refinement led to values of $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0| = 0.182$ and $r = \Sigma\omega(F_0^2 - |F_c|^2)^2/\Sigma\omega F_0^4 = 0.183$ 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.

SCHOOL OF CHEMISTRY MICHAEL G. ROSSMANN
UNIVERSITY OF MINNESOTA WILLIAM N. LIPSCOMB
MINNEAPOLIS 14, MINNESOTA

RECEIVED FEBRUARY 18, 1958

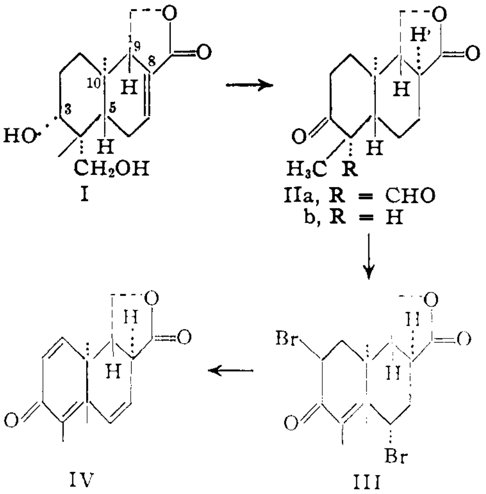
TERPENOIDS. XXXV.[1] THE STRUCTURE AND ABSOLUTE CONFIGURATION OF IRESIN[2]

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° ($CHCl_3$), $\lambda_{max}^{CHCl_3}$ 5.60, 7.75 and 5.85 μ; *anal.* found for $C_{15}H_{20}O_4$: 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° ($CHCl_3$), $\lambda_{max}^{CHCl_3}$ 5.61 and 5.84 μ; *anal.* found for $C_{14}H_{20}O_3$: 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 tribromination[4] of IIb which provided the 2,6-dibromo-Δ^4-3-ketone III (m.p. 154–157° (dec.), $[\alpha]_D$ +126° (diox.), λ_{max}^{EtOH} 262–264 mμ,[4] log ϵ 4.09; *anal.* found for $C_{14}H_{16}Br_2O_3$: Br, 41.49) and subsequent dehydrobromination to the 1,4,6-trien-3-one (IV) (m.p. 164–168°, λ_{max}^{EtOH} 224, 250 (shoulder) and 296 mμ, log ϵ 4.16, 3.96 and 4.12, $\lambda_{max}^{CHCl_3}$ 5.60, 6.01, 6.09, 6.16 and 6.23 (m)μ; *anal.* found for $C_{14}H_{14}O_3$: C, 73.25; H, 6.05). The spectroscopic data are typical of steroidal 1,4,6-trien-3-ones[5] 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 5,6-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 8β 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-5α-steroids[6] and the dispersion curve of the dibromo ketone III was antipodal to that of 2α,6β-dibromo-4-methyltestosterone acetate,[4] which in turn closely resembled that of 6β-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 cafestol[8] and eperuic acid[9]—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]

---

[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 2α,6β-dibromotestosterone acetate, m.p. 167–170° (dec.), $\lambda_{max.}$ 263.5 mμ, log ϵ 4.14.

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

[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).

DEPARTMENT OF CHEMISTRY
WAYNE STATE UNIVERSITY CARL DJERASSI
DETROIT, MICHIGAN S. BURSTEIN

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 flux[1] have been extended to investigate the effects of fission recoil fragment energy. Calcium nitrate solutions of various concentrations were impregnated with sufficient $U^{235}O_2(NO_3)_2$ 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).