p-Phenylphenacyl α-methyl-γ-phenylbutyrate, m. p. 62–63°. *Anal.* Calcd. for $C_{25}H_{24}O_3$: C, 80.65; H, 6.45. Found: C, 80.74; H, 6.56.

p-Phenylphenacyl β-methyl-δ-phenylvalerate, m. p. 66–67°. *Anal.* Calcd. for $C_{26}H_{26}O_3$: C, 80.83; H, 6.73. Found: C, 80.76; H, 6.79.

Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois
Herbert E. Carter

Received May 18, 1940

6-METHYL-5-NITRO-2-NAPHTHOIC ACID

Five grams of 1-nitro-2,6-dimethylnaphthalene[1] (m. p. 67–68°) was refluxed for two days in 50 cc. of water with 45 cc. of nitric acid added in portions. The crude product (5 g.) was collected by filtration and extracted with sodium bicarbonate to give 2 g. of 6-methyl-5-nitro-2-naphthoic acid; the neutral residue was a mixture of dinitrodimethylnaphthalenes. On recrystallization from 95% acetic acid, the acid formed rosets of colorless needles, m. p. 258–259°, neutral equivalent 230 (calcd. 231).

Anal. Calcd. for $C_{12}H_9O_4N$: C, 62.31; H, 3.94. Found: C, 62.61; H, 4.08.

The isomeric 6-methyl-1-nitro-2-naphthoic acid was prepared according to Meyer and Alken[1] in 3% yield, m. p. 238–239°.

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(1) Meyer and Alken, *Ber.*, **55**, 2280 (1922).

Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois
Charles C. Price

Received June 27, 1940

DERIVATIVES OF METHACROLEIN

The sample of methacrolein used for the preparation of the derivatives had the following physical constants: b. p. 73.5°; n^{20}_{D} 1.4191; d^{20}_{4} 0.830; M_D calcd., 21.37; M_D found, 21.31. The usual methods were used for the preparation of the derivatives.[1]

Semicarbazone of Methacrolein.—Colorless plates from 25% ethanol, m. p. 197.5–198°.

Anal. Calcd. for $C_5H_9ON_3$: N, 33.06. Found: N, 33.09.

p-Nitrophenylhydrazone of Methacrolein.—Orange crystals from xylene, m. p. 161–163°.

Anal. Calcd. for $C_{10}H_{11}O_2N_3$: N, 20.48. Found: N, 19.99.

2,4-Dinitrophenylhydrazone of Methacrolein.—Orange crystals from xylene, m. p. 206–206.5°

Anal. Calcd. for $C_{10}H_{10}O_4N_4$: N, 22.30. Found: N, 22.05.

1-Phenyl-4-methyl-Δ^2-pyrazoline.—Phenylhydrazine reacted with methacrolein to produce the pyrazoline and not the phenylhydrazone. It was recrystallized from petroleum ether, m. p. 73–74°.

Anal. Calcd. for $C_{10}H_{12}N_2$: N, 17.49. Found: N, 17.24.

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(1) Shriner and Fuson, "Systematic Identification of Organic Compounds," 2nd Edition, John Wiley and Sons, N. Y., 1940.

Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois
R. L. Shriner
A. G. Sharp

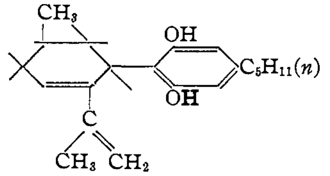
Received June 28, 1940

COMMUNICATIONS TO THE EDITOR

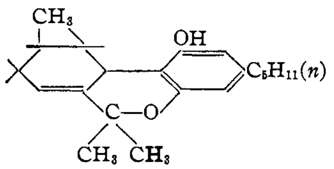
CONVERSION OF CANNABIDIOL TO A PRODUCT WITH MARIHUANA ACTIVITY. A TYPE REACTION FOR SYNTHESIS OF ANALOGOUS SUBSTANCES. CONVERSION OF CANNABIDIOL TO CANNABINOL

Sir:

