with a 50% xylene solution of chloroprene in a sealed glass tube for 5 hours at 150°. The contents of the tube gradually blackened and only a viscous mass was obtained. Extraction of this material with ether, acetone and benzene failed to give any material corresponding to an adduct. Hydroquinone, du Pont "terpene B" and *t*-butylcatechol did not appear to inhibit the formation of the viscous material.

A 1.8-g. sample of anthracene, 8.4 g. of chloroprene in 50% xylene solution using "terpene B" polymerization inhibitor was heated for 24 hours at 130° in a sealed glass tube. At the end of this time the anthracene was recovered unchanged.

Acknowledgment.—The carbon hydrogen analyses were performed by the Galbraith Laboratories and the nitrogen analyses by Mrs. Patricia Ramey.

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RECEIVED OCTOBER 1, 1951

The Structure of Ocimene

BY MAURICE D. SUTHERLAND

RECEIVED OCTOBER 9, 1951

The hydrocarbon which has been named ocimene was first isolated by van Romburgh[1] from the essential oil of *Ocimum basilicum* and has since been identified in many other essential oils. Formula II although generally accepted[2] appears to be incorrect and should be replaced by I.

I

II

III

Jones and Smith[3] isolated from the oil of flowering *Tagetes glandulifera* a substance closely similar in various physical and chemical properties to van Romburgh's ocimene and regarded these two substances as identical. The ocimene from this source has now been submitted to quantitative ozonolysis and found to yield 95–96% of the acetone expected on Formula I. This may be compared with acetone yields (96–97%) obtained from pure β-citronellol phenylazophenylurethan[4] prepared from β-citronellol, the infrared spectrum[5] of which indicated the presence of less than 1% of α-citronellol. As acetone in this case can result only from the isopropylidene group, the ocimene examined must be I, although the presence of a few per cent. of II is not excluded. In possessing the isopropylidene structure this sample of ocimene resembles the samples of myrcene, citronellol, geraniol, linalol and other acyclic terpenoids so far examined.[6]

The structure II for ocimene from *O. basilicum* is due to Enklaar who worked almost alone on the problem for about twenty years. Enklaar[7] at first suggested I in accordance with the 27% yield of acetone obtained from ocimene ozonide but later preferred II although the strongest evidence for this was a color reaction indicating a γ-dicarbonyl compound amongst the ozonolysis products. In 1938 Dupont and Desreux[8] after examining Raman spectra concluded that a sample of van Romburgh's ocimene was rich in I and that the dihydro ocimene obtained by sodium and alcohol reduction was free from III.

These results of Enklaar and of Dupont and Desreux show that ocimene from *O. basilicum* contains at least a substantial proportion of I. On the other hand, there is no very satisfactory evidence that II is present in any proportion and the results of Dupont and Desreux speak strongly for the absence of II. The close correspondence in physical properties between the ocimene of Eklaar and that of Jones and Smith also favors an identity in structure and an absence of II. Thus no acceptable evidence for the existence of II in essential oils has yet been put forward and the name ocimene should be reserved for the hydrocarbon of structure I first isolated from *Ocimum basilicum*.

Experimental

A sample of crude ocimene from *Tagetes glandulifera* (kindly provided by Professor T. G. H. Jones) was redistilled at 10 mm. pressure and a fraction of b.p. 63° (10 mm.), d^{25}_4 0.7947, $n^{25}\text{D}$ 1.4836 and $[\alpha]\text{D}$ +0.12° selected. The ozonolysis procedure of Kuhn and Roth[9] was modified principally by the use of 15–20 mg. samples, an ozonation period of 15 minutes at an oxygen flow rate of 20 ml. per minute, (ozone concentration 8% by weight) and a sufficient excess of $M/5$ $KMnO_4$ (20 ml.) to ensure that some remained unreduced at the end of the distillation. Under these conditions samples of ocimene yielded 94.9, 95.4 and 96.0% of the acetone calculated on formula I. Levulinic and pyruvic acids (10 mg.) processed separately resulted in iodine consumption equivalent to less than 1% of the acetone resulting from 15 mg. of ocimene.

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[1] P. van Romburgh, *Proc. K. Acad. Wetensch. Amsterdam*, **3**, 454 (1900).

