of HCN[11] furnished *dl*-4,7-dimethyl-4-carboxydihydrocoumarin, mp 105° after sublimation, identical with XIII in nmr, uv, and ir spectra and thin layer and gas chromatographic behavior.

Thus, the C_{12}-compound XIII, together with degradative fragments carbon dioxide, acetic acid, and isobutyric acid, represent all 19 carbon atoms of the C_{19}-diketone Ia. Consideration of the above evidence allows reconstruction only of structure Ia, as follows. The carbon skeleton of XIII is present in the enol lactone VIII which results from a decarboxylative dehydration of VIa. VIa and acetic acid are the hydrolysis products from Va. Va and isobutyric acid result from hydroxylation of the enone II and cleavage of the glycol and derived α-diketone. The enone II in turn is the internal enol ether of the 1,3-diketone Ia.

(11) J. Bredt and J. Kallen, *Ann.*, **293**, 363 (1896).

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The Structure of a C_{19} Acid Derived from Ryanodine[1]

Sir:

Periodate oxidation of ryanodol, the alcohol moiety of the pyrrole-α-carboxylic ester ryanodine,[2] furnishes two acidic products in nearly quantitative yield. One is the previously reported C_{19} 1,3-diketone[3] (50%) and the other is a C_{19} carboxylic acid (40%) to which we assign structure Ia on the basis of the following evidence.

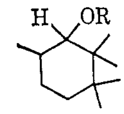
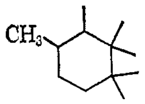
The acid[4] $C_{19}H_{28}O_8$ (Ia) (mp 163°; pK_a = 2.8; ν 3500–3300, 2700–2300, 1740–1715) and its methyl ester (Ib) (mp 139°; ν 3500, 1755, 1730, 1716) contain one secondary and one tertiary methyl, one isopropyl, one ethyl, one methylene between completely substituted carbons, and one proton on an acyloxylated carbon (nmr, Table I). Compound Ib further contains one hydroxyl (tritium exchange) and on oxidation (MnO_4^- or CrO_3) gives propionic, acetic, and isobutyric acids. The propionic acid originated from an ethyl ketone (shown as its hemiketal in Ia,b based on ir absorption), as shown by the nmr absorption pattern in which the methylene adjacent to the methyl appears as a quartet, δ 2.6. The high acidity of Ia indicates oxygen substitution on the α carbon, and this oxygen function was shown to be a (potential) hydroxyl by lithium aluminum hydride reduction to a polyol which on periodate oxidation gave formaldehyde.

The isopropyl group in Ia was proved to be present as an isobutyrate ester by the following: (1) lithium aluminum hydride reduction gave isobutyl alcohol; (2) both dilute alkaline hydrolysis and pyrolysis gave quantitatively isobutyric acid and carbon dioxide. The relative positions of the carboxyl and isobutyryloxy groups are assigned as shown in Ia to allow for their facile, concomitant elimination.

Ib with *t*-butoxide at 80° furnished quantitatively an acidic product, $C_{19}H_{26}O_7$ (II) (mp 237°; pK_a' = 5.4; λ_{max} 266 (7800), 305 (1900); $\lambda_{max}^{OH^-}$ 303 (16,000); ν 3400, 3300, 1730, 1706, 1660, 1619). Compound II, which is oxidized in air in the light, is a 1,3-diketone. Methylation (diazomethane) gave a mixture of isomeric methyl enol ethers, $C_{20}H_{28}O_7$, separated by crystallization into IIIa (mp 267°; λ_{max} 259 (9200); ν^{CHCl_3} 3500, 1728, 1682, 1613) and IIIb (mp 197°; λ_{max} 256 (7700); ν^{CHCl_3} 3500, 1723, 1666, 1618). Hydrogenation (1 mol) of II gave the β-hydroxy ketone $C_{19}H_{28}O_7$ (IV) (mp 243°; ν 3555, 3420, 1755, 1736, 1721). The nmr of IV shows two hydroxyl protons (deuterium exchange). The methylene next to the ketone carbonyl in II remains a singlet in IV, showing that the other carbonyl had been reduced. Appearance of a doublet at δ 3.9 (J = 4 Hz) in IV supports the introduction of a proton on a secondary alcohol carbon. IV in acidic aqueous ethanol undergoes dehydration to α,β-unsaturated ketone $C_{19}H_{26}O_6$ (V) (mp 260°; λ_{max} 238 (5800), 325–340 (60); ν 3600, 1752, 1710, 1645), with a new vinyl methyl at δ 1.8 coupled to the new vinyl proton at 6.25.

