Tetrahedron Letters,Vol.24,No.32,pp 3337-3340,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

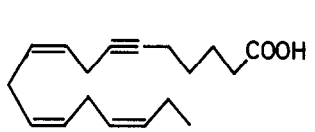
NOVEL CYCLOPENTENONYL FATTY ACIDS FROM MOSSES, DICRANUM SCOPORIUM AND DICRANUM JAPONICUM

Tetsuya Ichikawa, Misuzu Namikawa, Kaoru Yamada,
Kunikazu Sakai*, and Kiyosi Kondo
Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

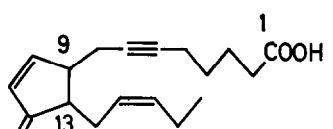
Summary: The novel cyclopentenonyl fatty acids, dicranenone A (III) and dicranenone B_1 (IV), were isolated from Japanese mosses.

Many bryophytes are known to resist to pests, such as insects and pathogenic bacteria. We were interested in this phenomenon and tried to isolate chemical substances from various mosses in expectation of finding a new physiologically active compound. Conventional bioassay technique using Piricularia oryzae (rice-blast) as pathogen was applied for identification of the desired compounds. In the course of this study, besides several known compounds, novel fatty acids having cyclopentenone ring similar to prostanoids and jasmonoids have been isolated from Dicranum scoporium (Kamoji-goke) and Dicranum japonicum (Shippo-goke). We report herein the isolation and structural identification of these novel cyclopentenonyl fatty acids named as dicranenone A (III) and dicranenone B_1 (IV).[1)]

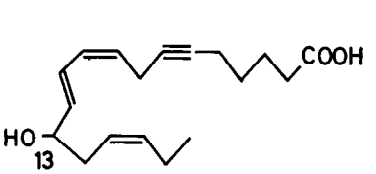
Dicranenoe A (III): This compound was found in the ether extract (oil, 6.7 g) of fresh Dicranum scoporium (460 g). The major components in the ether extract were 9(Z),12(Z),15(Z)-octadecatrien-6-ynoic acid (I) and its 15,16-dihydro derivative II[2)], and as a minor component, 13-hydroxy-9(Z),11(E)-15(Z)-octadecatrien-6-ynoic acid (V)[3)] was identified. Dicranenone A[4)] was obtained by repeated column chromatography on silica-gel and active charcoal



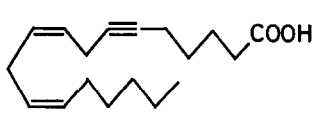
I



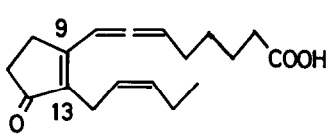
III



V



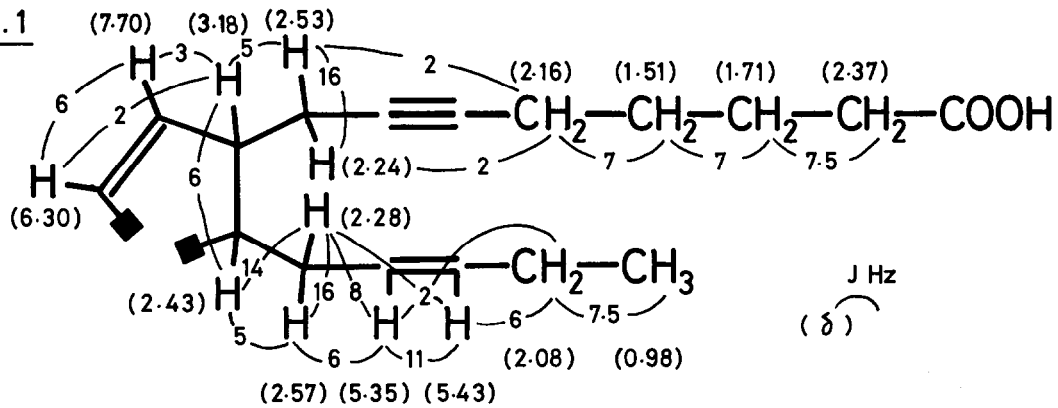
II



IV

as colorless oil (50 mg). The molecular formula of the compound was firstly assigned as $C_{18}H_{24}O_3$ by high resolution mass spectrometry (Obsd. m/z 288.1691; Calcd. 288.1723) and then following functional groups were deduced from IR and NMR spectra; 1,2-disubstituted triple bond (IR 2350 cm^{-1}, ^{13}C-NMR δ 77.2, 83.5), a cis-double bond (IR 730 cm^{-1}, ^{13}C-NMR δ 126.7, 133.3), a carboxyl group (IR 3200 cm^{-1}; also by chemical evidence of the formation of methyl ester by treatment of III with CH_2N_2), and a conjugate cyclopentenone ring system (IR 1710, 1590 cm^{-1}, UV λ_{Max}^{MeOH} 217 nm (ε 8,550), ^{13}C-NMR δ 133.4, 165.4, 210.1). The detailed decoupling analysis using 400 MHz ^{1}H-NMR spectroscopy revealed the relationship of all protones in dicranenone A as shown in Figure 1.

