dechlorination with the sulfides of palladium, platinum, rhodium, and ruthenium; no detectable debromination with platinum sulfide, trace debromination with rhodium sulfide, and appreciable debromination with palladium sulfide.

The selective hydrogenation of haloaryl nitro compounds also is applicable to polyhalo-substituted aromatics. For example, 2,5-dichloronitrobenzene was quantitatively hydrogenated to 2,5-dichloroaniline without dehalogenation when using a platinum sulfide catalyst.

Results of a large number of preparative experiments[3,6] plus development studies[6] have clearly demonstrated the superiority of platinum metal sulfide catalysts for the reductive alkylation of primary arylamines, or their nitro precursors, with aliphatic ketones. They usually produce a pure product with little or no side reactions, require no excess above the stoichiometric amount of ketone, and are active at relatively low pressures of hydrogen.

Platinum metal sulfide catalysts may be used for the reductive alkylation of aliphatic amines and their nitroalkane precursors with aliphatic ketones.[3] These catalysts might be of value when the feed contains a poison that prevents the use of other catalysts.

The platinum metal sulfides are useful for the selective hydrogenation of aryl disulfides to the corresponding thiophenols, *e.g.*, phenyl disulfide to thiophenol, without further reduction to the hydrocarbon and hydrogen sulfide.[3] Cleavage of the thioether linkage, as in phenyl sulfide, requires very severe conditions under which the thiophenol formed is further reduced to the hydrocarbon.[3] On the other hand, this lack of reactivity for carbon–sulfur bond cleavage permits the selective reduction of other functional groups in thioethers, *e.g.*, the previously mentioned conversion of a bis(nitrophenyl) sulfide to the corresponding bis(aminophenyl) sulfide.

Phenyl sulfone was very resistant to hydrogenation with a rhodium sulfide catalyst, there being no detectable reaction at 290° and over 122 atm.[3] There was little or no hydrogenation of arylsulfonic acids, arylsulfonic acid salts, or arylsulfonamides with a platinum sulfide catalyst at 240–250° and pressures of 95–122 atm.

The relative inactivity of these catalysts for the hydrogenation of aromatic rings, ketones, nitriles, esters, and some other functional groups, sometimes under severe reaction conditions, often permits useful selectivity in the hydrogenation of polyfunctional compounds. It also allows a wide choice of solvents for the hydrogenation reactions.

A typical reductive amination experiment follows. To a 600-ml. stainless-steel Magne-Dash autoclave were added 103.5 g. (0.54 mole) of 2,5-dichloronitrobenzene (Eastman Kodak 187), 230 ml. of methanol, and 3.0 g. of 5% platinum sulfide on carbon.[7] The autoclave was sealed and purged first with nitrogen and then with hydrogen. Hydrogen was added to a pressure of 41 atm. and the reaction mixture then was heated for 1.25 hr. at 85° and 34–54 atm., at which point gas absorption stopped at approximately the theoretical usage of hydrogen. The autoclave was cooled and vented, and its content filtered to remove the catalyst. The filtrate was made strongly alkaline with dilute sodium hydroxide and the methanol solution was concentrated by distillation. Benzene was added and the remaining methanol was removed by distillation. The benzene solution then was cooled and washed with water. The combined aqueous solutions gave a negative test for chloride anion with silver nitrate; thus there had been negligible dehalogenation. The benzene solution was distilled up to a pot temperature of 207° at atmospheric pressure. The residue consisted of 87 g. (99.5% yield) of 2,5-dichloroaniline that melted at 48–49.5°; there was no depression on a mixture melting point with an authentic sample.

A typical reductive alkylation experiment is here described. To a 600-ml. stainless-steel Magne-Dash autoclave were added 158 g (0.86 mole) of N-phenyl-*p*-phenylenediamine, 95.2 g. (0.95 mole) of methyl isobutyl ketone, and 3.2 g. of 5% platinum sulfide on carbon.[7] The autoclave was sealed and purged with nitrogen and then with hydrogen, and hydrogen was added to a pressure of 27 atm. The autoclave was heated for 4.5 hr. at 175–180° and 27–41 atm. The vessel was cooled and vented, and the reaction mixture was removed. The catalyst was removed by filtration. After topping the filtrate to a pot temperature of 188° at 32 mm. there was obtained 228 g. (99% yield) of N-(1,3-dimethylbutyl)-N′-phenyl-*p*-phenylenediamine as a residue product melting at 45–47°.

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(6) F. S. Dovell and H. Greenfield, unpublished work.
(7) Commercially available from Engelhard Industries, Inc.

