247–247.5° dec. Infrared ν_{max}^{Nujol}: 1773 cm.$^{-1}$ (ester), 1701 cm.$^{-1}$ (carboxyl), 1689 cm.$^{-1}$ (carbonyl).

Anal. Calcd. for $C_{19}H_{12}O_8$: C, 61.96; H, 3.29. Found: C, 62.17; H, 3.49.

The product was confirmed to be identical with authentic rhein diacetate.

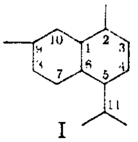
RESEARCH LABORATORIES
TAKEDA PHARMACEUTICAL INDUSTRIES, LTD.
JUSO, OSAKA, JAPAN

Structures of Carotol and Daucol[1]

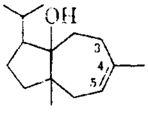
L. H. ZALKOW, E. J. EISENBRAUN,[2] AND J. N. SHOOLERY[3]

Received June 3, 1960

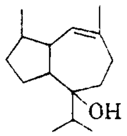
Three different carbon skeletons have been proposed for the sesquiterpenic alcohol carotol. Sorm and Urbanek[4] originally proposed formula I; carotol was represented as having a hydroxy group at C_{11} and a double bond at C_1—C_2. These workers[5] later suggested that the hydroxy group was at C_6 and the double bond at C_8—C_9 or C_9—C_{10}. Very recently Sorm and co-workers[6] proposed formula II for carotol on the basis of new degradative experimental work. At the time of the latter report there appeared another publication in which other workers[7] offered evidence in support of formula III.



I

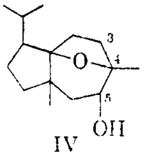


II

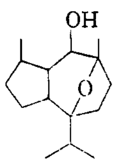


III

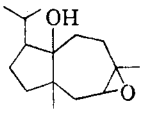
Daucol (carotol oxide), another sesquiterpenic constituent of the oil of *Daucus carota L.*, is also obtained from carotol on oxidation with peracids.[4] Originally daucol was believed to be the epoxide of carotol, but it was recently shown that oxidation of daucol gives a keto ether, $C_{15}H_{24}O_2$, and formula IV was proposed as the structure of daucol.[6]



IV



V



VI

We were in the process of determining the absolute configuration of carotol when the recent conflicting reports appeared. We wish to offer evidence which, together with the recent work of Sorm, *et al.*,[6] shows that structures represented by formulas I and III are untenable and that formula II or its isomer with the double bond at C_3—C_4 represents the correct structure of carotol.

Carotol was isolated from carrot seed oil, as previously described, and converted to daucol by oxidation with peracids.[4] The NMR spectrum of daucol is consistent only with formula IV. Formula V would represent daucol if carotol were correctly represented by formula III.

The two sharp lines at 64 cps (δ = 8.932) and 82 cps (δ = 8.632) in the NMR spectrum of daucol can be assigned to the bridgehead methyl group of IV and the methyl group at the tertiary carbon C_4, respectively, since neither line shows spin coupling to a neighboring proton. The methyl group attached to the five-membered ring of V would show a doublet character similar to that observed for each of the isopropyl methyls at 49 and 63 cps (δ = 9.184 and 8.950). The isopropyl methyl groups possess different chemical shift values in this compound (see reference 8 for discussion of this). Further evidence for IV in preference to V is the four line pattern at 224 cps (δ = 6.265) which arises from the proton attached to the same carbon atom as the hydroxy group in IV. The two protons of the adjacent CH_2 group couple their spins to this proton with different coupling constants, leading to the observed pattern. In the case of V, the single neighboring proton could not split the resonance of the proton in question into more than a doublet.

The acetate of daucol was prepared and its NMR spectrum showed the isopropyl methyls unshifted relative to daucol itself, while the bridgehead methyl and tertiary methyl group at C_4 showed small shifts. The large shift of the multiplet from 224 cps to 296 cps (δ = 5.070), a shift of 1.20 parts per million, is characteristic of the behavior of a proton adjacent to hydroxy upon acetylation of the hydroxy group. Therefore, the hydroxy group of daucol is adjacent to CH_2 and IV represents the correct structure; VI, which corresponds to the epoxide of II, is excluded. With the evidence available it is not possible to say with certainty whether the hydroxy group in IV is at position 5 or 3.