The 1,3-diketone II rapidly consumes 2 mol of

Table I. Selected Nmr Absorptions[a] of the C_{19} Acid and Its Derived Products

Compd			CH_3 (H)CH	—C— CH_2 C=O	CH_3 —C—	CH_3 CH_3 CH	CH_3 CH_3 CH
Ib	5.3 (d, 9)	0.85 (d, 6)	1.0 (t, 6)	2.8 (q, 18)[b]	1.3	2.5 (sep, 6)	1.1 (q, 6)
II	5.4 (d, 10)	0.9 (d, 6)	1.2	2.8 (s)	1.4	2.6 (sep, 6)	1.2 (q, 6)
IIIa	5.3 (d, 10)	0.9 (d, 6)	1.8	2.15 (s)	1.25	2.6 (sep, 6)	1.2 (q, 7)
IIIb	5.3 (d, 10)	0.9 (d, 6)	1.8	2.6 (s)	1.2	2.6 (sep, 6)	1.2 (q, 7)
IV	5.4 (d, 10)	0.9 (d, 6)	1.1 (d, 6)	2.8 (s)	1.2	2.5 (sep, 6)	1.1 (q, 6)
V	5.3 (d, 10)	0.9 (d, 6)	1.8 (d, 2)[c]	2.8 (s)	1.25	2.6 (sep, 6)	1.2 (d, 6)
VI	5.2 (d, 11)	0.8 (d, 6)	2.25[d]	2.8 (s)	1.3	2.4 (sep, 6)	1.2 (d, 6)

[a] δ values, followed in parentheses by multiplicity and coupling constants in hertz. [b] The ketonic carbonyl exists as a hemiketal in this compound. [c] This is now a vinyl methyl coupled to the vinyl proton at δ 6.25 as a quartet, J = 2 Hz; intensity ratio 1:3:3:1. [d] Acetyl methyl in this compound.

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(1) This work was sponsored by the U. S. Army Research Office, Durham. It was reported in part at the Tenth Organic Chemistry Conference, U. S. Army Natick Laboratories, Oct 4, 1966.

(2) Pertinent citations on ryanodine and its chemistry are given in ref 3.

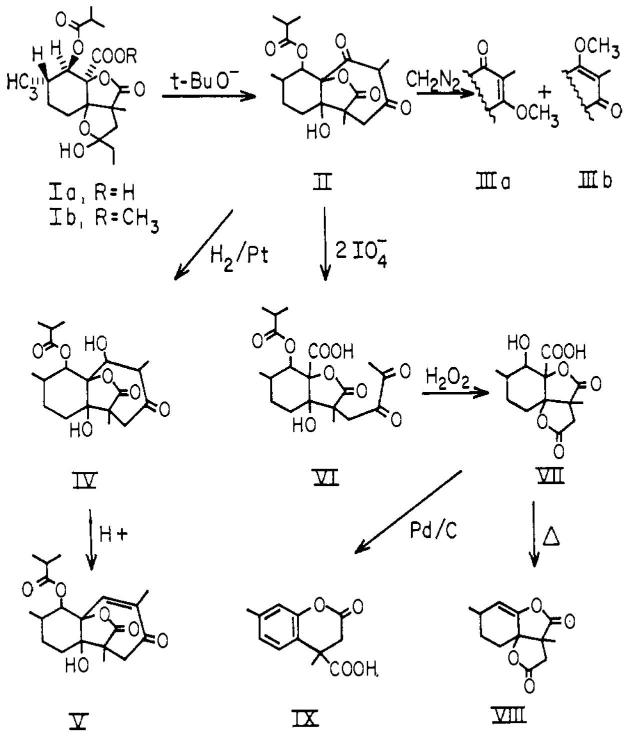
(3) U. Hollstein and H. Rapoport, *J. Am. Chem. Soc.*, **90**, 3864 (1968).

(4) Satisfactory elemental analyses and spectral data were obtained for all compounds reported; ultraviolet spectra were taken in ethanol and are reported in mμ (ϵ); infrared spectra (as KBr wafers unless otherwise specified) are reported in cm^{-1} only for the hydroxyl and carbonyl regions; nmr spectra were taken at 60 and 100 Mc in $CDCl_3$ with internal TMS (δ 0).

periodate (the first mole hydroxylates the α carbon, the second mole cleaves the α-hydroxy ketone), yielding the acid $C_{19}H_{26}O_9$ (VI) (mp 212°; ν 3500, 1770, 1755, 1720). Structure VI has been assigned arbitrarily; the data do not differentiate between the two possible modes of cleavage. VI is a 1,2-diketone as shown by quinoxaline formation with *o*-phenylenediamine; the presence of the acetyl group was clear from the nmr. VI, with alkaline hydrogen peroxide, gave acetic acid, isobutyric acid by accompanying hydrolysis, and the acid VII.