[2] (a) J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. 1, University Press, Cambridge, 1947, p. 19. (b) Maria Lipp in "Richter's Chemistry of the Carbon Compounds," Vol. II, edited by R. Anschutz, T. W. J. Taylor and A. F. Millidge, Elsevier, Amsterdam, 1938, p. 200. (c) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 2nd Ed., 1950, p. 1013.

[3] T. G. H. Jones and F. B. Smith, *J. Chem. Soc.*, **127**, 2530 (1925).

[4] M. D. Sutherland, THIS JOURNAL, **73**, 2385 (1951).

[5] R. Werner and M. D. Sutherland, accompanying paper.

[6] (a) Y. R. Naves, G. Brus and J. Allard, *Compt. rend.*, **200**, 1112 (1935); (b) J. Doeuvre, *Bull. soc. chim.*, [5] **3**, 613 (1936); (c) M. F. Carroll, *Perfumery and Essential Oil Record*, **38**, 226 (1947); (d) D. Barnard, *et al.*, *J. Chem. Soc.*, 915 (1950); (e) M. F. Carroll, R. G. Mason, H. W. Thompson and R. C. S. Wood, *ibid.*, 3457 (1950); (f) Y. R. Naves, *Bull. soc. chim.*, [5] **18**, 506 (1951).

[7] C. J. Enklaar, *Rec. trav. chim.*, **26**, 157 (1907); **27**, 422 (1908); **36**, 215 (1917); **45**, 337 (1926).

[8] G. Dupont and V. Desreux, *Bull. soc. chim.*, [5] **5**, 337 (1938).

[9] R. Kuhn and H. Roth, *Ber.*, **65**, 1285 (1932).

The Infrared Spectrum of α-Citronellol

BY R. L. WERNER AND MAURICE D. SUTHERLAND

RECEIVED NOVEMBER 1, 1951

In the published reports[1,2] of the infrared spectrum of various samples of citronellol, the absence of the bands characteristic of the isopropenyl group has been taken as proof of the virtual absence of α-citronellol, which itself has not been available for infrared examination.

The infrared spectrum of the previously de-

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[1] D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

[2] M. F. Carrol, R. G. Mason, H. W. Thompson and R. C. S. Wood, *ibid.*, 3457 (1950).

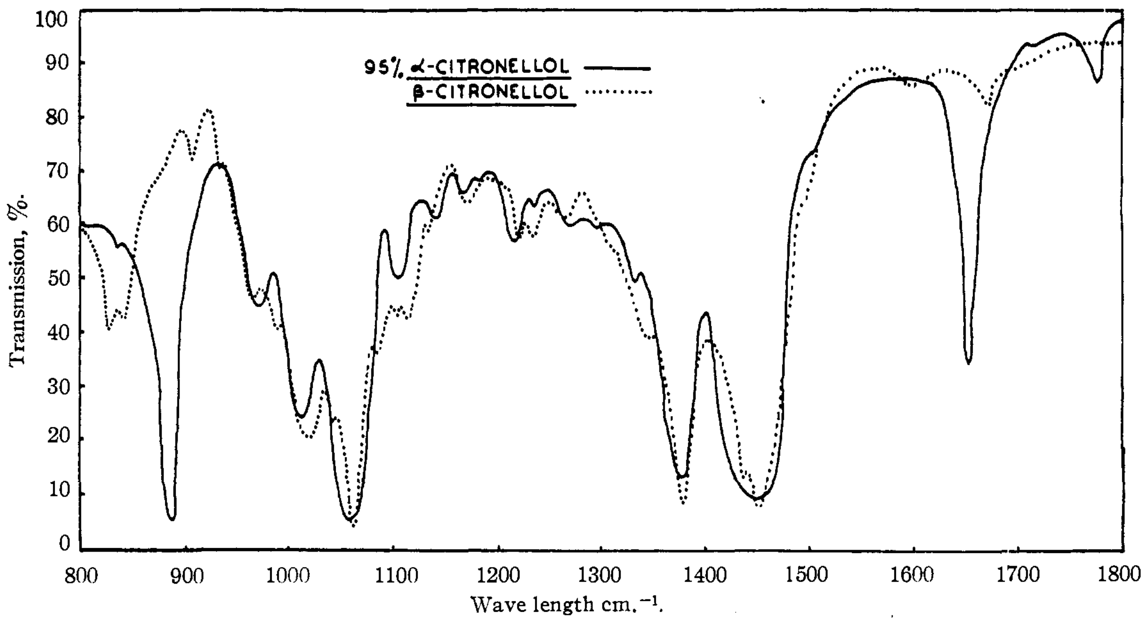

Fig. 1.

