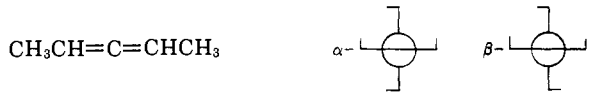


1,3-dimethylallene — A

1,2,1′,2′-tetramethylspiropentanes — C and D

When the arc is operated for 5–10 sec. with paraffin hydrocarbon covering the reaction vessel walls, less than a monomolecular film is deposited. After shutting off the arc, olefin was added at various time intervals and the product composition was determined for each of these experiments. When the C_1 is allowed to age 120 sec. or longer the sole products are C and D in 51:49 ratio, resulting from ^3P reacting with *cis*-2-butene.[1]

The products from *cis*-2-butene and C_1 aged 9, 17, and 30 sec. revealed that precursors of A and B disappear with a half-life of approximately 2 sec., and the precursors of E through J disappear with a half-life of approximately 15 sec.

Analysis of spectra from isolated carbon atoms results in a term system with two metastable states ^1D and ^1S which lie 30 and 60 kcal., respectively, above the ^3P ground state.[2] These forbidden transitions have not been observed. Radiative lifetimes have been predicted[3] on purely theoretical grounds: $^1D \rightarrow {}^3P$, $\tau_{1/2}$ 2000 sec. and $^1S \rightarrow {}^1D$, $\tau_{1/2}$ 2 sec.

Spiropentane formations from ^3P carbon atoms and *cis*-2-butene are 100% nonstereospecific in one of the addition steps, leading to equal quantities of C and D. With the metastable forms present C becomes the major product, indicating they react by stereospecific steps only and are therefore singlet.[4] Since the 10^{-5} sec. free flight from the arc plasma to the walls is long compared to the radiative decay of all higher C_1 states to ^3P, ^1D, and ^1S, these are the only species available for reaction with olefin. It is reasonable to assign to our 2-sec. half-life C_1 the ^1S state and to the 15-sec. C_1 the ^1D state. The reverse designation is unlikely since the 2-sec. species brings higher energies to the reactants than the 15-sec. species (*vide infra*).

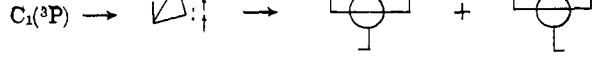
Although it is not yet apparent that ^1S carbon atoms do or do not react to produce C and E through J, the chemistry of the three varieties of C_1 can be summarized as follows for reactions with *cis*-2-butene.

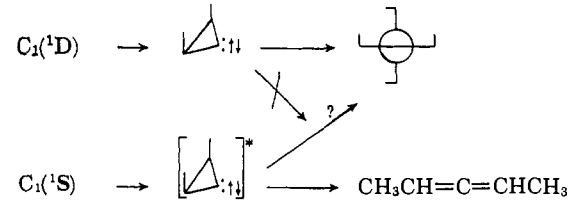
$$^3P \longrightarrow C, D$$

$$^1D \longrightarrow C, E\text{–}J$$

$$^1S \longrightarrow A, B\ (C, E\text{–}J)$$

In greater detail for reactions with identified products





There are a number of striking differences between the work cited here and the atomic carbon work reported by Wolfgang and co-workers.[5] For example, they find acetylene as a major reaction product with ethylene and we fail to find acetylene from interaction of a mixture of ^3P, ^1D, and ^1S carbon atoms with ethylene.[5a]

Benson[6] has suggested that singlet- and triplet-state designations are not required to explain nonstereospecificity in carbene–olefin addition reactions, nonstereospecificity being the resultant of excess energy in the cyclopropane. In condensed phase, dissipation of surplus vibrational energy to neighbors is probably fast compared to rotations about single bonds. Nonetheless, *the higher energy C_1 species add stereospecifically and the lower energy species nonstereospecifically.*

Acknowledgment. We acknowledge the financial support of the Air Force of Scientfic Research and the Army Research Office (Durham).

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The Biosynthesis of Psicofuranine[1]

Sir:

A number of nucleoside analogs and antibiotics that contain sugar moieties have been found in nature.[2,3] Very little is known concerning the biosynthesis of these nucleoside analogs or the sugar portion of these antibiotics. Suhadolnik, *et al.*,[4] have reported on the direct incorporation of adenosine into cordycepin (3′-deoxyadenosine), while glucose-C^{14} has been reported to be the direct precursor of the sugars in erythromycin-A[5] (L-cladinose and D-desosamine), in novobiosin[6] (noviose), and in magnamycin[7] (mycarose). This

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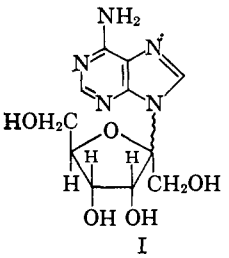
Table I. The Distribution of Carbon-14 in Psicofuranine

