of circular dichroism of two diastereoisomers of *cis*-α-pineneglycol.

An effective method has been reported by Bunnenberg and Djerassi[3] to introduce an appropriate chromophore to an ethylenic bond of optically active mono-unsaturated compound and to give rise to a Cotton effect in the relatively longer wavelength regions for the convenience of the measurement of ORD. They reported that the steroidal olefins reacted with osmium tetroxide to form the osmate esters, which exhibited a multiple Cotton effect in visible spectrum regions.

We have already mentioned that the sign of the Cotton effect of the osmate esters of optically active acryloyl esters,[4] α-olefins,[4] acryloyl-L-amino acids[5] and 1,2-glycols[6] can be associated with the configurations of these olefins. We measured ORD and CD curves of the osmate esters of optically active cyclic mono-unsaturated terpenes and tried to account for the correlation between the conformational structure of the osmate esters and the sign of CD maximum in 470 mμ regions.

Experimental

Menthene Isomers. (+)-*1-Menthene* 〔*1*〕. The crude (+)-1-menthene supplied by Nippon Terpene Chem. Co., was subjected in batches to preparative gas chromatography (Silicone DC 550, 2.6 m×10 mmϕ, 160°C), α_{589}^{17} +82.8° (neat).

(+)-trans-*2-Menthene* 〔*2*〕[7]. *l*-Menthyl toluene-*p*-sulphonate obtained by the reaction of *p*-toluenesulfonyl chloride with *l*-menthol was added to a solution of sodium in absolute ethanol. The mixture was refluxed for 6 hr in dry nitrogen. After ether extraction, the product was purified by preparative gas chromatography as above, α_{589}^{21}+109° (neat). The resulting product was found to contain (+)-*trans*-2-menthene (92%) and (+)-3-menthene (8%) by analytical gas chromatography (Dinonylphthalate, 3.7 m×3 mmϕ, 145°C).

(−)-trans-*2-Menthene* 〔*3*〕: The product obtained from α-menthyl tosylate by the method as above was found to contain (−)-*trans*-2-menthene (91%) and (−)-3-menthene (9%), α_{589}^{21} −108° (neat).

(+)-*3-Menthene* 〔*4*〕.[8] *l*-Menthol was added to metallic sodium in dry toluene and refluxed for 20 hr. To the reaction mixture was added ether solution of carbon disulfide and methyliodide. The yielded methyl (−)-menthyl xanthate was pyrolyzed to 〔*4*〕, which was purified by preparative gas chromatography. From the result of the analytical gas chromatography, it was found to contain (+)-*trans*-2-menthene (31%), α_{589}^{17} +83.2° (neat).

Dicyclic mono-terpenes.

The purity of the following compounds was determined by analytical gas chromatography (PEG 6000, 3 m×3 mmϕ, 130°C).

(+)-*α-Pinene* 〔*5*〕[9]: $[\alpha]_D^{11}$ +21.5° (neat), purity 97%.

(−)-*α-Pinene* 〔*6*〕[9]: $[\alpha]_D^{11}$ −26.5° (neat), purity 97%.

(−)-*β-Pinene* 〔*7*〕[9]: $[\alpha]_D^{11}$ −19.9° (neat), purity 97%.

(−)-*Camphene* 〔*8*〕[9]: $[\alpha]_D^{21}$ −28.3° (*c* 8, ethanol), purity 92.5%.

(+)-*Bornylene* 〔*9*〕[9]: $[\alpha]_D^{21}$ +8.3° (*c* 6, benzene), purity 87%.

Patchoulene Isomers.

α- and γ-Patchoulene 〔*10*〕, 〔*12*〕.[10] Phosphorus oxychloride was added into a solution of patchouli alcohol ($[\alpha]_D^{22}$ −120°, *c* 5, chloroform) in pyridine. The resulting patchoulene was separated into two components by preparative gas chromatography (PEG 6000, 2.6 m×10 mmϕ, 160°C). α-Patchoulene 〔*10*〕; α_{589}^{22} −45.10° (neat), purity 99%. γ-Patchoulene 〔*12*〕; purity 87% (containing 12% α-patchoulene).

