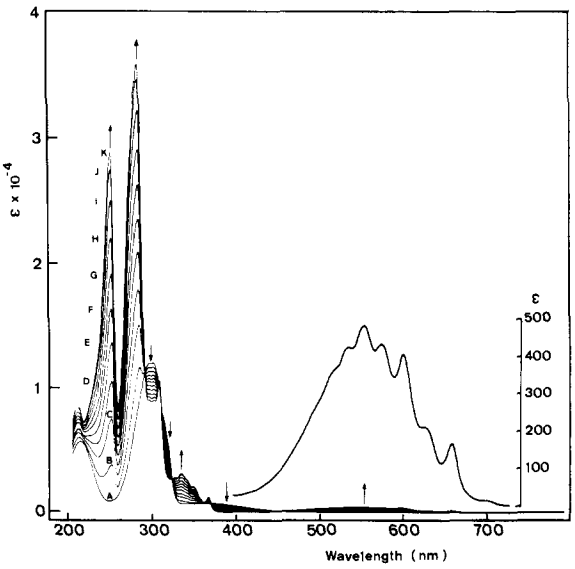

Figure 1. UV and visible spectral changes accompanying irradiation of a 4×10^{-5} M solution of 6-methoxytetracyclo[5.3.0.0^{2,4}.0^{3,5}]deca-6,8,10-triene (**1b**) in hexane. Features with an arrow pointing up and down are associated with the 4-methoxyazulene (**2b**) that is formed. Spectra A–K correspond to 0, 5.0, 10.5, 16.5, 23.0, 30.5, 39.5, 50.5, 65.5, 85.5, and 235.0-min irradiations.

sumably cis–anti–cis, **5a**) could be converted to bicyclobutane **6** by way of oxa-di-π-methane rearrangement (dry acetone/450-W high-pressure Hg lamp/3 h)[15,21] in 20–25% yield. Treatment of **6** with LDA at −35 °C followed by quenching at 0 °C with diphenyl disulfide[21c,d,22] afforded **7** in 73% yield. Oxidation of **7** (MCPBA/CH_2Cl_2/−78 °C) gave a 6:4 diastereomeric mixture of sulfoxide, **8a** and **8b**, quantitatively. Although the stereochemistry of each isomer was not fully characterized, the major one **8a**[23] suffers smooth elimination (CCl_4/45 °C/30 min) to afford **9** as a labile colorless liquid. With this efficient approach to the key intermediate **9** available, the stage was set to explore the crucial enol fixation. To our dismay, several usual attempts to effect O-alkylation, acylation, and silylation to the desired azulvalene[9] skeleton met with failure.[24] Success was finally achieved under very strictly controlled conditions (KO-*t*-Bu/HMPA + benzene/CH_3OFSO_2/0 °C).[25]

4-Methoxyazulvalene **1b** showed the following characteristics: air and acid-sensitive yellow plates, mp 71–73 °C (sealed capillary); MS, *m/e* 158 (M^+, 57%), 128 ($M^+ - CH_2O$, azulene cation, 100%), 115 (indenium ion, 93%); ^{1}H NMR (100 MHz, in $CDCl_3$ at 0 °C) δ 6.39–6.26 (m, 2 H, H-8,9), 6.10 (dd, 1 H, J = 2.2, 1.5 Hz, H-10), 4.08 (s, 3 H, OCH_3), 3.46 (t, 2 H, J = 2.5 Hz, H-3,4), 3.09 (dtd, 1 H, J = 4.0, 2.5, and 0.5 Hz, H-2), and 2.52 (dt, 1 H, J = 4.0, 2.5 Hz, H-5); UV (in hexane) λ_{max} 300 nm (ε 12 000) and 367 (689);[26] stable at room temperature under argon atmosphere.

On irradiation (100-W Hg lamp/hexane) at room temperature **1b** undergoes clean isomerization with six sharp isosbestic points (Figure 1) to 4-methoxyazulene (**2b**).[27]

In a preliminary experiment, the thermolysis of **1b** in isooctane at 110 °C was also found to produce **2b** as the final product with half-life of ca. 80 h. Whether the corresponding cyclobutene isomer is actually involved in the thermal isomerization of **1b** to **2b** as an intermediate or not could not be determined at the present stage. Further study on the detailed thermal and chemical behavior of **1b** as well as the independent synthesis of a cyclobutene isomer are being actively pursued.[28]

The preparation of a valence isomer of 4-methoxyazulene presents a new way to investigate the chemical and physical properties of this interesting molecule. The parent azulvalene **1a**, we believe, might be prepared from **1b** by way of hydride reduction, and studies are currently under way with the goal of achieving this transformation.

