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ISOPRELAUREFUCIN, NEW BROMO COMPOUND FROM LAURENCIA NIPPONICA YAMADA*

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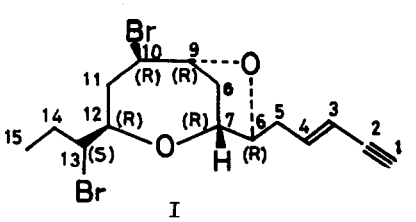
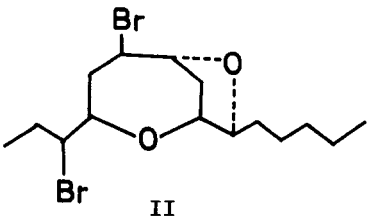
An extensive study of neutral essential oil from Laurencia nipponica Yamada (Rhodomelaceae; Urasozo in Japanese) led to isolation of a new bromo ether in 0.001% yield. It is designated as isoprelaurefucin and assigned structure I on the basis of chemical and spectral evidence and biogenetical point of view described below.

Isoprelaurefucin (I), oil, $(\alpha)_D$ -54.4°, $C_{15}H_{20}O_2Br_2$, m/e 394, 392 and 390 (M^+), 329, 327 and 325 ($M^+ - C_5H_5$), 271 and 269 ($M^+ - C_3H_6Br$). The UV (λ_{max} 224 (ε 13,200), λ_{inf} 232 (ε 9,800), 219 (ε 11,800) and 209 nm (ε 8,700)) and IR spectrum (ν_{max} 3300, 2130, 1620, 1196, 1178, 1139, 1107, 970 and 876 cm^{-1}) showed the presence of conjugated enyne and ether functions. The NMR spectrum displayed signals due to acetylenic proton at τ 7.34 (1H, d, J=2 Hz), two vinyl protons at τ 4.48 (1H, dd, J=16, 2) and 3.85 (1H, dt, J=16, 7) and methyl protons at τ 8.92 (3H, t, J=7). In addition, unresolvable six-proton multiplet appeared in the region of τ 6.4-5.2, which are ascribed to protons on carbons bearing bromine and ether oxygen. Isoprelaurefucin is, therefore, shown to be a bicyclic ether having $CH_3-CH_2-\underset{Br}{CH}-$, $CH{\equiv}C-CH{=}CH-$ and $-\underset{Br}{CH}-$ and these were further supported by following observations.



I

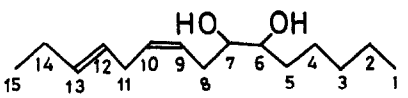


II

I consumed 3 moles of hydrogen over PtO_2 in ethanol to give hexahydroisoprelaurefucin (II), $(\alpha)_D$ -12.5°, $C_{15}H_{26}O_2Br_2$, m/e 400, 398 and 396 (M^+), 329, 327 and 325 ($M^+ - C_5H_{11}$), 277 and 275 ($M^+ - C_3H_6Br$); ν_{max} 1197, 1180, 1140 and 1108 cm^{-1}. The NMR spectrum exhibited two methyl signals at τ 9.07 (3H, br. t) and 8.93 (3H, sharp t, J=7), while the original signals due to acetylenic and olefinic protons in I disappeared.

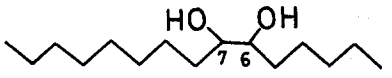
Treatment of hexahydroisoprelaurefucin (II) with Zn-acetic acid in ethanol gave unsaturated glycol (III), $C_{15}H_{28}O_2$, which was then hydrogenated to the corresponding saturated glycol (IV), $C_{15}H_{32}O_2$. These compounds, III and IV, were identical with the authentic samples derived from laurefucin (V)**(1) (H_2/PtO_2, $SOBr_2$ and Zn-AcOH) in all respect and consequently, antipode of III' and IV' derived from laureatin (2) and isolaureatin (3).

On the other hand, treatment with ethanolic potassium hydroxide effected dehydrobromination of II yielding an unsaturated monobromo ether (VI), $(\alpha)_D$ -58.5°, $C_{15}H_{25}O_2Br$, m/e 237 (M^+ - Br); τ 9.03 (3H, br. t), 8.42 (3H, d, J=5, $\underline{CH_3}$-CH=CH-), τ 5.5-6.6 (5H, m), 4.5-5.1 (2H, m, vinyl proton). On hydrogenation in acetic acid over Pd-C (5%), VI afforded two saturated compounds in the ratio of 1:3. The former was hexahydromonodebromoisoprelaurefucin (VII), $(\alpha)_D$ -65.4°, $C_{15}H_{27}O_2Br$, m/e 320 and 318 (M^+), 277 and 275 ($M^+ - C_3H_7$), 239 (M^+ - Br), 167 ($M^+ - C_5H_{11}$ - HBr); τ 9.10 (3H, br. t), 9.06 (3H, br. t), 5.5-6.5 (3H, m), and the other was hydrogenolysis product, hydroxy bromoether (VIII), $(\alpha)_D$ +9.45°, $C_{15}H_{29}O_2Br$, m/e 222 (M^+ - HBr - H_2O), 157 ($M^+ - C_6H_{12}Br$), 151 ($M^+ - C_5H_{11}$ - HBr - H_2O), 139 ($M^+ - C_6H_{12}Br - H_2O$); τ 9.16 (6H, br. t), 6.60 (1H, m), 6.10 (3H, m), ν_{max} 3420, 1180, 1130, 1088 and 960 cm^{-1}.