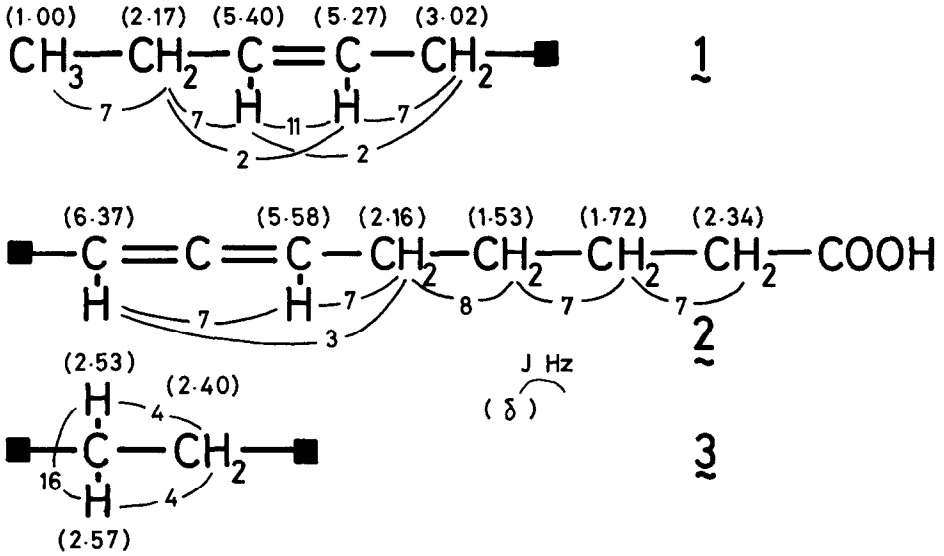
Fig. 1



On the basis of these spectral evidences, the structure III was assigned to dicranenone A. The structure III has two chiral centers on cyclopentenone ring at C-9 and C-13. Their stereochemical correlation is expected to be analogous to those in prostaglandin A series by comparison of $[\alpha]_D$ and CD[5].

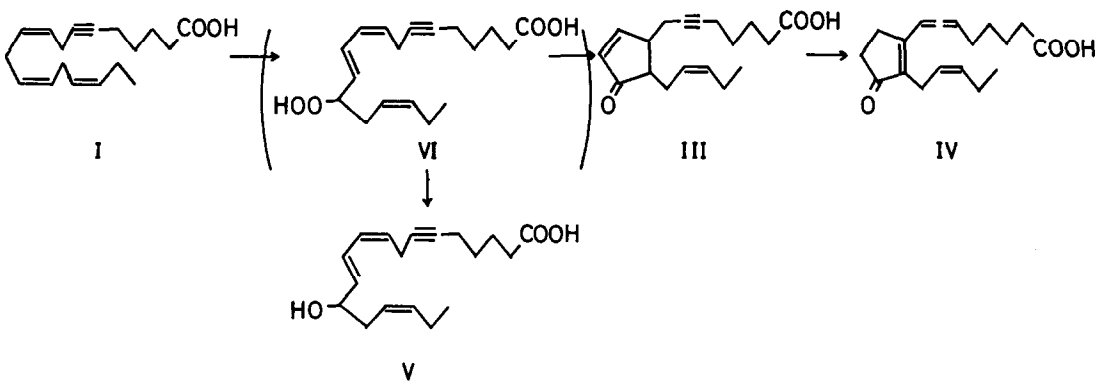
Dicranenone B_1 (IV)[4]: This compound was isolated in a similar manner as that of dicranenone A from the ether extract of fresh Dicranum japonicum. As only 1.4 mg of the compound could be obtained in pure form from 0.3 g of the crude extract, strucural analysis was performed principally by 400 MHz ^{1}H-NMR. Besides dicranenone B_1, a small amount of dicranenone A and other unsaturated fatty acids (I and II) were also observed in the ether extract. High resolution mass spectrum showed that dicranenone B_1 had the same molecular formula, $C_{18}H_{24}O_3$ (Obsd. m/z 288.1702; Calcd. 288.1723), with that of dicranenone A. IR spectrum of the compound (1710 cm^{-1}) strongly suggested the presence of a cyclopentenone ring. Decoupling analysis of ^{1}H-NMR revealed that it contained three independent partial structures 1, 2 and 3 (Fig. 2). The partial structure 1 is identical with that of C-13 side chain in dicranenone A. Protones in structure 3 showed ABX_2 coupling pattern and their chemical shifts and coupling constants well fitted for two methylenes in cyclopentenone ring. The functional groups in partial structure 2 were deduced by comparisone with C-9 side chain in dicranenone A. The coupling constant (7 Hz) between olefinic protons and a streching absorption peak at

Fig. 2



1950^{-1} clearly indicated the presence of an allenic bonding. From these observations and evidences, the structure IV and its 10-oxo isomer remained as the possible structure of dicranenone B_1 and we tentatively assigned the structure IV for dicranenone B_1 by analogy with dicranenone A (III) without stereochemical analysis around allenic configuration. We assume that dicranenone B_1 is not an artificial product formed from III during isolation procedure, because IV can not be detected in the ether extract of Dicranum scoporium.