(21) (a) Sugihara, Y.; Morokoshi, N.; Murata, I. *Tetrahedron Lett.* **1977**, 3887. (b) *Chem. Lett.* **1979**, 745. (c) Sugihara, Y.; Sugimura, T.; Murata, I. *Ibid.* **1980**, 1103. (d) Sugihara, Y.; Yamato, A.; Murata, I. *Tetrahedron Lett.* **1981**, 3257.

(22) Trost, B. M.; Salzman, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

(23) Because of easy crystallization, the major isomer could readily be separated from the minor isomer by trituration with carbon tetrachloride.

(24) We examined here LDA/THF/Me_2SO_4, LDA/THF/$MeOFSO_2$, LDA/THF/TMSiCl, LDA/THF/CH_3COCl, and $Bu_4N^+F^-$/$Me_3SiCH_2CO_2CH_3$/THF, all to no avail.

(25) Cf.: Press, J. B.; Shechter, H. *Tetrahedron Lett.* **1972**, 2677. All solvents used are deoxygenated by bubbling with argon before use. For a typical run, to a stirred ice cooled solution of KO-*t*-Bu (purified by sublimation, 53.5 mg, 0.478 mmol) in dry HMPA (3 mL) under argon a solution of **9** (prepared from 119 mg of **8a**) in dry benzene (0.7 mL) was slowly added. After 5 min of stirring, the resulting deep yellow solution of the enolate was treated with freshly distilled methyl fluorosulfonate (ca. 0.1 mL) for 2 min. The reaction mixture was quenched with water, extracted rapidly with hexane, washed with water, and then dried ($MgSO_4$); the solvent was then removed. The residue was separated by chromatography on a short column of alumina (deactivated with 10% H_2O, 0.6 × 1 cm) with hexane into four 0.5-mL fractions. The second and third fraction afforded ~10 mg of yellow crystals which on recrystallization from hexane gave pure **1b**.

(26) 6,6-Diethoxyfulvene showed an intense absorption at 293 nm (log ε 4.26), and no band corresponding to the weak, long wavelength maximum of fulvene, which may be submerged under the long wavelength slope of the high-intensity maximum, has been reported. Hafner, K.; Schulz, G.; Wagner, K. *Justus Liebigs Ann. Chem.* **1964**, *678*, 39.

(27) Reid, D. H.; Stafford, W. H.; Ward, J. P. *J. Chem. Soc.* **1958**, 1100. Shani, A. *Isr. J. Chem.* **1975**, *13*, 53. Very recently, 4-methoxyazulene (**2b**) has been synthesized via an unambiguous method by Takase and Yasunami. We are grateful to Professors K. Takase and M. Yasunami, Tohoku University, for communicating their results prior to publication.

(28) **Note Added in Proof**: After submittion of this paper we have prepared the corresponding cyclobutene isomer of **1b** starting from **5a** through the bromination (NBS in CCl_4/azobis(isobutyronitrile)), dehydrobromination–enolate formation (2 equiv of KO-*t*-Bu in HMPA + benzene), and methylation (CH_3OFSO_2 in HMPA + benzene/0 °C) sequence. Since the cyclobutene isomer was found to be thermally stable up to 120 °C for 48 h, the intervention of this compound during the thermal isomerization of **1b** to **2b** could be ruled out.

Chirally Selective Synthesis of Sugar Moiety of Nucleosides by Chemicoenzymatic Approach: L- and D-Riboses, Showdomycin, and Cordycepin

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Naturally occurring *C*-nucleosides have attracted a great deal of synthetic study because of their unique structures of C-glycosylated heterocycles and interesting biological properties such as antibiotic, antiviral, and antitumor activity.[1] Most of the synthetic approaches have been based on the utilization of natural carbohydrate precursors.[1a] Recent progress of the synthetic approaches starting from noncarbohydrate reactants or readily available meso compounds is noteworthy in the stereocontrolled approach to the sugar moiety of nucleosides.[2] However, they require a conventional optical resolution step, and recycling of the undesired enantiomer is required in a chirally economic synthesis.[2c,3] A chirally selective approach is indeed required for

(1) (a) Hanessian, S.; Pernet, A. G. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 111. (b) Ohno, M. "Anticancer Agents based on Natural Product Models"; Cassady, J. M.; Douros, J. D., Eds.; Academic Press: New York, 1980; pp 73–130.

