rearrangement of the phenylalanine side chain. A close biochemical analogy is the recently discovered methylmalonyl-coenzyme A $\leftrightarrows$ succinyl-coenzyme A isomerization.[13]

A less likely explanation of our results would involve a carboxylation reaction utilizing carbon dioxide produced by decarboxylation of the phenylalanine-1-C^{14}. If this were the case one would expect a much more general labeling of the alkaloids by the radioactive carbon dioxide. This expectation was realized in subsequent tracer experiments. Sodium bicarbonate-C^{14} (24.8 mg., 1.0 mc.) was fed to *Datura* plants as previously described and two weeks later radioactive hyoscyamine (5.5×10^5 d.p.m./mM.) and hyoscine (4.2×10^5 d.p.m./mM.) were isolated, representing a 0.008% incorporation of tracer into the alkaloids. Hydrolysis of the hyoscyamine yielded tropine (2.4×10^5 d.p.m./mM.) and tropic acid (3.1×10^5 d.p.m./mM.). Systematic degradation of the tropic acid as previously described indicated that it was non-specifically labeled, the percentage activity at C_1, C_2, C_3, and on the aromatic carbons being 16, 4, 16, and 65%, respectively.

We could speculate on the mechanism of the rearrangement of the phenylalanine side chain. However, we feel that scientific journals are currently being filled with far too many incontinent biogenetic hypotheses, and we will withhold our ideas until the completion of additional experimental work.

[13] *Cf.* R. Stjernholm and H. G. Wood, *Proc. Natl. Acad. Sci.*, **47**, 303 (1961), and ref. cited therein.

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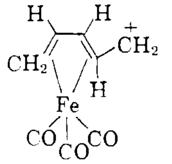
RECEIVED FEBRUARY 15, 1962

PENTADIENYL AND HEXADIENYL CARBONIUM IONS AS LIGANDS IN STABLE COMPLEX CATIONS

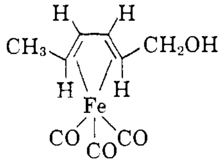
Sir:

Recently several cyclic unsaturated carbonium ions, *e.g.*, the tropylium,[1] cyclopentadienyl,[2] cyclohexadienyl,[3] cycloheptadienyl,[4] and cycloöctatrienyl[5] cations, have been found to bond with certain metal carbonyl groups in the formation of remarkably stable organo-metallic cations. Two major factors concerning the stability of these complex cations appear to be the donor properties of the π electrons and the "back donation" of electrons from the metal atom to the organic ligand through interaction of filled d orbitals of the metal with vacant π molecular orbitals of the carbonium ion ligand. This latter interaction is particularly important for, at the same time, it increases the metal-ligand bonding, decreases the electron density on the metal, and decreases the electrophilicity of the carbonium ion moiety. In each of the cyclic carbonium ions mentioned above, the sp^2 hybridized carbon atoms are fixed in a completely cisoid configuration and each presumably is involved directly in bonding to the metal atom.

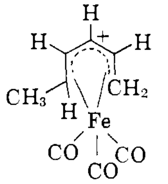
It is of interest then to determine whether linear unsaturated carbonium ions can act as ligands in similar complexes; such carbonium ions possess the required vacant, low energy molecular orbitals but, in contrast to the cyclic systems above, in certain *trans* configurations not all of the unsaturated carbon atoms can be simultaneously bonded to the metal. This may be the reason then why we have been unable to prepare the *trans*-pentadienyl-ion tricarbonyl cation (I) by direct hydride abstraction from *trans*-1,3-pentadiene-iron tricarbonyl using triphenylmethyl perchlorate. This reaction proceeds readily for the cyclic diene complexes.[3] Salts of two of the complexed linear carbonium ions have, however, been obtained from the corresponding alcohols. *trans-trans*-2,4-Hexadien-1-ol and $Fe(CO)_5$ reacted to form *trans-trans*-2,4-hexadien-1-ol-iron tricarbonyl (II).[6] (*Anal.* Calcd. for $C_9H_{10}O_4Fe$: C, 45.41; H, 4.23. Found: C, 45.67; H, 4.15.) Treatment of this alcohol with $HClO_4$ in acetic anhydride afforded a yellow crystalline precipitate of hexadienylium-iron tricarbonyl perchlorate in almost quantitative yield. (*Anal.* Calcd. for $C_9H_9O_7ClFe$: C, 33.73; H, 2.83; Cl, 11.07. Found: C, 33.49; H, 2.87; Cl, 10.89.) The structure (III) is assigned to this cation for several reasons. The salt reacted with $NaBH_4$ to produce hexadiene-iron tricarbonyl. Reaction of (III) with water gave a complex alcohol (IV), isomeric with (II). (*Anal.* Calcd. for $C_9H_{10}O_4Fe$: C, 45.41; H, 4.23. Found: C, 45.40; H, 4.57.) This new alcohol also generated the perchlorate of salt III when liberated with $HClO_4$. Decomposition of (IV) with $FeCl_3$ in alcoholic sodium acetate solution liberated a hexadienol which, on catalytic hydrogenation, absorbed 1.9 mole of hydrogen to give 2-hexanol. Compound (IV) must therefore be 1,3-hexadien-5-ol-iron tricarbonyl. Now since only dienes in the cisoid configuration produce stable diene–iron tricarbonyl complexes, carbon atoms 1 and 4 must now be *cis* with respect to the C_2–C_3 bond in (IV). Although it has not yet been definitely proven it would seem most likely that the geometrical inversion has taken place during



