

DIACETYLPYXINOL, A TRITERPENE ALCOHOL FROM A LICHEN: PYXINE ENDOCHRYSINA NYL

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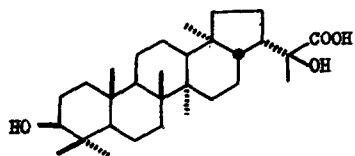
In the previous communication,<sup>1)</sup> we reported the structure of pyxinic acid(I), which was isolated from a lichen: Pyxine endochrysin Nyl. and characteristic by possessing OH function at C-3 of hopane skeleton among the lichen-triterpenoids. Further chemical study on the neutral fraction of the same lichen has led us to isolate a triterpene alcohol named diacetylpixinol. The present paper deals with the chemical evidence supporting the structure II.

Diacetylpixinol(II),  $C_{34}H_{56}O_6$ , mp.  $247^\circ$ ,  $[\alpha]_D +10^\circ (CHCl_3)$ ; IR(mujol,  $cm^{-1}$ ): 3420, 1735, 1245, 1235, 1020; NMR<sup>3)</sup> (100Mc,  $\tau$ ): 9.16(s, 2xMe), 9.13, 9.09, 9.01, 8.76, 8.55, 8.48(all s., 1Me each), 7.99 (2x Ac), 6.53(1H, sextet, J=2.9 & 6.4 cps.), 5.89(1H, t., J=6.4), 5.48(1H, q., J=6.5 & 8.2), exhibited a positive Libermann-Burchard color test and negative to tetranitromethane. On treatment with 5% KOH-MeOH or  $LiAlH_4$ , II gave pyxinol(III),  $C_{30}H_{52}O_4$ , mp.  $225-6^\circ$ ,  $[\alpha]_D +62.8^\circ (CHCl_3)$ ; IR( $CCl_4$ ): 3600, 3430, which lacks acetyl function and shows a diamagnetically shifted quartet at 6.73 $\tau$  (5.48 in II) and all the C-methyl singlets appearing above 8.70 $\tau$  in its NMR spectrum. Acetylation of II with  $Ac_2O-Py.$ ,  $Ac_2O-NaOAc$  or  $Ac_2O-p-TsOH$  yielded the same triacetate(IV),  $C_{36}H_{58}O_7$ , mp.  $180-1^\circ$ , which was also prepared by acetylation of III with  $Ac_2O-p-TsOH$ . These observations suggest that II is a triterpene possessing two acetoxy (a secondary and a tertiary), one secondary hydroxyl and oxygen function presumably of an ether linkage.

The  $CrO_3-Py.$  oxidation of III furnished monoketopyxinol(V),  $C_{30}H_{50}O_4$ , mp.  $184-5^\circ$ , and diketopyxinol(VI),  $C_{30}H_{48}O_4$ , mp.  $174-6^\circ$ , which were further converted by Huang-Minlon reduction to desoxy-pyxinol(VII),  $C_{30}H_{52}O_3$ , mp.  $196.5-7.5^\circ$  and didesoxypyxinol(VIII),  $C_{30}H_{52}O_2$ , mp.  $138.5-140^\circ$  respectively.

On the other hand, the similar oxidation converted II to diacetyl-monoketopyxinol(IX),  $C_{34}H_{54}O_6$ , mp.  $162^\circ$ ; IR: 1708, negative to Zimmermann color test.

The prominent fragment ions, tentatively ascribable<sup>4)</sup> to A,B rings of tetra- or penta-cyclic triterpenes, appearing at m/e 249, 189 of IV and 191 of VII, VIII in the mass spectra suggest that



I Pyxinic acid

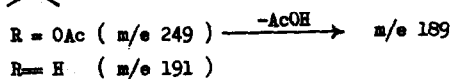
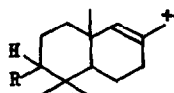
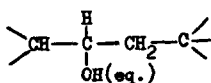
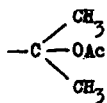


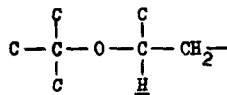
Chart 1



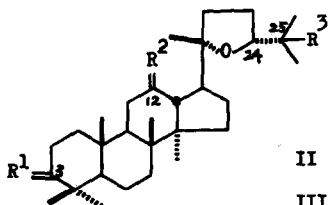
(A)



