excited t-$C_4H_9^+$ is formed in the gas phase and exhibits this by nonselective reactivity in the liquid phase. Two independent sets of experiments support this. When t-$C_4H_9^+$ is deexcited in the gas phase by collisions with added argon, its reaction selectivity toward liquid isobutylene increases. When reaction 1 takes place in the liquid phase, nonexcited t-$C_4H_9^+$ is formed which exhibits considerable reaction selectivity toward isobutylene.

Argon and neon were tested as deexciters for t-$C_4H_9^+$. Both can deexcite vibrational levels of molecules as well as act as moderators for translational energy.[4] Table I shows that reaction selectivity for the primary carbon increases from 53% with no added argon to 76% with 3 torr and above added argon. However, from 1 to 10 torr of neon shows no effect on the C_8 distribution. If neon and argon were acting entirely as translational energy moderators, 3 torr of Ar would be equivalent to 4.5 torr of neon.

The absence of ion translational energy effects on the C_8 distribution is also indicated by the lack of an applied field effect. We conclude that vibrational deexcitation is occurring and that argon is much more effective for vibrational deexcitation than is neon. Such a large difference in vibrational deactivation efficiency between neon and argon is somewhat surprising. However, deactivation of ions may be more sensitive to polarizability effects than is deactivation of neutral molecules. Further studies of this point are in progress.

The deexcitation experiments were done at a liquid isobutylene temperature of $-128°$ where the vapor pressure is 0.04 torr. $C_4H_9^+$ makes one to two collisions before reaching the liquid at this pressure under our experimental conditions. Maximum effective deexcitation by argon occurs at 3–4 torr which means that about 100 collisions of $C_4H_9^+$ with argon are necessary for maximum reaction selectivity. The selectivity of deexcited $C_4H_9^+$ never rises above 78%, whereas percentages approaching 90–100% are expected. The limiting observed value of 78% may be due to those $C_4H_9^+$ ions that are formed in a narrow layer above the liquid and are not deexcited before being injected.

Table II shows that the reaction selectivity of t-$C_4H_9^+$ can also be increased by lowering the liquid temperature. Lowering the temperature lowers the isobutylene vapor pressure. At 0.04 torr and above, $C_4H_8^+$ makes one or more gas-phase collisions with isobutylene to form vibrationally excited t-$C_4H_9^+$. However, below 0.04 torr more and more of the $C_4H_8^+$ ions are directly injected into the liquid. Reaction 1 then occurs in the liquid phase and the product t-$C_4H_9^+$ ion is vibrationally deexcited. At vapor pressures of only 0.004 torr the reaction selectivity reaches 90%. This suggests that thermal energy t-$C_4H_9^+$ ions are indeed quite selective in their reaction with isobutylene. In fact, 2,4,4-trimethylpentene-2 accounts for 84% of all the C_8 products.

Acknowledgment. This research was supported by the Air Force Rocket Propulsion Laboratory, Edwards, California.

(4) V. N. Kondrat'ev, "Chemical Kinetics of Gas Reactions," Addison-Wesley Inc., Reading, Mass., 1964, Chapter 6.

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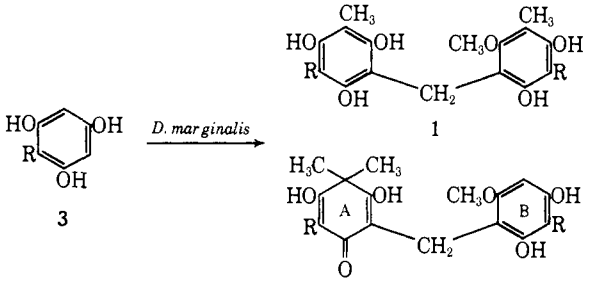
The Incorporation of Sodium Butyrate into Methylenebis(butyrylphloroglucinols) by a Novel Biosynthetic Pathway

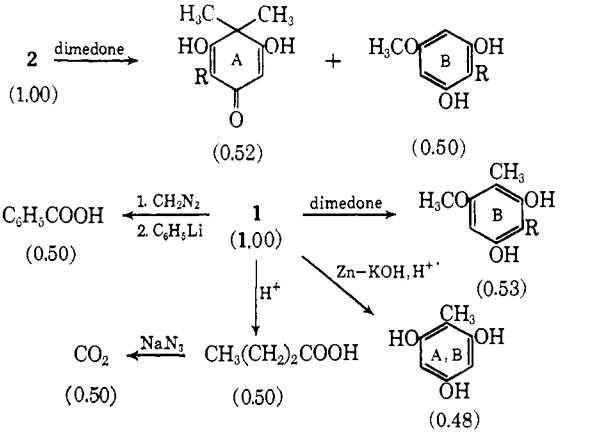
Sir:

