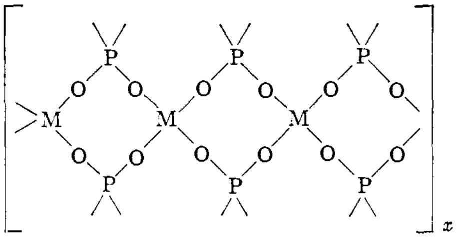
The structure of these polymers probably is related to that which we postulated for $[Cr(AcCHAc)(OPPh_2O)_2]_x$,[1] with double phosphinate bridges between metal atoms, *i.e.*



Evidence for this structure is afforded by the isolation and characterization of the beryllium dimer, $[Be(AcCHAc)(OPPh_2O)]_2$.[4] This was produced by a procedure similar to the one used to prepare $[Be(OPPh_2O)_2]_x$, except that the $Be(AcCHAc)_2$ rather than the $Ph_2P(O)OH$ was present in excess. The product gave an ebulliometric molecular weight in benzene of 661 (calcd. 650). The fiber-forming properties of $[Zn(OP(Ph)(Me)O)_2]_x$ constitute additional evidence that the structure is predominantly linear as opposed to crosslinked.

Thermogravimetric analysis indicates that initial weight loss starts at 530° for the polymer of composition $Be(OPPh_2O)_2$, at 495° for polymeric $Zn(OPPh_2O)_2$, and at 415° for polymeric $Zn(OP(Ph)(Me)O)_2$. In significant contrast we have found that $Cu(OPPh_2O)_2$ starts to lose weight at 293°. The Be and Zn polymers probably are more stable thermally than the Cu polymer, since a structure based on a square planar central atom offers a more facile decomposition mechanism than one based on a tetrahedral central element.

Acknowledgment.—This work was supported in part by the Office of Naval Research. Analyses were performed by our Analytical Department, and Dr. J. R. Soulen supervised the thermogravimetric analyses. Experimental assistance was provided by Mr. G. Mincarelli.

(4) B. P. Block, E. S. Roth, C. W. Schaumann and J. Simkin, *Inorg. Chem.*, **1**, in press (1962).

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RECEIVED JULY 5, 1962

ROTATORY DISPERSION AND ULTRAVIOLET ABSORPTION PHENOMENA OF SOME CONJUGATED KETONES[1]

Sir:

We have studied the rotatory dispersion (R.D.) curves of several diterpenoids of general structure I in which a keto group is in conjugation with an aromatic ring. Previously the R.D. curves of two such ketones, sugiol methyl ether and nimbiol methyl ether, had been reported as plain curves above 350 mμ.[2] We have found that using the acetate or the benzoate of these two ketones in place of their methyl ethers, measurements at lower wave length become feasible, revealing Cotton effect curves.

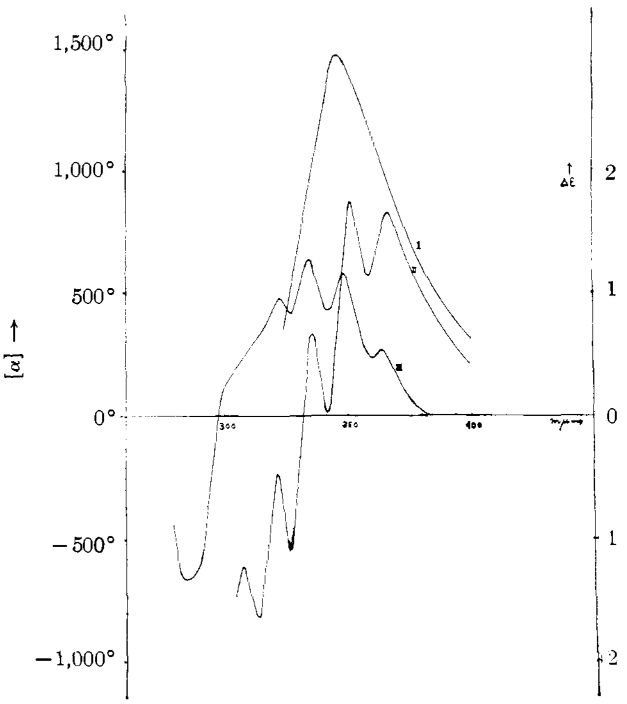
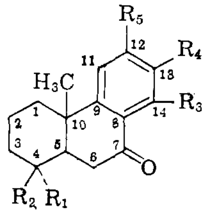


Fig. 1.—I, R.D. of methyl 7-oxo-O-methyl-podocarpate in methanol; II, R.D. of methyl 7-oxo-O-methyl podocarpate in isoöctane; III, C.D. of 7-oxo-O-acetyl-podocarpic acid in dioxane.



