ammonia and then dried with sodium carbonate and distilled.

Eb.—The remainder of the lower layer from Ea was dried with sodium carbonate and distilled.

F.—The procedure was the same as Eb except that an equimolar amount of water was added dropwise to the bromopentane during the hydrogen bromide addition.

G.—Moist air was blown through phosphorus tribromide for eight hours at room temperature. The residue was warmed for 20 minutes on the steam-bath. The bromopentane was added to this cooled material and the stoppered flask was kept in a Dry Ice–acetone-bath for two days and at room temperature for four days. The reaction mixture was worked up as in method D for the preparation of the halides with phosphorus tribromide.

H.—The bromopentane was refluxed for five hours at 123° flask temperature with the charge of 48% aqueous hydrobromic acid and concd. sulfuric acid that would have been used with an equimolar amount of alcohol in procedure B. The reaction mixture was diluted with water and extracted with ether. The black material formed during the refluxing period was filtered off and the ether solution was then dried with potassium carbonate and distilled.

I.—Seven grams of the bromopentane was shaken with 2.5 ml. of concd. sulfuric acid for 2.5 hours at room temperature. The mixture was diluted with water and the two layers were separated. The aqueous layer was made alkaline with solid sodium carbonate and then extracted twice with ether. The bromopentane layer was treated with solid sodium carbonate and added to the ether layers. The combined material was dried with sodium carbonate and distilled, 65% recovery of material boiling from 117.5–120° (uncor.).

5. Analytical.—The infrared spectra were taken at 30° against rock salt as standard with the bromopentane in a 0.03 mm. rock salt cell. A sing-beam memory-recording Beckman IR2T infrared spectrophotometer was used The analytical bands for 3-bromopentane were at wave lengths of 12.24 μ and 12.44 μ, while the characteristic peaks of 2-bromopentane were at wave lengths of 10.18, 13.23 and 13.39 μ. Mixtures of the bromides were analyzed in the usual manner by the application of the Beer–Lambert law at these five wave lengths. These two bromides were the only components present in the mixture with the one exception cited in Table II. The sensitivity of this method of analysis was checked by mixing accurately weighed amounts of bromide mixtures of known composition.

1-Bromopentane has a peak at 13.70 μ.

Acknowledgment.—The authors are grateful to Mr. E. Baclawski of Universal Oil Products Company for some of the infrared spectral analyses.

EVANSTON, ILL.

[A CONTRIBUTION FROM COLUMBIA UNIVERSITY AND UNIVERSITY OF RHODE ISLAND]

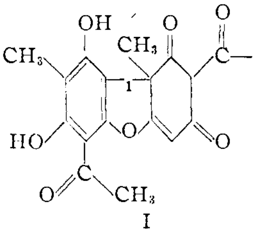
Ultraviolet Absorption Spectra of Derivatives of Usnic Acid

BY SCOTT MACKENZIE

RECEIVED JANUARY 16, 1952

Ultraviolet absorption spectra for usnetic acid, ethyl acetylusnetate, deacetyldecarbousnic acid, decarbousnic acid and the diacetates of the latter two substances, when compared with spectra for usnetol and its diacetate, confirm the accepted relationships among these derivatives. Spectra for dihydrousnic acid and its diacetate are analyzed in terms of previously proposed structures.

Structure I has been proposed for the lichen acid usnic acid, by Curd and Robertson.[1] Both they and Schöpf and Ross[2] have discussed those reactions[3] of usnic acid which can not be, as yet, reconciled with formula I.



I

Other reactions have been interpreted as demanding acceptance of I. The ozonolysis of diacetylusnic acid, giving a lactone (assigned structure II) and ethoxalylacetone,[2,4] has been thus construed, the assumption being made tacitly that substances similar to III could not exist. This assumption has been well supported for usnetol[5] and diacetyldecarbousnic acid[2] which have been ozonized.