β-Patchoulene 〔*11*〕.[10] This was prepared by dehydration of patchouli alcohol in concd. sulfuric acid and purified by preparative gas chromatography (PEG 6000, 2.6 m×10 mmϕ). α_{589}^{22} −37.8° (neat). Purity 99%.

α-Pineneglycols. (+)-(*1R*:*2R*:*3R*:*5R*)-trans- *and* (−)-(*1R*:*2R*:*3S*:*5R*)-cis-*α-Pineneglycol* 〔*13*〕, 〔*14*〕. (+)-2-Hydroxypinocamphone prepared by oxidation of chromic acid anhydride from (−)-α-pinene ($[\alpha]_D$ −26.9°) was reduced by lithium aluminum hydride. The mixture gave crude glycols which were chromatographed on silica

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[1] Studies on Optical Rotatory Dispersion Part VII. Part VI: N. Sakota, S. Tanaka, K. Okita, and N. Koine, *Nippon Kagaku Zasshi*, **91**, 265 (1970).

[2] Presented at the 13th Symposium on the Chemistry of Terpenes, Essential Oils and Aromatics, held at Kagoshima in 1969.

[3] I. Bunnenberg and C. Djerassi, *J. Amer. Chem. Soc.*, **82**, 5953 (1960).

[4] N. Sakota, T. Tanigaki, K. Okita, and N. Koine, *Nippon Kagaku Zasshi*, **90**, 593 (1969).

[5] N. Sakota and N. Koine, *ibid.*, **88**, 1087 (1967).

[6] N. Sakota, S. Tanaka, K. Okita, and N. Koine, *ibid.*, **91**, 265 (1970).

[7] W. Hückel and W. Tappe, *Ann. Chem.*, **543**, 191 (1940).

[8] L. Tschugaeff, *Ber.*, **32**, 3332 (1899).

[9] The samples were supplied by the Nippon Terpene Chem. Co., Ltd. except for (−)-α-pinene, which was supplied by the Yoneyama Chemical Co., Ltd.

[10] G. Büchi, R. E. Erickson, and N. Wakabayashi, *J. Amer. Chem. Soc.*, **83**, 927 (1961).

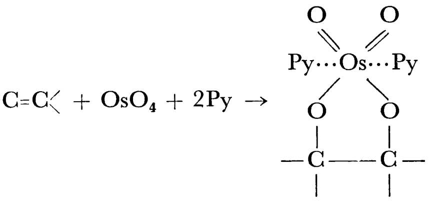
gel column with the mixture of ethyl acetate and *n*-hexane into *cis*- and *trans*-α-pineneglycol. The homogeneity of these glycols separated was checked by chromatostrip analysis. *cis*-Glycol 〔*14*〕, $[\alpha]^{11}_{589}$ −0.40° (*c* 5, chloroform). Lit[11] $[\alpha]^{25}_{D}$ −0.890° (*c* 7.91, chloroform), from (−)-α-pinene ($[\alpha]^{25}_{D}$ −39.9°). *trans*-Glycol 〔*13*〕, $[\alpha]^{26}_{589}$ −20.5° (*c* 1.5, ethanol), mp 153—156°C. Lit[8] $[\alpha]^{25}_{D}$ −33.1° (*c* 4.8, ethanol), mp 159—160°C, from (−)-α-pinene ($[\alpha]^{25}_{D}$ −39.9°).

