164~166°. The chloroacetate (70 mg.) and finely divided potassium iodide (1 g.) were refluxed for 4 hr. in 20 ml. of acetone. Recrystallization of the product from ethanol gave davallyl iodoacetate, needles, m.p. 175~176° (50 mg.). *Anal.* Calcd. for $C_{32}H_{51}O_2I$: C, 64.63; H, 8.65. Found: C, 64.37; H, 8.69.

Bromination of the Enone (XI)——To a boiling solution of 30 mg. of the $\alpha\beta$-unsaturated ketone (XI) in 2 ml. of glacial acetic acid was added 2 drops of bromine in 1 ml. of acetic acid. No absorption of bromine occurred. The starting material was recovered after refluxing the mixture for 2 hr, and allowing it to stand overnight.

The mass spectra were measured at Stanford University and some at Hitachi Co., Naka Laboratories. The authors are grateful to Professor C. Djerassi and Dr. H. Vorbrüggen for discussions and identification of davallene. The studies were carried out in close contact with the studies of fernene,[10] and we acknowledge this close cooperation.

Summary

The structure of davallic acid has been established as shown by I on the basis of chemical reactions and various physico-chemical data. The structure has received support from independent studies.

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131. Hideo Seki, Kenji Koga,*1 Hisayuki Matsuo,*1,*2 Sadao Ohki,*3 Ichiro Matsuo,*4 and Shun-ichi Yamada*1: Studies on Optically Active Amino Acids. V*5. Synthesis of Optically Active α-Aminoalcohols by the Reduction of α-Amino Acid Esters with Sodium Borohydride.

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It is generally accepted that sodium borohydride, a useful reducing agent for aldehydes and ketones, does not reduce carboxylic esters and orthoesters. This facts were shown by many instances in the literatures reported by Brown,[1] Chaikin[2], and other many researchers.[3] However, there are some "abnormal" cases[4~7] in which reduction of ester groups to the corresponding primary alcohols has been observed, especially in the field of sugar chemistry. Wolfrom, *et al.*[5] reported that sugar esters and lactones were reduced by sodium borohydride and other instances[6] were given in this region.

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*5 Presented at the 83rd Annual Meeting of Pharmaceutical Society of Japan, November, 1963, Tokyo. Part IV: This Bulletin, **11**, 1140 (1963).

1) H. C. Brown, E. J. Mead, C. J. Shoaf: J. Am. Chem. Soc., **78**, 3616 (1956).
2) S. W. Chaikin, W. G. Brown: *Ibid.*, **71**, 122 (1949).
3) R. Tschesche, G. Snatzke: Chem. Ber., 88, 1558 (1955); S. M. Kupchan, W. S. Johnson: J. Am. Chem. Soc., 78, 3864 (1956).

Moreover, the reduction of this type was also shown in the case of ketoesters[4] which did not only undergo the reduction of keto group but also that reduction of ester group to give the corresponding diols. The same results were obtained in the case of α-cyanoesters.

Schenker[8] has reviewed many of these instances in his excellent article entitled "Anwendung von komplexen Borhydriden und von Diboran in der organischen Chemie." He suggested that many of the compounds which undergo such abnormal reduction, contains neighboring functional groups, and these groups, in some way, take part in the reductions, although no suggestion was given on the mechanism of this effect. This assumption was visualized by the fact that the reduction of yohimbine afforded yohimbyl alcohol in a good yield.[8]

For our purpose to utilize α-amino acid, we were interested in preparing optically active α-amino alcohol from the corresponding α-amino ester. Lithium aluminium hydride reduction of amino esters by Karrer's method[9] was very elegant but too costful and troublesome for our purpose and then the use of sodium borohydride would be desirable, if possible. However, in the early literatures, we could find only a few reports on the reduction of this type.

Tanaka, *et al.* reported that L-glutamic acid methyl ester[10] and L-aspartic acid methyl ester[11] were reduced by sodium borohydride to afford L-proline and L-homoserine only in poor yields, respectively.