Were substances similar to III possible, an admissible structure for usnic acid could be written

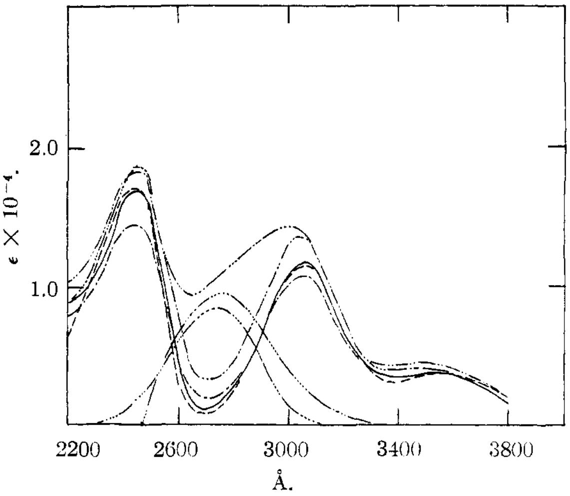


Fig. 1.———, usnetic acid; — — —, usnetol; —-—-—, deacetyldecarbousnic acid; —--—-—, ethyl acetylusnetate; —---—---, decarbousnic acid; —----—----, acetylacetone; —-----—----- values for decarbousnic acid less values for usnetol.

which would provide a ready explanation for both the acidity of usnic acid and its facile racemization. On the other hand, if this assumption regarding bond placement is, in general, valid for this type of substance, the ozonolysis information severely limits the number of formulas possible for this acid.

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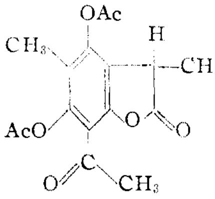
[1] F. H. Curd and A. Robertson, *J. Chem. Soc.*, 894 (1937).

[2] C. Schöpf and F. Ross, *Ann.*, **546**, 1 (1941).

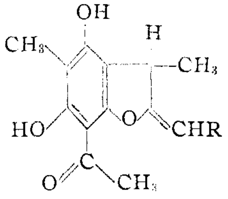
[3] Usnic acid is monobasic; further, racemic usnic acid is obtained when xylene solutions of active forms are refluxed.

[4] Confirmed by Y. Asahina and K. Okazaki, *J. Pharm. Soc. Japan.*, **63**, 618 (1943); *C. A.*, **45**, 5146 (1951).

[5] C. Schöpf, K. Heuck and A. Kraus, *Ann.*, **459**, 233 (1927).

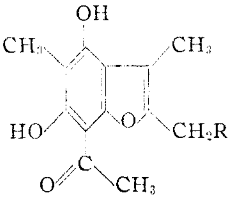


II



III

This important assumption has now been subjected to further scrutiny. Ultraviolet absorption spectra of IV, V, VI, VII and VIII are shown in



IV, usnetol, R = H[6]
V, deacetyldecarbousnic acid, R = $COCH_3$[7]
VI, usnetic acid, R = COOH[5]
VII, ethyl acetylusnetate, R = $COCH_2COOEt$[7]
VIII, decarbousnic acid, R = $COCH_2COCH_3$[5]

Fig. 1. The curve obtained by subtraction of the spectral values of usnetol from those of decarbousnic acid reproduces accurately the spectral values[8] of acetylacetone. This fact, and the very close correspondence of other spectra to that of usnetol, give assurance that all of these degradation products have a benzofuran nucleus. Thus, these

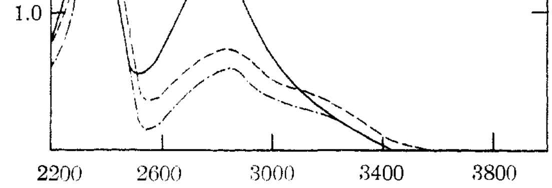
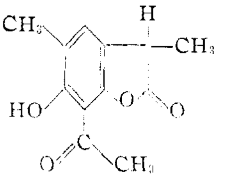


Fig. 2.———, diacetyldecarbousnic acid; —·—, diacetylusnetol; — — —, diacetyldeacetyldecarbousnic acid.

spectra fail completely to support structures of type III. Spectra of the diacetates of usnetol,[5] deacetyldecarbousnic acid[1] and decarbousnic acid[5] (Fig. 2) permit the same conclusion to be drawn for these substances.