(−)-(*1R*:*2S*:*3R*:*5R*)-cis-α-*Pineneglycol* 〔*15*〕.[12] Pinocarbonoxide mixture prepared from (−)-α-pinene (optical purity 71%, kindly supplied by Mr. Katsuhara), was reduced by lithium aluminum hydride. The resulting mixture was separated as shown above into two *cis*-α-pineneglycols and a *trans*-α-pineneglycol. The *trans*-glycol and the *cis*-glycols were identified to be 〔*13*〕, 〔*14*〕, and 〔*15*〕 respectively by the R_f values of thin-layer chromatography.

Measurements of ORD, CD and Visible Absorption Spectrum. Olefin (3—5 mg) was treated with two molar equivalents of pyridine dissolved in 1 m*l* of dichloromethane and one equivalent of osmium tetroxide. After standing for a certain time at room temperature, ORD, CD and visible absorption spectra were recorded on a Jasco Optical Rotatory Dispersion, Model UV-5 with an attached CD recorder using 1 mm and 2 mm cells. In the case of α-pineneglycol, 0.4% (v/v) pyridine - methanol was used as a solvent.

Results and Discussion

It has been reported[13] that the mono-unsaturated compounds react with one equivalent of osmium tetroxide and two equivalents of pyridine yielding the osmate esters (as di-pyridine adducts) as follows.



$$\rangle C{=}C\langle + OsO_4 + 2Py \rightarrow \begin{array}{c} O\ \ \ O \\ \backslash\!\backslash\ \ // \\ Py\cdots Os\cdots Py \\ /\ \ \ \ \backslash \\ O\ \ \ \ \ O \\ |\ \ \ \ \ \ | \\ -C\text{——}C- \\ |\ \ \ \ \ \ | \end{array}$$

The ORD, CD and visible absorption spectra of the osmate esters of mono-unsaturated terpenes differ markedly from each other in amplitude, fine structure and position of the extrema according to their chemical structures. However, general features of these spectra resemble each other. As two examples, the spectra of the osmate esters of monocyclic terpene, (+)-1-menthene and dicyclic terpene, (−)-β-pinene are shown in Figs. 1 and 2, respectively. When these terpenes are treated with pyridine and OsO_4 in dichloromethane, the maximum absorption is always obtained only after standing for 1—2 days at room temperature, and the spectra at the maximum absorption are shown in these figures. As shown in Fig. 1, the osmate esters of (+)-1-menthene 〔*1*-Os〕 exhibit a strong negative CD maximum at about 465 mμ with the corresponding Cotton effect. Because of the strong absorption exhibited below 410 mμ, the visible absorption band corresponding to the CD maximum at 465 mμ regions reveals itself merely as a shoulder, which is shifted to the shorter wavelength. In Fig. 2, the osmate ester of (−)-β-pinene 〔*7*-Os〕 exhibits a similar CD curve of opposite sign.

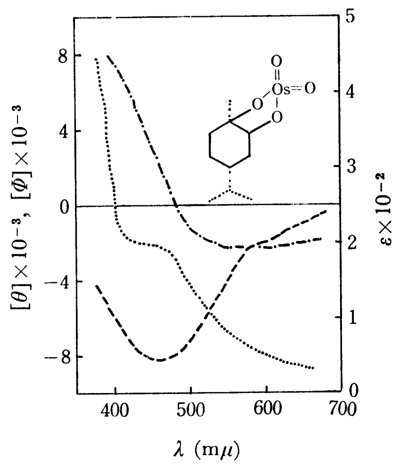


Fig. 1. CD (----), ORD (—·—) and visible absorption spectrum (······) of osmate ester of (+)-1-menthene in dichloromethane.

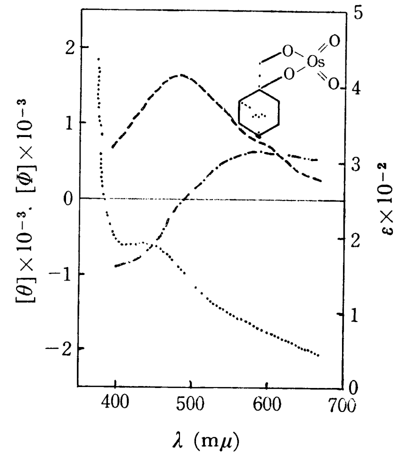


Fig. 2. CD(----), ORD(—·—) and visible absorption spectrum(······) of osmate ester of (−)-β-pinene in dichloromethane.