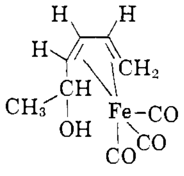
I



II



III



IV

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[1] H. J. Dauben and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).

[2] A. Davison, M. L. H. Green and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).

[3] E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).

[4] H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961).

[5] G. W. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).

[6] Decomposition of this complex by treatment with $FeCl_3$ in alcoholic sodium acetate regenerated the starting alcohol.

reaction of (II) with $HClO_4$, the driving force resulting from the increased bonding between the carbonium ion and the metal.

Reaction of *trans*-1,3-pentadien-5-ol with $Fe(CO)_5$ gave *trans*-1,3-pentadien-5-ol-iron tricarbonyl (V). (*Anal.* Calcd. for $C_8H_8O_4Fe$: C, 42.89; H, 3.59. Found: C, 43.29; H, 3.28.) Treatment of this with $HClO_4$ produced pentadienylium-iron tricarbonyl perchlorate (VI). (*Anal.* Calcd. for $C_8H_7O_7ClFe$: C, 31.35; H, 2.30; Cl, 11.57. Found: C, 31.48; H, 2.40; Cl, 12.09.) By analogy with the previous salt this cation is assigned the all-*cis* structure isomeric with I.

The two new cations reported here are remarkably stable as is evident from the fact that both alcohols (II) and (V) react with triphenylmethyl perchlorate to produce quantitative yields of triphenylmethanol and the perchlorate of salts III and VI, respectively.

We thank the Robert A. Welch Foundation and the Alfred P. Sloan Foundation for financial assistance.

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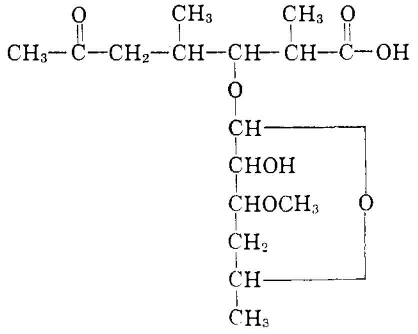
RECEIVED MARCH 9, 1962

A DEGRADATION PRODUCT OF CHALCOMYCIN: 2,4-DIMETHYL-3-CHALCOSYLOXY-6-OXOHEPTANOIC ACID

Sir:

Previous communications have shown that the antibiotic chalcomycin[1] contains two new sugars, chalcose[2] and mycinose.[3] We now wish to report the structural elucidation of a C_{16} acid (I, 2,4-dimethyl-3-chalcosyloxy-6-oxoheptanoic acid) which has been obtained as a degradation product of chalcomycin.



I

Oxidation of chalcomycin with periodate-permanganate[4] gave I, m.p. 103–104°, infrared ($CHCl_3$) 5.83 μ, $[\alpha]^{25}D$ $-23°$ (*c* 1.6%, water) [*Anal.* Calcd. for $C_{16}H_{28}O_7$ (332.38): C, 57.81; H, 8.49; OCH_3 (1), 9.34; $C\text{-}CH_3$ (4), 18.09. Found: C, 57.84; H, 8.54; OCH_3, 9.51; $C\text{-}CH_3$, 15.45; neut. equiv., 334; pK'_a (water), 4.5].