Expt.	Compd. added	% C^{14} in Adenine	% C^{14} in D-Psicose
1	Adenosine-U-C^{14}	98.0	2.0
2	Adenosine-U-C^{14}	86.0	14.0
3	Formate-C^{14}	99.5	0.5
4	Glucose-1-C^{14}	5.0	95.0
5	Glucose-6-C^{14}	25.0	75.0

Table II. Distribution of Carbon-14 in D-Psicose from Glucose-1-C^{14} and Glucose-6-C^{14}

Derivative	Carbon atoms	Glucose-1-C^{14}: C.p.m./mmole	Glucose-1-C^{14}: % C^{14}	Glucose-6-C^{14}: C.p.m./mmole	Glucose-6-C^{14}: % C^{14}
Psicosazone	1,2,3,4,5,6	52,200	100	4,580	100
Mesoxaldehyde-1,2-bisphenylhydrazone	1,2,3	42,000	81	0	0
Formaldimedone	6	5,000	10	4,020	88

communication reports the results on the incorporation of adenosine-U-C^{14}, formate-C^{14}, glucose-1-C^{14}, and glucose-6-C^{14} into the adenine and D-psicose of psicofuranine (6-amino-9-D-psicofuranosylpurine, I). The preparation of adenosine-U-C^{14} was reported earlier.[4] The labeled precursors were added to growing cultures



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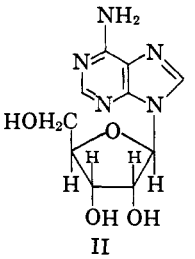

II

of *Streptomyces hygroscopicus*[8] two days after inoculation. Three days later, when the production of psicofuranine reached a maximum, the nucleoside was isolated.[9] Final purification of psicofuranine was achieved by paper chromatography. The chromatograms were developed in 1-butanol–3% ammonia (86:14). The psicofuranine was eluted and hydrolyzed.[10] After hydrolysis, the insoluble adenine sulfate was removed by filtration. Barium carbonate was added to the filtrate to remove the sulfuric acid. The mixture was filtered and the remaining adenine was removed by adsorption onto Dowex-50-H^+. The D-psicose which remained in solution was concentrated to a sirup at 60° with nitrogen. The distribution of carbon-14 in the psicofuranine is shown in Table I.

The distribution of radioactivity in the adenine-ribose of the adenosine-U-C^{14} used in these experiments was 40 and 60%, respectively. The per cent ratio of the radioactivity in the adenine-psicose moieties of psicofuranine was not the same (expt. 1 and 2, Table I). These data indicate that adenosine (II) does not serve as a direct precursor in the biosynthesis of psicofuranine. The lack of incorporation of formate-C^{14} into D-psicose supports the idea that psicofuranine is not derived directly from adenosine and a C_1 unit (as formate or formaldehyde). Although formate-C^{14} was incorporated into psicofuranine, 99.5% of the radioactivity resided in the adenine. This incorporation of formate is in agreement with the *de novo* synthesis of purine nucleotides. The fact that adenine-U-C^{14} was incorporated to a greater extent than was the D-ribose-U-C^{14} from the adenosine-U-C^{14} experiments (Table I) is taken as evidence that the purine moiety of psicofuranine arises from adenine. Both glucose-1-C^{14} and glucose-6-C^{14} were incorporated into psicofuranine. Most of the radioactivity resided in the D-psicose. To determine if the glucose were the direct precursor of D-psicose, this ketohexose from the glucose experiments was converted to the osazone[11] and degraded[12] to determine the distribution of radioactivity. The results of these studies are shown in Table II.

These findings indicate that the ketohexose D-psicose is arising from glucose or, more likely, a nucleotide–hexose intermediate.

Preliminary studies in our laboratory on the acid-soluble extracts from the mycelia from the glucose-1-C^{14} and glucose-6-C^{14} experiments show that a considerable amount of the radioactivity is retained on a Dowex-1-formate column. Studies are in progress to determine the nature of the radioactive intermediates in order to elucidate the mechanism by which glucose is converted to D-psicose by *S. hygroscopicus*.

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Biosynthesis of Berberastine[1]

Sir:

A new alkaloid, berberastine (II), was recently isolated[2] in minute quantity from extracts of *Hydrastis canadensis* L. The structure assigned[2] to berberastine differs from that of berberine, the major alkaloid of *H. canadensis*, by an additional hydroxyl group located at a site which in the biosynthesis of berberine is specifically derived from the benzylic carbon atom of dihydroxyphenylethylamine (dopamine).[3]

(1) Financial support by the National Institute of General Medical Sciences, U. S. Public Health Service (Grant No. GM-10043) and by the National Research Council of Canada is gratefully acknowledged.
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