reasonable analogy to earlier generalizations,[5] the bromo ketone was assigned[3] the expected 2β-bromo-2α-methylcholestan-3-one (I) formulation. We now wish to demonstrate that the situation is considerably more complicated as was uncovered by means of optical rotatory dispersion.[6]

According to the "axial haloketone rule,"[7,8] a 2β-bromo-2α-methyl-3-keto steroid in the chair form (IA) should exhibit a positive Cotton effect, contrary to the observed (Fig. 1) negative one of

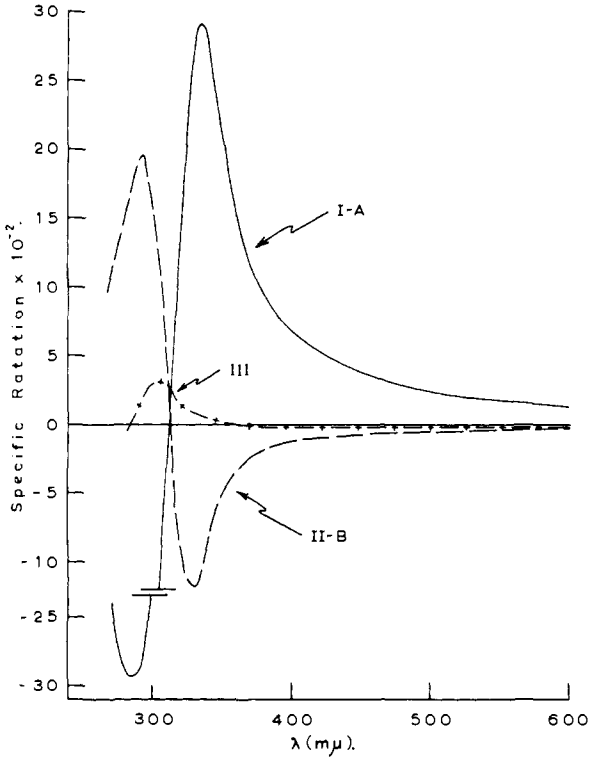
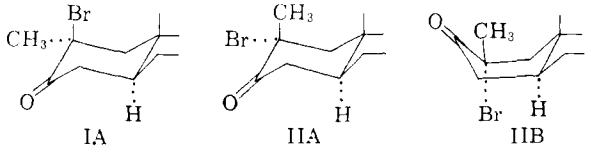


Fig. 1.

the bromo ketone (m.p. 136–138°).[3] The boat form IIB of the 2α-bromo-2β-methyl-3-keto isomer, however, satisfies all criteria, the bromine atom occupying an axial orientation and the "axial haloketone rule"[7,8] predicting a negative Cotton effect.



Conclusive support for this supposition is afforded by hydrogen bromide–acetic acid equilibration of 2α-bromo-2β-methylcholestan-3-one (II) (m.p. 136–138°) which yielded 2β-bromo-2α-methylcholestan-3-one (I) (m.p. 120–122°, $\lambda_{max}^{dioxane}$ 308 mμ, $\lambda_{max}^{CHCl_3}$ 5.85 μ) and 2α-methyl-4α-bromocholestan-3-one (III) (m.p. 140–141°, $\lambda_{max}^{CHCl_3}$ 5.77 μ, $\lambda_{inflect.}^{dioxane}$ 285 mμ). The position of the bromine atom was established by dehydrobromination, I yielding Δ¹-2-methylcholesten-3-one[3] and III giving 2α-methyl-Δ⁴-cholesten-3-one.[3,9] The spectral properties of I demonstrate that the bromine atom is axial and its powerful, positive Cotton effect curve (Fig. 1) is fully consistent[7,8] with the chair formulation IA. Similarly, the spectral and rotatory dispersion (Fig. 1) data show that the bromine atom in III is equatorially oriented. Identical isomers (I, II, III) were encountered in the 2α-methylandrostan-17β-ol-3-one series.

The above results have several important implications: (a) the "axial haloketone rule"[7] is applicable to boat as well as chair forms; (b) chair form IA is energetically favored over the boat IIB, but the latter is preferred over its corresponding chair form IIA. That this is due to the presence of the angular methyl group (the chair form IIA having the electrostatically unfavorable equatorial orientation of the bromine as well as a 1,3-diaxial dimethyl interaction, none of which are found in the boat IIB) will be demonstrated in a forthcoming paper reporting the bromination of analogous 19-nor steroids and where no boat form is encountered.