scribed[3] sample of 95% α-citronellol (impurity 5% β-citronellol) has now been examined, and found to show bands of high extinction coefficient at 887 and 1651 cm.$^{-1}$ (Fig. 1). There can be little doubt as to the correctness of the assignment of an isopropenyl group in this compound since many authors[1,2,4-7] have demonstrated that the spectra of substances with an isopropenyl group exhibit a strong absorption band about 890 cm.$^{-1}$ due to out of plane deformational modes of the hydrogen atoms, accompanied by a strong carbon–carbon double bond stretching frequency about 1640–1650 cm.$^{-1}$. It is of interest also to note the presence of the overtone of the hydrogen deformation frequency at 1778 cm.$^{-1}$ indicated by Colthup[8] as another characteristic of isopropenyl groups. On the other hand, β-citronellol exhibits characteristic bands at 830 and 1672 cm.$^{-1}$ of much lower extinction coefficient (Fig. 1).

In connection with the question of the composition of naturally occurring critonellols, we have examined mixtures of the α- and β-isomers in order to determine the lower limits of detectability of the one isomer in the other. Because of the lower extinction coefficients of the bands of the β-isomer and the absorption of the α-isomer in the same region, it was found difficult to detect small amounts of the former in the latter; in fact a lower reliable limit would be 10%. On the other hand, because of the high extinction coefficient of the 887 cm.$^{-1}$ band of the α-isomer, it was found possible to detect as little as 1% of this in the β-form (Fig. 2). These results confirm the work of Barnard, *et al.*,[1] who suggested, on the basis of known values of other extinction coefficients of the isopropenyl group at 890 cm.$^{-1}$, that 2% of the α-isomer could probably be detected in the β-isomer.

