III, is of interest because of its analogy to the high reactivity of enzyme-substrate complexes.[2b,5,6]

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(5) H. Morawetz and E. W. Westhead, Jr., *J. Polymer Sci.*, **16**, 273 (1955).

(6) M. L. Bender, THIS JOURNAL, **79**, 1258 (1957).

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RECEIVED APRIL 4, 1958

A NEW CRYSTALLINE MODIFICATION OF BORON

Sir:

We have found that the product of the pyrolytic decomposition of BI_3 on a surface heated at 800–1000° contains a crystalline modification of boron different from any hitherto reported. Substrates of tantalum, tungsten or boron nitride yield the same results. Above 1500° the new modification transforms to the rhombohedral form of boron recently reported by Sands and Hoard.[1] The new modification is stable to twenty-four hours heating at 1100° or below, but a similar heating at 1200° produces a few new lines in the X-ray diffraction pattern which match the strong lines of the high temperature form.

The new modification appears in the product prepared at 1000° as a red sandy, red glassy, or red microcrystalline material. These forms may be recovered from the total deposit by leaching with warm concentrated nitric acid. Clear red crystals about 0.25 mm. long have been collected from the product. These, when examined by X-ray emission, show about 0.04 weight per cent. iodine but no other impurities of $Z = 13$ or larger in concentration greater than 0.001% (the limit of detection for the amount of sample available). The carbon content was determined by vacuum fusion analysis to be 0.003%. The density of the crystalline material was determined to be 2.46 g./cc. as opposed to 2.33 g./cc. for normal boron.

A preliminary crystal structure determination has been made from the isolated red crystals. The structure is rhombohedral, space group $R\bar{3}m$, with $a = 5.06$ Å. and $\alpha = 58°4'$. The experimental density yields 12.0 for the number of atoms in the rhombohedral unit cell; they are in 2 sets of the special positions 6(h) with $x = 0.01$, $z = -0.35$, and $x' = 0.23$, $z' = -0.37$. The structure may be described as composed of units of nearly regular icosahedra in a slightly deformed cubic close-packing. There are two kinds of bonds between boron atoms of neighboring icosahedra. One-half of the atoms in an icosahedron are bound by conventional single bonds to atoms of other icosahedra. The other kind of binding consists of equilateral triangles formed by boron atoms from three icosahedra.

This new boron structure is essentially the same as the boron framework in boron carbide, B_4C.[2,3] There is the significant difference, however, that omission of the chains of three carbon atoms from the octahedral holes results in the closer approach of icosahedra and the formation of the new triangular boron bonds to replace the 3 bonds to 3 icosahedra formed by an end carbon of the three-carbon chains. The other bonds between icosahedra are the same in the two structures. Details of the preparation, properties, and structure will be published separately.

(1) D. E. Sands and J. L. Hoard, THIS JOURNAL, **79**, 5582 (1957).

(2) H. K. Clark and J. L. Hoard, *ibid.*, **65**, 2115 (1943).

(3) G. Zhdanov and N. Sevastjanov, *J. Phys. Chem. U.R.S.S.*, **17**, 326 (1943); *Compt. Rend. Acad. Sci. U.R.S.S.*, **32**, 432 (1941).

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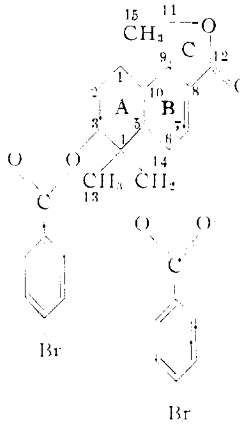
RECEIVED MARCH 28, 1958

MOLECULAR STRUCTURE AND STEREOCHEMISTRY OF AN IRESIN DIESTER

Sir:

Three-dimensional analysis of 1432 independent X-ray diffraction maxima from single crystals of the *p*-bromobenzoate diester of the sesquiterpenoid, iresin,[1,2,3] has yielded a complete molecular structure (I). Rings A and B are fused *trans* and



(I)

the angular methyl group is attached to C-10. Ring A has the chair form, and Rings B and C are nearly coplanar except for atom C-5. In agreement with chemical evidence (ref. 3, footnote 26), the OH group on C-3, the carbon atom bearing the primary hydroxyl function, and the 5–6 bond are all *cis*. Our results also provide an independent proof of all structural features of iresin except for the hydrogen atom positions.

The crystals are monoclinic with space group $P2_1$ and cell parameters $a = 28.75$, $b = 7.41$, $c = 6.40$A and $\beta = 92°$. The observed density of 1.526 g. cm.$^{-3}$ gives a molecular weight of 627 in agreement with the expected value of 632 for the diester. Three-dimensional Patterson, Fourier and difference syntheses plus nine cycles of least squares

(1) C. Djerassi, P. Sengupta, J. Herran and F. Walls, THIS JOURNAL, **76**, 2966 (1954).

(2) C. Djerassi, W. Rittell, A. L. Nussbaum, F. W. Donovan and J. Herran, *ibid.*, **76**, 6410 (1954).

(3) C. Djerassi and W. Rittell, *ibid.*, **79**, 3528 (1957).

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.

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RECEIVED FEBRUARY 18, 1958

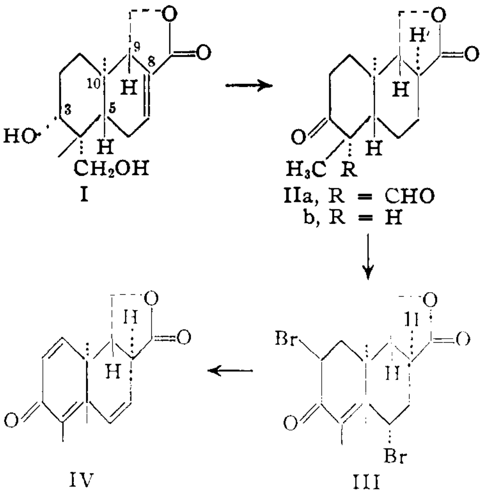
TERPENOIDS. XXXV.[1] THE STRUCTURE AND ABSOLUTE CONFIGURATION OF IRESIN[2]

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.), $\lambda_{\max}^{EtOH}$ 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°, $\lambda_{\max}^{EtOH}$ 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]

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[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).

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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 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).