been observed to react rapidly to Dry Ice temperature (−78°).[5] We are investigating the conversion of the methyl sulfinylation products of **9** (for NMR data, see footnote 6) to β-ketosulfinates. Mixtures containing some methyl sulfinates were obtained upon reaction of **1**, R = CH_2CH_2CN, or 1-hexene[7] with $CH_3F{\cdot}SbF_5$ in SO_2.

The reverse ene reaction Scheme II, occurred upon basic hydrolysis of sulfinates **2a** and **2b**, followed by acidification and extraction with CCl_4. The extracts gave clean NMR spectra identical with those of solutions quantitatively prepared from distilled samples of vinyl halides. Yields, given in Scheme II, were based on NMR and GC analyses of the extracts and the corresponding standard solutions.

Currently there is considerable interest in the use of sulfoxide and sulfone activating groups in synthetic procedures, including alkylations.[8] Conditions required for removal of the sulfur activating group limit the scope of such procedures, however. We are exploring the possibility that comparable synthetic procedures may be based on the introduction and removal of sulfinate ester groups via the reactions of Schemes I and II.

Acknowledgment. Support by the National Science Foundation is gratefully acknowledged (Grant GP 30683).

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(3) For **2a:** Anal. Calcd for $C_4H_7ClO_2S$: C, 31.07; H, 4.56; Cl, 22.92; S, 20.73. Found: C, 31.24; H, 4.63; Cl, 22.74; S, 20.82. For **2a,** δ, ^1H NMR, CCl_4, internal TMS, 3.65 (d, CH_2S) 3.75 (s, CH_3O), 5.45 (s, $=CH_2$); ^{13}C NMR, neat, internal TMS, 58.6 (CH_3O), 68.2 (CH_2S), 121.8 ($=CH_2$), 131.6 ($=CCl$).

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(6) NMR data for the methylsulfination product of **9,** X = CH_3, is as follows: ^1H, CCl_4, internal TMS, δ, 0.93 (t, CH_3), 1.45 (m, CH_2), 2.05, (q, CH_2), 3.62 (s, CH_2S), 3.72 (s, CH_3O), 5.65 (t, $=CH$); ^{13}C, $CDCl_3$, ppm from internal TMS, 13.57 (CH_3), 21.85 (CH_2), 27.91 (CH_2), 54.67 (OCH_3), 61.15 (CH_2S), 127.06 ($=CH$).

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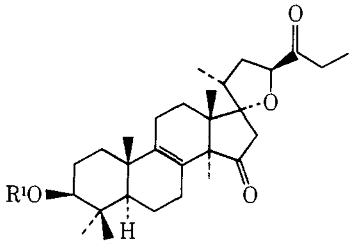
Received February 20, 1975

Eucosterol, a Novel Spirocyclic Nortriterpene Isolated from Bulbs of *Eucomis* Species

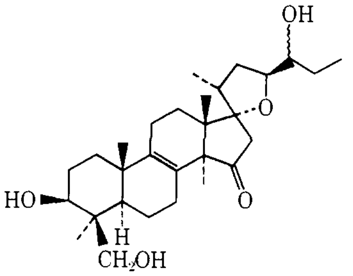
Sir:

During the past years a new class of natural products, the homoisoflavanones, has been discovered in the bulbs of several species of *Eucomis* (Liliaceae).[1-4] We now have isolated a hitherto unknown substance, which we name eucosterol (**1**), from the neutral extracts of the bulbs of *Eucomis autumnalis* (Mill.) Chitt., *Eucomis punctata* l'Hérit., and of a botanically undefined *Eucomis* species (ca. 60 mg per kilogram of undried bulbs). Eucosterol (**1**) proved to be a nortriterpene possessing a furanoid spirocyclic system as novel structural element. It crystallized as colorless needles from acetone, mp 221-223°; $[\alpha]^{25}D$ +20.4 ± 2° (chloroform). The molecular formula, $C_{29}H_{44}O_5$, was deduced from high resolution mass spectrometry.[5]