The formula of dihydrousnic acid[7] has also been controversial. Foster, Robertson and Healy[9] suggested that the aromatic nucleus was hydrogenated and this assumption appeared to receive support when dihydrousnic acid was destructively distilled in the presence of calcium chloride to give 6-hydroxy-3,5-dimethyl-7-acetylcoumaranone-2, (IX).[10]



IX

However, distillation, in the presence of calcium chloride, of the uncharacterized oxidation product of either dihydrousnic acid or tetrahydrodesoxyusnic acid gave 2,6-dihydroxy-3-methylacetophenone (X).[10] After postulating that IX was formed by secondary recombination, Schöpf and Ross[2] offered the inviting suggestion that a dihydrousnic acid having the structure XI would account for the origin of X.

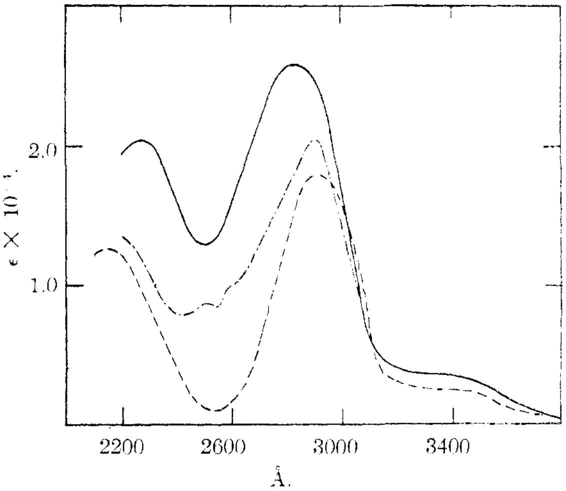
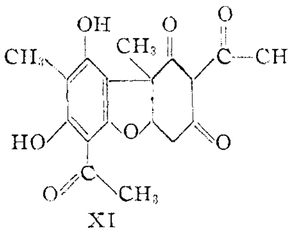
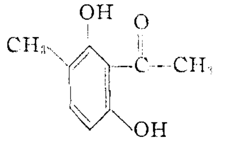


Fig. 3.———, dihydrousnic acid; —·—·—, values for dihydrousnic acid less values for acetyldimedon; — — — —, acetylmethylphloroglucinol (Morton and Sawires).



XI



X

The ultraviolet absorption spectrum of dihydrousnic acid is shown in Fig. 3. Also, the curve resulting by subtraction of the spectral values for C-acetylmethone (acetyldimedon)[11] is compared to the spectrum of acetylmethylphloroglucinol, this latter spectrum being reproduced here as accurately as possible from the excellent paper by Morton and Sawires,[12] who showed, it is important to note,

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[6] H. Salkowski, *Ber.*, **8**, 1459 (1875).

[7] Y. Asahina, M. Yanagita, S. Mayeda and Sh. Kawamura, *ibid.*, **70B**, 2462 (1937).

[8] Redetermined here under the conditions of the other experiments: solvent, 95% ethanol; c 10^{-4} molar. Under these conditions, ethyl acetoacetate showed barely measurable absorption.

[9] R. T. Foster, A. Robertson and T. V. Healy, *J. Chem. Soc.*, 1597 (1939).

[10] Y. Asahina and M. Yanagita, *Ber.*, **71B**, 2260 (1938); M. Yanagita, *ibid.*, **71B**, 2269 (1938).

[11] W. Dieckmann and R. Stein, *ibid.*, **37**, 3380 (1904).

[12] R. A. Morton and Z. Sawires, *J. Chem. Soc.*, 1052 (1940).

that the monoalkylation of substances of the type of phloracetophenone caused essentially no change in spectrum. The subtraction shown in Fig. 3 appears to produce reasonable agreement; both maxima of the spectrum of acetylmethylphloroglucinol are well reproduced.

