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.

1) D. H. R. Barton, P. de Mayo, J. C. Orr: J. Chem. Soc., **1958**, 2239; S. Huneck, J-M. Lehn: Bull. soc. chim. France, **1963**, 1702.

2) I. Yosioka, T. Nakanishi: This Bulletin, **11**, 1468 (1963).

3) I. Yosioka, T. Nakanishi, E. Tsuda: Tetrahedron Letters, **1966**, 607.

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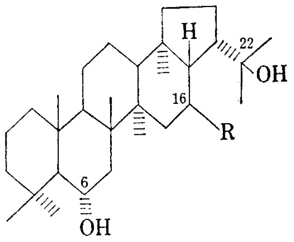
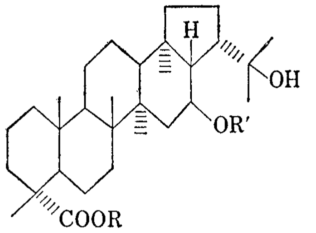
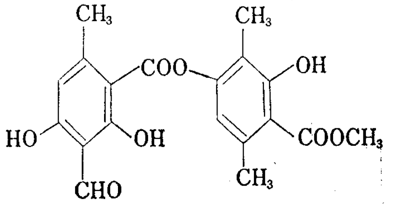
5) M. E. Hale, Jr.: Bryologist, **61**, 81 (1958); C. A., **55**, 702 (1961).



I: R=H zeorin
II: R=OH leucotylin



IIIa : R=R'=H leucotylic acid
IIIb : R=CH_3, R'=H
methyl leucotylate
V : R=CH_3, R'=Ac
Acid-U methyl ester
=methyl 16β-O-acetylleucotylate



IV: **atranorin**

Chart 1.

Acid-U Methyl Ester (V)——$C_{33}H_{54}O_5$, m.p. 176°, $[\alpha]_D$[*2] +95°, IR[*2] cm^{-1} : 3530 (OH), 1740 (OAc), 1715 ($COOCH_3$), 1240~1200, NMR[*2] (τ) : 6.33 ($COOC\underline{H}_3$), 7.91 ($OCOC\underline{H}_3$), 4.75 ($\underline{H}\overset{|}{\underset{|}{C}}$-OAc).

The existence of a tertiary hydroxyl function in the methyl ester was shown by lacking a proton attached to a carbon bearing hydroxyl in its nuclear magnetic resonance (NMR) spectrum and also by acetylation experiment where the hydroxyl was unreacted by ordinary procedure (acetic anydride-pyridine). On 5% potassium hydroxide-methanol hydrolysis, the methyl ester yielded methyl leucotylate (IIIb) thus indicating acid-U methyl ester to be methyl 16β-O-acetylleucotylate.[3] The identity of both compounds was achieved by IR, NMR and mixed m.p. comparisons.

