breast tissue. No difference from normal was noted in the case of the benign fibroadenoma. In carcinoma of the gastrointestinal tract an elevated concentration of the enzyme is apparent in 4 of 6 patients.

From these few cases there seems to be no correlation of the blood glucuronidase with the incidence of cancer. However, one may speculate as to the reason for the relatively high glucuronidase activity in mammary tumors. Since glucuronidase activity has been found associated with the action of the estrogenic hormones (*4*), this suggests the accumulation of significant amounts of sex hormone in the mammary tumor. In cancer of the gastrointestinal tract, the question arises as to whether or not excessive amounts of estrogen may be present, in view of the elevated glucuronidase content.

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Relabeling of the Cis and Trans Isomers of 1,3-Dimethylcyclohexane

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Evidence pointing to the necessity of relabeling the cis and trans isomers of 1,3-dimethylcyclohexane has been recently presented (*6*). The pertinent experimental facts may be summarized as follows: (a) The 1,3-dimethylcyclohexanes were synthesized by Skita and Schneck (*7*), who prepared a mixture of the cis and trans isomers by hydrogenating m-xylene, and who identified for the first time the lower-boiling and higher-boiling isomers as the trans and cis isomers, respectively, according to von Auwers' rule (*8*), and analogous to the isomers of 1,2-dimethylcyclohexane and 1,4-dimethylcyclohexane. (For these isomers, the lower-boiling one also has a lower refractive index and lower density.) (b) The low-temperature measurements of Oliver, Todd, and Huffman (*6*), coupled with values of the standard entropies of vaporization (*2*), yield experimental values for the standard entropy in the gaseous state at 25°C. such that, for the cis and trans isomers, the lower-boiling isomer has a standard entropy lower than that of the higher-boiling isomer by about 1–1.5 cal./deg. mole, in each of the three pairs, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, and 1,4-dimethylcyclohexane. (c) The energies of isomerization reported by Prosen, Johnson, and Rossini (*6*) for the gas state at 0° K are such that the three lower-boiling isomers have an energy content near 2 kcal./mole less than that of the corresponding higher-boiling isomer. (d) The data (*3*) giving the relative amounts of the cis and trans isomers formed in the hydrogenation (in the range 200°–250°C.) of each of the three xylenes show that the lower-boiling isomer is in each case the more abundant, the relative amounts being in accord, within the combined limits of uncertainty, with the values calculated (*4*) thermodynamically from the experimental entropies and heats of isomerization. The foregoing experimental facts are consistent in indicating a lower energy content, lower entropy, lower density, and lower refractive index for the lower-boiling isomer of the cis- and trans-1,2–, 1,3-, and 1,4-dimethylcyclohexanes.

It is also a matter of experimental fact that, among pairs of geometric isomers, the one possessing less steric hindrance has the lower energy content and usually has the lower boiling point, lower density, and lower refractive index. Various complex situations give exceptions to this rule. If the molecular configuration is such as to produce less steric hindrance in the trans isomer, the latter will normally have the lower boiling point, lower energy, etc., and the cis isomer will normally have the higher boiling point, higher energy, etc. This is the situation in the monoolefins (such as cis- and trans-2-butene) and in the cis- and trans-1,2-dimethylcyclopentanes, in which cases the trans isomer is the lower-boiling, etc.[1] In these cases, the name trans is synonymous with less steric hindrance.

But in the case of the cis and trans isomers of the 1,2-, and 1,3-, and the 1,4-dimethylcyclohexanes, Pitzer and Beckett (*6*) have shown that the trans configuration is not uniformly associated with the isomer of less steric hindrance. As has already been explained in detail by Pitzer, Beckett, and Spitzer (*6*), substantially all the molecules of cyclohexane are in the "chair" or symmetrically staggered configuration in which the successive CH_2 groups comprising the ring are alternately twisted up and down from a plane passing through the ring of carbon atoms. The result is that 6 of the hydrogen atoms lie in an equatorial belt extending out from the ring of carbon atoms, while the remaining hydrogen atoms are perpendicular to the plane through the ring of carbon atoms, three being above and called north polar, and three being below and called south polar. Of the 6 hydrogen atoms which are "cis" to one another, three may be described as north polar and three as equatorial. Of the two hydrogen atoms on each carbon atom, one is polar and one equatorial. If the 6 carbon atoms are all twisted through a single plane over to the opposite chair configuration, all hydrogen atoms originally polar become equatorial and vice versa. With this situation, there thus exists among the 1,2-, the 1,3-, and the 1,4-dimethylcyclohexanes two tautomeric forms for each isomer. Considering only the tautomeric form of lower energy in each case where the energies are different, the trans-1,2-, the cis-1,3-, and the trans-1,4-dimethylcyclohexanes each have both methyl groups equatorial, while the cis-1,2, the trans-1,3, and the cis-1,4-dimethylcyclohexanes each have one methyl group equatorial and one polar. Changing one methyl group from an equatorial to a polar position leads to an increase in the steric hindrance in the molecule and a consequent increase in its energy.