Marasmic Acid

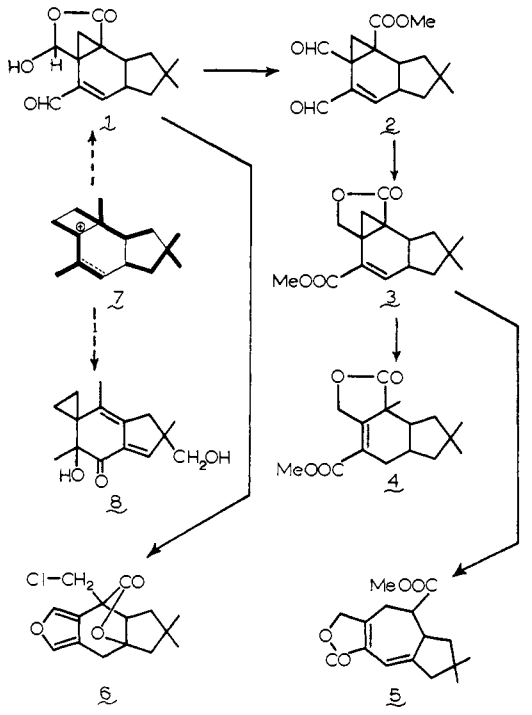
Sir:

The evidence presented here requires that the terpenoid antibiotic, marasmic acid, have the nonisoprenoid structure **1**. The natural occurrence of such a molecule provides circumstantial evidence for the existence of an interesting biosynthetic pathway in farnesyl ester cyclization from which other modified sesquiterpenoids are accessible.

Marasmic acid,[1] m.p. 173–174°, $[\alpha]_D$ +182°, has the empirical formula $C_{15}H_{18}O_4$.[2] One oxygen atom is present in an α,β-unsaturated aldehyde [λ_{max} 241 mμ (ϵ 9700); ν_{max} 1684 and 1631 cm.$^{-1}$; singlet, τ 0.53, 1 H] with a β-vinylic proton (doublet, τ ~3.50, J ~2 c.p.s.). The remaining three oxygen atoms are contained in a γ-lactol (ν_{max} 3350 and 1773 cm.$^{-1}$) in which there is a proton attached to the lactol ether terminus (singlet, τ 3.87, 1 H). On methylation (diazomethane) marasmic acid is converted into the methyl ester **2** (ν_{max} 1724 cm.$^{-1}$) of a dialdehydecarboxylic acid (doublet, τ 3.45, 1 H, J ~ 2 c.p.s.; singlet, τ 0.52,

(1) F. Kavanagh, A. Hervey, and W. J. Robbins, *Proc. Natl. Acad. Sci. U. S.*, **35**, 343 (1949).
(2) Adequate analyses have been recorded for all substances reported. Where not specifically mentioned all spectroscopic data are in agreement with the assigned structures.

1 H; singlet, τ 0.17, 1 H). Treatment with aqueous base induces an internal Cannizzaro reaction leading, after methylation, to **3** (m.p. 127–128°; $[\alpha]D$ +80°; λ_{max} 233 mμ (ϵ 6300); ν_{max} 1767, 1709, and 1634



cm.$^{-1}$; signals at τ 8.98 (3 H, singlet) 8.95 (3 H, singlet), 6.20 (3 H, singlet), 5.52 (2 H, AB pattern, J_{AB} = 10 c.p.s., $\delta_B - \delta_A$ = 20.7 c.p.s.), and 3.35 (1 H, doublet, $J \sim 2$ c.p.s.).

In these substances signals for two methyl groups attached to quaternary carbon can be discerned. Hydrogenation of **3** to the dihydro compound (**4**, m.p. 110–111°; $[\alpha]D$ +96°; λ_{max} 231 mμ (ϵ 10,100); ν_{max} 1773, 1709, and 1675 cm.$^{-1}$) gives, by 1,4-addition to the vinylcyclopropane system, a substance in which a signal for a third methyl group (τ 8.71) can be observed. The latter substance, unlike **3**, shows no signal for vinylic proton absorption but has a band at 4.83 (2 H, broad) for allylic protons on carbon bearing oxygen.

