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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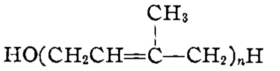
RECEIVED JULY 20, 1959

COENZYME Q. XI. THE STRUCTURE OF SOLANESOL

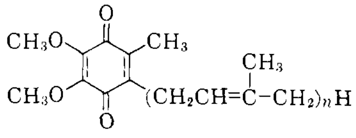
Sir:

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



$$\mathrm{HO(CH_2CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_2)_{\mathit{n}}H}$$

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.

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOLANESOL[a]

Band	τ[b]	Assignment
1	4.45	$-\mathrm{CH_2{-}CH{=}C}\!<$
2	5.10 5.21	$\mathrm{HO{-}CH_2{-}CH{=}}$
3	6.51	$=\overset{\vert}{\mathrm{C}}-\mathrm{CH_2{-}CH_2}-\overset{\vert}{\mathrm{C}}=$
4	6.71	$=\overset{\vert}{\mathrm{C}}-\mathrm{CH_3}$

[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	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.

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

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(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).

(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).

ston-Salem, N. C., for a generous initial sample of solanesol. Our simplified procedure for the isolation of solanesol from tobacco will be described later.

CONTRIBUTION FROM THE
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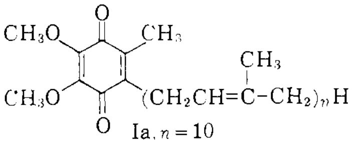
RECEIVED JULY 31, 1959

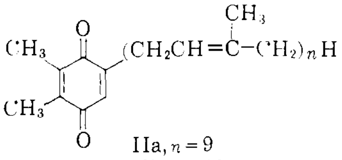
COENZYME Q. X. SYNTHESIS OF COENZYME Q_9, 2,3-DIMETHYL-5-SOLANESYLBENZOQUINONE (*Q-254*), AND A VITAMIN K ANALOG

Sir:

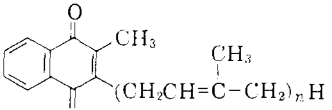
A polyisoprenoid alcohol, solanesol, was isolated from tobacco and evidence was presented indicating that it was composed of 10 isoprenoid units.[1] We obtained a sample of solanesol through the generosity of Dr. R. L. Rowland and Dr. M. Senkus[2] to condense with 2,3-dimethoxy-5-methylhydroquinone, because the reaction could be expected to give synthetic coenzyme Q_{10} (Ia).[3,4,5,6] The resulting 2,3-dimethoxy-5-methyl-6-solanesylbenzoquinone, m.p. 42–43.5°, $\lambda_{\max}^{\text{isooctane}}$ 271 mμ ($E_{1\text{cm}}^{1\%}$ 175). (*Anal.* Found: C, 81.06; H, 10.47) was different from coenzyme Q_{10}, but proved to be indistinguishable from coenzyme Q_9 (Ib)[3] with respect to m.p., R_f, ultraviolet, and infrared data. The structure of solanesol was reinvestigated[7] and it was found to be composed of nine isoprenoid units rather than ten.



Ia, $n = 10$
Ib, $n = 9$



IIa, $n = 9$
IIb, $n = 10$



IIIa, $n = 7$
IIIb, $n = 9$

A quinone (Q-254) has been isolated[8] from alfalfa and has been shown to be 2,3-dimethylbenzoquinone with a substituent in the 5-position composed of 9-isoprenoid units (IIa).[9] Kofler and co-workers[10] have proposed structure IIb which has a 10-isoprenoid unit side chain for a plant quinone believed to be identical with "Q-254." The structure having the 9-isoprenoid unit side chain has been confirmed by synthesis. 2,3-Dimethylhydroquinone was condensed with solanesol in the presence of boron trifluoride etherate, and the resulting hydroquinone was oxidized yielding 2,3-dimethyl-5-solanesylbenzoquinone (IIa), m.p. 43.5–45°, $\lambda_{\max}^{\text{isooctane}}$ 253 mμ ($E_{1\text{cm}}^{1\%}$ 239) and 261 mμ ($E_{1\text{cm}}^{1\%}$ 222) (*Anal.* Found: C, 84.87; H, 10.63). This compound is identical with "Q-254" with respect to m.p., R_f, ultraviolet, infrared and nuclear magnetic resonance data.