(2) (2) Noyori, R.; Sato, T.; Hayakawa, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2561. (b) Just, G.; Liak, T. J.; Lim, M.-L.; Potvin, P.; Tsantrizos, Y. S. *Can. J. Chem.* **1980**, *58*, 2024 and references cited therein. (c) Schmidt, R. R.; Lieberknecht, A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 769. (d) Gensler, W. J.; Chau, S.; Ball, D. B. *J. Am. Chem. Soc.* **1975**, *97*, 436.

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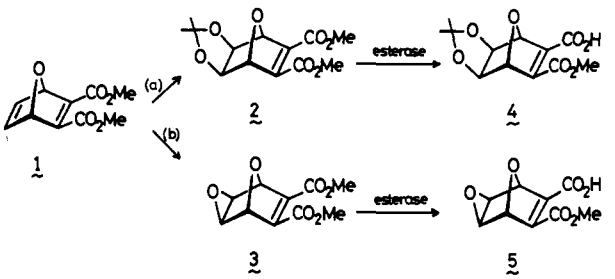
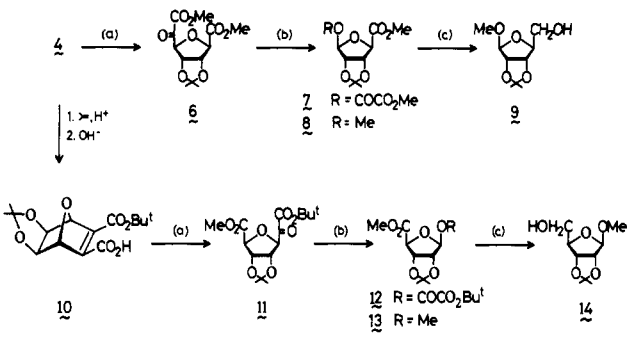
Scheme I



(a) 1. OsO_4, N-Methylmorpholine-N-oxide, t-BuOH, H_2O, THF; 2. 2,2-Dimethoxypropane, p-TsOH, Acetone (b) MCPBA, CH_2Cl_2

Scheme II

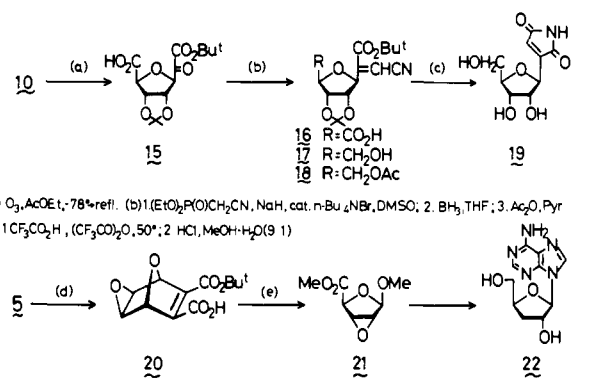


(a) O_3, MeOH, -78° (b) 1. MCPBA, CH_2Cl_2 2. HCl, MeOH (c) $LiAlH_4$, Et_2O

the synthesis of the biologically significant enantiomer of nucleosides. We wish to report here a chemicoenzymatic approach to the synthesis of L- and D-riboses, showdomycin, and cordycepin through the optically active half-esters **4** and **5** enzymatically generated starting from a Diels–Alder adduct **1** as shown in Schemes I–III.