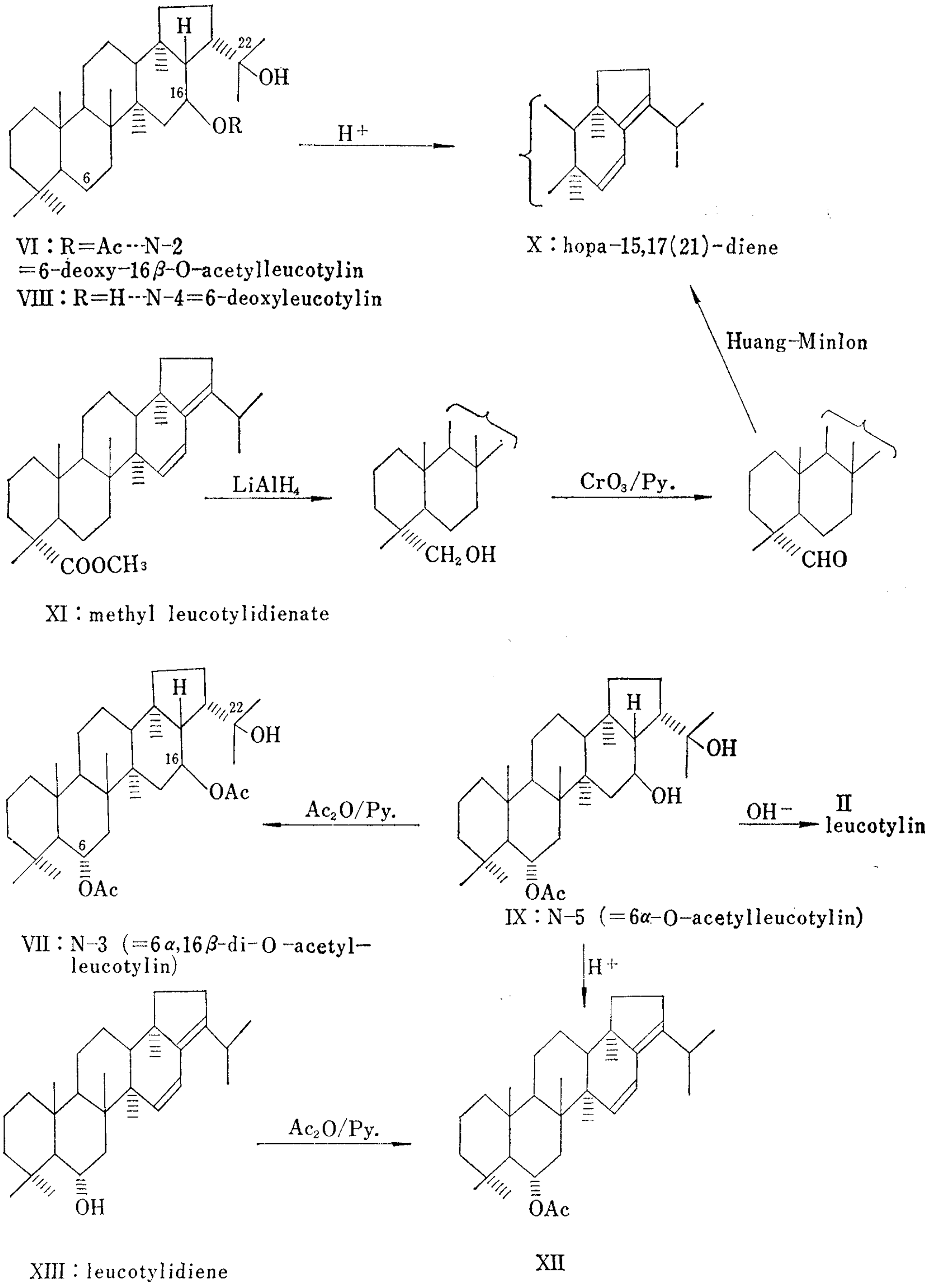
N-2 (VI) and N-4 (VIII)——N-2, $C_{32}H_{54}O_3$, m.p. 228°, $[\alpha]_D$ +52°, IR cm^{-1} : 3550 (OH), 1735, 1240~1200 (br.) (OAc), NMR (τ) : 7.90 ($OCOC\underline{H}_3$), 4.75 ($\underline{H}\overset{|}{\underset{|}{C}}$-OAc); N-4, $C_{30}H_{52}O_2$, m.p. 268°, $[\alpha]_D$ +68°, IR cm^{-1} : 3350 (OH).

On alkaline hydrolysis, N-2 gave N-4, which by reacetylation with acetic anhydride and pyridine produced N-2 again, thus proving N-2 is a monoacetyl derivative of N-4. Treatment of N-4 with 5% hydrochloric acid-ethanol yielded a diene (X), m.p. 152~153°, λ_{max} 243, 252, 261 mμ, $[\alpha]_D$ +90°, which was shown identical (mixed m.p.) with hopa-15,17(21)-diene[6] prepared from methyl leucotylidienate[3] as illustrated in Chart 2. From the biogenetical point of view, the coexistence of N-2, N-4 with leucotylin and its analogs would make it probable to assign structures (VI and VIII) having hydroxylic functions at C-16, C-22 for N-2 and N-4, respectively. A broad signal at τ 4.75 in the NMR spectrum of N-2 could be ascribed to 16α-H as in the case of V. The feasible formation of dienic compound[2,3] would also corroborate this assumption. The assigned structures for N-2 (VI) and N-4 (VIII) correspond to 6-deoxy-16β-O-acetylleucotylin and 6-deoxyleucotylin, respectively.