This sequence provides direct evidence for the presence of the cyclopropane ring for which spectroscopic evidence was also available. The position of this cyclopropane ring within the concatenation of carbonyl functions was shown by the conversion of **3** under more strongly basic conditions to **5** (m.p. 142–143°; $[\alpha]D$ +216°; λ_{max} 274 mμ (ϵ 7500); ν_{max} 1754, 1736, and 1686 cm.$^{-1}$; signals at τ 9.03 (3 H, singlet), 8.90 (3 H, singlet), 6.27 (3 H, singlet), 5.30 (2 H, singlet), and 3.86 (1 H, singlet). This transformation represents a vinylogous extension of the base-catalyzed opening of homocaronic acid.[3]

Treatment of marasmic acid with refluxing hydrochloric acid in acetic acid resulted in cleavage of the cyclopropane ring and cyclization to the lactonic furan **6** (m.p. 93–94°; $[\alpha]D$ −13°; λ_{max} 215 mμ (ϵ 5300); ν_{max} 1776 cm.$^{-1}$). The furan nature of **6** was shown by the formation of a Diels–Alder adduct with acetylenedicarboxylic ester. In addition, every proton with its expected coupling could be identified and clearly discerned in the n.m.r. spectrum[4] [signals at τ 8.92 (3 H, singlet), 8.80 (3 H, singlet), 8.04 (2 H, AB pattern, J_{AB} = 15 c.p.s., $\delta_B - \delta_A$ = 26 c.p.s.), 7.8–8.7 (2 H, AB of ABX), 7.08 (2 H, AB, J_{AB} = 17 c.p.s., $\delta_B - \delta_A$ = 23.5 c.p.s.), 7.3 (1 H, X of ABX, doublet of doublets), 6.12 (2 H, AB, J_{AB} = 12 c.p.s., $\delta_B - \delta_A$ = 21.9 c.p.s.), and 2.76 and 2.66 (1 H each, narrow with fine splitting)]. The lack of coupling between the pair of methylene protons in the cyclopentane ring required that they be separated by the geminal methyl groups. Confirmation of this and of the entire carbon skeleton was obtained by the classical method of dehydrogenation.

Reduction of marasmic acid with sodium borohydride and treatment with palladized charcoal at 300° gave two aromatic hydrocarbons. Spectroscopic data required that these be methylated indans, and the more substituted was identified as 2,2,4,5,6-pentamethylindan by direct synthesis.[5] This substance contains all the carbon atoms of marasmic acid except that present in the carboxyl function. Structure **1** follows unequivocally.

The structure of marasmic acid as here presented represents a new mode of cyclization of a farnesyl precursor. The most likely biogenetic route appears to be that through an ion such as **7**; in principle this may be obtained by a direct cyclization. It is pertinent that the formation of marasmic acid and of illudin-S (**8**)[6] represents two alternative migrations in the same cyclobutyl cation (**7**).

(3) G. Widmark, *Arkiv Kemi*, **11**, 195 (1957).

(4) Using deuterium chloride the resultant furan had incorporated three deuterium atoms. These were the two fuanic protons and one of the adjacent methylene protons. On irradiation of the deuterium, kindly performed by Dr. J. B. Stothers, a one-proton singlet was obtained instead of the AB pattern in the undeuterated material.

(5) The less substituted was identified as 2,2,4,5-tetramethylindan by synthesis of 2,2,4,6-tetramethylindan, the only other possible isomer.

(6) T. C. McMorris and M. Anchel, *J. Am. Chem. Soc.*, **85**, 831 (1963); M. Tuda, Y. Yamada, N. S. Bhacca, K. Nakanishi, and M. Ohashi, *Chem. Pharm. Bull.* (Tokyo), **7**, 853 (1964); K. Nakanishi, M. Tada, and Y. Yamada, *ibid.*, **7**, 856 (1964); T. C. McMorris and M. Anchel, *J. Am. Chem. Soc.*, **87**, 1594 (1965).

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Cyclopentadienone Ketals

Sir:

We wish to present an exceptionally convenient synthesis of the ketals of cyclopentadienone and to report the use of these active dienes in the preparation of 7-substituted norbornenes. Further, we wish to draw attention to the extraordinary influence of the ketal group on the reactivity of these dienes.

Cyclopentadienone would seem in theory to be the most suitable reagent for norbornenone syntheses. Unfortunately this dienone has but fleeting existence; spontaneous dimerization occurs even at very low temperatures. In 1962 DePuy[1] and Vogel[2] recognized independently that the ketals of cyclopentadienone would possess the synthetic utility of the parent ketone

(1) C. H. DePuy, B. W. Ponder, and J. D. Fitzpatrick, *Angew. Chem.*, **74**, 489 (1962); *J. Org. Chem.*, **29**, 3508 (1964).

(2) E. Vogel and E.-G. Wyes, *Angew. Chem.*, **74**, 489 (1962).