Recent work has shown that methylenebis(butyrylphloroglucinols) such as margaspidin (**1**) and desaspidin (**2**) are biosynthesized by oxidative dimerization of the methylated monomers of butyrylphloroglucinol (**3**)[1] and that all of the methyl groups are derived from methionine.[2]

Butyrylphloroglucinol (**3**) itself would seem to be derived from one butyrate and three malonate units or ultimately one acetate and four malonate units, all as their thiol ester or acyl carrier protein equivalents.[3] To



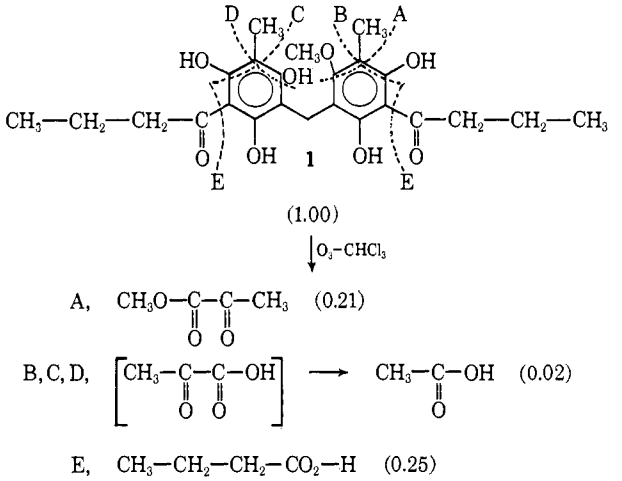
prove the former, sodium butyrate-1-^{14}C (3.6×10^{12} dpm/mole, 0.5 mCi) was administered to *Dryopteris marginalis* tubers during a period of 4 days (0.17% average incorporation). Degradation[2] of recovered **1** (4.73×10^8 dpm/mole) and **2** (4.8×10^8 dpm/mole) with dimedone showed that the activity was equally distributed between the two butyrylphloroglucinol moieties as expected. However, further degradation of the methyl ether of **1** with phenyllithium as well as decarboxylation of the derived butyric acid (Schmidt degradation)[4] showed that only one-half of the total activity of **1** was located at the carbonyl carbons of the side chain and that the remainder of the side chain was essentially inactive. Assuming the butyrate-plus-three-malonate hypothesis, this requires that the activity of the three malonate units derived from catabolism of butyrate sum fortuitously to the same radioactivity as the side chain.



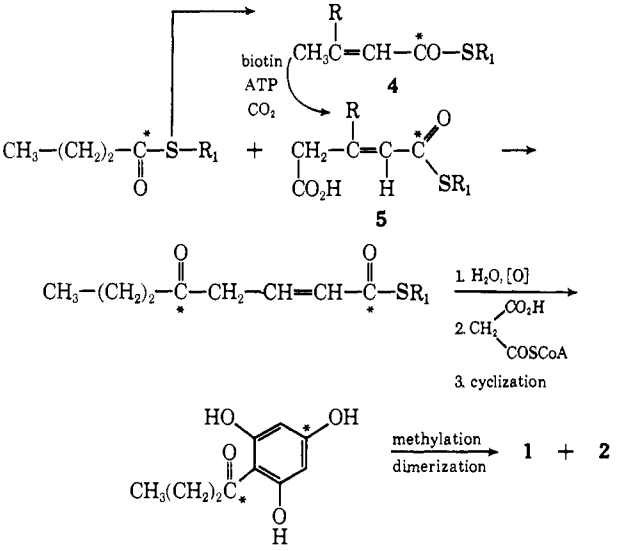
(1) A. Penttila and H. M. Fales, *J. Amer. Chem. Soc.*, **88**, 2327 (1966).
(2) A. Penttila, G. J. Kapadia, and H. M. Fales, *ibid.*, **87**, 4402 (1965).
(3) P. R. Vagelos, *Ann. Rev. Biochem.*, **33**, 139 (1964).
(4) R. O. Brady, R. M. Bradley, and E. G. Trams, *J. Biol. Chem.*, **235**, 3093 (1960).

