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PHOTOCHEMICAL REARRANGEMENTS OF CROSS-CONJUGATED CYCLOHEXADIENONES—VII

6,9-DIMETHYLSPIRO[4·5]DECA-6,9-DIEN-8-ONE[1]

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Abstract—The photochemical behaviour of the spiro dienone (VIII) in neutral media has been examined in an effort to obtain evidence concerning its intermediacy in the previously reported rearrangement of the dienone (I) to the linearly conjugated isomer (IX). The spiro dienone (VIII) was prepared by solvolysis of the tosylate (XVI). On irradiation in methanol or dioxane it was converted principally to the cyclopropyl ketone (IV), which, in turn, underwent further rearrangement to the dienone (IX). No evidence for the formation of the isomeric cyclopropyl ketone (XI) was detected. It is suggested that the selective formation of the photoproduct (IV) is attributable to the enhanced stability of the β-methyl substituted enone system of IV relative to that of the α-methyl isomer (XI). Although the behaviour of VIII is consistent with its intermediacy in the conversion of the dienone (I) to the dienone (IX), attempts to detect its presence in the irradiation of either the dienone (I) or the cyclopropyl ketone (II) were fruitless.

IT WAS recently reported that the cross-conjugated cyclohexadienone (I) undergoes photochemical rearrangement in either methanol or dioxane to give, ultimately, the linearly conjugated dienone (IX)[2]. This intriguing transformation was resolved into a sequence of at least three light-induced rearrangements involving the cyclopropyl ketones (II and IV) as discrete intermediates. We now wish to present evidence which is suggestive of the intervention of yet a third intermediate, the spiro dienone (VIII).

In originally considering the rearrangement of the initial photoproduct (II) to the isomeric cyclopropyl ketone (IV), we noted the possibility that this transformation is a two-step process involving VIII as an intermediate.[2] Previous studies had indicated that lumiproducts of type II, in the absence of interfering substituents on ring B, normally rearrange through spiro structures such as VI on irradiation.[3,4] Moreover, a subsequent rearrangement of VIII to the cyclopropyl ketone (IV) would be completely analogous to the conversion of I to II and would merely constitute yet another

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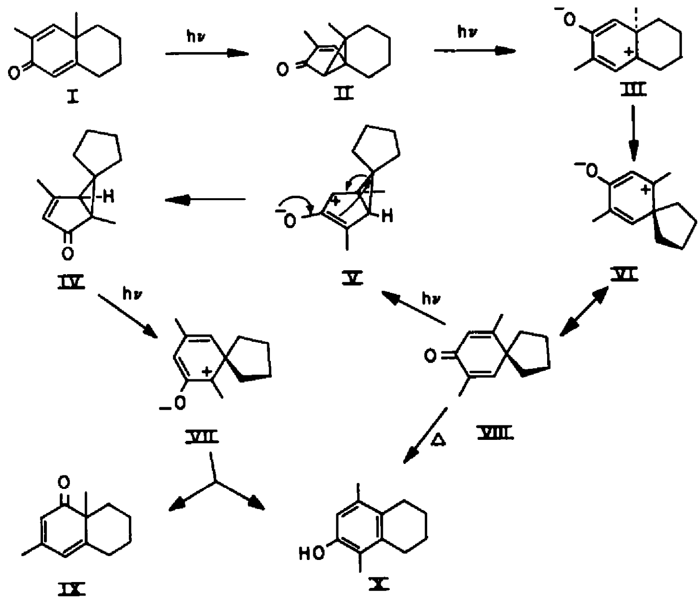
[1] Part VI: P. J. Kropp, *Tetrahedron Letters* 3647 (1964).

[2] P. J. Kropp, *J. Amer. Chem. Soc.* **86**, 4053 (1964).

[3] See discussion in P. J. Kropp, *J. Amer. Chem. Soc.* **85**, 3779 (1963), and Refs. cited therein.