The NMR spectrum of carotol itself showed a flat-topped peak in the olefinic region which is characteristic of an olefinic proton adjacent to a CH_2 group. Treatment of carotol with permanganate at 0° gave the previously reported triol.[4]

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[1] This work was supported in part by Frederick Gardner Cottrell Grant from the Research Corporation and the Research Foundation of Oklahoma State University.

[2] Department of Chemistry and Chemical Engineering, Stanford University, Stanford, Calif.

[3] Varian Associates, Palo Alto, Calif.

[4] F. Sorm and L. Urbanek, *Collection Czechoslov Chem. Communs.*, 13, 49, 420 (1948).

[5] F. Sorm, V. Herout, and V. Sykora, *Perfumery Essent. Oil Record*, 50, 679 (1959).

[6] V. Sykora, L. Novotny, and F. Sorm, *Tetrahedron Letters*, No. 14, 24 (1959).

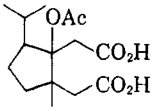
[7] G. Chiurdoglu and M. Descamps, *Chem. & Ind. (London)*, 1377 (1959); *Tetrahedron*, 8, 271 (1960).

[8] S. Goodwin, J. N. Shoolery, and L. F. Johnson, *J. Am. Chem. Soc.*, 81, 3065 (1959).

The NMR spectrum of this triol was also consistent with structure II for carotol.

A dicarboxylic acid was obtained by oxidation of the triol with chromic acid in acetic acid. This acid appears to be the same as the one recently reported by Sorm, *et al.*,[6] however, Chiurdoglu and Descamps[7] isolated an α-hydroxyketone by a similar oxidation.

The NMR spectrum of the above acid is consistent with the formula VII proposed by Sorm[6] for this acid. It is interesting that in the NMR spectrum of the acid the isopropyl methyl groups are equivalent and the doublet corresponding to them is found at 55 cps ($\delta = 9.083$), close to the average of the nonequivalent methyls in daucol. A similar situation prevails in carotol itself in which the isopropyl methyls are equivalent or nearly so and fall at 57 cps ($\delta = 9.050$).



VII

EXPERIMENTAL[9]

NMR spectra. The NMR spectra were obtained with a Varian V-4300C high resolution NMR spectrometer operating at 60 mc. in a magnetic field of 14,092 oersteds. Samples were examined in dilute deuterochloroform solution at 33°, contained in cylindrical glass cells 0.195″ o.d. and 0.165″ i.d. containing 0.4 ml. of solution. The magnetic field was swept through the spectrum at approximately 25 milligauss per minute from low to high field. A trace of tetramethylsilane was added to each sample to serve as an internal reference. The positions of single lines or centers of spin multiplets are designated by the field-independent symbol δ where $\delta = 10.00 - 10^6 \times (\nu - \nu_{\mathrm{SiMe_4}})/\nu_{\mathrm{SiMe_4}}$.

Daucol acetate. Carotol was obtained by distillation of commercial natural carrot seed oil (Magnus Mabee and Reynard, Inc.). The fraction of boiling point 80–81° at 0.1 mm. and n_D^{26} 1.4944 was used. Gas chromatography indicated that this fraction contained at least 90% carotol.

Carotol was converted to daucol with either perbenzoic acid or monoperphthalic acid as previously described.[4]

A solution prepared from 262 mg. of daucol (m.p. 117–118°), 2.5 ml. of pyridine, and 0.2 ml. of acetic anhydride was allowed to stand at room temperature for 5 hr., then warmed on the steam bath for 15 min. Daucol acetate, 239 mg., precipitated when the solution was poured on ice. Recrystallization from methanol-water gave colorless needles of constant m.p. 80–81°.

