four compounds. The nmr spectrum of the 2-norbornyl cation as the hexafluoroantimonate salt has been observed in SbF_5–liquid SO_2 solution;[5] it was noted that both the 1- and 7-norbornyl cations rapidly rearranged to the more stable 2-norbornyl cation at −10°. Thus, it is probable that the gaseous $C_7H_{11}^+$ ions formed upon electron impact from the four norbornyl bromides are identical, and that the values in Table I reflect the k/k' ratios.

Additional data obtained with the isomeric 2,3-dibromo- and 2,3-bromochloronorbornanes indicate that the more facile loss of *exo*-Br relative to *endo*-Br is general for the norbornyl system.[6] These and further studies will be described in the full article.

Acknowledgment. The mass spectrometer was purchased by Wayne State University with funds from a National Science Foundation Chemical Research Instrument grant.

(5) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*,86, 5679 (1964).

(6) D. C. DeJongh, S. R. Shrader, and N. A. LeBel, to be published.

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The Isolation and Structure of Echinodol, a Triterpene Acetate

Sir:

Echinodontium tinctorium Ellis and Ev. (Polyporaceae) is a wood-rotting fungus commonly found on conifers, particularly in the Northwest. According to French[1] the plant has been used as a bactericidal agent by the Wasco Indians, and preliminary tests of crude material also indicate tumor-inhibiting activity.[2] Petroleum ether extraction of the dried fungus afforded a good yield of crude material, shown by tlc to consist of at least ten components. Careful chromatography on alumina or repeated recrystallizations afforded the major component, Ia, named echinodol, in pure form.

Echinodol, $C_{32}H_{50}O_4$,[3] mp 236–238°, $[\alpha]^{25}D$ +48°, $\lambda_{max}^{CHCl_3}$ 3605, 3450 (broad), 1735, and 1240 cm^{-1}, was clearly an hydroxy acetate, confirmed by its nmr spectrum (Table I, and three-proton singlet at δ 2.01) and further chemical transformations. Acetylation gave the diacetate Ib, $C_{34}H_{52}O_5$,[4] mp 270–271°, $[\alpha]^{25}D$ +51°, which showed no hydroxyl group even when the infrared spectrum was taken using a concentrated solution. Saponification or lithium aluminum hydride reduction afforded the diol Ic, $C_{30}H_{48}O_3$, mp 228–229°, $[\alpha]^{25}D$ +47°, which showed no carbonyl band in the infrared. The above data suggest the presence of one ether linkage in these compounds. The nmr spectra of these compounds all showed the presence of one vinyl hydrogen, confirmed by catalytic reduction to a dihydro derivative, $C_{32}H_{52}O_4$, IIa, mp 186–187°, which formed a diacetate IIb, $C_{34}H_{54}O_5$, mp 178–180°. The presence of an isopropylidene group in I, suggested by the nmr six-proton doublet at about δ 1.7 (Table II), was confirmed by isolation of acetone[5] upon ozonolysis of Ia. The presence of a nonreducible, tetrasubstituted double bond in IIb was shown by chromic acid–acetic acid oxidation of IIb to a yellow diketone, mp 179–182°, λ_{max}^{alc} 270 mμ (ε 9200), $\lambda_{max}^{CHCl_3}$ 1739, 1671, and 1240 cm^{-1}, indicative of a Δ^2-ene-1,4-dione.[6] These data, coupled with the nmr evidence (Table II) showing six angular methyl groups and two vinyl methyl groups, clearly suggested a lanosterol skeleton. The nmr chemical shifts of the angular methyl groups in particular are in excellent agreement with those predicted on the basis of earlier data.[7]

Table I. Nmr Data (δ 3.0–5.5) on Echinodol Derivatives[a]

Compd	C_3–H	C_{16}–H	C_{22}–H	C_{23}–H	C_{24}–H
Ia	3.20 (m)	3.74 (m)	4.51 (t)[b]	4.10 (t)[b]	5.16 (bd)
Ib	4.50 (m)	3.74 (m)	4.52 (t)[b]	4.05 (t)[b]	5.16 (bd)[b]
Ic	3.20 (m)	3.70 (m)	2.96 (t)[b]	3.97 (t)[b]	5.20 (bd)[b]
Id	...	3.75 (m)	4.50 (t)[b]	4.04 (t)[b]	5.16 (bd)[b]
Ie	...	4.20 (m)	...	4.52 (d)[c]	5.31 (bd)[c]
If	...	3.80 (m)	2.97 (t)[b]	3.93 (t)[b]	5.19 (bd)[b]
IIa	3.20 (m)	3.50 (m)	4.48 (t)[b]	3.67 (q)[b]	...