Methyl 2,3-*O*-Isopropylidene-β-L-ribofuranoside (9). A combination of enzymatic and chemical procedures was taken as our synthetic strategy, and unsaturated half-esters **4** and **5** were considered to be versatile intermediates in the synthesis of the sugar moiety of various nucleosides, if they are formed in an opticall active form from Diels–Alder adducts **2** and **3**.[5] Pig liver esterase was employed as the enzyme as shown in the hydrolysis of β-hydroxy-β-methyl dimethyl glutarate[6] and dimethyl β-aminoglutarate.[7] The esterase hydrolyzed **2**[4] very efficiently (3 g of **2**, pH 8.0, 10% acetone, 0.1 M phosphate buffer, 4000 units of the esterase,[8] 30–32 °C, 4 h) and optically active half-ester **4** was obtained in 96% yield after usual workup. It was found to be an optically crude material, showing $[\alpha]^{20}_D$–37° (*c* 1.0, $CHCl_3$), and was recrystallized from CCl_4, showing mp 115.5–117.5 °C, $[\alpha]^{20}_D$–49°, R_f = 0.41 (AcOEt–AcOH = 20:1).[9] The absolute configuration of **4** as well the optical purity of **4** was determined by synthetic transformation to L-ribose derivative as described below. Thus, the half-ester **4** with $[\alpha]^{20}_D$–37° was directly subjected to ozonolysis in methanol at −78 °C for 15 min. As expected, decarboxylative cleavage took place smoothly and selectively to afford the desired product **6**[10] as a colorless oil. Further Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid (MCPBA) had occurred with virtually complete selectivity to yield an oxalate derivative **7**[9] [77% yield from 4; crude material, $[\alpha]^{22}_D$ +59.8° (*c* 1.0, $CHCl_3$), mp 65–82 °C; pure material recrystallized from $CHCl_3$–*n*-hexane (2:1), $[\alpha]^{22}_D$ +73.8° (*c* 0.95, $CHCl_3$), mp 92–93 °C]. The ^1H NMR[11] spectrum shows clearly the retention of configuration,[12] and the facile migration of tetrahydrofuran ring can be explained by participation of the oxygen of the ring, contrary to the oxidation of ethyl pyruvate.[13] Treatment of **7**, $[\alpha]^{22}_D$ +59.8°, with dry HCl/MeOH at room temperature for 2 h afforded **8** (R_f = 0.52, Et_2O–*n*-hexane = 1:1) as a colorless oil after usual workup and chromatography on silica gel. The methanolysis product **8** was reduced with lithium aluminum hydride (LAH), and an oily material obtained upon workup was distilled under a reduced pressure (~110 °C/0.3 mm), affording **9**[14] in 67% yield from **7**, $[\alpha]^{20}_D$ +63.2° (*c* 1.5, $CHCl_3$), R_f = 0.66 (5% methanolic $CHCl_3$). The absolute configuration of the ribofuranoside **9** was found to be L configuration with optical purity of 77% ee by comparison with the natural derivative **14** [$[\alpha]^{20}_D$ −82.2° (*c* 2.0, $CHCl_3$)] derived from D-ribose.[14,15]

Scheme III



(a) O_3, AcOEt, -78°-refl. (b) 1. $(EtO)_2P(O)CH_2CN$, NaH, cat. n-Bu_4NBr, DMSO; 2. BH_3, THF; 3. Ac_2O, Pyr (c) 1. CF_3CO_2H, $(CF_3CO)_2O$, 50°; 2. HCl, MeOH-H_2O (9:1)

(d) 1. $(COCl)_2$, CH_2Cl_2, refl.; 2. t-BuOH, n-BuLi, THF, 0°; 3. NaOH, aq Acetone (e) 1. O_3, MeOH, -78°; 2. MCPBA, CH_2Cl_2; 3. MeOH, p-TsOH

Methyl 2,3-*O*-Isopropylidene-β-D-ribofuranoside (14). A formal inversion of L enantiomers mentioned above to D enantiomers was carried out in the following way. *tert*-Butyl ester **10** was prepared in 91% yield by treatment of **4** with isobutene in the presence of catalytic H_2SO_4 followed by alkaline hydrolysis (0.25 N NaOH, 25 °C, 10 min), showing $[\alpha]^{20}_D$ +49.4° (*c* 1.16, $CHCl_3$) and mp 109–110.5 °C after recrystallization from ether–*n*-hexane (3:2). Successive treatment of the recrystallized **10** as described for **4** above (ozonolysis, Baeyer–Villiger reaction, methanolysis, and reduction) afforded **14** in 32% overall yield from **10**. The synthetic **14** ($[\alpha]^{20}_D$ −77.7° (*c* 1.5, $CHCl_3$) was confirmed to be methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside with optical purity of about 95% ee [lit.[14] $[\alpha]^{25}_D$ −82.2 °C (*c* 2.0, $CHCl_3$)] (Scheme II).

