an activity arbitrarily designated as 100%. A 1.233-g. portion was digested in 250 ml. of 0.05 *N* hydrochloric acid with 132 mg. of pepsin.[8] After dilution, the solution was dialyzed for five days against distilled water. The dialysates were collected daily, concentrated *in vacuo*, and lyphilized.

The combined product, a yellow solid, weighed 0.605 g. *Anal.* Found: N, 13.69; amino-N, 1.7. It showed an average assay value of 140%. The material was administered to a patient with rheumatoid arthritis, and found to be fully active[11] at a dosage of 18 mg., four times daily, in maintaining a remission obtained by previous treatment with ACTH.

In another experiment, the dialysate was collected after one day, and yielded a product having 12.63% nitrogen and 1.89% amino-nitrogen. It was fully active clinically in maintaining remission at a level of 10 mg., four times daily. In a third clinical trial, material obtained during the third day of dialysis was found fully active when given in four 12.5-mg. doses daily. We gratefully acknowledge the coöperation of Dr. Charles Ragan,[12] who carried out the clinical tests.

The chemical nature of the clinically active component(s) is being investigated.

Complete acid hydrolysis of ACTH and of the combined dialysates of the pepsin digest, followed by paper strip chromatography,[13] revealed in each the presence of at least seven or eight common amino acids. Paper chromatograms of the dialysate of the pepsin digest showed no substances which reacted with ninhydrin to give colored spots under the usual conditions for detecting amino acids.[13]

It is our understanding[14] that Dr. Li also prepared a pepsin digest of ACTH which was active in a case of rheumatoid arthritis.

(11) The effect was equivalent to the clinical response obtained with Armour Standard ACTH (L. A. 1050).

(12) Columbia University, College of Physicians and Surgeons, New York, N. Y., private communication.

(13) Consden, Gordon and Martin, *Biochem. J.*, **38**, 224 (1944); **41**, 590 (1947).

(14) Private communication.

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RECEIVED JANUARY 3, 1950

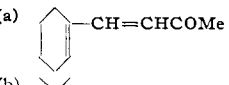
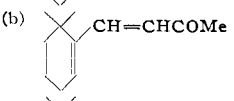
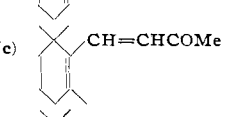
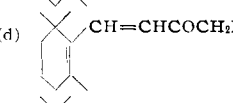
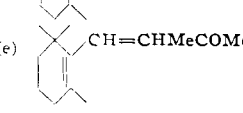
STRUCTURE AND LIGHT ABSORPTION OF METHYLIONONES

Sir:

In a recent communication, Lusskin and Winston[1] have recorded the ultraviolet light absorption properties of "*β-i*-methylionone" and conclude that the somewhat anomalous spectrum of this compound (see table) is incompatible with the structure (e) proposed by Köster.[2] Lusskin and Winston suggest that in view of its high-intensity band in the 2300 Å. region, *β-i*-methylionone is probably an enone rather than a dienone. This suggestion does not, however, account for the lower-intensity band near 2800 Å.; yet there is no reason to doubt that *β-i*-methylionone, regenerated from its pure semicarbazone, is a homogeneous compound.

We have recently reported and discussed[3] the spectral properties of a comprehensive series of natural and synthetic homologs of *β*-ionone and have shown that the anomalous absorption exhibited by *β*-ionone itself and by some of its homologs can be explained in terms of steric interference between the side-chain and methyl substituents in the ring. As a result of this interference, the unsaturated side-chain is displaced out of the plane of the cyclohexene ring and resonance interaction between the two parts of the molecule is decreased. As the inhibition of resonance increases, the intensity of the long wave length band near 2800 Å. characteristic of the dienone chromophore decreases, while the intensity of the short wave length band near 2300 Å. characteristic of the partial enone chromophore increases.

TABLE I

		"Enone" band		Dienone band		Steric inhibition
		Å. λ_{max}	ϵ_{max}	Å. λ_{max}	ϵ_{max}	
(a)		..	...	2810	20800[3]	
(b)		2280	4100	2810	13000[3]	
(c)		2230	6500	2960	10700[3]	
(d)		2200	6500	2950	9400[1]	
(e)		2280	11600	2780	4500[1]	

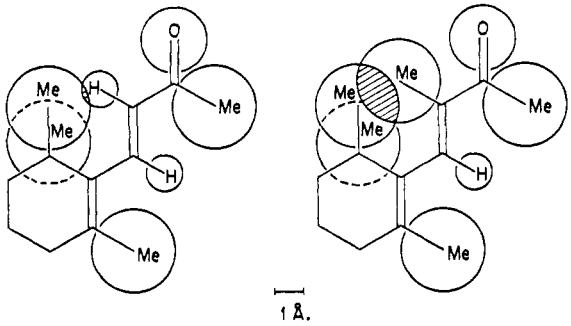
Increase

An approximate scale projection of formula (e) in the *s*-transconfiguration, using covalent radii which represent a measure of minimum interfering properties,[3] shows that the extra methyl group considerably increases steric interference in *β-i*-methyl ionone as compared with *β*-ionone. On the other hand, no additional interference is caused byt he extra methyl group in *β-n*-methylionone (d), the absorption of which is very similar to that of *β*-ionone (c). The spectral data for *β-i*-methylionone are thus fully in agreement with formula (e) and with the generalizations of Braude, Jones, Koch, Richardson, Sondheimer and Toogood.

(1) Lusskin and Winston, THIS JOURNAL, **71**, 2412 (1949).

(2) Köster, *Ber.*, **80**, 248 (1947).