The fact that the product of the kinetically controlled bromination is II, while the thermodynamic product is I appears to be contrary to the earlier generalizations.[5] We intend to comment on this point in another paper, together with additional experimental evidence.

(5) E. J. Corey, THIS JOURNAL, **76**, 175 (1954).
(6) See C. Djerassi, *Bull. Soc. Chim. France*, 741 (1957).
(7) C. Djerassi and W. Klyne, THIS JOURNAL, **79**, 1506 (1957).
(8) C. Djerassi, J. Osiecki, R. Riniker and B. Riniker, *ibid.*, **80**, 1216 (1958).
(9) J. A. K. Quartey, *J. Chem. Soc.*, 1710 (1958).
(10) Stanford University, Stanford, California.

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DEUTERIUM EXCHANGE OF DECABORANE WITH DEUTERIUM CHLORIDE UNDER ELECTROPHILIC CONDITIONS

Sir:

In contrast to the recently reported base catalyzed deuterium exchange reactions of decaborane[1,2] with such compounds as deuterium oxide and chloride, we wish to report the results of an electrophilic exchange study.

Four successive exchanges of a 10 mmole sample of decaborane with 130 mmole portions of deuterium chloride in the presence of 10 mmole of aluminum chloride and in carbon disulfide solvent (15 ml.) introduced six atoms of deuterium per molecule of decaborane. Each exchange was carried out for 90 hours at room temperature. The HCl–DCl gas mixtures were analyzed at equilibrium by an infrared method. After the third exchange reaction the hydrogen chloride content of the gas mixture was negligible and the recovered decaborane (9.5 mmole) analyzed[1] properly for $B_{10}H_8D_6$.

In the infrared this material exhibited B–H bridge, B–H terminal and B–D terminal stretching bands. No 7.30μ B–D bridge was observed.

(1) M. F. Hawthorne and J. J. Miller, THIS JOURNAL, **80**, 754 (1958).
(2) I. Shapiro, M. Lustig and R. E. Williams, *ibid.*, **81**, 838 (1959).

In the B^{11} nuclear magnetic resonance spectrum the doublet attributed[2] to the 2 and 4 borons was collapsed to a singlet as was the doublet attributed to the 5, 7, 8 and 10 positions of decaborane. The latter doublet normally appears as the high field portion of a triplet. The proton spectrum of this material was composed of the bridge hydrogen peak plus the four peaks assigned[2] to the composite 1, 3, 6 and 9 positions. The slight separation of each of these latter peaks into two equivalent peaks was suggested by the curve shape. The B^{11} and H^1 spectra substantiated each other nicely and this result corroborates the spectral assignments of Shapiro and co-workers.[2]

Electrophilic iodination of decaborane at the 2 and 4 positions was demonstrated recently.[3] Recently another diiododecaborane was isolated[4] and shown to be the 2,5-isomer. This previous work coupled with that reported here substantiates the fact that decaborane is sensitive to electrophilic attack at the 2, 4, 5, 7, 8 and 10 positions. The less saturated 1, 3, 6 and 9 borons[2] apparently are inert to such attack.

(3) R. Schaeffer, THIS JOURNAL, **79**, 2726 (1957).

(4) M. Hillman, Abstracts of the 135th Meeting of the American Chemical Society, April, 1959, p. 44-M.

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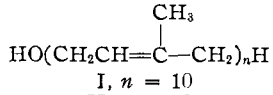
RECEIVED JULY 20, 1959

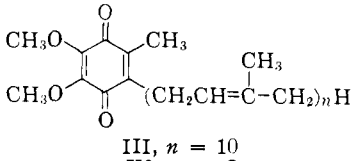
COENZYME Q. XI. THE STRUCTURE OF SOLANESOL

Sir:

The isolation and determination of the structure of solanesol (I), a polyisoprenoid alcohol from tobacco, has been described.[1] Since a synthesis[2]



I, $n = 10$
II, $n = 9$



III, $n = 10$
IV, $n = 3$

utilizing solanesol and 2,3-dimethoxy-5-methylhydroquinone did not give coenzyme Q_{10} (III), we reinvestigated the structure of solanesol. We wish to present new data which confirm the basic structure but support II rather than I.

The nuclear magnetic resonance spectrum of solanesol (Table I) provides confirmation of the isoprenoid structure, and relative area measurements of appropriate bands (Table II) support structure II.