I

In Table I are shown the results of R.D. measurements in methanol solution of a series of diterpenoid ketones. The corresponding ultraviolet absorption data in the 300–350 mμ range are reported in Table II. The close relationship between ultraviolet and R.D. spectra which is expected on theoretical grounds[3,4] has been demonstrated[5,6] experimentally for many types of compounds. The data in Tables I and II, however, show an apparent lack of correspondence between the ultraviolet spectra and R.D. curves in methanol solution. We have studied therefore the circular dichroism (C.D.) spectra of two diterpenoid ketones, sugiol benzoate and 7-oxo-O-acetylpodocarpic acid and

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(1) Molecular Rotation and Absolute Configuration, Part IV (presented at the Metropolitan Meeting of the New York and New Jersey sections of the American Chemical Society in New York, January 27, 1962). For Part III, see A. K. Bose, *Tetrahedron Letters*, no. 14, 461–467 (1961).

(2) P. Sengupta, S. N. Chaudhuri and H. N. Khastgir, *Tetrahedron*, **10**, 45 (1960).

(3) L. L. Jones and H. Eyring, *Tetrahedron*, **13**, 235 (1961).

(4) A. Moscowitz, *ibid.*, **13**, 48 (1961).

(5) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Company, Inc., New York, 1960.

(6) E. C. Olson and C. D. Alway, *Anal. Chem.*, **32**, 370 (1960).

found the C.D. spectra to consist of multiple peaks over the range 320–360 mμ (see Fig. 1). The center of these peaks is in the wave length region at which the R.D. curves in methanol cross the zero degree line.

TABLE I

ROTATORY DISPERSION DATA

Compound	R.D. peak mμ	Zero degree crossing, mμ
Sugiol (I, $R_1 = R_2 =$ Me, $R_3 =$ H, $R_4 =$ *i*-Pr, $R_5 =$ OH)	Plain up to 340	...
Sugiol benzoate	355	331
Nimbiol (I, $R_1 = R_2 = R_4 =$ Me, $R_3 =$ H, $R_5 =$OH)	Plain up to 350	...
Nimbiol benzoate	350	335
7-Oxototarol (I, $R_1 = R_2 =$ Me, $R_3 =$ *i*-Pr, $R_4 =$ OH, $R_5 =$ H)	Plain up to 300	...
7-Oxototarol benzoate	353	331
7-Oxototarol methyl ether	367	350[a]
7-Oxopodocarpic acid (I, $R_1 =$ Me, $R_2 =$ COOH, $R_3 = R_4 =$ H, $R_5 =$ OH)	342	312[a]
Methyl 7-oxo-O-methyl-podocarpate	346	318[a]
Methyl 7-oxo-O-methyl-13-acetyl podocarpate	340	315[a]
7-Oxo-O-acetyl-podocarpic acid	354	325
Methyl 7-oxo-dehydroabietate (I, $R_1 = CO_2Me$, $R_2 =$ Me, $R_3 =$ *i*-Pr, $R_4 =$ H)	350	325

[a] By extrapolation.

TABLE II

ULTRAVIOLET ABSORPTION DATA

Compound	$\lambda_{\max}^{\mathrm{MeOH}}$ (ε)	$\lambda_{320}^{\mathrm{MeOH}}$ (ε)	$\lambda_{350}^{\mathrm{MeOH}}$ (ε)
7-Oxototarol benzoate	233 (23,340) 283 (2,662) 296 (2,300)	656	34
Methyl 7-oxopodocarpate	225 (12,200) 277 (15,700)	4,200	41
Methyl 7-oxo-O-methyl-13-isopropyl podocarpate	230 (14,300) 279 (13,350)	1,300	49
Sugiol benzoate		291	61

In view of the multiple peaks in the C.D. spectra of these conjugated ketones, one has to expect corresponding multiple peaks in their ultraviolet spectra. It is known[5] that ketones conjugated with a double bond, *e.g.*, testosterone, show corresponding multiple peaks in their R.D. and ultraviolet spectra.