All samples were examined with a Perkin–

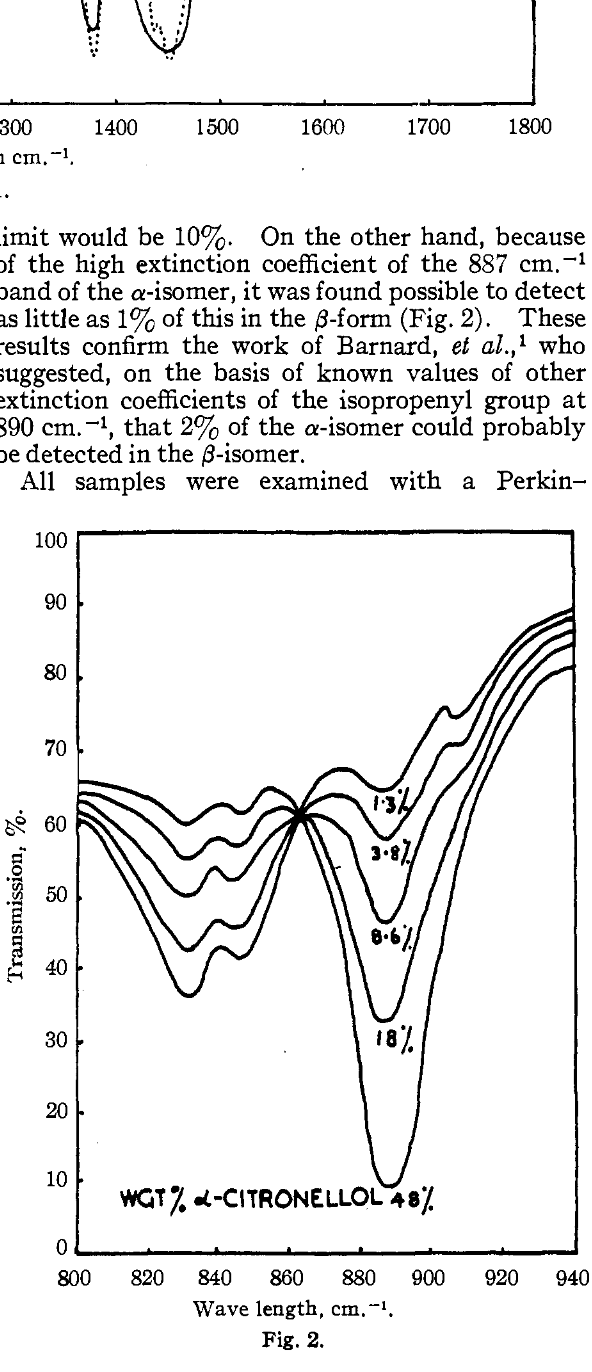

Fig. 2.

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(3) M. Sutherland, THIS JOURNAL, **73**, 2385 (1951). The boiling points reported herein have been found to be incorrect as a result of excessive heat loss along the metal well enclosing the stillhead thermocouple of the Podbielniak still. This difficulty arises only in distillations under reduced pressure. When the thermocouple junction is exposed to the vapor satisfactory boiling points (β-citronellol b.p. 108.4°) are obtained. The sign of the specific rotation reported for 95% α-citronellol should be positive instead of negative.

(4) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

(5) N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 1540 (1947).

(6) N. Sheppard and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **196**, 195 (1949).

(7) H. W. Thompson and D. H. Whiffen, *J. Chem. Soc.*, 1412 (1948).

(8) N. B. Colthup, *J. Optical Soc. Am.*, **40**, 6 (1950).

Elmer model 12C infrared spectrometer with rock salt optics calibrated against water vapor and ammonia,[9] using the same fixed rock salt cell of thickness about 0.025 mm.

(NOTE: The complete spectrum will be available through the American Petroleum Institute.—Ed.)

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[9] R. A. Oetjen, C. L. Kao and H. M. Randall, *Rev. Sci. Instruments*, **13**, 515 (1942).

JOINT CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE NEW SOUTH WALES UNIVERSITY OF TECHNOLOGY, SYDNEY, AND THE
CHEMISTRY DEPARTMENT, UNIVERSITY OF QUEENSLAND, BRISBANE, AUSTRALIA

Trinitrobenzene Complexes of Various Indole Compounds[1]

BY LOWELL E. WELLER, THEODORE L. REBSTOCK AND HAROLD M. SELL

RECEIVED DECEMBER 22, 1951

We have prepared a number of new 1,3,5-trinitrobenzene complexes of various indole derivatives for use in characterization of these substances.

The properties of these derivatives, prepared as previously described,[2,3] are summarized in Table I.

TABLE I

PROPERTIES OF 1,3,5-TRINITROBENZENE ADDUCTS OF INDOLE COMPOUNDS

Trinitrobenzene derivative of	M.p., °C.	Color	Formula	Dumas nitrogen, % Calcd.	Dumas nitrogen, % Found
Isatin (2,3-indolinedione)	116	Light brown	$C_{14}H_8O_8N_4$	15.6	15.7
Oxindole (2,3-dihydro-2-oxoindole)	123	Yellow	$C_{14}H_{10}O_7N_4$	16.2	16.3
Indole-3-aldehyde	144.5	Yellow	$C_{15}H_{10}O_7N_4$	15.6	15.8
Skatol (3-methylindole)[a]	184	Red	$C_{15}H_{12}O_6N_4$	16.3	16.4
Tryptophol (indole-3-ethanol)	109.5	Orange	$C_{16}H_{14}O_7N_4$	15.0	15.1
β-(Indole-3)-propionic acid	135	Orange	$C_{17}H_{14}O_8N_4$	13.9	14.1
2-Methylindole-3-acetic acid	208	Red	$C_{17}H_{14}O_8N_4$	13.9	13.8
β-(Indole-3)-*n*-butyric acid	152	Red	$C_{18}H_{15}O_8N_4$	13.5	13.4
2,3-Diphenylindole	160	Red	$C_{26}H_{18}O_6N_4$	11.6	11.6

[a] van Romburgh[4] reported the m.p. as 183°, but gave no analysis.

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[1] Journal Article No. 1307 from the Michigan Agricultural Experiment Station, East Lansing. This work was supported in part by the Horace H. Rackham Research Endowment of Michigan State College.