The reaction of solanesol with 3,4,5-triiodobenzoyl chloride yielded solanesyl triiodobenzoate, m.p. 53–54.5°, $E^{1\%}_{1cm} = 271$ at 234 mμ in *i*-octane. *Anal.*

(1) R. L. Rowland, P. H. Latimer and J. A. Giles, THIS JOURNAL, **78**, 4680 (1956).

(2) C. H. Shunk, R. E. Erickson, E. L. Wong and K. Folkers, *ibid.*, **81**, 5000 (1959).

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOLANESOL[a]

Band	τ[b]	Assignment
1	4.45	$-CH_2-CH=C\langle$
2	5.10 5.21	$HO-CH_2-CH=$
3	6.51	$=C-CH_2-CH_2-C=$
4	6.71	$=C-CH_3$

[a] Concentration, 14% in carbon tetrachloride. [b] $\tau = \gamma_0/40 + 3.50$ where γ_0 is the observed band position in c.p.s. relative to benzene as external standard. See G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

TABLE II

RELATIVE AREAS OF BANDS 1 AND 2 FOR SOLANESOL (TABLE I) AND RELATED COMPOUNDS[a]

Compound	No. of determinations	A_1/A_2 Calculated	A_1/A_2 Found	Found/calcd.
Coenzyme Q_{10} (III)[3]	6	5.0	5.2	1.04
2,3-Dimethoxy-5-methyl-6-farnesylbenzoquinone (IV)[4]	4	1.5	1.55	1.04
Solanesol (II)	5	4.5[b]	4.77	1.06

[a] Band 2 in III and IV is assigned to the methylene group attached to the quinone ring. [b] Calculated for structure II. The corresponding value for I is 5.0.

Calcd. for $C_{52}H_{75}I_3O_2$: C, 56.11; H, 6.79; I, 34.21. Calcd. for $C_{57}H_{83}I_3O_2$: C, 57.97; H, 7.08; I, 32.24. Found: C, 56.00, 55.81; H, 6.57, 6.79; I, 34.04, 34.52. The oxidation of solanesol with manganese dioxide yielded the corresponding aldehyde which was isolated as its 2,4-dinitrophenylhydrazone, m.p. 74–75°, $E^{1\%}_{1cm} = 360$ at 379 mμ in ethanol. *Anal.* Calcd. for $C_{51}H_{76}N_4O_4$: C, 75.70; H, 9.47; N, 6.92. Calcd. for $C_{56}H_{84}N_4O_4$: C, 76.67; H, 9.65; N, 6.39. Found: C, 75.86; H, 9.14; N, 7.19. These analytical data support structure II.

Similarly, farnesol yielded a triiodobenzoate, m.p. 46–47°, $E_{mol} = 31{,}000$ at 234 mμ in *i*-octane. *Anal.* Calcd. for $C_{22}H_{27}I_3O_2$: C, 37.52; H, 3.86. Found: C, 37.77; H, 3.87. Farnesaldehyde yielded a 2,4-dinitrophenylhydrazone,[5] m.p. 105–106°, $E_{mol} = 30{,}000$ at 380 mμ in ethanol. *Anal.* Calcd. for $C_{21}H_{28}N_4O_4$: C, 62.98; H, 7.05; N, 13.99. Found: C, 62.87; H, 6.88; N, 14.50. A calculation of the molecular weight of solanesol from these E_{mol} values for farnesol derivatives and the $E^{1\%}_{1cm}$ values of the corresponding solanesol derivatives leads to values of 658 and 655 which support structure II (mol. wt. = 631) rather than I (mol. wt. = 699).

The synthesis of "Q-254" from solanesol for confirmation of structure[6] and the synthesis of coenzyme Q_9 and a vitamin K analog is reported in an accompanying communication.[2]

We wish to thank Dr. R. L. Rowland and Dr. M. Senkus of the R. J. Reynolds Tobacco Co., Win-

(3) D. E. Wolf, C. H. Hoffman, N. R. Trenner, B. H. Arison, C. H. Shunk, B. O. Linn, J. F. McPherson and K. Folkers, *ibid.*, **80**, 4752 (1958).

(4) C. H. Shunk, B. O. Linn, E. L. Wong, P. E. Wittreich, F. M. Robinson and K. Folkers, *ibid.*, **80**, 4753 (1958).

(5) Y. R. Naves, *Helv. Chim. Acta*, **32**, 1798 (1949).

(6) N. R. Trenner, B. H. Arison, R. E. Erickson, C. H. Shunk, D. E. Wolf and K. Folkers, THIS JOURNAL, **81**, 2026 (1959).