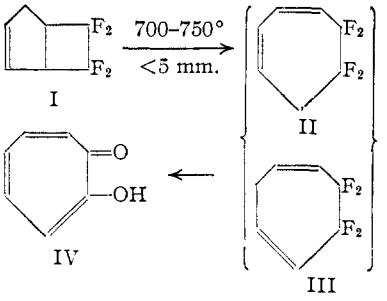
rearrangement of the tetrafluoroethylene–cyclopentadiene adduct, 6,6,7,7-tetrafluorobicyclo[3.2.0]hept-2-ene[1] (I), to tetrafluorocycloheptadienes (II) and (III). Tropolone (IV) is obtained by hydrolysis of these cycloheptadienes and the overall yield for the three steps is approximately 20%.



Thermal rearrangement of the bicycloheptene was accomplished by pyrolysis at 700–750° under pressures of less than 5 mm. The pyrolysate was fractionated, and selected fractions were further purified by gas chromatography to give *5,5,6,6-tetrafluoro-1,3-cycloheptadiene* (*II*), b.p. 63° (50 mm.), $n^{25}D$ 1.4141, λ-max 240 mμ (ϵ = 9460) (*Anal.* Calcd. for $C_7H_6F_4$: C, 50.61; H, 3.64. Found: C, 51.06; H, 4.29), and *6,6,6,7-tetrafluoro-1,4-cycloheptadiene* (III), b.p. 78° (50 mm.), $n^{25}D$ 1.4014 (*Anal.* Calcd. for $C_7H_6F_4$: C, 50.61; H, 3.64; F, 45.75; hydrogenation 0.0245 g. H_2/g. sample. Found: C, 50.95; H, 3.92; F, 45.99; hydrogenation 0.0231, 0.0232 g. H_2/g. sample). Infrared absorption and nuclear magnetic resonance spectra of these isomers confirmed the structure assignments. The combined yield of cycloheptadienes II and III was of the order of 50–65% at 50% conversion.

Hydrolysis of the mixture of tetrafluorocycloheptadienes obtained from the thermal rearrangement gave tropolone in 70% yield. The hydrolysis was accomplished by heating under reflux the cycloheptadienes in acetic acid containing potassium acetate and a small amount of water. Tropolone, m.p. 50–51°, was positively identified by comparison of its infrared spectrum with that of authentic material[2] and by conversion to the green copper chelate.

Acknowledgments.—The assistance of Drs. O. W. Webster and W. R. Brasen of This Laboratory is gratefully acknowledged.

(1) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949).

(2) Prepared by Dr. E. G. Howard of This Laboratory by bromination of 1,2-cycloheptanedione.

CONTRIBUTION NO. 452 FROM THE CENTRAL RESEARCH DEPARTMENT EXPERIMENTAL STATION E. I. DU PONT DE NEMOURS AND CO. WILMINGTON, DELAWARE

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RECEIVED DECEMBER 4, 1957

PHOTOREDUCTION OF TRIPHOSPHOPYRIDINE NUCLEOTIDE BY CHROMATOPHORES OF *Rhodospirillum rubrum*

Sir:

Reasoning from the knowledge gained about photosynthesis in green plants, it is thought that the primary photochemical reaction in bacterial photosynthesis is a splitting of water under the influence of light and bacterial chromatophores to produce an oxidative and a reductive system. In green plants the oxidative system is dissipated as molecular oxygen, but this is not the case with photosynthetic bacteria. Accordingly, the oxidative system so generated must be accommodated by oxidation–reduction reactions occurring in the cell. Back reaction of the oxidative system with the reductive system *via* an electron transport system maintained in the chromatophore occurs, and is linked to phosphorylation resulting in ATP formation.[1] This potential for the oxidative system to react back either directly through such an electron transport system contained in the chromatophore, or indirectly through a series of cytoplasmic reactions, probably accounts for the inability to demonstrate directly a reduction of the pyridine nucleotides with illuminated extracts of photosynthetic bacteria. Repeated experiments directed toward this goal by the author have not been successful. This is in contrast to plant chloroplasts, which can be shown to reduce both diphosphopyridine nucleotide (DPN) and triphosphopyridine nucleotide (TPN) under the influence of light, with an accumulation of the reduced forms, DPNH and TPNH.[2,3]