[*2] Optical rotations, IR spectra were taken in $CHCl_3$, NMR spectra in $CDCl_3$ unless stated otherwise.
6) Y. Tsuda, K. Isobe : Tetrahedron Letters, **1965**, 3337.

N-3 (VII)——$C_{34}H_{56}O_5$, m.p. 232°, $[\alpha]_D$ +109°, IR cm^{-1} (Nujol) : 3400 (OH), 1730, 1245 (OAc), NMR (τ) : 7.90, 7.93 ($2\times OCOC\underline{H}_3$), 4.80 (2H, broad, $2\times \underline{H}\overset{|}{\underset{|}{C}}$-OAc). The NMR spectrum shows two secondary acetoxyl functions in N-3, which on 5% potassium hydroxide-methanol treatment gave leucotylin (Ⅱ), thus indicating N-3 could be 6α,16β-O-acetylleucotylin$^{2)}$ (Ⅶ). The identification of N-3 with Ⅶ was performed by IR, NMR and mixed m.p. comparisons.

N-5 (IX)——$C_{32}H_{54}O_4$, m.p. 225°, $[\alpha]_D$ +36°, IR cm^{-1} : 3400 (OH), 1720, 1250 (OAc), NMR (τ) : 7.95 ($OCOC\underline{H}_3$), 4.80 ($\underline{H}\overset{|}{\underset{|}{C}}$-OAc), 5.90 ($\underline{H}\overset{|}{\underset{|}{C}}$-OH). Acetylation of N-5 with acetic anhydride and pyridine afforded 6α,16β-di-O-acetylleucotylin (Ⅶ), while on alkaline hydrolysis N-5 gave leucotylin (Ⅱ), suggesting N-5 to be a monoacetyl derivative of Ⅱ.



VI : R=Ac…N-2 =6-deoxy-16β-O-acetylleucotylin

Ⅷ : R=H…N-4=6-deoxyleucotylin

X : hopa-15,17(21)-diene

XI : methyl leucotylidienate

VII : N-3 (=6α,16β-di-O-acetyl-leucotylin)

IX : N-5 (=6α-O-acetylleucotylin)

XIII : leucotylidiene

XII

Chart 2.

Quite resemblance of C-methyl signal region in the NMR spectrum*[3] of N-5 with other leucotylin and leucotylic acid derivatives possessing 16β,22-dihydroxyl functions, especially peaks corresponding to methyls attached to C, E rings, would support locating an acetoxyl function of N-5 at C-6.

The acidic treatment of N-5 as for Ⅷ yielded a diene (Ⅻ), $C_{32}H_{50}O_2$, m.p. 221°, IR cm^{-1}: 1730, 1240 (OAc), 1645 (C=C), which was proved to be identical with 6α-O-acetylleucotylidiene prepared from leucotylidiene[2)] (XⅢ) by IR, mixed m.p.

Accordingly, the structure of N-5 was established as 6α-O-acetylleucotylin (Ⅸ).

N-1——$C_{30}H_{50}O$, m.p. 258°, $[\alpha]_D$ −12°, IR cm^{-1}: 1720 (CO), exhibiting negative to tetranitromethane and Zimmermann tests, positive to Liebermann-Burchard color test, is probably a ketonic triterpenoid.

The chemical structures of N-1 and a pigment entothein are under study in our laboratory. It is quite interesting to note that the title lichen contains several triterpenoids having analogous patterns of hydroxylation and acetylation with common hopane skeletons.

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*[3] The NMR analyses in detail concerning to lichen triterpenoids hitherto isolated in our laboratory will be discussed in our full paper.