Showdomycin (19). The half-*tert*-butyl ester **10** was considered to be a useful intermediate for the synthesis of various *C*-nucleosides, since it can be easily converted to anomerically func-

(3) A chirally economic synthesis is characterized by recycling of the undesired isomer. See: (a) Kozikowski, A. P.; Floyd, W. C., Kuniak, M. P. *J. Chem. Soc., Chem. Commun.* **1977**, 582. (b) Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1981**, *103*, 3923. (c) Fischli, A.; Klaus, M.; Mayer, H.; Schonholzer, P.; Rüegg, R. *Helv. Chim. Acta* **1975**, *58*, 564. (d) Fischli, A. *Chimia* **1976**, *30*, 4.

(4) (a) Diels, O.; Olsen, S. *J. Prakt. Chem.* **1940**, *156*, 285. (b) Stork, G.; van Tamelen, E. E.; Friedman, L. J.; Burgstahler, A. W. *J. Am. Chem. Soc.* **1953**, *75*, 384.

(5) (a) Compound **2** was first used in the synthesis of *C*-nucleosides by Just et al. Just, G.; Martel, A. *Tetrahedron Lett.* **1973**, 1517. (b) For compound **3**, see: Zefirov, N. S.; Davydova, A. F.; Abdulvaleeva, F. A.; Yuřev, Y. K. *Zh. Obshck. Kim.* **1966**, *36*, 197.

(6) Huang, F.; Lee, L. F. H.; Mittal, R. S. D.; Ravikumar, P. R.; Chain, J. A.; Sih, C. J.; Caspi, E.; Eck, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4144.

(7) Ohno, M.; Kobayashi, S.; Iimori, T.; Wang, Y.-F.; Izawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 2405.

(8) This was purchased from Sigma Co.

(9) All materials described here gave IR, ^1H NMR, and MS spectra consistent with their structures.

(10) The α-keto ester **6** in racemic form was originally considered as a key intermediate for the synthesis of *C*-nucleosides by Just and his co-workers but not easily accessible and obtained by multistep synthesis from a Diels–Alder adduct of furan and methyl nitroacrylate.[5a]

(11) ^1H NMR of **7** ($CDCl_3$/Me_4Si): δ 6.32 (s, 1 H), 5.26 (d, 1 H, *J* = 5.5 Hz), 4.82 (d, 1 H, *J* = 5.5 Hz), 4.79 (s, 1 H), 3.90 (s, 3 H), 3.75 (s, 3 H), 1.51 (s, 3 H), 1.32 (s, 3 H).

(12) H. O. House "Modern Synthetic Reactions", 2nd ed.; Benjamin Cummings: Menlo Park, CA, *1972*, p. 324.

(13) Karrer, P.; Haab, F. *Helv. Chim. Acta* **1949**, *32*, 950.

(14) (a) Leonard, N. J.; Carraway, K. L. J. *Heterocycl. Chem.* **1966**, *3*, 485. (b) For the cleavage to ribose, see: Levene, P. A.; Stiller, E. T. *J. Biol. Chem.* **1934**, *102*, 187.

(15) Although optically crude materials were used in this case to confirm the optical purity of **4** enzymatically formed, the use of recrystallized **7** ($[\alpha]^{22}_D$ +73.8°) was found best for optically pure **9** (>98% ee).

tionalized derivatives of tetrahydrofuran with the desired absolute configuration. Showdomycin[16] was efficiently synthesized in 9 steps from **2** by the present chemicoenzymatic approach (Scheme III).