[4] In accord with a growing concensus that photochemical rearrangements of cross-conjugated cyclohexadienones and the cyclopropyl ketones derived from them involve, at least ultimately, dipolar intermediates having negative character localized on oxygen and positive character distributed through the conjugated system of the carbon skeleton [see, among others, H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.* **84**, 4527 (1962); C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **45**, 2403 (1962); O. L. Chapman and L. F. Englert, *J. Amer. Chem. Soc.* **85**, 3028 (1963); and M. H. Fisch and J. H. Richards, *Ibid.* **85**, 3029 (1963)], we have depicted such intermediates here. Although the present results are consistent with the intervention of intermediates of this type, they offer no direct proof and afford little insight into the important question of their mode of formation.

Chart 1



example of the well-documented photochemical conversion of cyclohexadienones to cyclopropyl ketones.

There was, however, the problem that none of the spiro dienone (VIII) could be detected when either I or II was irradiated for varying periods of time. Moreover, VIII, being unsymmetrically substituted, *a priori* could give rise to two isomeric photoproducts, the cyclopropyl ketones (IV and XI)—whereas no evidence for the formation of the isomer XI or of any of its expected secondary photoproducts could be detected in the irradiation of the dienone (I).[5]

It has now been found that the spiro dienone (VIII) is converted predominantly, if not exclusively, to a single product, the cyclopropyl ketone IV, on irradiation in neutral media. As outlined in Chart 2, dienone VIII was prepared by $Ar_1^{\ominus}$-5 solvolysis of the tosylate XVI, in analogy to the similar formation of the unsubstituted analog XVIII.[6,7] The product obtained exhibited the anticipated IR absorption at 6·00 and 6·16 μ and UV absorption at 246 mμ (ϵ 15,600). In the NMR spectrum the α- and β-vinylic protons appeared appropriately as quartets at 3·90 and 3·28 τ (J_{AB} = 1·0

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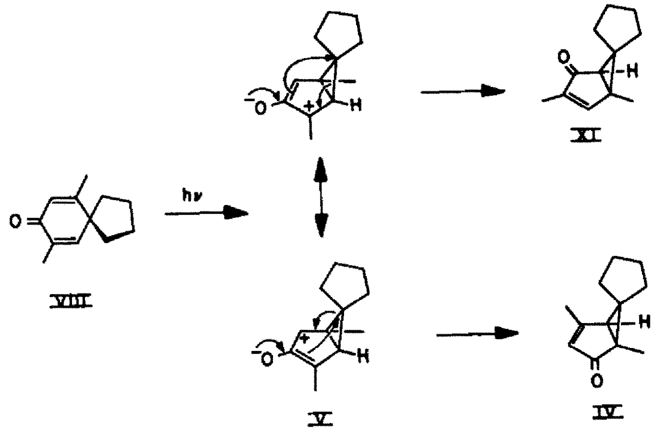
[5] It should be noted that C. Ganter, F. Greuter, D. Kägi, K. Schaffner and O. Jeger, *Helv. Chim. Acta* 47, 627 (1964), have recently reported the isolation of photoproducts analogous to II, IV and IX from the irradiation of a steroidal analog of dienone I (17β-hydroxy-2-methylandrosta-1,4-dien-3-one acetate). They established a sequence of rearrangements analogous to I-II-IV and also suggested the intermediacy of a spiro dienone of type VIII. Indeed, their structural assignments for the products related to IV and IX were based in part on the assumed intermediacy of a spiro dienone analogous to VIII. However, "Das dabei zu erwartende Dienon . . . entzog sich bisher der Isolierung."