Berlinguet[12] showed that the reduction of ethyl acetamidomalonate and ethyl acetamidocyanoacetate by sodium borohydride, followed by hydrolysis gave DL-serine in 40 ~60% yields in both cases but the reduction of ethyl aminomalonate under the same condition was fruitless.

Schenker's suggestion[8] described above leads us to investigate the sodium borohydride reduction of α-amino esters whose α-amino group would facilitate the ester reduction by its neighboring effect.

In 1963, the present authors[13] reported that L- and DL-phenylalanine ethyl ester hydrochloride were reduced with sodium borohydride in abs. ethanol to give L- and DL-phenylalaninol in excellent yields.

On the basis of this finding, further investigation on the reduction condition and application of this method to other several kinds of α-amino acid esters were carried out to obtain the good results and some findings, with which the present paper concerns.

In order to find out the optical condition, the reduction of L-phenylalanine ethyl ester hydrochloride (L-Phe (OEt)·HCl) was further investigated under various conditions. a) Amounts of sodium borohydride used: On the reduction of L-Phe (OEt)·HCl with various molar ratio of sodium borohydride in boiling abs. ethanol in which the solvolysis

4) H. Heyman, L. F. Fieser: *Ibid.*, **73**, 5252 (1951); Cl. Daesslé, H. Schinz: Helv. Chim. Acta, **40**, 2270 (1957); N. J. Leonard, K. Conrow, R. W. Fulmer: J. Org. Chem., **22**, 1445 (1957); V. Boekelheide, R. J. Windgassen Jr.: J. Am. Chem. Soc., **81**, 1456 (1959). and others in ref. 8).
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7) J. A. Meschino, C. H. Bond: J. Org. Chem., **28**, 3129 (1963); G. W. K. Cavill, F. B. Whitfield: Proc. Chem. Soc., **1962**. 380.
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9) P. Karrer, P. Portmann, M. Suter: Helv. Chim. Acta, **31**, 1617 (1948).
10) M. Tanaka, T. Kishi, S. Kinoshita: Nippn Nogei-Kagaku Kaishi, **34**, 972 (1960).
11) *Idem*: Agr. Biol. Chem. **25**, 678 (1961).
12) L. Berlinguet: Canad. J. Chem., **33**, 1119 (1955).
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rate of sodium borohydride would be comparatively slower as reported by Brown, *et al.*,[14] the results that obtained are shown in Table I.

Reaction was followed by thin-layer chromatography using silica gel as the stationary phase. From Table I, it was revealed that the use of more than 4 moles sodium borohydride afforded the higher yields of L-phenylalaninol, while the yield decreased with less than 3 moles. Therefore, all experiments in this paper were carried out by using 4 moles of sodium borohydride.

Table I. Reduction of L-Phe(OEt)·HCl in abs. Ethanol at the Boiling Point with Various Molar Ratio of Sodium Borohydride

Molar ratio ($NaBH_4$/Ester)	Reaction time (hr.)	Yield (%)	Molar ratio ($NaBH_4$/Ester)	Reaction time (hr.)	Yield (%)
6	24	91	3	16.5	70
6	13	83	2	27	57
4	15	80			

b) Effect of water-addition : As shown in Table I, the use of abs. ethanol as a solvent required the prolonged reaction time for the completion of the reaction. In order to shorten the time, the examination of the effect of water-addition, whose promoting effect on the reaction rate was already reported by Brown and his co-workers.[14]

Reduction of L-Phe (OEt)·HCl in the mixture of ethanol-water of various concentrations at their boiling points was carried out by using 4 moles of sodium borohydride and results thus obtained are summarized in Table II. As was expected, the time

Table II. Effect of Water-addition on the Reduction of L-Phe(OEt)·HCl with 4 moles of Sodium Borohydride

Solvent system	under reflux		with ice-cooling	
	Time (hr.)	Yield (%)	Time (day)	Yield (%)
abs. EtOH	15	80	5	92
50% EtOH	4.5	84	2	84
25% EtOH	4	82		
H_2O	3	61	1	91

required for the complete disappearance of the starting ester on the thin-layer chromatogram was markedly reduced in aqueous solvents in comparison with the case of non-aqueous solvent. In boiling water, although the reduction rate of ester was accelerated, the hydrolysis of the starting ester was accompanied to some extent which was recognized by thin-layer chromatography. In order to restrain the competitive hydrolysis occurred in aqueous solvent, the reduction at low temperature was investigated. Under this condition, it was proved that the ester reduction was preferable to the hydrolysis, even though the reduction rate was markedly retarded as shown in Table II. Moreover, racemization was not observed during the reduction under these reaction conditions.