Pyrolysis of VII to produce VIII, analogous to the previous conversion VIa*[5] to VIII, gave a much poorer yield, ascribed to the hydroxyl and carboxyl in VII being *trans*. A *trans* relationship between the secondary hydroxyl and adjacent carbonyl is assigned as the original configuration in both I and I*. In I, the facile and parallel decarboxylation and elimination of isobutyric acid on treatment with alkali supports this stereochemistry. It remains unchanged throughout the degradation as witnessed by the coupling constant between the protons on the hydroxyl-bearing carbon and the adjacent methyl-bearing carbon (J = 9–11 Hz, *trans* diaxial protons).

In I* the same relationship holds initially (J = 11 Hz). However, acid-catalyzed formation of the internal enol ether II* causes an inversion at the secondary alcohol carbon, and the coupling constant between these two protons becomes, and remains, 2 Hz. Thus in VIa* the hydroxyl and carboxyl are now *cis* and consistent with a ready thermal decarboxylation–dehydration, giving VIII in excellent yield.



Treatment of hydroxy acid VII with palladium on carbon (di-*n*-hexyl ether, 200°) caused decarboxylation and aromatization to dihydrocoumarin IX, identical with the compound previously reported.[3] Thus dihydrocoumarin IX is the end product of this sequence (I → II → VI → VII → IX) as it was in the degradation of the C_{19} 1,3-diketone.[3] The nature of the reactions employed and the properties of the intermediates establish the structures as shown, with stereochemistry in the cyclohexane as given for I. The recent[6] structure presented for ryanodol must also accommodate the C_{19} acid and the C_{19} 1,3-diketone,[3] both now of established structure, which along with formic acid are the products of the action of 3 mol of periodate.

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(5) Starred numerals refer to compounds obtained in another degradation sequence, as presented in ref 3.

(6) S. N. Srivastava and M. Przybylska, *Can. J. Chem.*, **46**, 795 (1968), have presented a structure for ryanodol *p*-bromobenzyl ether based on X-ray diffraction studies.

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The Thermal Racemization of Aryl Arenethiolsulfinates. An Extraordinary Rate Acceleration of the Inversion of Sulfoxide Sulfur

Sir:

Unsymmetrically substituted sulfoxides, $R_1S(O)R_2$, are known to be optically stable substances which may undergo thermal racemization *via* pyramidal inversion only under forcing conditions. Recent data[1] indicate typical activation parameters for such inversion to be $\Delta H^{\ddagger}$ = 40 kcal/mol, $\Delta S^{\ddagger}$ = 0 eu, yielding conveniently measurable racemization rates in the neighborhood of 200°.

Although no quantitative information is available on other sulfoxidic substances such as sulfinate or sulfite esters, these also appear to be optically stable under normal conditions and in the absence of acid and nucleophilic catalysis.[2]

In contrast to this behavior, another class of sulfoxidic substances, the aryl arenethiolsulfinates, ArS(O)SAr, which have been recently prepared in an optically active form[3] exhibit exceptionally high optical lability.[3] Mechanistic studies in our laboratory and in that of Kice have revealed that racemization of thiolsulfinates can be achieved by several mechanisms, including a nucleophile-catalyzed route[4] and a concerted nucleophile- and electrophile-catalyzed route.[5] In this communication we wish to report that racemization of thiolsulfinates may also occur in an uncatalyzed path which appears to involve pyramidal inversion at the sulfoxide sulfur. The evidence follows.

Optically active thiolsulfinates, in solution and in the absence of nucleophilic and/or electrophilic substances, lose optical activity without undergoing any appreciable chemical change. The uv absorption spectrum remains unchanged during racemization and the product recovered after 10 half-lives is identical with the starting material except for optical activity. Racemization rates for two substrates under a variety of conditions are reported in Table I.

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(1) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3138 (1966).

(2) H. F. Herbrandson and R. T. Dickerson, Jr., *ibid.*, **81**, 4102 (1959).

(3) (a) W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965); (b) J. L. Kice and G. B. Large, *Tetrahedron Letters*, 3537 (1965).

(4) P. Koch, unpublished.

(5) J. L. Kice and G. B. Large, *J. Am. Chem. Soc.*, in press. We are indebted to Dr. Kice for letting us know their results in advance of publication.