Recently, Zimmerman et al.[6] showed the existence of a series of enzymes including hydroperoxide cyclase in flaxsees and many other plants, which performed the in vitro synthesis of 8-[2-(2(Z)-pentenyl)-1-oxo-4-cyclopenten-3-yl]octanoic acid[7] (12-oxophytodienoic acid) from linolenic acid. On the basis of their observation, we can rationalize the biosynthesis of these dicranenones in mosses as follow. The unsaturated fatty acid I which was observed as the major component in D. scoporium and D. japonicum would firstly be attacked by a lipoxygenase to produce an n-6 hydroperoxide intermediate VI,



which would then be cyclized to dicranenone A by the action of the cyclase. The 13-hydroxy fatty acid V corresponding to the intermediate VI could be detected as a minor component in D. scoporium. Although there is no precedent for the isomerization of III to IV, the process would also be catalyzed by an enzyme.

Acknowledgements: We are grateful to Dr. H. Inoue of National Science Museum and Prof. N. Takagi of Aichi-gakuin University for the classification of mosses. We also thank to Prof. N. Otake and Prof. H. Seto of Institute of Applied Microbiology, the University of Tokyo for the measurement of 400 MHz ^{1}H-NMR spectroscopy, and to Prof. T. Tsuyuki and Dr. T. Murae of Faculty of Science, the University of Tokyo for the measurement of high resolution mass spectroscopy.

References and notes:

1) Both dicranenone A and B_1 showed antibiotic activity against Piricularia oryzae and Bacillus cereus at 60 and 400 ppm levels, respectively.

2) These acetylenic fatty acids (I and II) have already been isolated from other mosses: Fontinalis antipyretica, G. R. Jamieson and E. H. Reid, Phytochemistry, 1976, 15, 1731; Dicranum clongatum, P. Karunen and H. Mikola, ibid., 1980, 19, 317; Ceratodon purpureus, Fontinalis pyretica, Sulacomnium turugidum, Brium tortifolium, and Dicranum montanum, B. Andersson, W. H. Anderson, J. R. Chigault, E. C. Ellison, J.L. Gellerman, J. H. Hawkins, and H. Schlenk, Lipids, 1974, 9, 506.

3) The 13-hydroxy fatty acid V has not been found previously and was assigned by 400 MHz ^{1}H-NMR and ^{13}C-NMR; ^{1}H-NMR, 2.37(t,J=7.5;C-2) 1.74(tt,J=7.5,7.5; C-3) 1.54(tt,J=7.5,7.5;C-4) 2.19(tt,J=7.5,2.5;C-5) 3.04(dtd,J=7.5,2.5,1.5; C-8) 5.46(dtd,J=11,7.5,<1;C-9) 6.02(dtd(J=11,1.5,-;C-10) 6.50(dddd,J=15,1, <1,-;C-11) 5.75(dd,J=15,6.5;C-12) 4.23(dtd,J=6.5,6.5,1;C-13) 2.34(ddd,J= 7.5,6,2;C-14) 5.35(dtt,J=11,7,1;C-15) 5.57(dtt,J=11,7,2;C-16) 2.07(qdd,J= 7.5,7,1.5;C-17) 0.97(t,J=7.5;C-18).

4) These cyclopentenonyl fatty acids could be detected easily by TLC, on which they appeared as an yellow spot when the plate was treated with celium sulfate.

5) Dicranenone A $[\alpha]_D^{25.5}$ +191° (c 0.3, MeOH), PGA_2 $[\alpha]_D$ +140°; CD dicranenone A $[\theta]_{320}^{MeOH}$ -4.3×10^3, $[\theta]_{225}^{MeOH}$ $+8.2\times10^4$, PGA_2 $[\theta]_{320}^{MeOH}$ -5.2×10^3, $[\theta]_{230}^{MeOH}$ $+5.25\times10^4$: For $[\alpha]_D$ of PGA_2, E.J.Corey and G.Moinet, J. Am. Chem. Soc., 1973, 95, 6831 and for CD of PGA_2, O. Karrer, Recueil, 1969, 88, 1070.

6) B. A. Vick, P. Feng, and D. C. Zimmerman, Lipids, 1980, 15, 468 and references cited in.

7) Recently, 12-oxophytodienoic acid has been found in a kind of chrysanthemun (Chrumolaema morii) by F. Bohlmann et al., Phytochemistry, 1982, 21, 125.

(Received in Japan 4 April 1983)