The molar elipticities at maximum wavelength ($[\theta]_{\max}$) of the osmate esters of mono-, di- and tricyclic mono-unsaturated terpenes are summarized in Fig. 3. The general features of the CD curves are similar to those of the osmate esters of the open chained mono-unsaturated compounds[4—6] and also to those of the osmate esters of steroidal olefins.[3] Notable results are obtained from Fig. 3 as follows. The osmate esters of monocyclic terpene, 1-, 2- and 3-menthene exhibit fairly large $[\theta]_{\max}$ values compared to those of di- and tricyclic terpenes. Menthene reacts with osmium tetroxide, when a pair of diastereoisomers of the osmate esters are produced owing to the direction of the *cis*-addition. The ratio of the formation of these two stereoisomers might differ according to the stereoselectivity of the menthene to osmium tetroxide. As an example, the use of OsO_4 for (±)-*trans*- and (±)-*cis*-2-menthene is reported to take place in the

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[11] T. Suga, T. Shishibori, T. Hirata, and T. Matsuura, This Bulletin, **41**, 1180 (1968).

[12] J. Katsuhara, *ibid.*, **41**, 2700 (1968).

[13] R. Criegee, B. Marchand, and H. Wannowius, *Ann. Chem.*, **550**, 107 (1942).

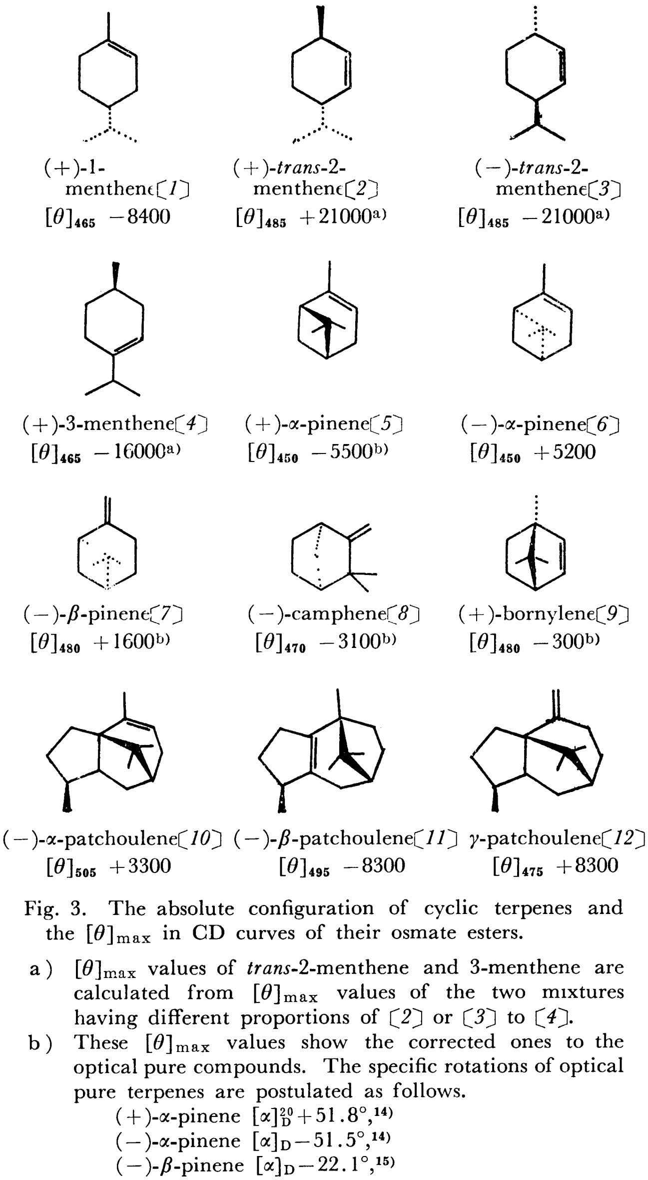

Fig. 3. The absolute configuration of cyclic terpenes and the $[\theta]_{\max}$ in CD curves of their osmate esters.