Finding a diterpenoid (methyl O-methyl-7-oxopodocarpate) of adequate solubility in isooctane, its R.D. and ultraviolet spectra were determined in this non-polar medium. The R.D. spectrum (see Fig. 1) now revealed a set of multiple peaks in the same area where the C.D. peaks occur for this type of compound.[7] The ultraviolet spectrum in isoöctane ($\lambda_{\max}^{\text{isooctane}}$ 358 (149), 345 (415), 331 (626), 310 (686), 291 (2683), sh 282, sh 276, 267.5 (17,727), 226 (17,141), 219.5 (17,568)) shows a close correspondence with the C.D. and the R.D. curves.

Djerassi and co-workers[5] have reported the absence of any noticeable ultraviolet absorption peaks (in methanol) in the region where 2α-iodocholestane-3-one shows a Cotton effect curve. We have now studied the C.D. of this ketone (in dioxane) and find a peak at 295 mμ. Cholestane-3-one has a peak at 299 mμ in its C.D. spectrum. The ultraviolet absorption spectrum of 2α-iodocholestane-3-one in isoöctane or in carbon tetrachloride failed, however, to show any absorption maxima in the 300 mμ region.

According to Eyring and co-workers[8] the rotational strength R_k of a chromophore is related to an induced dipole moment, $\mu_e{}^k$, and a magnetic dipole moment, $\mu_m{}^k$, as shown in the equation: $R_k = \mu_e{}^k \cdot \mu_m{}^k$. For ultraviolet absorption, the greater the induced electric dipole moment the greater is the intensity of transition. To account for the strong C.D. and R.D. spectra of the diterpenoid ketones and 2α-iodocholestane-3-one and the corresponding exceedingly weak ultraviolet absorption maxima, one has to assume that for these chromophores the induced electrical dipole moment is very small, but the magnetic dipole moment is sufficiently large.

Acknowledgment.—We are very thankful to Dr. L. Velluz for the circular dichroism spectra reported here, to Dr. P. Sengupta for derivatives of sugiol, to Gilbert Suarez for running some ultraviolet spectra, to R. Bruce and R. J. Izdebski for technical help and to Dr. U. Weiss for valuable discussions. This work was supported in part by a research grant from the National Science Foundation.

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[7] Solvent effects on optical rotatory dispersion have been attributed to various factors including shifts in absorption spectra and conformational changes in the molecule; see N. C. Knelen, N. J. Krause, T. O. Carmichael and O. E. Weigang, *J. Am. Chem. Soc.*, **84**, 1738 (1962), and C. Tanford, *ibid.*, **84**, 1747 (1962).

[8] E. V. Condon, W. Altar and H. Eyring, *J. Chem. Phys.*, **5**, 753 (1937).

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RECEIVED MAY 14, 1962

THE EFFECT OF RADIATION ON THE REACTIONS OF RECOIL CARBON-11 IN AMMONIA[1]

Sirs:

The ammonia system[2] in which carbon-14 recoil atoms[3] are produced by the $N^{14}(n,p)C^{14}$ reaction was the first in which essentially all of the radioactive carbon produced could be accounted for in isolable and identifiable species.

One of the factors affecting the chemistry of the system is the radiation[4] from all sources that the

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. Y. Yang and A. P. Wolf, *J. Am. Chem. Soc.*, **82**, 4488 (1960).

[3] The literature prior to 1960 has been reviewed in A. P. Wolf, *Ann. Rev. Nucl. Science*, **10**, 259 (1960).

[4] *Cf.* ref. 2 and A. P. Wolf, C. S. Redvanly and R. C. Anderson, *J. Am. Chem. Soc.*, **79**, 3717 (1957).