

refinement led to values of $R = \frac{\sum |F_0|}{\sum F_0} = 0.182$ and $r = \frac{\sum \omega(F_0^2 - |F_0|^2)}{\sum \omega F_0^4} = 0.183$ for all observed reflections. Anisotropic temperature motion, introduced for the Br atoms only, was unusually large.

We wish to acknowledge the interest of Professor C. Djerassi who supplied us with the iresin, and Dr. P. Tomboulion, who prepared the diester for us. The 39 hours of computing time on the Remington Rand 1103 UNIVAC SCIENTIFIC was contributed by the University of Minnesota.

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RECEIVED FEBRUARY 18, 1958

TERPENOID. XXXV.¹ THE STRUCTURE AND ABSOLUTE CONFIGURATION OF IRESIN²

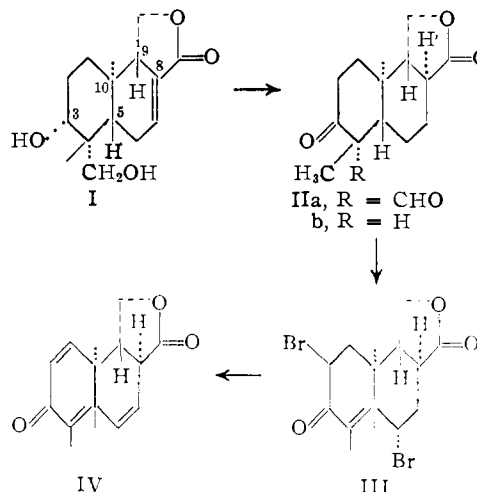
Sir:

Iresin—an important link in the terpene biogenetic scheme—possesses^{1,3} structure I (without the stereochemical assignment) or the variant with the angular methyl group at C-5. This remaining structural point as well as its absolute configuration now have been established.

Chromium trioxide oxidation of isodihydroiresin^{1,3} led to the keto aldehyde IIa (m.p. 184–189°, $[\alpha]_D +48^\circ$ (CHCl₃), $\lambda_{\max}^{\text{CHCl}_3}$ 5.60, 7.75 and 5.85 μ ; *anal.* found for C₁₅H₂₀O₄: C, 68.26; H, 7.85; O, 23.78), which upon heating with aqueous ethanolic hydrochloric acid afforded 13-nor-3-dehydroisodihydroiresin (IIb) (m.p. 153–155°, $[\alpha]_D +8^\circ$ (CHCl₃), $\lambda_{\max}^{\text{CHCl}_3}$ 5.61 and 5.84 μ ; *anal.* found for C₁₄H₂₀O₃: C, 71.06; H, 8.56; O, 20.54). Evidence for the location of the angular methyl group at C-10 rather than at C-5 was adduced by tribromination⁴ of IIb which provided the 2,6-dibromo- Δ^3 -3-ketone III (m.p. 154–157° (dec.), $[\alpha]_D +126^\circ$ (diox.), $\lambda_{\max}^{\text{EtOH}}$ 262–264 m μ ,⁴ log ϵ 4.09; *anal.* found for C₁₄H₁₆Br₂O₃: Br, 41.49) and subsequent dehydrobromination to the 1,4,6-trien-3-one (IV) (m.p. 164–168°, $\lambda_{\max}^{\text{EtOH}}$ 224, 250 (shoulder) and 296 m μ , log ϵ 4.16, 3.96 and 4.12, $\lambda_{\max}^{\text{CHCl}_3}$ 5.60, 6.01, 6.09, 6.16 and 6.23 (m) μ ; *anal.* found for C₁₄H₁₄O₃: C, 73.25; H, 6.05). The spectroscopic data are typical of steroidal 1,4,6-trien-3-ones⁵ and since the unsaturated ketones III and IV can only be formed if the angular methyl group is located at C-10 (rather than C-5), the structure of iresin is now securely established as I.

Evidence for the stereochemistry of the C-3 hydroxyl group, the primary alcoholic function and the $\delta,6$ -bond already has been recorded.³ A 9,10-*anti* backbone now has been established by the hydrogenation of iso-iresin (I with 8,9-double bond)

to dihydroiresin (I with 8 β H).^{1,3} The rotatory dispersion curve of the 13-nor-3-ketone IIb exhibited a negative Cotton effect curve in contrast to the positive one of 4-methyl-3-keto-5 α -steroids⁶



and the dispersion curve of the dibromo ketone III was antipodal to that of 2 $\alpha,6\beta$ -dibromo-4-methyltestosterone acetate,⁴ which in turn closely resembled that of 6 β -bromotestosterone acetate.⁷

Consequently, iresin possesses the absolute configuration shown in I, which is opposite to that of the steroids and higher terpenes. Iresin is thus still another higher terpenoid—the other being cafestol⁸ and eperuic acid⁹—for which the "wrong" absolute configuration has been established and in each instance the rotatory dispersion technique^{6,7} has played a crucial role in uncovering this unexpected stereochemical feature.¹⁰

(6) C. Djerassi, O. Halpern, V. Halpern and B. Riniker, *ibid.*, **80**, in press (1958).