a) $[\theta]_{\max}$ values of *trans*-2-menthene and 3-menthene are calculated from $[\theta]_{\max}$ values of the two mixtures having different proportions of [2] or [3] to [4].

b) These $[\theta]_{\max}$ values show the corrected ones to the optical pure compounds. The specific rotations of optical pure terpenes are postulated as follows.

(+)-α-pinene $[\alpha]_D^{20}+51.8°$,[14)]
(−)-α-pinene $[\alpha]_D-51.5°$,[14)]
(−)-β-pinene $[\alpha]_D-22.1°$,[15)]
(−)-camphene $[\alpha]_D^{20}-99.4°$,[16)]
and
(+)-bornylene $[\alpha]_D^{17}+23.9°$.[17)]

formation of a single epimer in each case.[18)] In these cases, the stable conformation of the osmate esters must be the one in which cyclohexane ring takes one of the two possible chair forms.

The molecular model shows that the five membered ring containing an osmium chromophore is twisted and forms gauche structures, which seem to be more stable than the plain one with respect to the O–C–C–O angle. If the two gauche structures are defined as δ- and λ forms as shown in Fig. 4, it is reasonable to consider that the stable conformation of [3-Os] is the δ form and [2-Os] is the λ form. Experimental results show that the sign of CD maximum at 470 mμ is negative for [3-Os] and positive for [2-Os]. This suggests that the sign of CD maximum at 470 mμ can be correlated to the gauche structure of the five membered ring. In contrast, the chiralities of [1-Os] and [4-Os] are so little effected by the stereoselectivity of 1- and 3-menthene to osmium tetroxide that the predominant twisted conformation is not easy to predict. However, if the above mentioned rule is applicable for [1-Os] and [4-Os], the negative sign of the Cotton effect of their osmate esters is ascribed to the predominance of δ form in the chirality of their five membered ring.

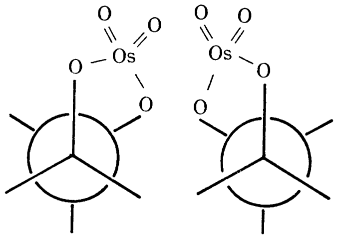

Fig. 4. The gauche structures of the osmium chromophore.

Bunnenberg and Djerassi[3)] measured the ORD spectra of the osmate esters of four steroidal cholestenes which have a more rigid and twisted conformation than those of menthene isomers. Their results also show that λ- and δ structure of five membered ring exhibit the positive and negative Cotton effect near 470 mμ, respectively. In previous papers, it was suggested that the sign of the 460 mμ CD maximum in osmate esters of open chained (S)-1,2-glycols $CH_2(OH)CH(OH)R$[6)] and open chained (S)-α-olefins $CH_2{=}CHR$[4,5)] was affected by the conformation of the five membered ring. It is well known that the metal complexes of ethylenediamine and propylenediamine have gauche structures.[19)] Dwyer *et al.*[20)] also showed that the stable conformation of the propylenediamine-cobalt complex is the gauche structure, in which the conformation of the methyl group is equatorial. The stable conformation of the osmate esters of (S)-open chained compounds is suggested to be δ structure in which R group is equatorial, and can explain the negative CD maxima.