From the results described above, the following conditions were found to be the most practically suitable for the reduction of L-Phe (OEt)·HCl without racemization :

i) Sodium borohydride more than 4 moles must be used.

ii) The solvent systems, a) 50% ethanol under reflux and b) water with ice-cooling were practically favored.

14) H.C. Brown, K. Ichikawa : J. Am. Chem. Soc., 83, 4372 (1961).

On the basis of this conclusion, the reduction of several optically active α-amino acid esters was carried out.

The starting esters and their hydrochlorides, L-Phe (OEt),[15] L-Try (OEt)·HCl,[16] L-Met (OEt)·HCl,[17] D-Thr (OEt),[18] and L-Ileu (OEt)*[6,19] were prepared by the esterification of the corresponding α-amino acids with abs. ethanol and thionyl chloride in a similar manner as reported previously[13,20] or by the usual method using abs. ethanol and dry hydrogen chloride.

Table III. Reduction of Optically Active Amino Acid Ethyl Esters and Their Hydrochlorides with 4 moles of Sodium Borohydride

Ester	Solvent	Temp. (°C)	Time (hr.)	Yield (%)	Product		$[\alpha]_D$ reported
					m.p. (b.p.)	$[\alpha]_D$ obs. (EtOH)	
L-Phe(OEt)·HCl	50% EtOH	reflux	4.5	84	91~93°	−25.6	−24.7 (EtOH)
	〃	0~10	2 days	84			
L-Phe(OEt)	100% EtOH	reflux	10	87		−24.1	
L-Try(OEt)·HCl	50% EtOH	〃	5.5	39		−18.7	−2.77[a] (EtOH)
	75% EtOH	〃	8	77			
L-Met(OEt)·HCl	〃	〃	9	58	(110~132°/5)	−9.7	(D-) +14.06 (neat)
	〃	0~10	2 days	67			
L-Ileu(OEt)	〃	reflux	5.5	63	(87~89°/10)	−3.6	
D-Thr(OEt)	〃	0~10	2 days	47		+6.4	

a) P. Karrer, *et al.*[24] reported this value −2.77°, but based on their calculation formula in their report, this value seemed to be −27.7°.

As shown in Table III, it was revealed that either esters or their hydrochloride were reduced under the similar condition as in the case of L-Phe (OEt)·HCl described above to afford the corresponding α-aminoalcohols without racemization in fair yields, respectively. Only with L-Met (OEt)·HCl and D-Thr (OEt), lower yields were obtained. This was considered to be due to the higher water-solubility of the reduction products, L-methioninol and D-threoninol, and to their difficulty of the extraction with organic solvent.

Thus, it was revealed that sodium borohydride could reduce the ester having amino group at its α-position with retention of configuration.

Recently, however, Rapoport, *et al.*[21] reported that the reduction of heteroaromatic, aromatic, and aliphatic esters with great excess of sodium borohydride in methanolic solution gave the corresponding alcohol derivatives and deduced that the ester groups were not resistant to reduction by sodium borohydride, although the rate of reduction was much slower than for aldehydes and ketones and it was obvious that no special structural features were necessary for reduction of esters by sodium borohydride to occure at least to some extent. Therefore, there still remained the interesting problem which would be pertinent in the reduction of this type, Schenker's neighboring effect or Rapoport's proposal.

Discussion on this point will be reported in future.

*6 Abbreviation used : L-Try(OEt)·HCl for L-tryptophan ethyl ester hydrochloride; L-Met(OEt)·HCl for L-methionine ethyl ester hydrochloride; D-Thr(OEt) for D-threonine ethyl ester; L-Ileu(OEt) for L-isoleucine ethyl ester.