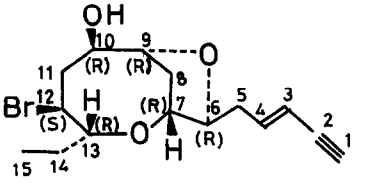
III C-6,C-7; R

III' C-6,C-7; S

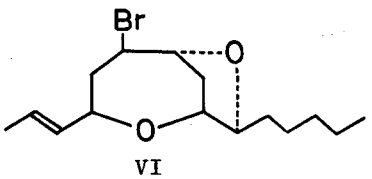


IV C-6,C-7; R

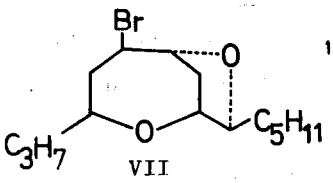
IV' C-6,C-7; S



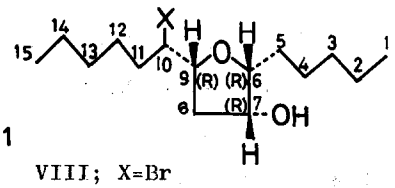
V



VI



VII



VIII; X=Br

IX; X=H

Treatment of VIII with Raney Ni gave hydroxy ether (IX), mp. 36-38°, $(\alpha)_D$ -11.1°, $C_{15}H_{30}O_2$, m/e 171 ($M^+ - C_5H_{11}$), 157 ($M^+ - C_6H_{13}$); ν_{max} 3630, 1134, 1088 and 1034 cm^{-1}; τ 9.13 (3H, br. t) and 9.10 (3H, br. t), which was identical with authentic sample derived from laurefucin (V) (1) (H_2/Pt, $SOCl_2$, Zn-AcOH, H_2/Pt and Raney Ni) in all respect.

These above results show that the structure of isoprelaurefucin are represented by formula I, in which the configurations at C-6, C-7 and C-9 were confirmed from those of hydroxy cyclic ether (IX) and the others at C-10, C-12 and C-13 were proposed by chemical properties and biogenetical point of view as follows.

It has been presumed that the bromo cyclic ether compounds, laurencin (4,5), laureatin (2), isolaureatin (3) and laurefucin (V) (1) isolated from the same species, Laurencia nipponica Yamada, would be formed from the same precursor, hexadeca-4,7,10,13-tetraenoic acid via laurediol (6) and noteworthily, in the all case the stereochemical relationship between C-12 and C-13 having either bromine or ether oxygen has been decided to be erythro and additionally, R-configuration to carbon bearing ether oxygen and S-configuration to carbon bearing bromine.

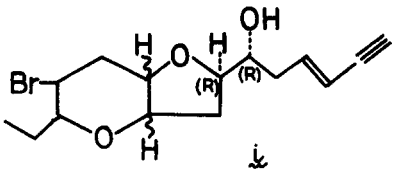
Moreover, 12-trans double bond of III should be arised from erythro configuration on Zn-acetic acid degradation of II, which might be considered to proceed through E_2 mechanism to 1,2-haloether oriented as trans. Therefore, R-configuration would be assigned to C-12 and S to C-13 in I.

Similarly, on the basis of the biogenetical point and chemical observation the stereochemical relationship concerning C-9 and C-10 would be presumed to be threo and consequently, the configuration of C-10 are assigned as R.

References

* Part XXII of "Constituents of marine plants". Part XXI; E. Kurosawa, A, Furusaki, M. Izawa, A. Fukuzawa and T. Irie, Tetrahedron Letters, in press.

** In previous paper (1), the structure of laurefucin, $C_{15}H_{21}O_3Br$, has been represented by formula i on the basis of chemical and spectral properties. However, from the result of crystallographic study and chemical experiments afterwards, the formula i had to be revised to V. The details will be reported in near future.



i

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(2) T. Irie, M. Izawa and E. Kurosawa, Tetrahedron Letters, 2091 (1968); Tetrahedron, 26, 851 (1970); See also part XXI of this series.

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