Anal. Calcd. for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41; O, 17.24. Found: C, 73.27; H, 9.87; O, 17.08. $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.78 μ, 8.00 μ. Rotatory dispersion in methanol *c* 0.494; $[\alpha]_{700\mathrm{m}\mu}$ +4.05°; $[\alpha]_{589\mathrm{m}\mu}$ +10.5°; $[\alpha]_{255\mathrm{m}\mu}$ +170°.

Preparation of acid VII. Carotol was converted to the triol, $C_{15}H_{26}O_3$, m.p. 137–139°, as previously described.[4] The triol, 4.62 g., was dissolved in 400 ml. of acetic acid, 10.3 g. of chromic anhydride added, and the solution maintained at 80° with stirring for 13 hr. The solution was concentrated with the water aspirator and the residue taken up with ether. Extraction of the ether layer with bicarbonate solution followed by acidification of the bicarbonate extract gave 125 mg. of a colorless solid, m.p. 169–170°.

Anal. Calcd. for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05; O, 31.96. Found: C, 60.16; H, 7.93; O, 31.92; neut. equiv., 129. The neutralization equivalent indicates that saponification of the acetate occurred. Rotatory dispersion in methanol *c* 0.460; $[\alpha]_{700\mathrm{m}\mu}$ −2.6°; $[\alpha]_{589\mathrm{m}\mu}$ −3.0°; $[\alpha]_{305\mathrm{m}\mu}$ −31.3°; $[\alpha]_{255\mathrm{m}\mu}$ +53.9°.

Evaporation of the neutral ether layer gave a viscous oil the infrared spectrum of which showed no O—H band but two carbonyl bands one at 5.63 μ and the other at 5.83 μ.

Acknowledgment. We wish to thank Professor Carl Djerassi for the rotatory dispersion data. We are indebted to Mr. J. G. Houston for technical assistance.

Department of Chemistry
Oklahoma State University
Stillwater, Okla.

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[9] All melting points are uncorrected. Microanalysis by Dr. Alfred Bernhardt, Max Planck Institute, Mulheim, Germany.

Generation of Nitroethylene *in Situ* for Use in Diels-Alder Reactions[1a]

Ralph B. Kaplan[1b] and Harold Shechter[1c]

Received July 25, 1960

Diels-Alder addition of α,β-unsaturated nitro[2] compounds and conjugated dienes is an important preparative reaction. In a synthesis of derivatives of 3-nitroadipic acid,[3] it became of advantage to prepare 4-nitrocyclohexene. 4-Nitrocyclohexene was first obtained (see Experimental) in the present work in 78–92% yields by condensation of nitroethylene and 1,3-butadiene at 105–107° in either glacial acetic acid or benzene or in the absence of a solvent. The condensation, although adequate, offered the disadvantages that (1) nitroethylene is a viscous lacrymatory liquid which deteriorates on storage and is readily polymerized by heat, light, water, or traces of alkali[4] and (2) preparation of nitroethylene from nitroethanol, either *via* 2-nitroethyl acetate (88% yield from nitroethanol) and subsequent reaction with sodium acetate (considerable polymerization) or by reaction with phthalic anhydride at 170°

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[1] (a) Financial support for this research was provided by the Office of Naval Research, 1950. (b) Present address, Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Del. (c) To whom inquiries should be made.

[2] K. Alder, H. F. Rickert, and E. Windemuth, *Ber.*, **71**, 2451 (1938); H. L. Holmes, *Org. Reactions*, **4**, 136 (1948); W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952); E. E. van Tamelin and R. J. Thiede, *J. Am. Chem. Soc.*, **74**, 2615 (1952); W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954); K. Klager, *J. Org. Chem.*, **20**, 650 (1955); W. E. Noland, H. I. Freeman, and M. S. Baker, *J. Am. Chem. Soc.*, **78**, 188 (1956); and W. E. Noland, *J. Am. Chem. Soc.*, **82**, 2022 (1960).

[3] To be published separately.

[4] (a) H. Wieland and E. Sakellarios, *Ber.*, **52**, 898 (1919); (b) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

[5] L. Zeldin, Ph.D. dissertation, The Ohio State University, 1951.