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.

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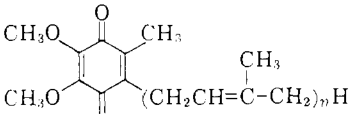
DIVISION OF MERCK & CO., INC.
RAHWAY, N. J.
ROBERT E. ERICKSON
CLIFFORD H. SHUNK
NELSON R. TRENNER
BYRON H. ARISON
KARL FOLKERS

RECEIVED JULY 31, 1959

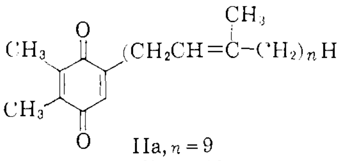
COENZYME Q. X. SYNTHESIS OF COENZYME Q_9, 2,3-DIMETHYL-5-SOLANESYLBENZOQUINONE (Q-254), AND A VITAMIN K ANALOG

Sir:

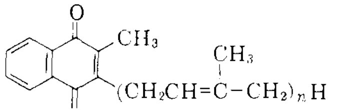
A polyisoprenoid alcohol, solanesol, was isolated from tobacco and evidence was presented indicating that it was composed of 10 isoprenoid units.[1] We obtained a sample of solanesol through the generosity of Dr. R. L. Rowland and Dr. M. Senkus[2] to condense with 2,3-dimethoxy-5-methylhydroquinone, 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).

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[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).

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[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).

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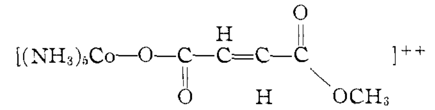
DIVISION OF MERCK & CO., INC.
RAHWAY, NEW JERSEY
CLIFFORD H. SHUNK
ROBERT E. ERICKSON
EMILY L. WONG
KARL FOLKERS

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



$$[(\mathrm{NH_3})_5\mathrm{Co{-}O{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{{=}}\underset{\mathrm{H}}{\mathrm{C}}\mathrm{{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}OCH_3}]^{++}$$

(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.