metal derivatives with such macrocyclic di- and polyacetylenes provide a novel means for investigating mechanisms of acetylene di- and oligomerizations; further studies of this type are in progress in this laboratory.

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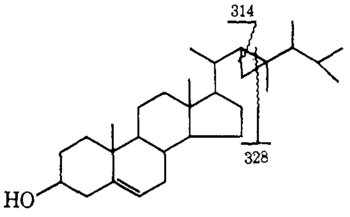
## New Marine Sterol Possessing a Side Chain Cyclopropyl Group: 23-Demethylgorgosterol[1]

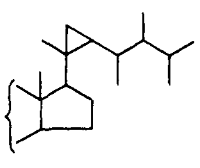
*Sir:*

A recent report[2] emanating from several laboratories showed that the marine sterol, gorgosterol,[3] possesses a biogenetically unprecedented side chain including the unusual features of carbon substitution at positions 22 and 23 and a cyclopropane ring located at either C-22,23 or C-20,22 as shown in **1** or **2**, respectively. An X-ray diffraction analysis[4] of $3\beta$-bromogorgostene has subsequently shown that gorgosterol is (22*R*,23*R*,24*R*)-22,23-methylene-23,24-dimethylcholest-5-en-$3\beta$-ol, in agreement with the nonstereochemical formula **1**. Discovery of the cyclopropane ring in gorgosterol was cited[2] as the first evidence in support of the postulate[5] that cyclopropanes may be intermediates in the introduction of methyl groups into the side chain of sterols, although it was also emphasized[2] that cyclopropanation might be only a terminal step in the biosynthesis of gorgosterol. We wish to report the isolation of a new marine sterol for which mass spectral and nmr data support a structure which includes a cyclopropane moiety bridging positions 22 and 23 of the sterol side chain but lacks the methyl group at C-23 present in gorgosterol.

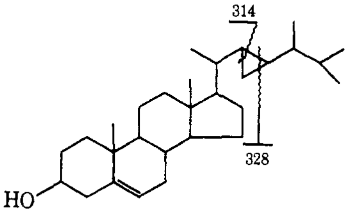
The new sterol was isolated by gas-phase chromatography (2% OV-17)[6] from the complex mixture of sterols, including gorgosterol, extracted from either of the coelenterates *Gorgonia flabellum* L.[7a] or *G. ventilina* L.[7a,b] The recrystallized sterol, mp 162–163°, $C_{29}H_{48}O$ (high-resolution mass spectrometry[8]), exhibits a rotation, $[\alpha]^{21}{}_{D}$ $-34.5°$, in the range characteristic of $3\beta$-hydroxy-$\Delta^5$-sterols.[9] A conventional C-19 steroid nucleus is indicated for this sterol by the series of peaks found at *m/e* 299–301, 271–273, 255–257, 231, 229, 217, 215, and 213 which are characteristic of the common sterols with an unsaturated side chain.[10] The presence of fragment ions at *m/e* 369 ($M^+ - C_3H_7$), 351 [$M^+ - (C_3H_7 + H_2O)$], and 341 ($M^+ - C_5H_{11}$) support the formulation of the terminal portion of the side chain as a $-CH(CH_3)CH(CH_3)_2$ moiety. The base peak in the mass spectrum of the new sterol is found at *m/e* 314 ($C_{22}H_{34}O$) and a second odd-electron fragment (relative intensity 32%) appears at *m/e* 328-($C_{23}H_{36}O$). The base peak in the spectrum of gorgosterol[2,11] also occurs at *m/e* 314 and is ascribed[2] to a cleavage of the cyclopropane ring as shown in **1**. Alternate fragmentation of the cyclopropane ring as shown in **1** would give rise to an *m/e* 328 ion. The occurrence of a *m/e* 328 peak in the spectrum of both gorgosterol,[11] **1**, and **3** coupled with the fact that nmr data (see below) exclude the C-20,22 positions for the cyclopropane ring in **3** leads us to conclude that the new C-29 sterol is 23-demethylgorgosterol.



**1**



**2**



**3**

The two C-24 ethylidene sterols, fucosterol and $\Delta^5$-avenasterol ($C_{29}H_{48}O$), would also be expected[10,12] to give rise to intense *m/e* 314 ions, but these sterols were excluded from structure considerations by nmr data (see below) and by the failure to obtain any low molecular weight carbonyl compounds upon attempted ozonolysis of the new sterol. Furthermore the infrared spectrum of **3** lacked the absorption bands at 12.14 and 12.30 $\mu$ characteristic of the 24-ethylidene sterols.[12]

The 220-MHz nmr spectrum[13] of **3** exhibits signals at $\delta$ 0.20 (2 H, distorted triplet,[14] $J \simeq 6$ cps), 0.28–0.41

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(1) Chemistry of Coelenterates. XXII. Part XXI: F. J. Schmitz and E. D. Lorance, *J. Org. Chem.*, in press.