Thus the chiral structure of five membered ring of the osmate esters can be correlated to the sign of the CD maximum near 470 mμ. A similar conclusion has been reported by Djerassi *et al.*,[21)] who showed that the sign of the Cotton effect attributed to π–π* and n–π* transition of the steroidal trithiocarbonate depends upon the chirality of the trithiocarbonate chromophoric ring. In dibenzoate compounds, the

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14) F. H. Thurber and R. C. Thielke, *J. Amer. Chem. Soc.*, **53**, 1030 (1931).

15) G. Dupont, J. Allard, and R. Dulou, *Bull. Soc. Chim. Fr.*, [**4**], **53**, 602 (1933).

16) Golbev, *J. Russ. Phys. Chem. Soc.*, **36**, 1107 (1904).

17) I. M. McAlpine, *J. Chem. Soc.*, **1932**, 545.

18) A. Killen Macbeth and W. G. P. Robertson, *ibid.*, **1953**, 895.

19) K. Nakatsu, M. Shiro, Y. Saito, and T. Kuroya, This Bulletin, **30**, 795 (1957).

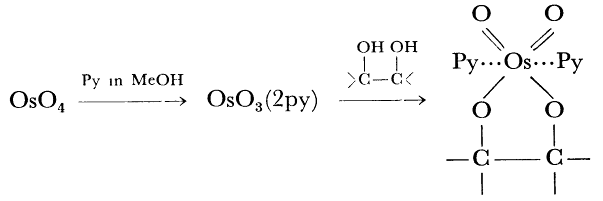
20) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **85**, 2913 (1963); F. P. Dwyer, A. M. Sargeson, and L. B. James, *ibid.*, **86**, 590 (1964).

21) C. Djerassi, H. Wolf, D. A. Lightner, E. Bunnenberg, K. Takeda, T. Komeno, and K. Kuriyama, *Tetrahedron*, **19**, 1547 (1963).

same consideration was reported by Harada and Nakanishi.[22] For the octahedral metal complexes, the possibility of a correlation between the octant sign and the sign of the Cotton effect for identified transitions within certain symmetry groups is mentioned.[23]

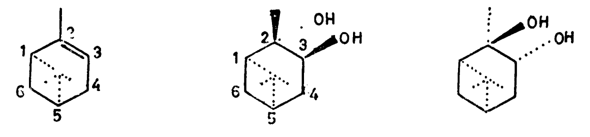
However, the molecular structure of the osmate esters of dicyclic monoterpenes, α-pinenes and bornylene, 〔*5*-Os〕, 〔*6*-Os〕 and 〔*9*-Os〕 are more rigid than those of the monocyclic terpenes, and their gauche structures of the chelate ring are less twisted. Thus, it is difficult to predict whether their stable chiral structure is to be λ or δ. In the case of the osmate esters of β-pinene 〔*7*-Os〕 and camphene 〔*8*-Os〕, not only the skeleton of the terpene moiety but also the whole molecular structure of the osmate ester should be taken into account for the evaluation of the stability of the five membered ring since the double bond is situated in exo position. Thus, for these osmate esters, the existence of a puckered conformation as mentioned above is difficult to predict. It is well established that in general the puckered chromophore contributes much more to the amplitude of the CD maximum than the plain chromophore. In Fig. 3, the molecular elipticities at CD maximum of the osmate esters of dicyclic terpenes are recognized to be smaller than those of monocyclic terpenes. This suggests the puckered conformation for the osmate esters of monocyclic terpenes. In the case of the osmate esters of patchoulene isomers, the situation seems to be more complicated.

