1–8 if it is assumed that –HgX is considerably larger than –H, but smaller than $-CH_3$.[6]

The potential advantages of mercury–proton splitting in the structural determination of olefinic compounds, as well as in conformational analysis, are numerous. Methoxymercuric halide adducts of olefins can be prepared as rapidly and conveniently as the corresponding dibromides, are more stable, and are free from complications due to carbonium ion rearrangements and conjugate addition.[7] They are generally hydrophobic solids which crystallize in analytical purity from ethanol–water mixtures and are abundantly soluble in carbon tetrachloride. The original olefins can be readily regenerated, if necessary.

Work now in progress in this laboratory suggests that the magnitude of mercury–proton 4σ coupling is highly sensitive to electronic effects of substituents, foreshadowing some utility in theoretical studies as well.

(6) F. R. Jensen and L. H. Gale [*J. Am. Chem. Soc.*, **82**, 145 (1960), and preceding papers] showed that –HgBr exhibits little or no conformational preference as a substituent on the cyclohexane ring, implying that the long (2.33 Å.) C–Hg bond minimizes 1,3-axial,axial repulsions. That mercury behaves as a large atom toward β-substituents in acyclic compounds is evident from the magnetic nonequivalence of the $-CH_2$-HgCl protons in compounds **1**, **7–9**, and **11–15**. (The methylene protons in **10** are apparently accidentally equivalent.) Magnetic nonequivalence is especially easy to establish in these compounds, since *there are two different* H^1–C–Hg^{199} *coupling constants;* this is apparently the first reported case in which geminal protons couple nonidentically with a nucleus attached to the same saturated carbon atom. The n.m.r. spectra of compounds **13–15** are particularly striking, since both methylene groups appear as widely spaced AB quartets (J_{AB} = 12–15 c.p.s., $\Delta\nu_{AB}$ = 8–38 c.p.s.) with sharply resolved proton–proton 4σ coupling (J = 1–1.5 c.p.s.) superimposed on the low-field half of each quartet. The stereoelectronic implications of this result will be discussed in a subsequent communication.

(7) T. G. Traylor, *J. Am. Chem. Soc.*, **86**, 244 (1964), and references cited therein. Breakdown of stereospecificity resulting from the duality of mechanisms discussed by Traylor might prove troublesome with certain strained olefins.

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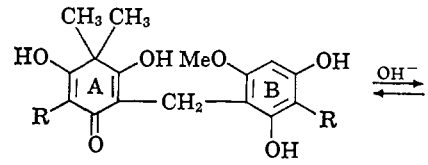
The Biosynthesis *in Vivo* of Methylenebisphloroglucinol Derivatives

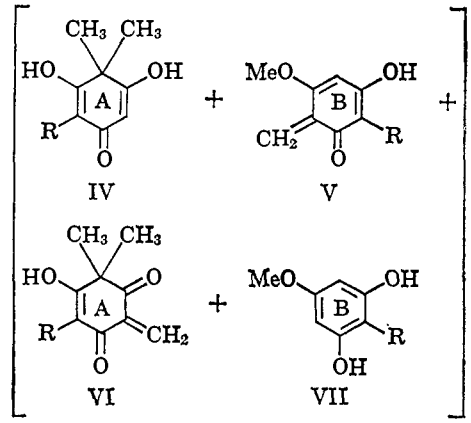
Sir:

Dimeric acylphloroglucinol derivatives such as desaspidin (I), margaspidin (II), and albaspidin (III)[1] are presumably derived from acetate and malonate units in the same manner as griseofulvin and quercetin, etc.[2] We have been concerned with later aspects of the biosynthesis, in particular, the source of the methyl and methylene units, the mechanism of the dimerization process, and the sequence in which these events occur.

Methionine-methyl-C^{14} (specific activity 11.7 curies/mole, 48.8×10^6 d.p.m. total) was injected into adult *Dryopteris marginalis* ferns and the aforementioned compounds were isolated (incorporation: 0.76% in raw filicin), purified, and degraded by taking advantage of the "rottlerone change."[3] The methylene carbon



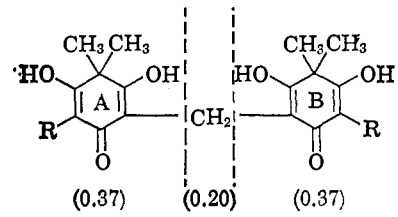
I (0.24 mcurie/mole = 1.00)