15) E. Fischer, W. Schöller : Ann., **357**, 14 (1907).
16) C. P. Berg, W. C. Rose, C. S. Marvel : J. Biol. Chem., **85**, 207 (1929).
17) D. Fleš, A. Markovac-Prpić : Croat. Chem. Acta, **29**, 79 (1957).
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19) C. W. Roberts : J. Am. Chem. Soc., **76**, 6203 (1954).
20) M. Brenner, W. Huber : Helv. Chim. Acta, **36**, 1113 (1953).
21) M. S. Brown, H. Rapoport : J. Org. Chem., **28**, 3261 (1963).

Experimental*7

Sodium Borohydride——Obtained from Daiichi Pure Chemical Co., Ltd., and E. Merck A. G.

Starting Materials——The optically active amino acid ethyl esters and their hydrochlorides were prepared by the esterification of the appropriate amino acids with abs. EtOH and $SOCl_2$ in the similar manner described previously by Yamada, *et al.*[13] or the usual method using abs. EtOH and dry HCl.

D-Threonine Ethyl Ester (D-Thr(OEt))——To an ice-cold suspension of 20 g. (0.168 mole) of D-threonine ($[\alpha]_D^{24}$ +28.1° (c=1.147, H_2O)), in abs. EtOH (200 ml.) was added dropwise 30 g. (0.252 mole) of $SOCl_2$ and the resulting mixture was refluxed for 4.5 hr. After the evaporation of EtOH, the oily residue was dissolved in $CHCl_3$ and made alkaline with 10% Na_2CO_3. The organic layer was washed with a small portion of satd. NaCl solution, dried over anhyd. Na_2SO_4 and evaporated to afford pale yellow crystals (13.7 g., 56%). Repeated recrystallizations from ether-petr. ether gave colorless needles of m.p. 52~54°. $[\alpha]_D^{24}$ −0.23° (c=2.584, EtOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 3190, 1728, 1226, 1143, 1027. *Anal.* Calcd. for $C_6H_{13}O_3N$: C, 48.97; H, 8.90; N, 9.52. Found: C, 48.95; H, 8.94; N. 9.26. The reported constants: L-Thr(OEt) m.p. 52~54°, $[\alpha]_D^{20}$ +0.95° (c=5, EtOH).

Reduction——All the reductions were carried out in a similar manner.

L-Phenylalaninol——i) From L-Phe(OEt)·HCl: To a solution of $NaBH_4$ (3.5 g., 0.092 mole) in 50% EtOH (50 ml.) was added dropwise a solution of L-Phe (OEt)·HCl (5.0 g., 0.022 mole, $[\alpha]_D^{21}$ −10.5° (c=1.128, H_2O)) in 50% EtOH (50 ml.). After the resulting mixture was refluxed for 4.5 hr., EtOH was evaporated *in vacuo*. The aqueous solution thus obtained was then extracted with AcOEt, and the extracts were washed with satd. NaCl solution and dried over anhyd. Na_2SO_4. Evaporation of AcOEt under reduced pressure afforded L-phenylalaninol (2.8 g., 84%) as a pale yellow solid of m.p. 85~92°. Recrystallization from ether gave colorless crystals of m.p. 91~93°, $[\alpha]_D^{25}$ −25.6° (c=1.037, EtOH)[22,23], which were identical with the authentic specimen by IR spectra comparison and mixed melting point method.

ii) From L-Phe(OEt): To the solution of $NaBH_4$ (5.2 g., 0.137 mole) in abs. EtOH (210 ml.), was added dropwise a solution of L-Phe(OEt) (5.0 g., 0.026 mole) in EtOH (50 ml.) and the whole was refluxed for 10 hr. After evaporation of EtOH, the residual white solid was again dissolved in H_2O, and aqueous solution was extracted with AcOEt. Worked up as usual to afford L-phenylalaninol (3.4 g., 87%) of m.p. 76~85° as a pale yellow solid. Recrystallization from ether gave colorless needles of m.p. 91~93°, $[\alpha]_D^{23}$ −24.1° (c=1.994, EtOH), whose mixed melting point and IR spectra were identical with those of the authentic specimen.