The recrystallized *tert*-butyl ester **10** was subjected to ozonolysis in ethyl acetate (−78 °C, 30 min), and the resultant solution was warmed at reflux temperatures for 1 h, affording decarboxylated cleavage product **15** in quantitative yield as an oily material. The reaction of **15** with $(EtO)_2POCH_2CN$/NaH in absolute Me_2SO in the presence of n-Bu_4NBr under Ar atmosphere (25 °C, 6 h) affording Wittig product **16** in 61% yield from **10** as a syrup after workup and chromatography on silica gel [$[\alpha]^{20}_D$ −10.7° (c 1.0, $CHCl_3$); R_f = 0.65 (AcOEt–AcOH = 20:1)]. Reduction of **16** with diborane afforded a primary alcohol **17**[9] in 52% yield [$[\alpha]^{22}_D$ −22.2° (c 0.57, $CHCl_3$), R_f = 0.32 (AcOEt–n-hexane = 1:1)]. After acetylation of **17** with Ac_2O (**18**, 96% yield), ring closure was effected with $(CF_3CO)_2O$ (50 °C, 8 h), and removal of the protective groups with HCl in MeOH afforded showdomycin (**19**) in 30% yield from **18**. The product **19** was confirmed to be identical with authentic natural showdomycin in all respects (mixed mp, $[\alpha]_D$, IR, ^1H NMR).[17]

Cordycepin (3′-Deoxyadenosine) (22). The epoxy half-ester **5** was considered to be a chiral starting material for the synthesis of nucleosides having a different sugar moiety. Cordycepin,[18] which belongs to N-nucleosides with 3-deoxyribose moiety, was selected as a synthetic target. The symmetric epoxy diester **3**[5a] was treated with pig liver esterase as described in the hydrolysis of **2** to yield **5** [mp 120–122 °C, $[\alpha]^{20}_D$ −32° (c 0.50, $CHCl_3$)] in quantitative yield (Scheme I). A formal inversion of **5** to **20** was effected by treatment with excess oxalyl chloride followed by esterification[19] with t-BuOLi and alkaline hydrolysis (1 N NaOH, aqueous acetone, 5 °C, 20 min). *tert*-Butyl half-ester **20** was obtained in 56% yield from **5**, showing mp 121–124 °C, $[\alpha]^{20}_D$ +33° (c 0.5, $CHCl_3$). The successive treatment of **20** as described above (ozonolysis, Baeyer–Villiger reaction, and methanolysis) afforded **21** in a fair overall yield. Reduction of **21** with LAH gave exclusively methyl 3-deoxy-β-D-ribofuranoside in 79% yield [$[\alpha]^{20}_D$ −63° (c 0.4, $CHCl_3$)], a known precursor for cordycepin.[18] In order to determine the optical purity of **20**, the 3-deoxyribofuranoside was converted to 3′-deoxynucleoside **22** according to the procedures by Walton et al.[18] Cordycepin synthesized in 12 steps from **3** by the present study showed mp 222–224 °C, $[\alpha]^{20}_D$ −34° (c 0.25, H_2O), and was found to be about 77% ee on the basis of a reported value[18] (Scheme III).

The key features of the present methodology include the following: (1) pig liver esterase efficiently hydrolyzed unsaturated[20] meso compounds **2** and **3** with high optical purity; (2) it was found that half-esters **4** and **5** enzymatically formed correspond to the L series sugar moiety of nucleosides; the half esters were successfully transformed into the D series sugar moiety by esterification and controlled hydrolysis (**4** to **10**, and **5** to **20**); (3) a combination of chirally selective hydrolysis (enzyme process) and decarboxylative ozonolysis directly provided the versatile intermediate **15** suitable for the synthesis of C-nucleosides; (4) highly selective Baeyer–Villiger oxidation made possible to elaborate various types of sugar moiety including L- and D-riboses and 3-deoxyribofuranoside.

Further investigation of the present chemicoenzymatic approach to other C- and N-nucleosides and carbocyclic nucleosides are in progress in our laboratory, and the results will be reported in due course.

Acknowledgment. This work was financially supported in part by Grant-in-Aid for Cancer Research from the Ministry of Education, Science, and Culture of Japan. We express our gratitude to Professor I. Kuwajima of Tokyo Institute of Technology for a generous gift of natural showdomycin.

(16) For recent synthesis of **19**, see: Inoue, T.; Kuwajima, I. *J. Chem. Soc., Chem. Commun.* **1980**, 251 and references cited therein and ref 3b.

(17) Synthetic sample showed $[\alpha]^{23}_D$ +49.1° (c 0.5, H_2O) [lit. $[\alpha]^{22.5}_D$ +49.9° (c 1, H_2O)] and satisfactory combustion data of **19** was also obtained.[9] For the optical rotation, see: Nakagawa, Y.; Kanō, H.; Tsukuda, H.; Koyama, H. *Tetrahedron Lett.* **1967**, 4105.