IV + V + VI + VII

dimedone

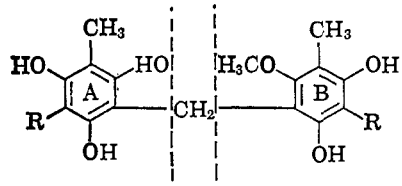
IV (0.50) + VII (0.24) + HCHO dimedone (0.24)



(0.37) (0.20) (0.37)

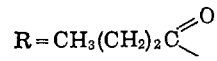
III (0.13 mcurie/mole = 1.00)

+



(0.25) (0.50)

II (0.12 mcurie/mole = 1.00)



was withdrawn from the equilibrium as the dimedone adduct of formaldehyde, and the radioactivity of the liberated monomers (*e.g.*, IV and VII) was used as a measure of the activity of their contained methyl groups.

As expected, the C- and O-methyl groups are derived from methionine (presumably *via* S-adenosylmethionine), and in common with analogous processes[4] all of the methyl carbons are derived with the same efficiency, suggesting that the complete synthesis of a given molecule occurs from one methyl pool.[5]

(1) For the most recent paper in this series see A. Penttila and J. Sundman, *Acta Chem. Scand.*, **18**, 1292 (1964). Margaspidin is a new compound: A. Penttila and G. J. Kapadia, *J. Pharm. Sci.*, in press. This paper was presented in part at the Sixth Annual Meeting of the American Society of Pharmacognosy, June 17, 1965.

(2) For a review see A. J. Birch, *Proc. Chem. Soc.*, 3 (1962).

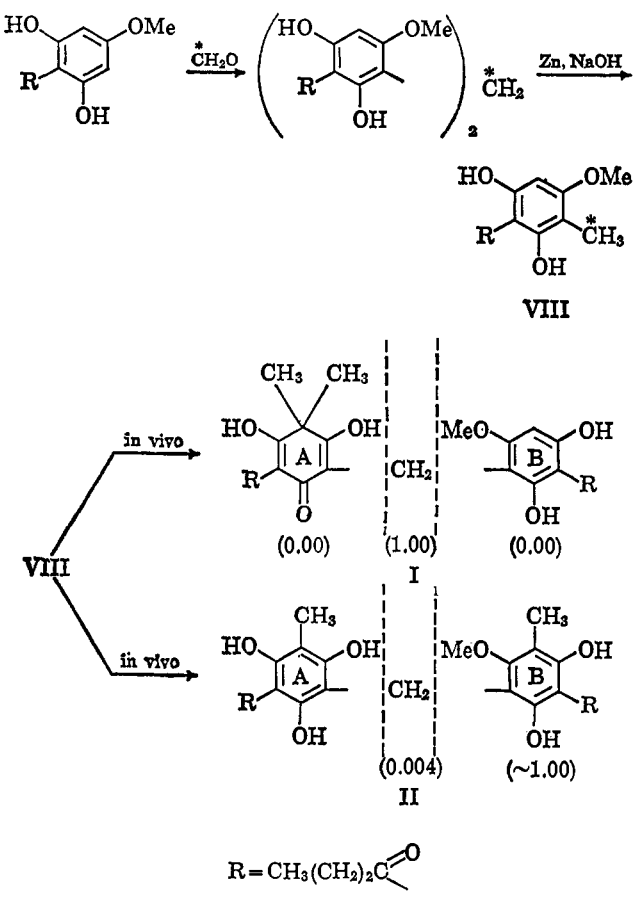
(3) T. Backhouse, A. McGookin, J. Matchet, A. Robertson, and E. Tittensor, *J. Chem. Soc.*, 113 (1948).

(4) J. F. Snell, A. J. Birch, and P. L. Thomson, *J. Am. Chem. Soc.*, **82**, 2402 (1960).

(5) However, the fact that I has a higher specific activity than either II or III when corrected for the number of methyl and methylene groups present suggests that the sites of their synthesis may differ. In addition, the different activities observed fortuitously remove the objection that equilibration among the various compounds may have occurred in nature or during isolation, *via* the "rottlerone change." Subsequent isolations gave still other ratios of activities between I, II, and III.

The methylene bridge also is derived from methionine with the same efficiency, suggesting that it has evolved from the methyl group of a monomeric species perhaps *via* an *o*- or *p*-quinone methide[6] such as V or VI (or their hydration products).