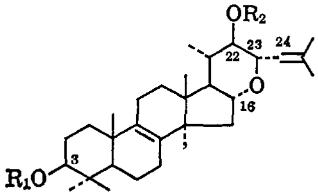
[a] All spectra were recorded in $CDCl_3$. Chemical shifts are given in parts per million relative to internal tetramethylsilane. Chemical shifts of multiplets are approximate. Abbreviations: bd, allylically broadened doublet; d, doublet; q, quartet; t, triplet; m, multiplet. [b] J = 9 cps. [c] J = 8 cps.

Table II. Chemical Shifts of Angular Methyl Groups

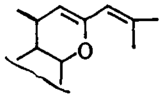
Compd	C_{18}	C_{19}	C_{21}	$C_{26,27}$	C_{30}	C_{31}	C_{32}
Ia	0.69	1.00	0.90 (d)[a]	1.69 (d)[b]	0.82	1.00	1.05
Ib	0.68	1.00	0.90 (d)[a]	1.67 (d)[b]	0.87	0.87	1.05
Ic	0.68	0.99	Obs[c]	1.67 (d)[b]	0.82	0.99	1.03
Id	0.70	1.07	0.92 (d)[a]	1.70 (d)[b]	1.08	1.08	1.06
Ie	0.82	1.08	Obs[c]	1.70 (d)[b]	1.08	1.08	1.13
If	0.71	1.08	Obs[c]	1.70 (d)[b]	1.08	1.08	1.08

[a] J = 7 cps. [b] J = 1.5 cps. [c] Obs, obscured by other peaks.

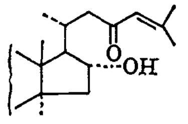
The position and nature of the acetate and ether linkages[8] were shown by further degradation and extremely informative nmr data. Jones oxidation of Ia afforded the 3-keto derivative Id, $C_{32}H_{48}O_4$, mp 227–229°, whereas similar oxidation of Ic gave the valuable diketone Ie, $C_{30}H_{44}O_3$, mp 168–171°, $\lambda_{max}^{CHCl_3}$ 1698 cm^{-1}.



Ia, R_1 = H, R_2 = Ac
b, R_1 = Ac, R_2 = Ac
c, R_1 = H, R_2 = H
d, 3-keto, R_2 = Ac
e, 3-keto, 22-keto
f, 3-keto, R_2 = H



III (3-keto)



IV (3-keto)

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(1) Private communication from Dr. D. H. French, Reed College, Portland, Ore.

(2) Private communication from Dr. J. L. Hartwell, National Cancer Institute, Bethesda, Md.

(3) Satisfactory microanalyses have been obtained for all compounds with cited empirical formulas.

(4) Molecular weight confirmed by mass spectrometry.

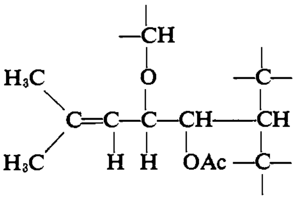
(5) As its 2,4-dinitrophenylhydrazone derivative in 46% yield.

(6) J. Fried, P. Grabowich, E. F. Sabo, and A. I. Cohen, *Tetrahedron*, 20, 2297 (1964).

(7) A. I. Cohen, D. Rosenthal, G. W. Krakower, and J. Fried, *ibid.*, 21, 3171 (1965).

(8) The nmr data in Tables I and II, as well as molecular rotational changes, clearly point to the presence of a C-3 hydroxyl group.

The nmr of diketone Ie shows the ether O–C–*H* protons as a *doublet* and multiplet, shifted downfield from the triplet and multiplet in previous compounds. Clearly the former proton must be on a carbon adjacent to the acetate bearing carbon. In addition, this same proton in Ie is coupled to the downfield vinyl hydrogen, and indeed returns to a triplet when Ie is catalytically reduced. The evidence thus far presented indicates the presence of the following group in Ia



This arrangement is most satisfactorily explained by formula Ia, the stereochemical assignments in the tetrahydropyran ring neatly explaining the noted diaxial coupling.[9] Chemical confirmation was obtained by saponification of Id to If, $C_{30}H_{46}O_3$, mp 186–187°, which was dehydrated ($POCl_3$–pyridine, room temperature) in high yield to vinyl ether III, $C_{30}H_{44}O_2$, mp 189–190°, $\lambda_{\max}^{\text{alc}}$ 233 mμ (ϵ 12,450), $\lambda_{\max}^{\text{CHCl}_3}$ 1610 cm^{-1}. The conjugated diene III was then opened (6 *N* H_2SO_4 in THF) albeit in low yield to give hydroxyenone IV, $C_{30}H_{46}O_3$, mp 185–188°, $\lambda_{\max}^{\text{alc}}$ 238 mμ (ϵ 11,800), $\lambda_{\max}^{\text{CHCl}_3}$ 1698, 1680, and 1615 cm^{-1}. Final confirmation of the ether attachment to a five-membered ring D was obtained by micro-Jones oxidation of IV to an oil which in the infrared showed one additional carbonyl band at 1741 cm^{-1}.