Vitamin K_2 recently has been shown to have the formula IIIa.[11] We have now synthesized the corresponding naphthoquinone in which the side chain contains nine isoprenoid units (IIIb). 2-Methylnaphthohydroquinone was condensed with solanesol in the presence of boron trifluoride etherate. Oxidation of the product yielded 2-methyl-3-solanesylnaphthoquinone (IIIb), m.p. 60–61°, $\lambda_{\max}^{\text{isooctane}}$ 243, 248, 260, 269 and 322 mμ ($E_{1\text{cm}}^{1\%}$ 218, 232, 212, 210 and 38 resp.) (*Anal.* Found: C, 85.01; H, 10.39).

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

[2] R. J. Reynolds Tobacco Co., Winston-Salem, North Carolina.

[3] R. L. Lester, F. L. Crane and Y. Hatefi, THIS JOURNAL, **80**, 4751 (1958).

[4] 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).

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

[6] R. A. Morton, U. Gloor, O. Schindler, G. M. Wilson, L. H. Chopard-dit-Jean, F. W. Hemming, O. Isler, W. M. F. Leat, J. F. Pennock, R. Ruegg, U. Schwieter and O. Wiss, *Helv. Chim. Acta*, **41**, 2343 (1958).

[7] R. E. Erickson, C. H. Shunk, N. R. Trenner, B. H. Arison and K. Folkers, THIS JOURNAL, **81**, 4999 (1959).

[8] F. L. Crane and R. L. Lester, *Plant Physiol.*, **33** (Suppl.), VII (1958).

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

[10] M. Kofler, A. Langemann, R. Ruegg, L. H. Chopard-dit-Jean, R. Rayroud and O. Isler, *Helv. Chim. Acta*, **42**, 1283 (1959).

[11] O. Isler, R. Ruegg, L. H. Chopard-dit-Jean, A. Winterstein and O. Wiss, *ibid.*, **41**, 786 (1958).

CONTRIBUTION FROM THE
MERCK, SHARP & DOHME
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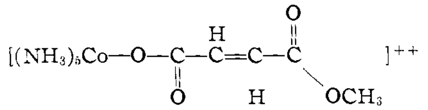
RECEIVED JULY 31, 1959

ACTIVATION OF BRIDGING GROUPS IN ELECTRON TRANSFER. II. THE POSITION OF BOND-BREAKING IN ESTER HYDROLYSIS[1]

Sir:

It has been shown that when certain half-esters function as bridging groups for electron transfer, ester hydrolysis accompanies electron transfer. The point of bond scission in these hydrolyses is a matter of interest, and forms the subject of this communication. The reaction of Cr^{++} with



$$\left[(NH_3)_5Co{-}O{-}\underset{\underset{O}{\|}}{C}{-}\overset{H}{C}{=}\underset{H}{C}{-}\overset{\overset{O}{\|}}{C}{\diagdown}OCH_3\right]^{++}$$

(the ligand is the methyl half ester of fumaric acid, containing oxygen of normal isotope composition) was carried out in aqueous solution 8.5-fold enriched in O^{18} and containing 0.3 *M* $HClO_4$. The fumaric acid was removed as described earlier,[2] and after purification was heated with $Hg(CN)_2$ and $HgCl_2$[3] to convert oxygen to CO_2. The CO_2 was found to be enriched in O^{18} by only a factor of 1.048 above that of a sample derived from acid of normal isotopic composition. Thus it appears

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[1] Supported by the A.E.C. under Contract AT(11-1-)-378.

[2] R. T. M. Fraser, D. K. Sebera and H. Taube, THIS JOURNAL, **81**, 2906 (1959).

[3] M. Anbar and S. Guttmann, private communication.