1-propanol (*R*(+)-Ⅷa) in a 71% yield as colorless oil, $b.p._{5.5}$ 88~90.5°, α_D^{24} +0.717° (1=0.1, neat)(optical purity 40%[10]). This alcohol gave α-naphthyl urethane derivative (*R*(+)-Ⅷb), m.p. 102.5°, α_D^{23} +5.9° (c=0.988, EtOH). *Anal.* Calcd. for $C_{20}H_{19}O_2N$: C, 78.66; H, 6.27; N,4.59. Found : C, 78.87; H, 6.32; N, 4.58. IR ν_{max}^{KBr} cm^{-1} : 3260, 1688, 1600, 1530. The alcohol (+)-Ⅷa was treated with phosgene in benzene, followed with sodium azide in aq. methanol to afford *R*(+)-2-phenyl-1-propyl azidoformate (*R*(+)-Ⅸ) in a 93% yield, α_D^{23} +0.222° (1=0.1, neat). IR ν_{max}^{Cap} cm^{-1} : 2185(sh), 2140, 1756, 1730, 1230, 1150, 700. The thermal decomposition of *R*(+)-Ⅸ in diphenyl ether[1] at 200±10°, followed by the purification using the procedure as reported previously[1] gave (+)-4-methyl-4-phenyl-2-oxazolidinone ((+)-Ⅶ) in a 4% yield, m.p. 68.5~74.5°, α_D^{25} +43.9° (c=1.026, EtOH). Infrared spectrum of this (+)-Ⅶ in solid state showed that this sample was contaminated with a fair amount of DL-Ⅶ,[*1] but in chloroform it was superimposable with those of DL-Ⅶ[*1] and (+)-Ⅶ obtained from *S*(+)-Ⅳa. Thin-layer chromatography of this sample in two different solvent systems showed a single spot respectively, whose Rf value was as same as those of DL-Ⅶ.[*1] Rf value : 0.2 ($CHCl_3$), 0.6 (hexane-AcOEt=1:1). Recrystallizations of crude (+)-Ⅶ twice gave (+)-Ⅶ with a low optical purity as white plates, m.p. 80.5~81.5°,[*2] $[\alpha]_D^{17}$ +9.3° (c=0.172, EtOH). *Anal.* Calcd. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.91. Found : C, 67.90; H, 6.43; N, 8.11. Infrared spectra of this sample were identical with those of DL-Ⅶ[*1] in solid state and chloroform solution.

From the results obtained above, it has been concluded that the absolute configuration of (+)-α-methylphenylglycine ((+)-Ⅳa) should be shown to be *S*-configuration on the assumption that the thermal decomposition of azidoformate proceeded with the retention of configuration, and this conclusion is in agreement of Cram's proposal. In this case, the retention percentage of the reaction was also nearly 100%. The determination of the absolute configuration of Ⅳa using chemical correlation method is now in progress in our laboratory.

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[*1] DL-Ⅶ was prepared from DL-Ⅳa similarly to (+)-Ⅶ.[7] m. p. 81.5~82.5°. (lit.,[7] m.p. 79.6~80°).

[*2] Mixed melting point with (+)-Ⅶ obtained from (+)-Ⅳa showed m.p. 73.5~78°.

10) E. L. Eliel, J. P. Freeman : J. Am. Chem. Soc., **74**, 923 (1952).

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14(7) 802~804 (1966)]

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Synthesis of Bisanhydroaklavinone

In 1956, Strelitz, *et al.*[1] isolated a pigment antibiotics, aklavine, from Streptomyces. Afterwards, in 1960, Ollis, *et al.*[2] obtained aklavinone (I), the aglycone of the antibiotics, on a mild acid hydrolysis of aklavine and also bisanhydroaklavinone by dehydration of I, and established their structures by the degradative and physical methods. We have prepared methyl 2-ethyl-5,7-dihydroxy-6,11-dioxo-6,11-dihydro-1-naphthacenecarboxylate

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1) F. Strelitz, H. Flon, U. Weiss, I. N. Asheshov : J. Bacteriol., **72**, 90 (1956).

2) W. D. Ollis, J. J. Gordon, L. M. Jackmann, I. O. Sutherland : Tetrahedron Letters, No. 8, 28 (1960).

