

オニヒトデからC30ステロール、ゴルゴスタノールの分離

誌名	日本水産學會誌
ISSN	00215392
著者	金沢, 昭夫 手島, 茂夫 富田, 茂夫 安藤, 哲夫
巻/号	40巻10号
掲載ページ	p. 1077-1077
発行年月	1974年10月

Short Paper

Gorgostanol, a Novel C₃₀ Sterol from an Asteroid, *Acanthaster planci**1

Thirty years ago, a C₃₀ sterol was isolated from the gorgonian, *Plexaura flexuosa*, and named gorgosterol. In 1970, gorgosterol was reported as an unique C₃₀ sterol possessing a cyclopropane ring at C(22)–C(23) by HALE *et al.*¹⁾ Furthermore, as cyclopropane-containing sterols, 23-demethylgorgosterol²⁾ and acansterol³⁾ have been isolated from coelenterates and asteroids, respectively. On the other hand, SMITH and GOAD⁴⁾ have demonstrated that asteroids are capable of synthesizing Δ⁷-cholesterol from cholesterol via cholestanol. The authors attempted to clarify the occurrence of gorgostanol (saturated C₃₀ sterol) which is presumed as an intermediate in the bio-conversion of gorgosterol (Δ⁵-C₃₀ sterol) into acansterol (Δ⁷-C₃₀ sterol) by asteroids.

An unknown compound (comp. Y) was isolated by silver nitrate-impregnated silicic acid (AgNO₃-SiO₂) column chromatography and preparative GLC from *Acanthaster planci* collected at Aguni Island in Okinawa. Comp. Y was assumed to be a saturated C₃₀ sterol from the relative retention time (RRT) (2.39) to cholesterol in GLC on 1.5% OV-17 and from the mobility on AgNO₃-SiO₂ column chromatography. The mass spectrometry of comp. Y (acetate) gave the molecular ion peak (M⁺) at m/e 470 and other prominent peaks at m/e 427 (M⁺-C₅H₇), 410 (M⁺-60), 372 (M⁺-C₇H₁₄), 358 (M⁺-C₈H₁₆), 344 (M⁺-C₉H₁₇-1H), 339 (M⁺-C₈H₁₆-60), 315 (M⁺-R-2H, R=side chain), 312 (M⁺-C₇H₁₄-60), 298 (M⁺-C₈H₁₆-60), 285 (M⁺-C₉H₁₇-60), 283 (M⁺-C₉H₁₇-2H-60), 257 (M⁺-R-60), 255 (M⁺-R-2H-60), 215 (M⁺-R-42-60), and 213 (M⁺-R-2H-42-60). The presence of molecular ion peak indicated that comp. Y is not a Δ⁵-steryl acetate. Since the peaks at m/e 315, 257, 255, 215, and 213 are characteristic of sterols with an unsaturated side chain⁵⁾ and a saturated steroid nucleus, it was considered that the side chain of comp. Y is composed of C₁₁H₂₁ (Fig. 1). The prominent peaks at m/e 358 and 298 were ascribed to the cleavage of a cyclopropane ring in the side chain.¹⁻³⁾ Furthermore, the peaks at m/e 372 and 312 indicated the presence of a cyclopropane ring located at C(22)–C(23).³⁾ The sterols with double bonds at C(23) and C(22) exhibited fragment ions of M⁺-C(20)–C(22) and M⁺-C(20)–C(22)–1H, respectively,⁵⁾ but comp. Y gave two

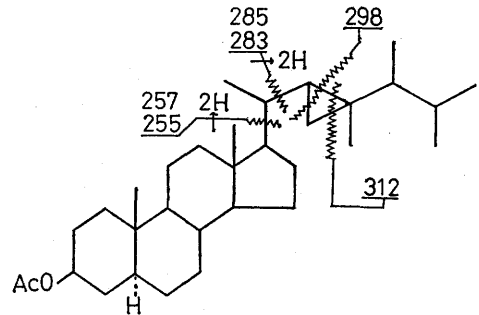


Fig. 1 Gorgostanol

fragment ions of M⁺-C(20)–C(22) and M⁺-C(20)–C(22)–2H. The RRT and mass spectrum of comp. Y were identical with those of gorgostanol derived by hydrogenation of gorgosterol isolated from the coelenterate, *Cladiera cligitulata*.⁶⁾ From these results, it was concluded that comp. Y is gorgostanol.

In coral reefs, *A. planci* takes the corals containing gorgosterol as a diet and can convert dietary Δ⁵-sterol into Δ⁷-sterol. Gorgostanol isolated from *A. planci* may be an intermediate in the biosynthesis of acansterol from gorgosterol, and this could be the first case where gorgostanol was isolated from the natural source.

Akio KANAZAWA,*2 Shin-ichi TESHIMA,*2
Shigeo TOMITA,*2 and Tetsuo ANDO*2
Faculty of Fisheries, University of Kagoshima,
Kagoshima, Japan

References

- 1) R. L. HALE, J. LECLERCQ, B. M. TURSCH, C. DJERASSI, R. A. CROSS, Jr., A. J. WEINHEIMER, K. GUPTA, and P. J. SCHEUER: *J. Am. Chem. Soc.*, **92**, 2179–2180 (1970).
- 2) F. J. SCHMITS and T. PATTABHIRAMAN: *ibid.*, **92**, 6073–6074 (1970).
- 3) Y. M. SHEIKH, C. DJERASSI, and B. M. TURSCH: *Chem. Comm.*, 217–218 (1971).
- 4) A. G. SMITH and L. J. GOAD: *Febs Lett.*, **12**, 233–235 (1971).
- 5) S. G. WYLLIE and C. DJERASSI: *J. Org. Chem.*, **33**, 305–313 (1968).
- 6) A. KANAZAWA, S. TESHIMA, and T. ANDO: *Comp. Biochem. Physiol.*, in press.

Received July 20, 1974

*1 オニヒトデから C₃₀ ステロール, ゴルゴスタノールの分離

*2 金沢昭夫・手島新一・富田茂夫・安藤哲夫: 鹿児島大学水産学部