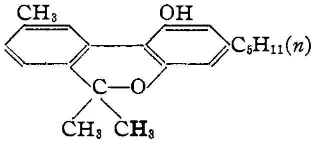
Cannabidiol, which has been shown in previous papers to have structure I with doubt merely as to the position of the double bond in the left-hand ring, isomerizes in the presence of pyridine hydrochloride, ethanolic hydrogen chloride, hydrogen chloride in ether, sulfamic acid, ethanolic phosphoric acid or zinc chloride to give tetrahydrocannabinol (II). Undoubtedly other reagents of a similar character will be found to be equally effective for the isomerization. The tetrahydrocannabinol (II) is a colorless highly viscous oil (b. p. 188–190° (2.5 mm.), found: C, 79.90; H, 9.52). It has a constant boiling point regardless of the method of synthesis, but its rotation varies depending on the conditions used; under specified conditions two products of constant rotation are produced, $[\alpha]^{27}_{D}$ $-160°$ and $[\alpha]^{32}_{D}$ $-240°$. Apparently the reagents sometimes cause a shift in the double bond or an interchange of diastereoisomers. The structure of compound II was demonstrated by dehydrogenation to cannabinol (m. p. 75–76.5°) (III) which has been proved by synthesis to have that formula,



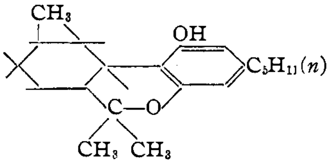
I



II



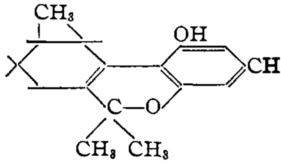
III



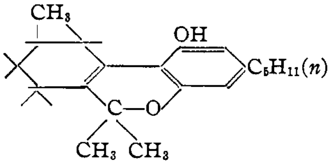
IV

The interesting fact is that the tetrahydrocannabinol (II) product, independent of its rotation, has a potent marihuana activity. Upon reduction the tetrahydrocannabinol, regardless of the rotation it possesses, gives a hexahydrocannabinol (IV) of constant rotation (colorless, viscous oil, b. p. 153–155° (0.10 mm.), $[\alpha]^{27}\mathrm{D}$ $-70°$, found: C, 79.35; H, 10.43); this reduction product is also physiologically active.

A superb method for preparing pyrans of the type III and IV has been devised. It consists in condensing ethyl 5-methylcyclohexanone-2-carboxylate with orcinol and phosphorous oxychloride, followed by treatment with methylmagnesium iodide; compound V (white crystals, m. p. 115.5–116°, found: C, 78.98; H, 8.75) was prepared thus. If, however, olivetol is used in place of orcinol, a tetrahydrocannabinol (VI) will result which upon dehydrogenation should give cannabinol and upon reduction a hexahydrocannabinol (IV), the racemic or a diastereoisomeric form of the same substance obtained from isomerization of cannabidiol and reduction. These synthetic products, at least the reduced one, it is expected will have marihuana activity.



V



VI

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
IN COLLABORATION WITH THE
TREASURY DEPARTMENT, NARCOTICS
LABORATORY, WASHINGTON, D. C.
AND DR. S. LOEWE AT THE
PHARMACOLOGICAL DEPARTMENT
CORNELL MEDICAL SCHOOL

ROGER ADAMS
D. C. PEASE
C. K. CAIN
B. R. BAKER
J. H. CLARK
HANS WOLFF
R. B. WEARN

RECEIVED JULY 23, 1940

RELATION OF LIGHT INTENSITY TO THE LATERAL GROWTH ON A PHOTOGRAPHIC PLATE

Sir:

While investigating the dependence of the diameters of photographic images of stars (artificial and natural) upon several parameters, we found a certain failure in reciprocity with respect to the relation between diameter, time and intensity which is very much greater than the usual reciprocity failure for photographic density. We find that the greatly predominant factor upon which the width of the photographic image depends is the intensity. To investigate the effect of wave length, we used a Hilger Quartz Spectrograph in addition to "star sources." During certain experiments we were able to vary independently the time of development, temperature of development, time of exposure, intensity of exposure and the plate characteristics.

The following results were obtained:

1. The width of the photographic image appears as a nearly linear function of the logarithm of the intensity.
2. In most cases the widths of the images were not at all or only slightly influenced by increases of exposure time.
3. In cases in which the width of the images of corresponding lines increased with the increase of the logarithm of the exposure time, such increase was in no case more than one-tenth the increase with the logarithm of the intensity.