(2) R. L. Hale, L. Leclercq, B. Tursch, C. Djerassi, R. A. Gross, Jr., A. J. Weinheimer, K. Gupta, and P. J. Scheuer, *J. Amer. Chem. Soc.*, **92**, 2179 (1970).

(3) W. Bergmann, M. J. McLean, and D. J. Lester, *J. Org. Chem.*, **8**, 271 (1943); L. S. Ciereszko, M. A. Johnson, R. W. Schmidt, and C. B. Koons, *Comp. Biochem. Physiol.*, **24**, 899 (1968); K. C. Gupta and P. Scheuer, *Steroids*, **13**, 343, (1969).

(4) N. C. Ling, R. L. Hale, and C. Djerassi, *J. Amer. Chem. Soc.*, **92**, 5281 (1970).

(5) E. Lederer, *Biochem. J.*, **93**, 449 (1964); E. Lederer, *Quart. Rev., Chem. Soc.*, **23**, 453 (1969).

(6) Separation can also be effected on OV-225 and HI-EFF 8BP. We are grateful to Drs. H. H. Wotiz, S. Clark, and Mr. R. Okerholm at Boston University Medical School for their assistance in evaluating the effectiveness of several stationary phases for accomplishing this separation.

(7) (a) F. M. Bayer, "The Shallow-Water Octocorallia of the West Indian Region," Martinus Mijhoff, The Hague, Netherlands, 1961, pp 259 and 262. (b) We thank Dr. A. J. Weinheimer for specimens of *G. ventilina*.

(8) Kindly provided by personnel in Dr. K. Biemann's laboratory, Massachusetts Institute of Technology.

(9) W. Bergmann, *Comp. Biochem.*, **3**, Part A, 113 (1962).

(10) B. A. Knights, *J. Gas. Chrom.*, 273 (1967); S. G. Wyllie and C. Djerassi, *J. Org. Chem.*, **33**, 305 (1968).

(11) (a) We thank Dr. R. Grigsby, Texas A&M University, College Station, Texas, for the spectrum of gorgosterol, mp 183–184°, isolated by preparative gc of the sterol mixture from *G. flabellum;* (b) R. A. Gross, M.S. Thesis, University of Oklahoma, Aug 1969.

(12) (a) R. B. Bates, A. D. Brewer, B. A. Knights, and J. W. Rowe, *Tetrahedron Lett.*, 6163 (1968); (b) J. P. Dusza, *J. Org. Chem.*, **25**, 93 (1960).

(13) Kindly determined by Mr. Robert B. Bradley through arrangement with Dr. U. Weiss at the National Institutes of Health. All spectra were obtained in pyridine-$d_5$ solution unless otherwise noted.

(broad unresolved multiplet, *ca.* 1 H), and 0.56 ppm (*ca.* 3 H, unresolved multiplet) consistent with the presence of a cyclopropane moiety bearing four hydrogens and two additional protons absorbing at unusually high field. Gorgosterol[2] and 9,11-secogorgost-5-ene-3,11-diol-9-one[15] also exhibit high-field ($\delta$ ∼0.27 ppm) noncyclopropyl proton absorption; other instances of high-field absorption by methylene protons proximate to cyclopropane and epoxide rings have also been reported.[16] Irradiation[17a] at $\delta$ 0.56 ppm (100 MHz) changes the apparent distorted triplet at $\delta$ 0.20 ppm to what appears to be a broadened doublet, $J \simeq 7$ Hz.[17b] Further decoupling experiments ($CDCl_3$) revealed that the broad signal at $\delta$ 3.35 ppm (1 H), ascribable to a proton attached to a carbon bearing oxygen, was coupled to the lowest field portion of the allylic proton absorption in agreement with the $3\beta$-hydroxyl-$\Delta^5$ partial structure suggested by rotational data (see above). Also consistent with the $3\beta$-hydroxy-$\Delta^5$ structure and a normal steroid nucleus is the presence of only one vinyl hydrogen absorption ($\delta$ 5.33 ppm, 220 MHz, $CDCl_3$) and two quaternary methyl signals, $\delta$ 0.66 and 1.09 ppm. Doublet methyl signals were observed at $\delta$ 0.91 ($J \simeq$ 6.5 Hz), 0.94 ($J \simeq$ 6.5 Hz), 0.99 ($J \simeq$ 6.0 Hz), and 1.01 ppm ($J \simeq$ 6.0 Hz) and, since mass spectral evidence cited above supports a C-19 nucleus, these four secondary methyl groups must be part of the side chain. The structure **3** which we propose for the C-29 sterol is compatible with all of the above data. The nearly identical chemical shifts observed for the cyclopropyl methylene protons strongly suggest *trans* substitution for that ring since this configuration would provide essentially equivalent chemical shielding of these protons.[18] Further efforts are under way to clarify this point as well as to determine the absolute configuration of **3**.