When a second feeding experiment produced identical results, the location of activity within the ring was determined by carefully controlled ozonolysis of **1**. Methyl pyruvate, acetic acid, and butyric acid were isolated and quantitated by gas chromatography.[5]

Essentially all of the activity on the ring[6] was found in the methyl pyruvate, derived by the indicated cleavage (A). The acetic acid (cleavages B, C, and D) contained 2% of the original activity, proving, along with the previous butyric acid degradations, that conversion of butyrate to acetate plays a minor role in this system.



We must conclude that *two discrete four-carbon units* have joined *head to tail* prior to combination with a single two-carbon unit. Although chain initiation by butyrate is well documented,[7] we know of no precedent for the subsequent coupling reaction. β-Methylcrotonyl-CoA (**4**, R = CH_3) is a substituted vinylog of acetyl-CoA and has been shown to undergo biotin-dependent carboxylation in leucine metabolism to give **5** (R = CH_3).[8] A similar reaction with crotonyl-CoA (**4**, R = H, derived from butyrate)[9] would provide the necessary activation for its condensation with butyryl-CoA.[9]



The generality of the reaction and the nature of the intermediate are under current investigation.

(5) Reoplex 400, 20% on Gas-Chrom P (HMDS treated), 100–120 mesh (Applied Science Laboratories, Inc.), 6 ft × 1/8 in. column, 130°, flash heater 178°, gas flow 35 cc/min. Retention times: methyl pyruvate 8.1 min; acetic acid 15.3 min; butyric acid 34.6 min. Similar conditions were employed for the preparative glpc except that the column was 7 ft × 1/4 in at 125°.

(6) Average of two determinations.

(7) S. J. Wakil and J. Ganguly, *J. Amer. Chem. Soc.*, **81**, 2597 (1959); M. G. Horning, D. B. Martin, A. Karmen, and P. R. Vagelos, *Biochem. Biophys. Res. Commun.*, **3**, 101, (1960); R. W. Long and J. W. Porter, *J. Biol. Chem.*, **234**, 1406 (1959).

(8) A. Del Campillo-Campbell, E. E. Dekker, and M. J. Coon, *Biochim. Biophys. Acta*, **31**, 290 (1959).

(9) Dr. R. O. Brady (National Institutes of Health) has pointed out that tetrolyl-CoA ($CH_3C{\equiv}CCOSCoA$) could also function as a plausible intermediate in the reaction. The intermediacy of acetoacetate is a third possibility but the methylene carbon atom is already activated and coupling at this point would lead to a different labeling pattern.

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Book Reviews

Gas-Phase Reaction Rate Theory. By HAROLD S. JOHNSTON, University of California, Berkeley, Calif. The Ronald Press Co., 15 East 26th St., New York, N. Y. 1966. ix + 362 pp. 16 × 23.5 cm. $10.00.

This book is intended as a text for an introductory course in gas kinetics. It begins, as texts of this kind must, by drawing together the necessary array of widely diversified background information. The first seven chapters contain a well-balanced survey of experimental techniques, a discussion of tunneling, qualitative features of potential surfaces and particle dynamics, a quick introduction to normal coordinates, and elementary material drawn from statistical thermodynamics and the kinetic theory of gases. The stage is thus set for the beginning of the book proper at page 117.

The main focus is on the kinetics of elementary bimolecular reactions. Chapters 8 and 9 present a careful derivation of the transition-state theory under conditions of chemical equilibrium—the assumptions inherent in its use under other conditions are clearly identified—and a corresponding treatment from the collisional point of view, along with comparisons of the two. Chapter 10, the longest and best in the book, covers the bimolecular exchange reaction of three hydrogen atoms in a thorough and up-to-date way. The next three chapters extend the discussion to other reactions. Appropriately, Professor Johnston's own research results appear frequently in these.

Other classes of reaction are discussed in less detail. Recombination reactions, at the level of iodine atoms and unsophisticated theory, are allotted 10 pages. The selection of material carries a mild implication that this field has been stagnant since 1960, with which some experimentalists will surely disagree. Unimolecular reactions occupy more space (35 pages) but are treated in a less even way; quantum-statistical effects are well covered and the Slater