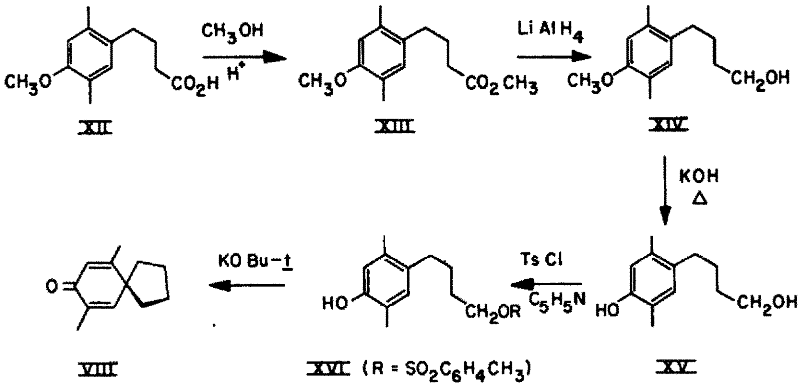
[6] R. Baird and S. Winstein, *J. Amer. Chem. Soc.* **84**, 788 (1962).

[7] Also obtained in minor yield in the present work was a phenolic product which exhibited major peaks in the mass spectrum at m/e = 135, 163 and 222. This material, which was not further investigated, was assumed to be the ethyl ether (XVIII) which arose from attack of ethanol impurity on the tosylate (XVI).



and 1·4 c/s), respectively.[8] The product was found to be exceptionally labile, undergoing facile thermal rearrangement to the expected phenolic product, the tetrahydronaphthol (X).[9,10]

Chart 2



In a typical experiment, irradiation of a specimen of the spiro dienone (VIII) in methanolic solution for 1 hr gave a mixture containing the cyclopropyl ketone (IV[2]; 63%), the linearly conjugated dienone (IX[2]; 16%) and the phenol (X;[9,10] 10%). When another sample was similarly irradiated, except for an extended period (3·75 hr), the dienone (IX) was obtained in 63% yield, accompanied by a small amount of the phenol (X; 2%). These results are essentially identical with those obtained previously from irradiation of either the dienone (I) or the cyclopropyl ketone (II).[2,11]

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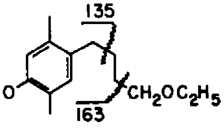
[8] See discussion in Ref. 2, footnote 25.

[9] L. F. Fieser and W. C. Lothrop, *J. Amer. Chem. Soc.* **58**, 2050 (1936); K. Paranjpe, N. L. Phalnikar, B. V. Bhide and K. S. Nargund, *Rasayanam* **1**, 233 (1943) [*Chem. Abstr.* **38**, 4266 (1944)]; M. Yanagita, S. Inayama, M. Hirakura and F. Seki, *J. Org. Chem.* **23**, 690 (1958).

[10] M. Yanagita and R. Futaki, *Ibid.* **21**, 949 (1956).

[11] Although the formation of small amounts of the phenol (X) from irradiation of the cyclopropyl ketone (IV) in neutral media was observed previously,[9] it is likely that at least part of the phenolic product obtained in the present work, particularly after limited irradiation periods, arose from thermal rearrangement of unreacted portions of the highly labile spiro dienone (VIII).

No evidence for the formation of any of the isomeric cyclopropyl ketone (XI) could be detected in the above experiments. Moreover, the high yields of ketone (IV) and its secondary rearrangement products (IX and X) indicate that IV is formed at least preferentially, if not exclusively. This selective formation of IV is yet another example of the marked influence which alkyl substituents exert on the photochemical behaviour of unsaturated ketones.[2,12] The selectivity observed in this case does not appear to be attributable to steric factors and quite possibly reflects the greater stability of the β-methyl substituted enone system of IV relative to that of the α-substituted isomer (XI).



