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.

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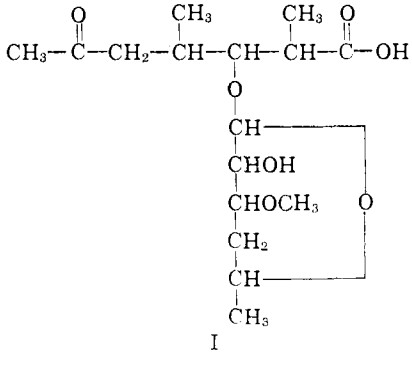
A DEGRADATION PRODUCT OF CHALCOMYCIN: 2,4-DIMETHYL-3-CHALCOSYLOXY-6-OXOHEPTANOIC ACID

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 (C-HCl_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-CH_3 (4), 18.09. Found: C, 57.84; H, 8.54; OCH_3, 9.51; C-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 δ = 0.94 (3 hydrogens) and at δ = 1.2 (6 hydrogens), *J*'s = 6 cps.], one methyl ketone (singlet, δ = 2.1), one methoxyl group (singlet, δ = 3.4), and a total of 28 hydrogens (signal area integration based on two exchanging hydrogens centering at δ = 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 (λ_{max}^{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 (δ = 3.8 to 4.4), two hydrogens not α to oxygen (δ = 2.0 to 2.6), two secondary methyl groups or one isopropyl group (two sets of doublets centering at δ = 1.33 and δ = 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

(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).

2,4-dimethylpentane-1,3,5-triol or the alternative 2,3-dimethylpentane-1,4,5-triol. The latter was eliminated because X did not take up any periodate. The infrared spectrum of X is identical with that of 2,4-dimethylpentane-1,3,5-triol [m.p. 54–56°, $[\alpha]^{25}D$ −14.0° (*c* 2%, methanol)] isolated as a degradation product of erythromycin.[7] Hence, the triol X is the enantiomorph of the "*act*-triol" from erythromycin.

The above data establish the structure of I as 2,4-dimethyl-3-chalcosyloxy-6-oxoheptanoic acid.

(7) K. Gerzon, E. H. Flynn, M. V. Sigal, Jr., P. F. Wiley, R. Monahan and U. C. Quarck, *J. Am. Chem. Soc.*, **78**, 6396 (1956).

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OPTICALLY ACTIVE AMINES. I. N-ISOPROPYLIDENE DERIVATIVES OF OPTICALLY ACTIVE OPEN CHAIN PRIMARY AMINES AND THEIR ROTATORY POWERS[1]

Sir:

Recently Bergel and co-workers[2] reported that optically active α-amino acid esters and amides containing a primary amino group, and other optically active open chain primary amines examined in ketonic solvents (Table I) exhibit rotatory powers which change greatly with time, eventually reaching a constant value, highly levorotatory for L-α-amino acid esters and amides. They concluded[2b] that the mutarotation is due to the formation in ketonic solvents of unstable Schiff bases, $R_2C{=}NCHR'R''$, (I), and suggested that the maximal rotation of an α-amino acid ester in a ketonic solvent may help to decide its absolute configuration.

TABLE I

MOLECULAR ROTATIONS[a] OF SOME L-α-AMINO ACID DERIVATIVES AND (S)-(+)-AMPHETAMINE[3] IN ETHANOL AND IN ACETONE AS REPORTED BY BERGEL[2]

Code	Compound	$[\phi]^{22}D$ in ethanol	$[\phi]^{22}D$ in acetone	Time to reach constant $[\phi]D$ in acetone, min
IIa	Ethyl L-alaninate	+ 4	−153	160
IIIa	(S)-(+)-Amphetamine	+45	+114	240
IVa	Ethyl L-phenylalaninate	+43	−242	60
IVb	Ethyl L-tyrosinate	+38	−259	60
IVc	L-Tyrosinamide	−41	−133[b]	days

[a] Calculated as $[\alpha]D \times$ mol. wt. of free base/100 from $[\alpha]D$'s reported in Ref. 2. [b] 1:1 methanol–acetone as solvent.