If pyridine nucleotides were being reduced by bacterial chromatophores and rapidly reoxidized by the oxidative system generated simultaneously, it might be possible to demonstrate such a reduction by trapping the reduced pyridine nucleotides with thermodynamically favorable enzyme systems. Such a system for TPNH would consist of oxidized glutathione and glutathione reductase, while one for DPNH would be pyruvate and lactic dehydrogenase. These systems were used earlier for demonstration of DPNH and TPNH formation by plant chloroplasts in the light.[4,5] The results of such experiments using chromatophores from *Rhodospirillum rubrum* are presented in Table I. It is possible to demonstrate TPNH formation by illuminated chromatophores by such a coupled reaction. A requirement for spinach pyridine nucleotide reductase (the enzyme from plants necessary for pyridine nucleotide reduction by illuminated chloroplasts) indicates a similar mechanism of pyridine nucleotide reduction in both plant and bacterial systems. Preliminary experiments indicate that *R. rubrum* chromatophores are much more efficient in affecting TPN photoreduction when compared with DPN. Thus, a system similar to the one listed in Table I, but substituting DPN for TPN and utilizing a pyruvate–lactic dehydrogenase system to trap DPNH formed, produced only 0.06 μmole of lactate as a function of illumination. It is significant that the photoproduction of lactate in the DPN system is stimulated by the addition of TPN, while the photo-

(1) A. W. Frenkel, *J. Biol. Chem.*, **222**, 823 (1956).

(2) A. San Pietro and H. M. Lang, *Science*, **124**, 118 (1956).

(3) D. I. Arnon, F. R. Whatley and M. B. Allen, *Nature*, **180**, 182 (1957).

(4) D. D. Hendley and E. E. Conn, *Arch. Biochem. Biophys.*, **46**, 454 (1953).

(5) W. Vishniac and S. Ochoa, *J. Biol. Chem.*, **195**, 75 (1952).

production of glutathione in the TPN system is inhibited by the addition of DPN. Thus, it would appear that TPN is preferentially reduced by the photochemical reducing system produced in bacterial photosynthesis. However, this could be due to the use of spinach pyridine nucleotide reductase, which is specific for TPN with chloroplasts.[3]

TABLE I

PHOTOREDUCTION OF TPN BY *Rhodospirillum rubrum* CHROMATOPHORES AS DEMONSTRATED BY COUPLED ENZYMIC REDUCTION OF OXIDIZED GLUTATHIONE

The reaction mixture consisted of 20 μmoles phosphate buffer *p*H 7.4, 1.2 μmoles TPN, 40 μmoles oxidized glutathione neutralized to *p*H 7.0, 5.4 mg. of a glutathione reductase preparation prepared according to reference 4, 1.8 mg. of a pyridine nucleotide reductase preparation prepared according to directions furnished by A. San Pietro, and *R. rubrum* chromatophores equal to 0.20 mg. bacterial chlorophyll in a final volume of 3.2 ml. The reaction mixture was placed in a Thunberg tube, made anaerobic by evacuations with four alternate flushings with nitrogen gas, following which half the mixture was placed in the side arm and covered with aluminum foil. The Thunberg tube (thus containing an internal dark control of identical composition) was immersed in a water-bath at 30° and illuminated for two hours at approximately 2000 foot candles. Following illumination the glutathione content of the illuminated and non-illuminated portions was determined according to the method of Grunert and Phillips.[6]

Conditions	μmoles GSH present: Light	Dark	Light − dark
Complete system	1.81	0.85	0.96
Minus TPN	0.30	.33	− .03
Minus oxidized glutathione	.13	.20	− .07
Boiled GSH reductase	.48	.53	− .05
Boiled pyridine nucleotide reductase	.68	.72	− .04
Boiled chromatophores	.46	.32	.14

(6) R. R. Grunert and P. H. Phillips, *Arch. Biochem.*, **30**, 217 (1951).

DEPARTMENT OF CHEMISTRY
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RECEIVED NOVEMBER 22, 1957

TERPENOIDS. XXXIII.[1] THE STRUCTURE AND PROBABLE ABSOLUTE CONFIGURATION OF CAFESTOL

Sir:

Recently[2] we proposed structure I—without the stereochemical implications—for the coffee constituent cafestol and rigorous evidence for the furanoperhydrophenanthrene skeleton was adduced by dehydrogenation[3] and synthesis.[2] The nature of the substituted cyclopentane ring follows from a series of reactions[2,3,4] but its point of attachment is so far based only on the virtual identity of the rotatory dispersion curves[5] of certain 17-nor-16-ketones (II) in the cafestol and phyllocladene series where this structural point has been established[6] by dehydrogenation to retene. The angular methyl group of cafestol (I) was placed[2] at C-10 by analogy to phyllocladene,[6] which in turn is based on analogy to other diterpenes. Quite recently, Haworth and Johnstone[7]—on the basis of certain dehydrogenations—have suggested that the angular methyl group in cafestol (and by inference[8] also in the other members of the phyllocladene group of diterpenes) should be placed at C-5, which would be of considerable biogenetic significance. We wish now to place on the record certain relevant experiments which show that our original[2] structure I with the angular methyl group at C-10 is correct and that Haworth's dehydrogenation results[7] are probably best interpreted as involving rearrangements or reduction of a carboxyl group to methyl.