Acid oxalate: White needles of m.p. 173° (decomp.) from aq. EtOH (Reported m.p.[9] 161~163°). $[\alpha]_D^{24}$ −10.7° (c=0.850, H_2O). IR ν_{max}^{KBr} cm^{-1}: 3400, 3140, 1745, 1050. *Anal.* Calcd. for $C_{11}H_{15}O_5N$: C, 54.77, H, 6.27; N, 5.81. Found: C, 54.89; H, 5.99; N, 5.67.

L-Tryptophanol——A solution of L-Try(OEt)·HCl (3.5 g., 0.013 mole, $[\alpha]_D^{26}$ +22.1° (c=0.778, EtOH)) prepared from L-tryptophan ($[\alpha]_D^{18}$ −33.6° (c=1.050, H_2O)) with abs. EtOH and dry HCl, in 75% EtOH (60 ml.) was added dropwise to a solution of $NaBH_4$ (2.0 g., 0.053 mole) in 75% EtOH (40 ml.) and the whole was refluxed for 8 hr. EtOH was evaporated *in vacuo*, the residue was extracted with ether (ca. 550 ml.), and then ethereal layer was dried over anhyd. Na_2SO_4. Evaporation of ether gave L-tryptophanol (1.9 g., 77%) as an oil of $[\alpha]_D^{15}$ −18.7° (c=5.42, EtOH). IR $\nu_{max}^{Cap.}$ cm^{-1}: 3340, 1040. No absorption band was observed in the carbonyl region of IR spectrum.

Acid oxalate: White needles, m.p. 206.5° (decomp.)[24] from aq. EtOH. $[\alpha]_D^{18.5}$ −25.1° (c=0.976, H_2O). IR ν_{max}^{KBr} cm^{-1}: 3410, 3210, 1744, 1053. *Anal.* Calcd. for $C_{13}H_{16}O_5N_2$: C, 55.71; H, 5.75; N, 10.00. Found: C, 55.89; H, 5.78; N, 9.93.

L-Isoleucinol——A solution of L-Ileu(OEt) (2.0 g., 0.013 mole) prepared from L-isoleucine ($[\alpha]_D^{24}$ +15.4° (c=1.059, H_2O)) with abs. EtOH and dry HCl, in 75% EtOH (30 ml.) was added dropwise to a solution of $NaBH_4$ (1.9 g., 0.050 mole) in 75% EtOH (30 ml.). The mixture was refluxed for 5.5 hr. Working up as above afforded a pale yellow oil (0.93 g., 63%), which was purified by the distillation under reduced pressure to give a colorless oil (0.72 g.), $b.p_{10}$ 87~89°,[25] $[\alpha]_D^{25}$ −3.6° (c=1.776, EtOH). IR $\nu_{max}^{Cap.}$ cm^{-1}: 3330, 1070.

Acid oxalate: Fine needles from EtOH, m.p. 133.5~134° (decomp.). $[\alpha]_D^{24}$ +7.7° (c=1.974, H_2O). IR ν_{max}^{KBr} cm^{-1}: 1730, 1610, 1053. *Anal.* Calcd. for $C_8H_{17}O_5N$: C, 46.37; H, 8.27; N, 6.76. Found: C, 46.61; H, 8.13; N, 6.74.

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*7 All melting points and boiling points are not corrected. IR spectra were measured with Koken DS-301 spectrophotometer and optical rotations were measured with Yanagimoto photomagnetic direct reading polarimeter model OR-20.

22) H. Ôeda: Bull. Chem. Soc. Japan, **13**, 465 (1938). The reported melting point of this compound is 92~94°.

23) J. H. Hunt, D. McHale: J. Chem. Soc., **1957**, 2073; Brit. Pat., 746,058. $[\alpha]_D^{25}$ −24.7° (c=3.1, EtOH) for this compound was reported.

24) P. Karrer, P. Portmann: Helv. Chim. Acta, **32**, 1034 (1949). Reported m.p. 204~205°.