(7) C. Djerassi, J. Osiecki, R. Riniker and B. Riniker, *ibid.*, **80**, 1216 (1958).

(8) C. Djerassi, M. Cais and L. A. Mitscher, *ibid.*, **80**, 247 (1958).

(9) F. E. King and G. Jones, *J. Chem. Soc.*, 658 (1955); J. D. Cocker and T. C. Halsall, *ibid.*, 4262 (1956); C. Djerassi and D. Marshall, *Tetrahedron*, **1**, 238 (1957).

(10) The A/B *trans* juncture—demonstrated by the rotatory dispersion and bromination experiments—and the location of the angular methyl group have been established also by three-dimensional X-ray diffraction analysis of iresin *bis-p*-bromobenzoate (M. G. Rossmann and W. N. Lipscomb, *THIS JOURNAL*, **80**, 2592 (1958)).

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RECEIVED FEBRUARY 24, 1958

FISSION RECOIL DECOMPOSITION OF CALCIUM NITRATE SOLUTIONS

Sir:

The experiments on irradiation of calcium nitrate solutions in a mixed fast neutron- γ flux¹ have been extended to investigate the effects of fission recoil fragment energy. Calcium nitrate solutions of various concentrations were impregnated with sufficient U²³⁵O₂(NO₃)₂ to ensure that, in the Harwell experimental reactor BEPO (thermal neutron flux *ca.* 1.2×10^{12} n. cm.⁻² sec.⁻¹), more than 95% of the ionizing energy deposited was kinetic energy

(1) R. G. Sowden, *THIS JOURNAL*, **79**, 1263 (1957).

(1) Paper XXXIV, C. Djerassi, F. W. Donovan, S. Burstein and R. Mauli, *THIS JOURNAL*, **80**, 1972 (1958).

(2) Supported by grant No. CY-2919 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service.

(3) C. Djerassi, W. Rittel, A. L. Nussbaum, F. W. Donovan and J. Herran, *THIS JOURNAL*, **76**, 6410 (1954); C. Djerassi and W. Rittel, *ibid.*, **79**, 3528 (1957).

(4) Tribromination of 4-methyldihydrotestosterone acetate yields 2 $\alpha,6\beta$ -dibromotestosterone acetate, m.p. 167–170° (dec.), λ_{\max} , 263.5 m μ , log ϵ 4.14.

(5) C. Djerassi, G. Rosenkranz, J. Romo, St. Kaufmann and J. Pataki, *THIS JOURNAL*, **72**, 4534 (1950).

of fission recoil fragments. The thermal neutron dose during irradiation was monitored using high purity cobalt wire, and energy deposition (extending to 5×10^{21} e.v. per g. of solution) was calculated assuming 160 Mev. of recoil energy released per fission event,² and a thermal neutron fission cross-section for U^{235} of 580 barns.³ The main products were hydrogen, oxygen and nitrogen, with smaller amounts of carbon dioxide, and, in the case of concentrated nitrate solutions, nitrous oxide. With more dilute solutions, precipitation of some UO_4 during irradiation was encountered. As this phenomenon would have introduced uncertainty into energy deposition data, it was prevented by adding about 100 p.p.m. of iron as ferric nitrate to the solutions; this presumably catalyzed the deposition of H_2O_2 sufficiently to prevent peroxide precipitation. No peroxide and only traces of nitrite were found in solution after irradiation.

A plot of G_{H_2} vs. $(NO_3^-)^{1/2}$ is linear, and obeys an equation of the type $G_{H_2} = A - k(NO_3^-)^{1/2}$, (1) where $A = 2.0$ and $k = 0.8$: the G_{H_2} data of Boyle and Mahlman for $Th(NO_3)_4-U^{235}O_2(NO_3)_2$ solutions also lie on this line. The results can therefore be explained qualitatively in terms of a theory¹ involving reaction of diffusing H atoms with $\dot{N}O_3^-$: $NO_3^- + H \rightarrow NO_2 + OH^-$ (2), where the parameter k is a measure of the probability of reaction (2).

Values of G_{N_2} are more than an order of magnitude greater than those obtained for fast neutron- γ energy. Figure 1 shows a log-log plot of

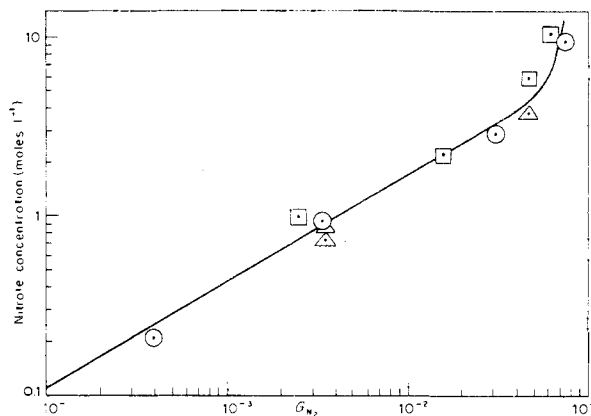


Fig. 1.—Log-log plot of G_{N_2} vs. $[NO_3^-]$: O, present results; □, data of Boyle and Wahlman; Δ, data of Bidwell.