The positive Liebermann-Burchard test[6,7] and the formation of a 2,4-dinitrophenylhydrazone suggested the presence of a steroid or triterpene containing a double bond, a carbonyl, and hydroxyl groups. These results were supported by the ir spectrum (KBr) which exhibited absorptions at 1710 and 1728 cm^{-1} (C=O); 3290 and 3350 cm^{-1} (OH), and the uv spectrum with maxima at 290 (log ε 1.72) and 196 nm (log ε 3.77) (ethanol). The latter absorption suggested the presence of a tri- or tetrasubstituted double bond[8] and a cyclopentanone system. The 100-MHz ^1H NMR spectrum ($CDCl_3$) of **1** indicated the presence of four tertiary methyl groups (singlets at 0.96, 0.98, 1.28, and 1.41 ppm) of one secondary methyl group (doublet at 1.15 ppm, J = 7 Hz) and of an ethyl group attached to a carbonyl function (triplet at 1.09 ppm and quartet at 2.51 ppm, J = 7 Hz). The elimination of $C_3H_5O^+$ in the mass spectrum confirmed the latter assignment. The presence of one primary and one secondary hydroxyl group was detected in the ^1H NMR spectrum in $(D_3C)_2SO$ (multiplet at 4.08 ppm and doublet at 4.98 ppm, respectively). Accordingly, acetylation of **1** yielded a diacetate **2,** $C_{33}H_{48}O_7$, mp 168-170°; M^+ at m/e 556). Treatment of **1** with $CuSO_4$ in acetone[9] yielded the *O*-isopropylidene derivative **3,** $C_{32}H_{48}O_5$, mp 203-204°, M^+ at m/e 512. This result, together with the findings that eucosterol (**1**) is not oxidized by KIO_4, indicated a 1,3-relationship of the two hydroxyl groups. Catalytic hydrogenation of **1** with PtO_2 in glacial acetic acid gave dihydroeucosterol **4,** $C_{29}H_{46}O_5$, mp 245-246°, $[\alpha]^{27}D$ +37 ± 2° (chloroform), M^+ at m/e 474. The ir spectrum showed only one carbonyl group at 1731 cm^{-1}. Upon treatment of **1** with CrO_3 in H_2SO_4-acetone, the keto aldehyde **5** ($C_{29}H_{40}O_5$, mp 205-213, $[\alpha]^{26}D$ +1.8 ± 2° (chloroform), M^+ at m/e 468) was formed. In the ir it exhibited several absorption bands between 1700 and 1735 cm^{-1}. The signal at 9.3 ppm (singlet) in the 100-MHz ^1H NMR spectrum is assigned to the aldehyde group.



1, $R^1 = R^2 = H$
2, $R^1 = R^2 = Ac$
3, $R^1 = R^2 = C(CH_3)_2$
6, $R^1 = H$; $R^2 = p\text{-}BrC_6H_4SO_2-$



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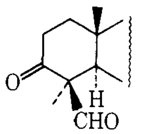

5

Treatment of eucosterol **1** with *p*-bromobenzenesulfonyl chloride in pyridine at 25° yielded the *p*-bromobenzene-

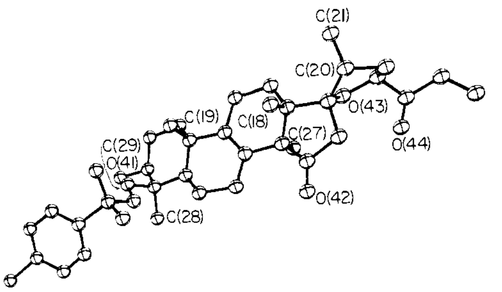

Figure 1. A perspective drawing of the *p*-bromobenzenesulfonate derivative of eucosterol (**1**). Hydrogens are not shown, and a standard triterpene numbering system is employed.

sulfonate **6**, colorless plates from benzene-*n*-hexane of mp 158-159°, $M^+ - C_6H_4BrO_3S$ at *m/e* 454.