Criegee *et al.*[13] has reported that glycols as well as α-olefins react with osmium tetroxide and pyridine to produce the osmate esters which resemble those from α-olefins:

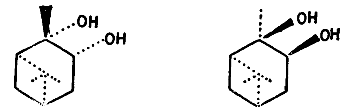


$$OsO_4 \xrightarrow{\text{Py in MeOH}} OsO_3(2py) \xrightarrow{\overset{\text{OH OH}}{>C-C<}}$$

In order to gain further insight into the osmate esters of (—)-α-pinene 〔*6*-Os〕, a *trans*- and two *cis*-α-pineneglycols, in which the configuration differs from each other only at C_2 and C_3 positions, were synthesized and the CD of these osmate esters was measured. Addition of osmium tetroxide to *trans*-α-pineneglycol 〔*13*〕 does not exhibit the CD maximum at 470 mμ, which denies the possibility of the trans addition of OsO_4 to olefins. The absolute configuration of *cis*-α-pineneglycol 〔*14*〕 obtained from (+)-2-hydroxypinocamphone was assigned to be 〔C〕 in Fig. 5 by Suga *et al.*,[11] but Schmidt[23] and Katsuhara[12] assigned 〔D〕 to it. Another *cis*-α-pineneglycol 〔*15*〕 having the opposite configuration at C_2 and C_3 was obtained from (—)-pinocarbonoxide. The CD curves of these two osmate esters were measured, and the $[\theta]_{max}$ values were obtained as +6400 and —12000, respectively (Table 1). The osmate ester of (—)-α-pinene 〔*6*-Os〕 consists of two isomeric esters of *cis*-α-pineneglycols 〔C-Os〕, 〔D-Os〕. The fraction of 〔D-Os〕 is considered to be larger than that of 〔C-Os〕, because the cis addition of osmium tetroxide to the double bond should be affected by the steric hinderance of the geminate dimethyl. The results in Table 1 show that 〔*6*-Os〕 mainly consists of 〔*14*-Os〕, and the absolute configurations of 〔*14*〕 and 〔*15*〕 should be assigned to 〔D〕 and 〔C〕, respectively. The trans glycol 〔*13*〕 obtained from (+)-2-hydroxypinocamphone should also be assigned to 〔B〕.



(—)-α-pinene 〔*6*〕 (+)-(1R:2S:3S:5R)-*trans*-α-pineneglycol 〔A〕 (+)-(1R:2R:3R:5R)-*trans*-α-pineneglycol 〔B〕



(—)-(1R:2S:3R:5R)-*cis*-α-pineneglycol 〔C〕 (—)-(1R:2R:3S:5R)-*cis*-α-pineneglycol 〔D〕

Fig. 5. The absolute configuration of (—)-α-pinene and *trans*-, *cis*-α-pineneglycols.

TABLE 1. THE $[\theta]_{max}$ IN CD CURVES OF THE OSMATE ESTERS OF α-PINENEGLYCOLS

Osmate ester	$[\theta]_{max}$ a)
〔*13*-Os〕	0
〔*14*-Os〕	+6400
〔*15*-Os〕	−12000
〔*6*-Os〕	+5200

a) These values are the corrected ones in relation to the optical pure compounds.

If we supposed that the sign of CD is dependent only upon the twisting of the five membered ring affected by the inherent α-pinene skeleton, both the CD maximum of 〔*14*-Os〕, and 〔*15*-Os〕 should have the same sign. However, the experimental results show different signs for them. This means that when osmium tetroxide reacts with (—)-α-piene from upper side or lower, the twisting of the chromophoric five membered ring might be reversed, *viz.*, the stable conformation of (—)-α-pinene skeleton is reversed. Accordingly, the chromophore in 〔*14*-Os〕 and 〔*15*-Os〕 should be a twisted five membered ring, whose conformation should be affected by the steric effects not only from the terpene moiety but also from the whole molecule.

We acknowledge the generosity of Mr. Katsuhara of Sun Star Research for providing the samples. We also wish to thank the Nippon Terpene Chem., Ltd. and the Yoneyama Chemical Industry Co., Ltd. for gifts of samples.

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22) N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, **91**, 3991 (1969).
23) C. J. Hawkins and E. Larsen, *Acjta Chem. Scand.*, **19**, 185 (1965).
24) H. Schmidt, *Chem. Ber.*, **93**, 2485 (1960).