G_{N_2} vs. (NO_3^-) , and includes the present data, those of Boyle and Mahlman,⁴ and those of Bidwell, *et al.*,⁶ obtained from experiments with critical assemblies of uranyl nitrate solutions (the Los Alamos "water boilers"). The continuity of the curve indicates that cation variation has little effect on nitrogen yields. The present data were obtained at about 80° , while the American data cor-

(2) S. Glasstone, "Source Book on Atomic Energy," Macmillan, 1950.

(3) Brookhaven National Laboratory, "Neutron Cross Sections," B.N.L.-235, Supplement 1 (1957).

(4) J. W. Boyle and H. A. Mahlman, *Nucl. Sci. Eng.*, **2**, 492 (1957).

(5) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

(6) R. M. Bidwell, L. D. P. King and W. R. Wykoff, *Nucl. Sci. Eng.*, **1**, 452 (1956).

respond to temperatures ranging from 37° to 300° ; temperature has therefore no significant effect on G_{N_2} .

Below a nitrate concentration of about $4M$, nitrogen yields can be expressed by the empirical relationship $G_{N_2} = 0.004(NO_3^-)^{1.5}$ (3), though nothing can be said at this stage about the mechanism of nitrogen formation.

A complete account of the work, with due acknowledgments, will be published elsewhere.

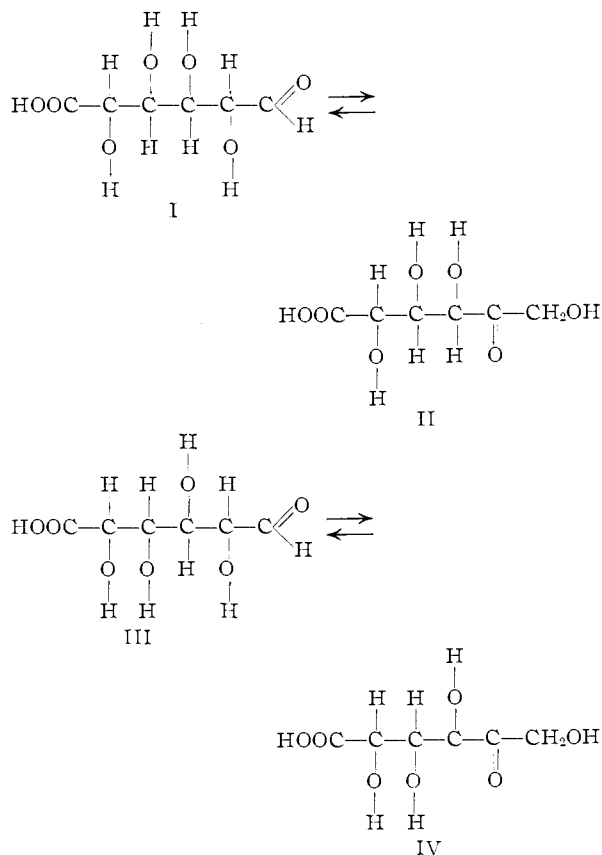
(7) Vacation Student, University of St. Andrews, Scotland.

ATOMIC ENERGY RES. EST. R. G. SOWDEN
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RECEIVED MARCH 6, 1958

ENZYMATIC FORMATION OF D-TAGATURONIC AND D-FRUCTURONIC ACID

Sir:

Various microorganisms have been shown to metabolize uronic acids rapidly although little is known about the nature of the primary reaction products formed.^{2,3,4} In the present study, D-tagaturonic acid (II) and D-fructuronic acid (IV) have been identified as the first products in a new pathway for the metabolism of D-galacturonic acid (I) and D-glucuronic acid (III), respectively.



Cultures of *E. coli* (ATCC 9637) were grown aéro-

(1) D-Tagaturonic acid may also be designated as 5-keto-D-altronic acid, 5-keto-t-galactonic acid or, systematically, D-arabino-5-hexulosonic acid. Similarly, D-fructuronic acid may be designated as 5-keto-D-mannonic acid, 5-keto-L-gulonic acid or D-lyxo-5-hexulosonic acid.

(2) S. S. Cohen, *J. Biol. Chem.*, **177**, 607 (1949).

(3) P. J. Heald, *Biochem. J.*, **50**, 503 (1952).

(4) M. P. Starr, J. DeLey and W. W. Kilgore, *Science*, **125**, 929 (1957).