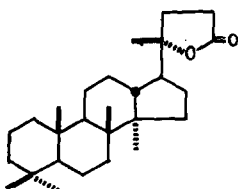
(B)



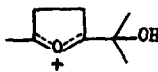
(C)



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	
II	-OAc, ...H	-OH, ...H	OAc	<u>diacetylpyxinol</u>
III	-OH, ...H	-OH, ...H	OH	pyxinol
IV	-OAc, ...H	-OAc, ...H	OAc	
V	=O	-OH, ...H	OH	
VI	=O	=O	OH	
VII	H <sub>2</sub>	-OH, ...H	OH	
VIII	H <sub>2</sub>	H <sub>2</sub>	OH	
IX	-OAc, ...H	=O	OAc	
X	H <sub>2</sub>	H <sub>2</sub>	OAc	
XI	-OCOPhBr(p) ...H	-OCOPhBr(p) ...H	OH	
XIII	-H, ...OH	-OH, ...H	OH	triterpene C



XII



(D)

only one hydroxyl of III locates in A or B ring (Chart 1). A positive Zimmermann color test of V in addition to a characteristic NMR signal pattern at  $5.48 \tau$ <sup>1)</sup> of II confines the location of one secondary acetoxy of II at C-3.

The partial structures in regard to the remaining three oxygen functions of II have been disclosed as follows. A secondary hydroxyl, as the location of which A or B ring is eliminated, may contribute to a partial structure(A) based on the NMR signal pattern at  $6.53 \tau$  of II. A tertiary acetoxy of II, on the other hand, may participate in an acetoxy-isopropyl side chain(B) on the basis of the following observations: (i) Two singlets(3H each) at  $8.55$  and  $8.48 \tau$  of II attributable to methyls attached to a carbon having an oxygen function are diamagnetically shifted (above  $8.70$ ) in the NMR spectrum of III; (ii) The hydroxyl function of didesoxyptyxinol (VIII) (IR:3553) resists the  $\text{Ac}_2\text{O}$ -Py. acetylation under ordinary condition, but is acetylated with  $\text{Ac}_2\text{O}$ -p-TsOH to yield a monoacetate(X), whose NMR spectrum shows two methyl signals at  $8.52 \tau$  similarly in II. Finally, as for the ether linkage, only a single proton is concerned to the system as revealed by the NMR signals such as at  $6.25 \tau$  (1H, t.,  $J=6$ ) in VIII and at  $6.09 \tau$  (1H, t.,  $J=6.6$ ) in X. Furthermore, the signal patterns corroborate to depict the partial structure as (C).

To elucidate the carbon framework of diacetyptyxinol(II), the X-ray analysis has been performed using a di-p-bromobenzoate(XI) as described in the following paper<sup>5)</sup>. The result has enabled us to illustrate the structures of diacetyptyxinol(II) possessing S configuration at  $\text{C}_{20}$  and all the derivatives as shown in this paper.

In addition, a  $\gamma$ -lactone,  $\text{C}_{27}\text{H}_{44}\text{O}_2$ , mp.  $192-5^\circ$ ; IR( $\text{CCl}_4$ ): 1775; NMR: six methyls singlets, lacking a signal due to  $\text{C}_{24}\text{-H}$ , obtained by Kiliani oxidation of VIII, is now formulated unambiguously as XII and the base peaks of  $m/e$  143 in the mass spectra of III, VII, and VIII are attributable to the ion as shown (D)<sup>6)</sup>.

Diacetyptyxinol(II) is the first example of a dammarane triterpene isolated in the lichen family, and pyxinol corresponds to a C-3 epimer of triterpene C (XIII) from *Betula platyphylla* var. *japonica*, which was recently disclosed by Tanaka et al.<sup>6)</sup>.

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#### REFERENCES

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- 2) Satisfactory analytical values were obtained in all compounds given with chemical formulae.
- 3) Unless mentioned otherwise, the NMR spectra were determined in  $\text{CDCl}_3$  solution at 60Mc using

TMS as an internal standard, and the signals were given in  $\tau$  values.

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