For this reason, methyl-labeled aspidinol (VIII)[7] was prepared as shown and fed (12.7 curies/mole, 16.8×10^6 d.p.m. total) with radioactivity recovered (incorporation: 1.17% in raw filicin) in both I (26.5 μcuries/mole) and II (112 μcuries/mole). Degradation of I, as above, showed that all of its activity resides in



the methylene bridge, strongly indicating that VIII is the precursor of both the B ring and methylene bridge, *via* the aforementioned oxidation process. By contrast, only traces of activity were found in the methylene carbon of II,[8] most of the activity residing in the B ring section. Here, VIII is directly the precursor of the B ring while the methylene bridge and A ring are presumably derived from a naturally occurring C-methyl isomer of VIII.

Lederer[9] has recently drawn attention to the function of methylene quinones such as V and VI in oxidative phosphorylation. Desaspidin is in fact a potent uncoupling agent,[10] and we suggest that the function of these compounds in the plant may be to act as oxidative phosphorylation regulators whose efficiency in this process is modified by the degree of methyl substitution.

(6) A. B. Turner, *Quart. Rev.* (London), **18**, 347 (1964).

(7) Monomers such as VIII have been isolated (*e.g.*, R. C. Blakemore, K. Bowden, J. L. Broadbent, and A. C. Drysdale, *J. Pharm. Pharmacol.*, **16**, 464 (1964)), but recent studies (A. Penttila and J. Sundman, unpublished results) show that VIII, at least, never occurs in nature and must be considered an artifact arising from excess heat or alkali during isolation.

(8) To the extent that activity resides in the bridge carbon, methylation of VIII must have occurred. Although further confirmation is required on this point, this suggests that aromatic C-methylation occurs *after* the polyketone stage; *cf.* ref. 2.

(9) E. Lederer, *J. Biol. Chem.*, **93**, 449 (1964).

(10) L. Runeberg, Thesis, University of Helsinki, 1963, Societas Scientiarum Fennica, Commentationes Biologicae, XXVI, 7.

(11) Fulbright Research Scholar, 1964-1965, on leave from Medica Ltd., Helsinki, Finland.

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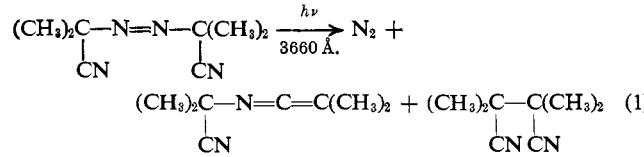
Photochemistry of Adsorbed Organic Molecules. II. "Cage" Effects in the Photolysis of Azobisisobutyronitrile and Tetramethyl-1,3-cyclobutanedione on Silica Gel[1]

Sir:

We[1] and others[2] have previously reported that physical adsorption strongly perturbs electronic absorption spectra of relatively polar organic molecules. Obviously, then, the electronic configurations of the bound, or adsorbed, species are not the same as the species "free" in solution. One could, and should, therefore, expect different photochemical behavior in the two different environments on this ground alone, but also it is highly reasonable that the secondary reactions will also be considerably different.

We wish now to report two photochemical reactions that are profoundly affected by physical adsorption in solvent–silica gel matrices

Azobisisobutyronitrile (AIBN) in benzene solvent has been reported to undergo photodecomposition with light of 3660 Å. to yield approximately 60% of the ketenimine, dimethyl-N-(2-cyano-2-propyl)ketenimine (eq. 1),[3] the remainder being tetramethylsuccinonitrile.



The quantum yield for destruction of AIBN (in benzene) was measured by Smith and found to be 0.46. The ketenimine has a very characteristic absorption band at about 2900 Å., and our own observations of the photolysis of AIBN in benzene show the pronounced appearance of this band with time and a corresponding disappearance of the n–π* (at 3300–3500 Å.) band of the azo compound. We have found that when the medium is changed to benzene–silica gel, AIBN decomposes at a virtually identical rate, but *no ketenimine is formed*, the sole product being the tetramethylsuccinonitrile. Irradiations were carried out in 0.1-cm.-path-length cells at 3660 Å.; the ultraviolet spectrum was scanned at various time intervals. The n–

(1) Number I of this series is: P. A. Leermakers and H. T. Thomas, *J. Am. Chem. Soc.*, **87**, 1620 (1965).

(2) For an excellent review see A. Terenin, *Advan. Catalysis*, **15**, 227 (1964).

(3) P. Smith and A. M. Rosenberg, *J. Am. Chem. Soc.*, **81**, 2037 (1959).