These crystals proved to be suitable for a structural analysis by X-ray diffraction belonging to the common monoclinic space group $P2_1$ with $a = 18.61$ (2) Å, $b = 7.84$ (1) Å, $c = 12.09$ (2) Å, and $\beta = 106.31$ (3)°. The calculated density for two molecules of $C_{35}H_{53}O_7SBr$ per unit cell was 1.31 g/cm^3. All unique diffraction maxima with $\theta \leq 55°$ were collected on a fully automated four-circle diffractometer using θ-2θ scans. A total of 2317 reflections were collected in this manner of which 1823 were judged observed after correction for Lorentz, polarization, and background effects ($F_o \geq 3\sigma(F_o)$).

A three-dimensional Patterson synthesis[10] was readily deconvoluted to yield both the bromine and sulfur atomic positions. Subsequent electron density syntheses revealed all 44 nonhydrogen atoms. Full-matrix least-squares refinement, followed by a difference electron density synthesis showed all nonmethyl hydrogens. Full-matrix least-squares refinements with anisotropic temperature factors for nonhydrogen atoms, and anomalous scattering corrections for bromine and sulfur lowered the conventional discrepancy index to 0.061 and 0.062 for the structure and its mirror image, respectively.[11] A careful remeasurement of the ten most enantiomorph sensitive reflections also showed that the absolute configuration depicted correctly predicted the difference ten out of ten times. The final X-ray model is shown in Figure 1. All bond distances and angles generally agree well with accepted values. See paragraph at end of paper regarding supplementary material.

The absolute configuration is that anticipated for triterpenes. The A/B and C/D ring junctions are trans and there is a C(8)-C(9) double bond. The most novel feature is the spiro-fused furanoid system at C(17).

Nortriterpenes which lack the carbon atom at the terminus of the side chain are rare. The biogenetic implications of the eucosterol structure will be considered in a later publication.

Acknowledgments. The investigations in Basel were supported by the "Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung" (Projects No. 2.48.68, 2.460.71, and 2.675.72), which is gratefully acknowledged.

Supplementary Material Available. The fractional coordinates (Table I), bond distances (Table II), and important bond angles (Table III) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3518.

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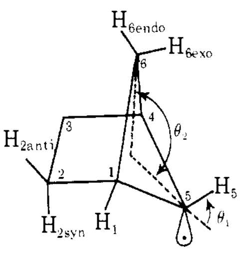
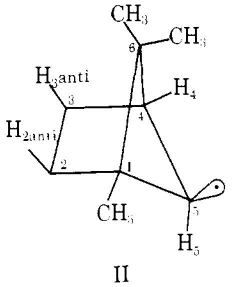
Electron Spin Resonance Study of Bicyclo[2.1.1]hex-5-yl Radicals

Sir:

The bicyclo[2.1.1]hex-5-yl radical is of interest with respect to the geometry around the radical-center carbon atom and the stereoselective delocalization of the odd electron. In this communication we report electron spin resonance (ESR) spectra and stable configurations of the bicyclo[2.1.1]hex-5-yl (I) and the 1,6,6-trimethylbicyclo[2.1.1]hex-5-yl (II) radicals.



I



II

An ESR spectrum shown in Figure 1A was observed during photolysis of bis(bicyclo[2.1.1]hexane-5-carbonyl) peroxide[1] in cyclopropane[2] at −90°. Figure 1B shows the spectrum of the lowest field group of absorptions which was obtained by seven accumulations.[3] The spectra were analyzed as two sets of doublets (26.8 and 9.42 G) split into 1:4:6:4:1 quintets (0.76 G) further into 1:3:3:1 quartets of 0.50 G. Wiberg and his coworkers[1c] reported that the thermolysis of *tert*-butyl bicyclo[2.1.1]hexane-5-peroxycarboxylate in cymene gives bicyclo[2.1.1]hexane (via I) with a fairly high yield without skeletal rearrangement. When a cyclopropane solution of a mixture of the diacyl peroxide and nitrosodu-