(II) by the following scheme and confirmed that compound II was identical with bisanhydroaklavinone.

3-Methoxyphthalic anhydride (III)[3] was condensed with methyl 2-ethyl-5-hydroxy-1-naphthoate (IV)[4] in acetylene tetrachloride in the presence of anhydrous aluminum chloride to give the single keto-acid (V, R=H), m.p. 106~107° (IR ν_{max}^{KBr} cm^{-1} : 1724 (C=O), 1689 (C=O), 1623 (C=O)), which was methylated with methyl iodide and potassium carbonate to the keto-ester (V, R=CH_3), m.p. 163~164° (IR ν_{max}^{KBr} cm^{-1} : 1724 (C=O), 1656 (C=O)). Reduction of V (R=CH_3) with zinc powder in aqueous sodium hydroxide solution gave the dicarboxylic acid (VI), m.p. 175~176° (IR ν_{max}^{KBr} cm^{-1} : 1687 (C=O), 1664 (C=O)), which was cyclized by heating in polyphosphoric acid at 100° for 10 minutes to 2-ethyl-11-oxo-5,7-dimethoxy-6,11-dihydro-1-naphthacenecarboxylic acid (VII, R=H), m.p. 247~248° (IR ν_{max}^{KBr} cm^{-1} : 1729 (C=O), 1649 (C=O)).

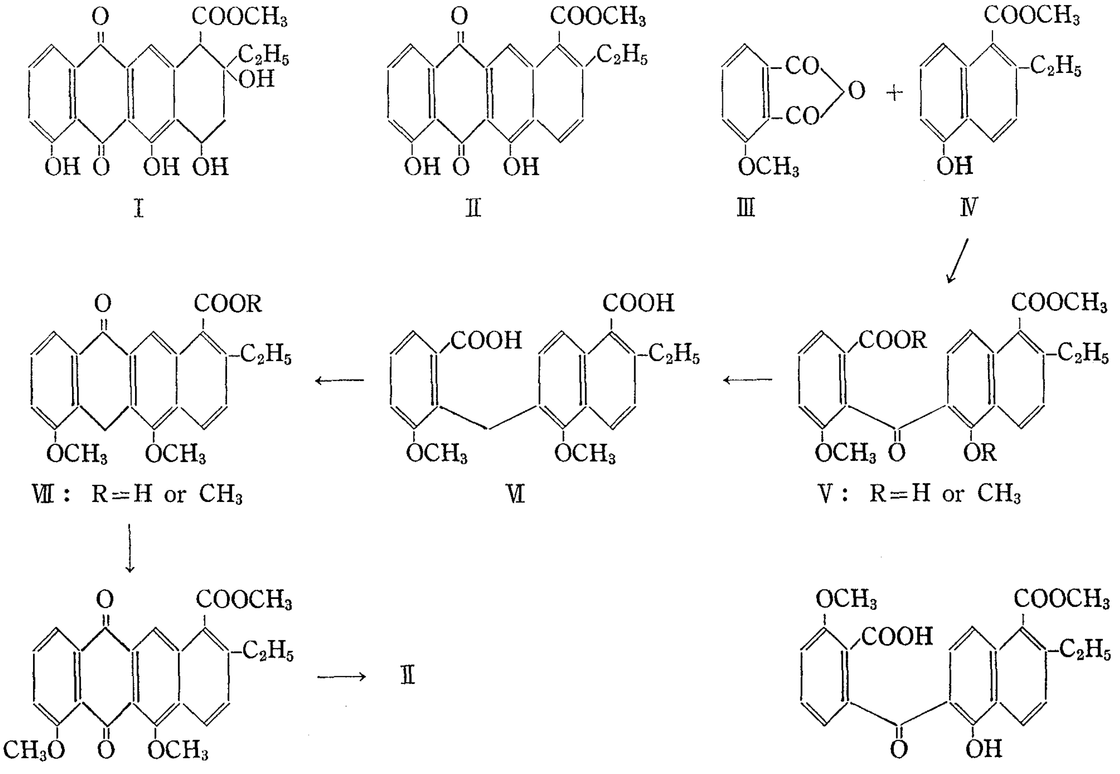

Chart 1.