(3) Braude, Jones, Koch, Richardson, Sondheimer and Toogood, *J. Chem. Soc.*, 1890 (1949).



β-Ionone *β-i-Methylionone*

Fig. 1.

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RECEIVED SEPTEMBER 8, 1949

SOME CHARACTERISTICS OF A CRYSTALLINE COMPOUND DERIVED FROM VITAMIN B_{12}

Sir:

Vitamin B_{12},[1] 23.7 mg., was stirred with 80 mg. of platinum catalyst in an atmosphere of hydrogen for twenty hours at atmospheric pressure as described by Kaczka and co-workers.[2,3] During the period, 1.12 ml. of hydrogen was taken up, corresponding to about 3 mols. The color changes described elsewhere[2] were noted. About 18 mg. of red crystals (I) was obtained from acetone–water solutions of the resultant product. Further purification, accompanied by the removal of brown material, was accomplished by silicic acid chromatography, using the same procedure employed for vitamin B_{12b},[4] followed by recrystallization. The absorption spectrum maxima following this procedure and after drying at 110° for twenty hours at 1 mm. over phosphorus pentoxide, were as follows: 273 mμ, $E^{1\%}_{1\,cm.}$ 132; 351 mμ, 159; 525 mμ, 54. These maxima and extinction coefficients are characteristic of vitamin B_{12b}. Upon adding sodium hydroxide to a concentration of 0.01 *N*, the absorption spectra of I and of vitamin B_{12b} were found to undergo identical bathochromic shifts of the two main absorption bands to 357 mμ and 536 mμ, respectively. No such shifts were observed with vitamin B_{12}. The infrared absorption spectrum[5] of I was similar to that of vitamin B_{12b} and both showed the absence of a band at 2140 $cm.^{-1}$. The presence of a band at this point was observed with vitamin B_{12}.[6] The biological activity of I was compared with those of vitamins B_{12} and B_{12b} using *L. leichmannii*[7] and chicks.[8] All three preparations had the same activity within the limits of error of the assay methods. In contrast, vitamin B_{12a}, also produced by hydrogenation of vitamin B_{12},[2] was reported to have only 20% of the activity of vitamin B_{12} for *L. leichmannii*[2,9] and 30 ± 15% of the activity vitamin B_{12} for chicks.[2] A band in the absorption spectrum of vitamin B_{12a} was reported at 315 mμ ($E^{1\%}_{1\,cm.}$ 80).[2] This band was absent from the absorption spectra of both I and vitamin B_{12b}.[6] The present experimental results indicate that, under our conditions, vitamin B_{12b} was produced by hydrogenation of vitamin B_{12}.

(1) Purchased from Merck and Co., Rahway, New Jersey.

(2) E. Kaczka, D. E. Wolf and K. Folkers, THIS JOURNAL, **71**, 1514 (1949).

(3) The hydrogenation was carried out by Mr. W. Fulmor.

(4) J. V. Pierce, A. C. Page, Jr., E. L. R. Stokstad and T. H. Jukes, THIS JOURNAL, **71**, 2952 (1949).

(5) Kindly measured by Dr. R. C. Gore, Stamford Research Laboratories, American Cyanamid Company.

(6) J. V. Pierce, A. C. Page, Jr., E. L. R. Stokstad and T. H. Jukes, THIS JOURNAL, **72**, in press (1950).

(7) C. E. Hoffmann, E. L. R. Stokstad, B. L. Hutchings, A. C. Dornbush and T. H. Jukes, *J. Biol. Chem.*, **181**, 635 (1949).

(8) E. L. R. Stokstad, T. H. Jukes, J. V. Pierce, A. C. Page, Jr., and A. L. Franklin, *ibid.*, **180**, 647 (1947).

(9) D. Hendlin and H. B. Woodruff, paper presented at 116th meeting, American Chemical Society, Atlantic City, N. J.; September, 1949.

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RECEIVED DECEMBER 21, 1949

A NEW IRON CARBIDE IN HYDROCARBON SYNTHESIS CATALYSTS

Sir:

During the course of hydrocarbon synthesis investigations in this laboratory, X-ray diffraction patterns of certain catalyst samples have indicated the presence of a new iron carbide phase. Iron catalysts in the hydrocarbon synthesis process using CO and H_2 have been characterized by the presence of iron carbide either as Fe_2C (Hägg) or Fe_2C (hexagonal).[1] There has been great interest in these carbides because of the role they may play in the catalytic process.[2]

The catalyst used in these investigations was obtained from reduced, promoted mill scale which analyzes approximately 97.0% total iron, with minor amounts of Mn, Cu, Ni, Al, S and P, and 0.7% K_2CO_3 as promoter. The new iron carbide appeared along with Fe_3O_4 and Fe_2C (Hägg) during the course of a fluidized synthesis run at 27 atm. pressure and 360°, and eventually it constituted approximately 90% of the total catalyst charge.

The X-ray diffraction pattern of this carbide phase is shown in Fig. 1(b). In this pattern some faint lines are attributed to Fe_3O_4 and Fe_2C (Hägg).[3] For comparison, the diffraction pattern for Fe_2C (Hägg) is shown in Fig. 1(a), and that for α-Fe is shown in Fig. 1c. These diffraction patterns were obtained with a 0.6-mm. extruded sample in a 71.6-mm. powder camera using radia-

(1) Hofer, Cohn and Peebles, THIS JOURNAL, **71**, 189 (1949).

(2) Storch, "Advances in Catalysis and Related Subjects," Vol. I, Academic Press, Inc., New York, N. Y., 1948, pp. 115–156.

(3) Jack, *Proc. Roy. Soc.* (*London*), **195A**, 56 (1948).