The statistical calculations (*6*) lead to values of the standard entropy lower for trans-1,2-, cis-1,3-, and trans-1,4-, respectively, than for cis-1,2-, trans-1,3-, and cis-1,4-dimethylcyclohexane. The analysis of the molecular structure also indicates that, in each pair (cis and trans), the isomers of lower energy should be trans-1,2-, cis-1,3-, and trans-1,4-dimethylcyclohexane. Furthermore, the calculated values of these differences agree quantitatively with the experimental

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[1] See, however, G. Chiurdoglu (*Bull. Soc. Chim. Belg.*, 1944, 53, 45), who has concluded, on the basis of rates of reaction, that in the 1,2-dimethylcyclopentanes, the cis isomer is the lower-boiling. We are not inclined to regard this type of evidence as at all conclusive.

values within experimental error. The statistical and molecular structure calculations, therefore, lead to the necessity of relabeling the cis and trans isomers of 1,3-dimethylcyclohexane.

Since preparing this manuscript, we have belatedly come upon the work of Mousseron and Granger (*5*), which seems also to have been overlooked by others. Mousseron and Granger prepared the cis and trans isomers of 1,3-dimethylcyclohexane from appropriate optically active starting materials and found the optically active isomer, which must be trans (*6*), to be the higher-boiling member of the pair. This completely confirms the conclusion presented above.

For these reasons, a change has been made, as of March 31, 1947, in the naming of the cis and trans isomers of 1,3-dimethylcyclohexane in the tables of physical and thermodynamic properties and in the catalogues of spectrograms issued by the American Petroleum Institute Research Project 44. The change is such that the lower-boiling isomer, formerly labeled "trans," is now labeled "cis," and the higher-boiling isomer, formerly labeled "cis," is now labeled "trans."

The following notation will be used in the tables and catalogues of spectrograms listing these compounds:

cis-1,3-Dimethylcyclohexane.[2]

trans-1,3-Dimethylcyclohexane.[3]

In addition to the foregoing changes in connection with the work of the American Petroleum Institute Research Project 44, corresponding changes have been made in the work of the American Petroleum Institute Research Project 6 and in the cooperative program on standard samples of the National Bureau of Standards and the American Petroleum Institute.

All workers in other laboratories dealing with cis-1,3-dimethylcyclohexane or trans-1,3-dimethylcyclohexane are invited to relabel these two compounds in the manner described above. It is also recommended that, whenever either of the two names is written, one or more properties also be recorded for adequate identification apart from the name cis or trans. This latter step will completely eliminate any confusion which may arise from this relabeling.

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[2] This isomer, formerly labeled "trans," has the following properties (*1*): boiling point at 1 atm., 120.09°C.; refractive index, n_D at 25°C., 1.4206; density at 25°C., 0.7620 g/ml.

[3] This isomer, formerly labeled "cis," has the following properties (*1*): boiling point at 1 atm., 124.45°C.; refractive index, n^D at 25°C., 1.4284; density at 25°C., 0.7806 g/ml.

The Dark Reductions of Photosynthesis[1]

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Although green plants have been shown (*4*) to fix CO_2 in the dark, the conditions influencing that fixation and the compounds formed were unknown. We are investigating these variables.

The conditions of the experiments were as follows: A sample of actively growing algae was split into two parts (approximately 1 cc. algae/15 cc. suspension). One part (I) was kept in the dark, exposed to 4 per cent CO_2 in N_2 for about 8 hours. The other (II) was exposed to the light of a 150-watt tungsten lamp (.7 g.cal./cm.^{2}/min.) for one hour, during which time it was kept free of CO_2 by constant flushing with N_2. The two samples were then evacuated, kept in the dark, and simultaneously exposed to the same gas containing $C^{14}O_2$ in N_2 for a period of 5 minutes. At the end of this period, the algae were killed by an acetic acid-HCl mixture and the remaining active $C^{14}O_2$ pumped off.

The total nonvolatile radiocarbon content of the two samples was then measured and its chemical distribution determined. The preliminary results are given in Table 1.

From these results alone, it is clear that the reduction of CO_2 to sugars and the intermediates in that reduction does not involve the primary photochemical step itself. This is further substantiated by the appearance of an appreciable fraction (up to 15 per cent) of the radiocarbon in the methylene groups of the succinic acid isolated from sample I of the table (*3*). It is thus confirmed that the photochemical process establishes a reservoir (small, to be sure) of reducing power which can subsequently carry out all of the reduction steps necessary to bring CO_2 to sugar.

TABLE 1

Dark Fixation of CO_2 by *Chlorella*

Pretreatment	I CO_2 in the dark	II Light in the absence of CO_2
Total (relative units)	1	5.5
Succinic acid*	70%	6%
Fumaric acid	3%	1%
Malic acid	—	6%
Cationic substances† (not extractable by ether from pH 1—probably amino acids)	15%	30%‡
Anionic substances† (not extractable by ether from pH 1)	9%	10%
Neutral (sugars)	<.1%	1.5%
Unidentified (extractable by ether from pH 6)	2%	6%
Unidentified (extractable by ether from pH 1)	—	25%

* The succinic acid was isolated without carrier and identified by extraction coefficient, equivalent weight, C and H analysis, melting point, and X-ray powder pattern.

† Absorbed by Duolite ion exchange resins C-3 and A-3, respectively.

‡ Largely alanine.

Using some of the reactions already established in animal tissue and bacteria (*5*), it is possible to account for the above

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