25) O. Vogl, M. Pöhm: Monatsh., **84**, 1097 (1953). Reported $b.p_{10}$ 120~125° for DL-isoleucinol.

D-Threoninol——To an ice-cold solution of $NaBH_4$ (4.1 g., 0.108 mole) in 75% EtOH (60 ml.) was added dropwise a solution of D-Thr(OEt) (4.0 g., 0.027 mole, $[\alpha]_D^{24}$ −0.23° (c=2.584, EtOH) in 75% EtOH (40 ml.). The mixture was stirred with ice-cooling for 2 days, and concentrated to a volume of 10 ml. The precipitate that deposited was filtered off and the filtrate was extracted with ether, and evaporation of ether afforded a viscous oil (520 mg.). The aqueous layer was subjected to further 104 hrs'. continuous extraction with ether, from which an oil (840 mg.) was obtained. Total yield of D-threoninol was 1.36 g. (47%). $[\alpha]_D^{24.5}$ +6.4° (c=1.257, EtOH).

Neutral oxalate: m.p. 188~189° (decomp.), colorless leaflets from 90% EtOH. $[\alpha]_D^{22.5}$ +3.2° (c=1.078, H_2O). IR ν_{max}^{KBr} cm^{-1}: 3300, 3080, 1575, 1066, 1048. *Anal.* Calcd. for $C_{10}H_{24}O_8N_2$: C, 39.99; H, 8.06; N, 9.33. Found: C, 39.99; H, 7.91; N, 9.13.

L-Methioninol——To an ice-cold solution of $NaBH_4$ (1.45 g., 0.038 mole) in 75% EtOH (20 ml.), was added a solution of L-Met(OEt)·HCl (2.0 g., 0.009 mole, m.p. 85~88°, $[\alpha]_D^{25.5}$ +21.8° (c=1.878, EtOH)[26]) prepared from L-methionine ($[\alpha]_D^{24}$ −10.6° (c=1.017, H_2O)), in 75% EtOH (30 ml.) and the whole was stirred with ice-cooling for 2 days and then concentrated *in vacuo* to remove EtOH. The aqueous layer was extracted with $CHCl_3$. Worked up as usual to give L-methioninol as a pale yellow oil (0.85 g., 67%). $[\alpha]_D^{21}$ −9.7° (c=1.481, EtOH).[27] IR $\nu_{max}^{Cap.}$ cm^{-1}: 3400, 1055. No absorption band was observed in the carbonyl region.

Acid oxalate: m.p. 161~161.5° (decomp.), colorless needles from EtOH, $[\alpha]_D^{24}$ +6.4° (c=0.720, H_2O). IR ν_{max}^{KBr} cm^{-1}: 3130, 1722, 1077. *Anal.* Calcd. for $C_7H_{15}O_5NS$: C, 37.32; H, 6.71; N, 6.22. Found: C, 37.59; H, 7.19; N, 6.10.

O,N-Di-*p*-nitrobenzoate: m.p. 171~171.5°,[28] pale yellow needles from EtOH. $[\alpha]_D^{22}$ +5.9° (c=0.372, dioxane)[28]. IR ν_{max}^{KBr} cm^{-1}: 1730, 1643, 1528, 1285, 1135. *Anal.* Calcd. for $C_{19}H_{19}O_7N_3S$: C, 52.55; H, 4.42; N, 9.69. Found: C, 52.41; H, 4.26; N, 9.47.

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Summary

A facile reduction of optically active α-amino acid esters and their hydrochlorides took place with sodium borohydride in ethanol or aqueous ethanol to give the corresponding optically active α-aminoalcohols in fair yields. The reaction conditions were investigated.

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26) ref. 17: Reported m.p. 81~82°, $[\alpha]_D^{20}$ +18.7° (c=2.245, EtOH).
27) R. R. Gebhard, P. Karrer: Helv. Chim. Acta, 38, 915 (1955). Reported $[\alpha]_D^{20}$ +14.06° (neat) for D-methioninol.
28) Ref. 27: Reported m.p. 173~174°, $[\alpha]_D^{22}$ +11.3° (c=1.10, tetrahydrofuran).