In another connection we had prepared a considerable number of optically active α-amino acid esters and other open chain primary amines, all of known absolute configurations, and it was decided to compare their rotatory powers in ethanol and in acetone (Table II) in order to provide a somewhat broader base for testing the reliability of Bergel's suggested method for assigning the absolute configurations of such open chain compounds.

(1) This work was supported by a grant (G14524) from the National Science Foundation.

(2) (a) F. Bergel and G. E. Lewis, *Chem. and Ind.*, 774 (1955); (b) F. Bergel, G. E. Lewis, S. F. D. Orr and J. Butler, *J. Chem. Soc.*, 1431 (1959); (c) F. Bergel and J. Butler, *ibid.*, 4047 (1961).

(3) Absolute configurational designations according to R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).

TABLE II

MOLECULAR ROTATIONS[a] OF SOME OPTICALLY ACTIVE α-AMINO ACID ESTERS AND OTHER OPEN CHAIN PRIMARY AMINES IN ETHANOL AND IN ACETONE

Code	Compound	$[\phi]D^{21-28}$ in ethanol[b]	$[\phi]D^{21-28}$ in acetone	Time to reach constant $[\phi]D$ in acetone, min.
IIa	Ethyl L-alaninate	+ 3	− 70[c]	390
IIb	Ethyl D-phenylglycinate	−217	− 68	350
IIc	(R)-(+)-α-Phenylethylamine	+ 36	+110	1330
IId	(S)-(−)-α-*p*-Tolylethylamine	− 33	−115	1360
IIIb	(S)-(+)-2-Aminobutane	+ 2	+ 72	1210
IVa	Ethyl L-phenylalaninate	+ 43	−249	1170
IVd	Methyl L-tyrosinate	+ 54[d]	−278	1000
IVe	Ethyl L-leucinate	+ 34	−252	1890
IVf	Ethyl L-methioninate	+ 13	−224	540
IVg	Ethyl (S)-(−)-β-aminohydrocinnamate[e]	− 13	−117	330
Va	Ethyl L-isoleucinate	+ 60	−249	1130
Vb	Ethyl L-alloisoleucinate[f]	+ 54	−174	2630

[a] Calculated as $[\alpha]D \times$ mol. wt. of free base/100. [b] No change in $[\phi]D$ with time. [c] 1:1 Ethanol–acetone as solvent. [d] Methanol as solvent. [e] (R)-Isomer used. [f] D-Isomer used.

The possible confirmation of Bergel's simple method seems especially important because for many of these compounds the direction and magnitude of the optical rotation is not certainly predicted with rules, such as the Atomic and Conformational Asymmetry Rules of Brewster.[4]

As seen by an inspection of Tables I and II, our results where comparable are essentially the same as those reported by Bergel, except that the times required for the attainment of constant optical rotations in acetone were somewhat longer, due perhaps to the prevailing humidity, traces of water in the acetone being known[2] to diminish the rate of change of rotatory power. Evidently the cause of these slower rates had no great effect on the magnitudes of the the rotatory powers finally observed in acetone (*cf.* IVa in Tables I and II).

From an inspection of Table II it is clear that at least one D-α-amino acid ester is highly levorotatory in acetone. The rotatory power of ethyl D-phenylglycinate in acetone is, indeed, displaced in a positive direction but is still nevertheless levorotatory. The work of Bergel[2] and these data indicate, however, that the absolute configurations of these Schiff bases formed in acetone can be related to their rotatory powers using Brewster's Atomic and Conformational Asymmetry Rules[4] and thus measurements of this kind will be useful in the deduction of the absolute configurations of amines of this type.

Thus, using Brewster's rules in conjunction with the rotational ranks tabulated by him[4] and considering the rotatory powers of the N-isopropylidene derivatives of code II (Tables I and II), all expected to show atomic asymmetry and the simplest type of conformational asymmetry, one obtains the empirical polarizability sequence of the substituent attachment atoms as decreasing in the order

(4) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959); *Tetrahedron* **13**, 106 (1961).