Wolff–Kishner reduction of this triketone under forcing conditions[10] gave a mixture of dienes,[11] mp 73–79°. Chromatography of this mixture on a silver nitrate impregnated silica gel column afforded the major diene, mp 80.5–81°, in 46% yield. This material was identical in all respects with an authentic sample of lanosta-8,24-diene.[12]

We are currently investigating the nature of other components of the crude extract as well as degradation of echinodol to trimethylprogestane derivatives. The interesting biogenetic features of this unusually highly oxygenated lanosterol derivative are also under study.

Acknowledgments. We acknowledge the generous financial support of the U. S. Public Health Service through Grant GM 10963. The nmr spectra were run on an instrument purchased with the assistance of the National Science Foundation. We wish to thank Professors W. G. Dauben and B. Weinstein for assistance in obtaining spectral data.

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[9] With the exception of C-16 where the stereochemistry is assigned solely on the basis of analogy with other triterpenes.

[10] J. F. McGhie, M. K. Pradham, and J. F. Cavalla, *J. Chem. Soc.*, 3176 (1952).

[11] Tlc on SiO_2–Ag^+ plates showed three components, with the major corresponding in retention time and color to authentic lanosta-8,24-diene.[12]

[12] Kindly provided by Professor J. F. McGhie.

[13] National Science Foundation Undergraduate Research Participant.

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Mass Spectrometry in Structural and Stereochemical Problems. CXIX.[1] Interaction of Remote[2] Functional Groups in Mass Spectrometry

Sir:

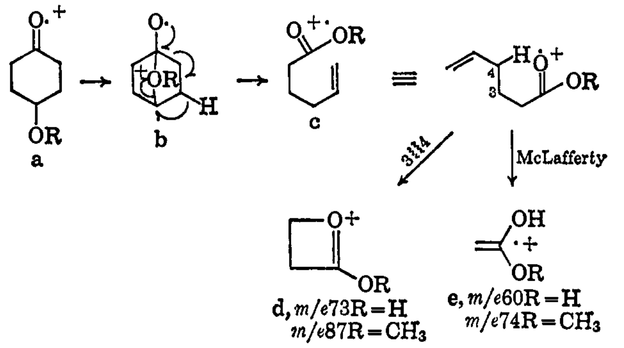
In connection with work under way in our laboratory[3] on the rearrangement of groups other than hydrogen in mass spectral fragmentations, we have encountered a case of electron-impact-induced oxygen rearrangement which is of considerable mechanistic interest and may be the prototype of other remote[2] functional group interactions in mass spectrometry.

One of the most abundant ions (relative abundance 78%, Σ_{20} 6.2%) in the mass spectrum of 4-hydroxycyclohexanone (I) corresponds to $C_2H_4O_2$ (*m*/*e* 60).[4] Analogously the base peak (Σ_{20} 9.1%) in the spectrum of 4-methoxycyclohexanone (II) corresponds to $C_3H_6O_2$ (*m*/*e* 74).[4] The presence of two oxygen atoms in a two-carbon fragment from I and a three-carbon fragment from II requires the intervention of an oxygen rearrangement in each case. The mass spectra of the three deuterated analogs III–V have shed some light on the most probable fragmentation pathway.

Replacement of the hydrogen atoms α to the carbonyl group in II by deuterium (V) resulted in a 2 mass unit shift of *m*/*e* 74 to 76, thus indicating that only one of the α-carbon atoms is retained in the rearrangement ion. Of crucial importance is the observation that approximately one-half of the *m*/*e* 60 peak is shifted to *m*/*e* 61 in III and IV, since this leads to the conclusion that one of the hydrogen atoms at C-3 or C-5 becomes equivalent to the C-4 hydrogen atom.

Another significant oxygen rearrangement ion occurs at *m*/*e* 73 ($C_3H_5O_2$;[4] relative abundance 28%, Σ_{20} 2.2%) in the mass spectrum of I and analogously at *m*/*e* 87 ($C_4H_7O_2$;[4] relative abundance 12%, Σ_{20} 1.1%) in that of II. The *m*/*e* 87 ion is shifted to *m*/*e* 89 in V while the *m*/*e* 73 ion remains unchanged in the mass spectrum of IV and is moved to *m*/*e* 75 in III. A plausible rationalization[5] consistent with these data is shown in Scheme I.

Scheme I



At the present time, no information is available on the details of the proposed rearrangement step (*i.e.*, bridged

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[1] For paper CXVIII see P. Brown, J. Kossanyi, and C. Djerassi, *Tetrahedron*, in press.

[2] "Remote" is meant to designate numbers of bonds rather than spatial relationships.

[3] C. Djerassi, A. M. Duffield, F. Komitsky, Jr., and L. Tökés, *J. Am. Chem. Soc.*, **88**, 860 (1966); M. Fischer and C. Djerassi, *Chem. Ber.*, **99**, 750 (1966), and references cited therein.

[4] High-resolution measurements were performed on all relevant ions in the labeled as well as unlabeled compounds.

[5] Two-electron transfers could equally well be used.