Methylation of the acid (VII, R=H) with diazomethane and subsequent oxidation[5] of the resulting ester (VII, R=CH_3), m.p. 192~194° (IR ν_{max}^{KBr} cm^{-1} : 1720 (C=O), 1666 (C=O)), with an excess of chromium trioxide in glacial acetic acid gave methyl 2-ethyl-5,7-dimethoxy-6,11-dioxo-6,11-dihydro-1-naphthacenecarboxylate (VIII), bright yellow plates, m.p. 196~197° (IR ν_{max}^{KBr} cm^{-1} : 1727 (C=O), 1669 (C=O), 1609, 1585, 1565 (arom.)). Compound VIII was demethylated[5b] with boron tribromide in methylene chloride at −60° to give methyl 2-ethyl-5,7-dihydroxy-6,11-dioxo-6,11-dihydro-1-naphthacenecarboxylate (II), orange needles, m.p. 234~236° (IR ν_{max}^{KBr} cm^{-1} : 1724 (C=O), 1667 (C=O), 1616 (C=O), 1600, 1572 (arom.); UV λ_{max}^{hexane} mμ ($\varepsilon \times 10^{-4}$) : 242 (4.5), 255 (4.3), 262 (4.8), 279 (1.8), 290 (1.9); λ_{max}^{hexane} mμ ($\varepsilon \times 10^{-4}$) : 445 (1.9), 462 (1.5), 475 (1.6)). The infrared spectrum of this compound was exactly superimposed with that of natural bisanhydroaklavinone, kindly provided by

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[3] E.D. Amstutz, E.A. Fehnel, C.R. Neumoyer : J. Am. Chem. Soc., **68**, 349 (1946).

[4] Z. Horii, T. Momose, Y. Tamura : This Bulletin, **13**, 651 (1965).

[5] cf. *a*) Z. Horii, T. Momose, Y. Tamura : This Bulletin, **13**, 740 (1965). *b*) *Idem* : *Ibid.*, **13**, 797 (1965).

Professor W. D. Ollis. In addition, the presence of a non-chelated quinone carbonyl band[5,6] at 1672 cm^{-1} in the spectrum of II excluded a possibility of the alternative structure (Va) to the product derived from the Friedel-Crafts condensation of III with IV.

All substances mentioned in this paper gave satisfactory elemental analyses.

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6) cf. Z. Horii, T. Momose, Y. Tamura: *Ibid.*, **10**, 1013 (1962).

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On the Triterpenic Constituents of a Lichen, *Parmelia entotheiochroa* Hue.; Zeorin, Leucotylin, Leucotylic Acid, and Five New Related Triterpenoids

In an attempt of comparative study on the chemical constituents of several lichens belonging to *Parmelia* genus, we have isolated six triterpenoids[*1] in addition to known triterpenoids; zeorin[1] (I), leucotylin[2] (II), leucotylic acid[3] (IIIa), a depside atranorin[4] (IV), (Chart 1) and hitherto unelucidated pigment entothein[5] from the title lichen collected at Sugio, Osaka-fu. In this communication, we are presenting the chemical structures of five of these new triterpenoids.

After removing atranorin (yield: 1.1%), which crystallized on concentration of the ether extract of the lichen, the ethereal solution was treated with 5% sodium bicarbonate, 10% sodium carbonate and 10% sodium hydroxide succesively. From sodium bicarbonate soluble part, there was obtained a yellow pigment known by the name of entothein[5] (0.026%). Both sodium carbonate and sodium hydroxide fractions gave a mixture of triterpenic acids, which were separated into two components as their methyl esters by means of methylation (CH_2N_2) and subsequent alumina chromatography giving methyl leucotylate (IIIb) (0.14%) and acid-U methyl ester (V) (0.03%). Furthermore, the remaining neutral fraction has been found to contain seven triterpenoids such as N-1 (0.0016%), N-2 (VI) (0.002%), N-3 (VII) (0.0026%), N-4 (VIII) (0.006%), N-5 (IX) (0.13%), zeorin (I) (0.4%), and leucotylin (II) (0.4%).

The separation of these was accomplished by repeated column chromatography on alumina and silica gel.

[*1] The natural occurrence of these compounds in the title lichen was confirmed by thin-layer chromatography of the crude extract.

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