(18) Walton, E.; Holly, F. W.; Boxer, G. E.; Nutt, R. F.; Jenkins, S. R. *J. Med. Chem.* **1965**, *8*, 659.

(19) Compounds of the epoxy series were found unstable to acidic conditions, resulting in easy cleavage.

(20) The corresponding saturated meso compound derived from furan maleic anhydride was hydrolyzed very slowly with the esterase. For the Diels–Alder adduct, see: Daniels, R.; Fischer, J. L. *J. Org. Chem.* **1963**, *28*, 320.

A New Bridging Ligand, the Hydrogen Oxide Ion ($H_3O_2^-$)

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The hydrated hydroxide has been the subject of many investigations,[1-3] but unlike the hydrated proton, structural data on this unit is scarce and limited. Although the existence of species like $H_3O_2^-$, $H_6O_4^{2-}$, $H_7O_4^-$ etc., was proposed on the basis of spectroscopic results,[1,2] it was only recently that the isolation and structural characterization of the first hydroxide hydrate was reported.[4] The X-ray structure analysis in that work showed the existence of a very short and symmetric hydrogen bond in the hydrogen oxide ion, $H_3O_2^-$. This anion was found to lie on a crystallographic inversion center with an O–O distance of 2.29 (2) Å and linked through hydrogen bonds to four adjacent water molecules. The participation of bridging $H_3O_2^-$ ligands in transition states of some redox reactions was proposed by Dodson et al.[5] There have been no reports of the isolation or structural characterization of stable species containing this ligand.

We wish to report the preparation and X-ray structure determination results of the first transition-metal complex containing $H_3O_2^-$ as a bridging ligand between two metal atoms.

Recently we have reported the synthesis and structure of a new class of metal atom cluster compounds having the general formula $[M_3(\mu_3\text{-}X)_2(O_2CR)_6L_3]^{n\pm}$ (M = Mo, W; X = O, CCH_3; L = H_2O, O_2CR).[6] One such W(IV) compound $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3](BF_4)_2\cdot 5.5H_2O$ was crystallized by elution of the cationic cluster from an ion-exchange column with HBF_4 and slow evaporation of the eluant.[6a] It was shown that the triangular 2+ cation possessed a nearly D_{3h} symmetry with average W–W distance of 2.745 (3) Å and average W–O(H_2O) distance of 2.09 (2) Å. We have found now that if HBr or KBr are used for the elution of this ion or its molybdenum analogue[7] from the ion-exchange column, a new class of compounds are obtained. We describe here three compounds, all having the general formula $[M_3O_2(O_2CC_2H_5)_6(H_2O)_2\text{-}(H_3O_2)\text{-}M_3O_2(O_2CC_2H_5)_6(H_2O)_2]$-

(1) Zundel, G. "The Hydrogen Bond, Recent Developments in Theory and Experiment. Structure and Spectroscopy"; Shuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland Publishing Co.: Amsterdam, 1979; Vol. II, Chapter 15.

(2) (a) Gennick, I.; Harmon, K. M.; Hartwig, J. *Inorg. Chem.* **1977**, *16*, 2241–2248. (b) Harmon, K. M.; Gennick, I. *Ibid.* **1975**, *14*, 1840–1845. (c) Harmon, K. M.; Gennick, J. *J. Mol. Struct.* **1977**, *39*, 39–49.

(3) Joesten, M. D.; Schaad, L. J. "Hydrogen Bonding"; Marcel Dekker: New York, 1974; Chapter 2.

(4) (a) Abu-Dari, K.; Raymond, K. N.; Freyberg, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 3688–3689. (b) Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 2427–2433.

(5) (a) Silverman, J.; Dodson, R. W. *J. Phys. Chem.* **1952**, *56*, 846–852. (b) Dodson, R. W.; Davidson, N. *Ibid.* **1952**, *56*, 866. (c) Hudis, J.; Dodson, R. W. *J. Am. Chem. Soc.* **1956**, *78*, 911–913.

(6) (a) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Kuppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245–3253. (b) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243–244.

(7) $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ is obtained by refluxing $Mo(CO)_6$ in a propionic acid/propionic anhydride mixture for 24 h and diluting the solution with H_2O.

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