The n.m.r. spectrum[5] of I in deuteriochloroform indicates the presence of three C-methyl groups each α to one hydrogen [doublets centering at $\delta = 0.94$ (3 hydrogens) and at $\delta = 1.2$ (6 hydrogens), *J*'s = 6 cps.], one methyl ketone (singlet, $\delta = 2.1$), one methoxyl group (singlet, $\delta = 3.4$), and a total of 28 hydrogens (signal area integration based on two exchanging hydrogens centering at $\delta = 6.9$).

Reduction of I with sodium borohydride gave an oil which exhibited absorption in the infrared at 5.81 μ and no γ-lactone band, thus indicating that in I the carbonyl group is not γ to the carboxyl group. Acid hydrolysis of I yielded chalcose and an acidic aglycone II (5.75 μ). The sodium salt of II showed no absorption in the carbonyl region (5.5–6.0 μ), suggesting hemiketal formation involving the methyl ketone and the hydroxyl group generated by acid hydrolysis. Oxidation of I with sodium hypoiodite gave iodoform and acid III (5.84 μ). Acid hydrolysis of III yielded chalcose and a γ-lactonic acid IV (5.64, 5.83 μ). These data indicate that chalcose is γ to the methyl ketone group, as in I, but not γ to the carboxyl group.

Esterification of the γ-lactonic acid IV with methyl iodide–silver oxide gave the lactonic methyl ester V (5.61, 5.74 μ). Treatment of V with sodium methoxide in methanol yielded, through elimination, the α,β-unsaturated ester VI, which shows the expected ultraviolet absorption ($\lambda_{\max}^{\text{MeOH}}$ 216 mμ, $\epsilon \sim 1.2 \times 10^3$) and infrared spectrum (5.78, 5.85, 6.04 μ; no OH band at 3 μ). VI was ozonized and then hydrolyzed to give pyruvic acid and α-methylsuccinic acid, both identified by paper chromatography and infrared spectroscopy. The above data are thus consistent with structure I and eliminate alternative structures having the methyl ketone γ to the carboxyl group.

Compound I was simultaneously O-methylated and esterified by treatment with methyl iodide and silver oxide to give VII, which then was oxidized with trifluoroperacetic acid[6] to give acetate VIII; the latter was reduced with lithium aluminum hydride to give dialcohol IX. Methanolysis of IX yielded the oily methyl-2-O-methylchalcoside and triol X, m.p., 52.5–54°, $[\alpha]^{23}D$ $+11°$ (*c* 1.5%, methanol) [*Anal.* Calcd. for $C_7H_{16}O_3$: C, 56.73; H, 10.88. Found: C, 56.55; H, 11.24]. X reacted with acetic anhydride in pyridine at room temperature to give a triacetate [*Anal.* Calcd. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08; acetyl (3), 47.08. Found: C, 57.09; H, 8.00; acetyl, 48.09]. The n.m.r. spectrum of X[5] in deuterium oxide shows five hydrogens α to oxygens ($\delta = 3.8$ to 4.4), two hydrogens not α to oxygen ($\delta = 2.0$ to 2.6), two secondary methyl groups or one isopropyl group (two sets of doublets centering at $\delta = 1.33$ and $\delta = 1.36$, *J*'s = 7 cps.), but no primary or tertiary methyl groups. The analytical and n.m.r. data establish the structure of X as either

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[1] Parke, Davis & Company, Belgian Patent 587,213, August 2, 1960.

[2] (a) P. W. K. Woo, H. W. Dion and Q. R. Bartz, *J. Am. Chem. Soc.*, **83**, 3352 (1961); (b) P. W. K. Woo, H. W. Dion and L. F. Johnson, *ibid.*, **84**, 1066 (1962).

[3] H. W. Dion, P. W. K. Woo and Q. R. Bartz, *ibid.*, **84**, 880 (1962).

[4] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

[5] Obtained at 60 Mc.; chemical shifts are given in p.p.m. relative to tetramethylsilane as 0.

[6] W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).