Hydrogenolytic opening of the furan ring of epoxynorcafestadiene (III)[3] with platinum oxide in acetic acid led to several products including the 3-hydroxy-4-ethyl derivative (m.p. 130–132°, $[\alpha]_D$ −64° (all rotations in $CHCl_3$), found for $C_{19}H_{32}O$: C, 82.58; H, 11.81; O, 6.07) which upon chromium trioxide oxidation and passage over *alkaline* alumina yielded the ketone V (m.p. 86–88°, $\lambda_{max.}^{CHCl_3}$ 5.84 μ, found for $C_{19}H_{30}O$: C, 83.42; H, 11.02; O, 5.99), while a similar reaction sequence on cafestadiene (IV) (m.p. 69–70, $[\alpha]_D$ −156°, found for $C_{20}H_{28}O$: C, 84.05; H, 9.86) provided the ketone VI (m.p. 81–83°, found for $C_{20}H_{32}O$: C, 83.32; H, 11.19). *Both ketones exhibited a negative single Cotton effect curve* (*cf.* ref. 5) *in contrast to the positive one* of 4α-ethyl-cholestan-3-one (m.p. 120–122°, $[\alpha]_D$ +38°, $\lambda_{max.}^{CHCl_3}$ 5.83 μ, found for $C_{29}H_{50}O$: C, 83.69; H, 11.92) prepared by lithium–ammonia reduction of 4-ethyl-Δ^4-cholesten-3-one[9] (m.p. 87–89°, $\lambda_{max.}^{EtOH}$ 251 mμ, log ε 4.07, found for $C_{29}H_{48}O$: C, 84.20; H, 12.04; O, 4.19).

It has been demonstrated[10] with the triterpene ketone friedelin, where the same A/B stereochemistry obtains, that an angular methyl group at C-5 favors the production of an axial alcohol in the lithium aluminum hydride reduction while the equatorial epimer is formed with lithium–ammonia. On the other hand, if the angular methyl group is located at C-10, both methods of reduction should provide the equatorial alcohol as shown by the formation of 4α-ethylcholestan-3β-ol (m.p. 141–143°, $[\alpha]_D$ +24°, found for $C_{29}H_{52}O$: C, 83.62; H, 12.23) from the model 4α-ethylcholestan-3-one. When the ketone V, derived from cafestol, was subjected to *either* reduction procedure, the principal product in each case was the *same* alcohol VII (m.p. 151–153°, $[\alpha]_D$ −73°, found for $C_{19}H_{32}O$: C, 82.69; H, 11.38; O, 5.98) with an equatorial hydroxyl group.[11]

(1) Paper XXXII, C. Djerassi and J. S. Mills, THIS JOURNAL, **80**, Feb. (1958).

(2) H. Bendas and C. Djerassi, *Chemistry and Industry*, 1481 (1955).

(3) C. Djerassi, H. Bendas and P. Sengupta, *J. Org. Chem.*, **20**, 1046 (1955).

(4) See A. Wettstein, F. Hunziker and K. Miescher, *Helv. Chim. Acta*, **26**, 1197 (1943), and earlier references cited therein.

(5) C. Djerassi, R. Riniker and B. Riniker, THIS JOURNAL, **78**, 6362 (1956).

(6) C. W. Brandt, *New Zealand J. Sci. Technol.*, **34B**, 46 (1952).

(7) R. D. Haworth and R. A. W. Johnstone, *J. Chem. Soc.*, 1492 (1957).

(8) See *Ann. Repts. Chem. Soc.*, **53**, 209 (1957).

(9) Synthesized from Δ^4-cholesten-3-one by the same procedure used recently for the corresponding 4-methyl analog (G. D. Meakins and O. Rodig, *J. Chem. Soc.*, 4679 (1956); F. Sondheimer and Y. Mazur, THIS JOURNAL, **79**, 2906 (1957)).

(10) *Cf.* G. Brownlie, F. S. Spring, R. Stevenson and W. S. Strachan, *J. Chem. Soc.*, 2419 (1956).

(11) The orientation of the hydroxyl group in this and several other alcohols derived from cafestol was confirmed by infrared data (alcohol and acetate) and by the elegant quantitative micro-oxidation procedure of J. Schreiber and A. Eschenmoser (*Helv. Chim. Acta*, **38**, 1529 (1955); *cf. ibid.*, **40**, 1391 (1957)).