Although it is possible that 23-demethylgorgosterol is a biosynthetic dead end, this sterol may be an intermediate in the biosynthesis of gorgosterol from a $\Delta^{22}$ precursor. The latter possibility provides further stimulation of our ongoing search for other new sterols related to gorgosterol and 23-demethylgorgosterol.

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(14) Multiplicity description is rendered difficult by virtue of the fact that these protons conform to an AA'XX' combination which can display a complex pattern; *cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon, New York, N. Y., 1965, p 392 ff.

(15) Private communication from Dr. A. J. Weinheimer of data presented at IUPAC Meeting, Riga, Latvia, June 1970.

(16) *Cf.*, for example, R. S. Boikess and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 343 (1963); P. R. Jefferies, R. S. Rosich, and D. E. White, *Tetrahedron Lett.*, 1853 (1963).

(17) (a) We are grateful to the Joelco Co., Medford, Mass., for carrying out the decoupling experiments; acquisition of decoupling data was rendered difficult by the limited amount of sample available for spectral analysis. (b) The converse double-irradiation experiments are as yet inconclusive due to the partial overlap of the lower field cyclopropyl absorption with the C-18 methyl and one of the unidentified upfield hydrogen resonances.

(18) D. E. Minnikin, *Chem. Ind.* (*London*), 2167 (1966).

(19) Recipient of a National Institutes of Health Special Fellowship (GM 13941) while on sabbatical leave at Woods Hole Oceanographic Institution (1969–1970) from the University of Oklahoma; to whom correspondence should be addressed.

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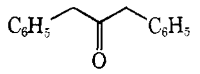
## Photochemistry of Dibenzyl Ketone

*Sir:*

Because the reported[1] photolability of dibenzyl ketone (**1**) seemed inconsistent with its inclusion in a table[2] of potential triplet photosensitizers, we were prompted to investigate the photochemistry of this compound. The following unusual results have emerged: (1) photodecarbonylation in solution is very efficient and proceeds from the triplet state, (2) the lifetime of this triplet state is shorter than that of the singlet, and (3) the triplet energy of **1** is considerably higher than the reported value of 72.2 kcal.



**1**

By comparison of the rate of gas evolution from **1** with that from 2,3-diazabicyclo[2.2.1]heptene-2, whose nitrogen quantum yield is known[3] to be unity, it was determined that $\Phi_{CO}$ is 0.7 at 313 nm in benzene at 30°. This number must be taken as a minimum however, since a uv spectrum of the irradiated solution showed enhanced absorption in the 300-nm region. The cause of this absorption is not presently known; however, since we have confirmed that CO is produced in 100 ± 1% yield,[1] it must be due either to a compound which loses CO or to one produced in very small amounts.

In order to determine the nature of the excited state undergoing decarbonylation, quenching studies with two dienes were carried out. The results shown in Figure 1 indicate that 1,3-cyclohexadiene decreases the efficiency of CO formation more than it inhibits ketone disappearance. This effect, which was also noted in more concentrated solutions of 1,3-pentadiene, is attributed to capture of short-lived phenylacetyl radicals by diene. Robbins and Eastman[4] have reported capturing phenylacetyl radicals using a stable nitroxide free radical as scavenger.

The fact that dienes inhibit the disappearance of starting material is strong evidence for quenching of an electronically excited state. Although this state would traditionally be taken as a triplet, recent studies[5–8]

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(1) G. Quinkert, K. Opitz, W. Wiersdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963).

(2) W. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(3) B. Solomon, T. Thomas, and C. Steel, *ibid.*, **90**, 2249 (1968).

(4) W. K. Robbins and R. H. Eastman, *ibid.*, **92**, 6077 (1970).

(5) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(6) T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, **91**, 5898 (1969).