A second subtraction has been carried out and is represented in Fig. 4. The spectral values for acetylmethone are subtracted from those for the diacetate of dihydrousnic acid. Since Morton and Sawires[12] showed that complete acetylation of acetylmethylphloroglucinol resulted in a severe decrease in those values of ϵ attributable to the existence of phenolic groups, the assumption is now made that acetylation of two hydroxyl groups would largely suppress those spectral values of acetylmethylphloroglucinol due to these groups. Accordingly, the spectral values obtained in the subtraction represented in Fig. 4 are compared in Table I to spectral values for *o*-hydroxy and *o*-methoxyacetophenone.[13]

TABLE I

	o-Hydroxy-acetophenone[13]		*o*-Methoxy-acetophenone[13]		Values by subtraction, Fig. 4	
	λ, Å.	$\epsilon \times 10^{-4}$				
α_2 max.	3250	0.35	2970	0.35	3200	0.60
min.	2680	.016	2600		2750	0.22
α_1 max.	2510	.90	2410	0.80	2500	1.00
min.	2300				2350	0.78
	Renewed rise		Renewed rise		Renewed rise	

The values obtained from Fig. 4 show a striking correlation with the spectral values of *o*-hydroxyacetophenone. Correlation with values for *o*-methoxyacetophenone is less satisfactory, made so, in part, by the excellence of the former agreement. While the suggestion that diacetyldihydrousnic acid may have structural features accurately represented by these comparisons cannot be ignored,[14] it must be remembered that the fundamental question asked by the comparisons of Figs. 3 and 4 was whether, *by these subtractions of values for acetylmethone,* values reasonably comparable to those for the appropriately substituted acetophenone could be obtained. It is felt that an affirmative answer must be given to this question. Accordingly, the present work supports the formula (XI) for dihydrousnic acid proposed by Schöpf and Ross[2] and, consequently, the formula (I) for usnic acid proposed by Curd and Robertson.

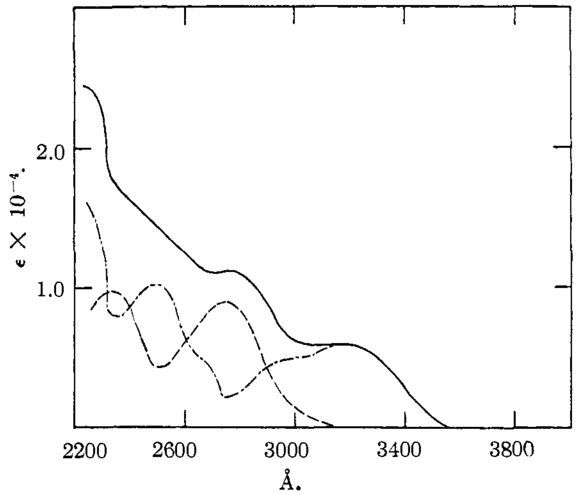

Fig. 4.——, diacetyldihydrousnic acid; —-—-—, values for diacetyldihydrousnic acid less values for acetyldimedon; — — — —, acetyldimedon.

The facile racemization of an optically active substance possessing a quaternary asymmetric carbon atom has appeared so improbable that some workers have rejected I as the formula for usnic acid. However, the racemization of a substance of formula I is not inexplicable. This formulation for usnic acid suggests that the racemization involves thermal, homolytic loosening of bond 1 with formation of a resonance stabilized biradical. A study of the racemization of usnic acid is currently underway in these laboratories.

Acknowledgment.—This work was made possible by the kindness of Professor L. F. Fieser, who sent a substantial sample of usnic acid to us.

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(13) N. A. Valyashko and Yu. S. Rozum, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 755 (1947); *C. A.*, **42**, 2588 (1948). Values shown in Table I were obtained with hexane solutions. The values for an ethanol solution of *o*-hydroxyacetophenone were reported to be characterized by a somewhat greater height of α_2 and a slight shift of α_1 to longer λ. Values for an ethanol solution of *o*-methoxyacetophenone were reported to be characterized by minor shifts only.

(14) Dihydrousnic acid and its diacetate are being studied further.