[2] C. T. Redemann, S. H. Wittwer and H. M. Sell, THIS JOURNAL, **73**, 2957 (1951).

[3] J. J. Sudborough, *J. Chem. Soc.*, **109**, 1339 (1916).

[4] M. P. van Romburgh, *Rec. trav. chim.*, **14**, 67 (1895).

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Synthesis of β-Acetamido-β,β-dicarbethoxypropionaldehyde and DL-Aspartic Acid[1]

BY OWEN A. MOE AND DONALD T. WARNER

RECEIVED DECEMBER 6, 1951

Previous publications[2-4] from this Laboratory have disclosed the syntheses of γ-acetamido-γ,γ-dicarbethoxybutyraldehyde and other closely related aldehydo compounds, and the utilization of these aldehyde intermediates in the production of diverse amino acids. This report concerns the synthesis of the lower aldehydo homolog, namely, β-acetamido-β,β-dicarbethoxypropionaldehyde.

Ethyl allylacetamidomalonate[5] was prepared by the allylation of the corresponding malonic ester with allyl bromide. The action of ozone on the allyl derivative yielded the ozonide which in turn was converted by reductive cleavage to the desired aldehydo compound, a crystalline product melting at 80–81°. The β-acetamido-β,β-dicarbethoxypropionaldehyde was further characterized as the 2,4-dinitrophenylhydrazone melting at 117–119°. Oxidation of the aldehyde by alkaline permanganate yielded the corresponding acid diester melting at 147–148°. Hydrolysis by refluxing in concentrated hydrochloric acid converted the acid diester to DL-aspartic acid.

Experimental

β-Acetamido-β,β-dicarbethoxypropionaldehyde.—Ethyl allylacetamidomalonate[5] (30 g.) was dissolved in 50 cc. of absolute ethanol. The resulting alcoholic solution was treated with ozone at 0–5° for a period of 5 hours. The water-clear alcoholic solution of the ozonide was diluted with absolute ethanol to a total volume of 200 cc. Five per cent. palladium-on-charcoal (2 g.) was added and the reductive cleavage[6] of the ozonide was accomplished at an initial pressure of 30 p.s.i. After 90 minutes the reduction was complete. The reaction mixture was refrigerated overnight and then the catalyst was removed by filtration. The water-clear filtrate gave no test for ozonide and it was concentrated *in vacuo*. A solid crystalline cake resulted which possessed a pungent odor of formaldehyde. The yield of crude aldehydo compound melting at 65–67° was 29.3 g. Purification by crystallization from ethanol increased the melting point to 80–81°.

Anal. Calcd. for $C_{11}H_{17}O_6N$: C, 50.93; H, 6.61; N, 5.40. Found: C, 50.58; H, 6.39; N, 5.87.

The 2,4-dinitrophenylhydrazone of β-acetamido-β,β-dicarbethoxypropionaldehyde was prepared following the conventional procedure and after purification by crystallization from ethanol melted at 117–119°.

Anal. Calcd. for $C_{17}H_{21}O_9N_5$: C, 46.44; H, 4.82; N, 15.94. Found: C, 46.33; H, 4.41; N, 15.85.

The Diester Acid.—A water solution containing 3.3 g. of the aldehydo compound was mixed with 5–10 drops of 10% aqueous sodium hydroxide. The resulting clear solution was treated with portions of a saturated aqueous solution of potassium permanganate until a slight excess was indicated. The oxidation of the aldehydo compound was very rapid and it was necessary to cool the reaction mixture in a cold water-bath in order to avoid an increase in the reaction temperature. After the oxidation was complete, the manganese dioxide was removed by filtration and the mixture acidified to *p*H 3. The excess permanganate was

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[1] Paper 126, Journal Series, General Mills, Inc., Research Department.

[2] O. A. Moe and D. T. Warner, THIS JOURNAL, **70**, 2763 (1948).

[3] D. T. Warner and O. A. Moe, *ibid.*, **70**, 2765 (1948).

[4] D. T. Warner and O. A. Moe, *ibid.*, **70**, 3918 (1948).

[5] N. F. Albertson, *ibid.*, **68**, 450 (1946).

[6] H. S. Mason, *ibid.*, **67**, 420 (1945).