XVII

The efficient conversion of the spiro dienone (VIII) to the cyclopropyl ketone (IV) rendered the intermediacy of VIII in the rearrangement of the dienone I to IV a particularly attractive hypothesis. With knowledge of the general properties of the spiro dienone (VIII) in hand, the photochemical rearrangements of the dienone (I) and the cyclopropyl ketone (II) in neutral solvents were re-examined. However, no evidence for the presence of VIII could be detected in either reaction mixture. If VIII is indeed formed as a ground-state intermediate, its rate of destruction under these conditions must be greater than its rate of formation from the cyclopropyl ketone (II).[13]

The conversion of the spiro dienone (VIII) to the cyclopropyl ketone (IV) is of additional interest in light of a recent study of the unsubstituted analog (XVIII), which was found to give rise to a mixture of the tetrahydronaphthols (XX and XXI) on irradiation in a variety of solvents.[14] It was assumed that these products were formed *via* the cyclopropyl ketone (XIX), although this intermediate was not isolated. By analogy with the present work, this assumption appears to be well founded.

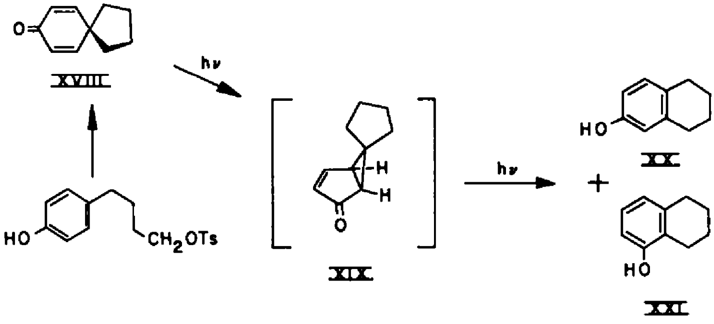
Finally, it should be noted that the closely related spiro dienone (XXII) has recently been reported to give a mixture of photoproducts in ether solution which are quite different from those afforded by either VIII or XVIII.[15] However, the case of XXII is complicated by the factors of extended conjugation and additional strain introduced by the three-membered ring.

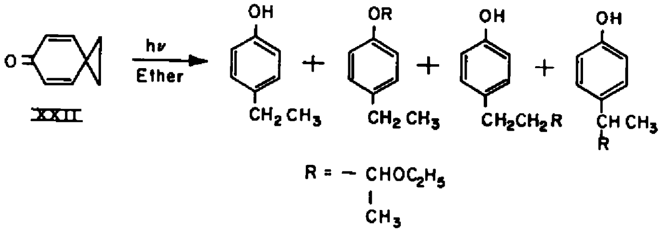
[12] P. J. Kropp, *J. Org. Chem.* **29**, 3110 (1964); D. Caine and J. B. Dawson, *Ibid.* **29**, 3108 (1964); P. J. Kropp and W. F. Erman, *J. Amer. Chem. Soc.* **85**, 2456 (1963); H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **45**, 2346 (1962).

[13] The data do not rule out an alternative possibility noted earlier,[3] that the rearrangement of II proceeds through an excited species of VIII which rearranges to IV more rapidly than conversion to the ground state occurs.

[14] A. A. Griswold, Ph.D. dissertation, Iowa State University (1963).

[15] D. I. Schuster and C. J. Polowczyk, *J. Amer. Chem. Soc.* **86**, 4502 (1964).





EXPERIMENTAL[16]

4-(4-*Methoxy-2,5-xylyl)butyric acid, methyl ester* (XIII)

Treatment of 48·3 g of acid XII[10] with 75 ml MeOH and 9 ml conc. H_2SO_4 according to the Fischer method[17] gave 44·8 g of the methyl ester (XIII) as a colourless liquid, b.p. 95–100° at 0·1 mm, n_D^{25} 1·5118, λ_{max} 5·78 μ; NMR spectrum: 3·12 and 3·38 (2s, 2, CH-6 and CH-3),[18] 6·22 and 6·34 (2s, 6, —OCH_3 and —CO_2CH_3) and 7·72 and 7·84 τ (2s, 6, CH_3-2 and -5). (Found: C, 71·1; H, 8·4. $C_{14}H_{20}O_3$ requires: C, 71·2; H, 8·5%.)

4-(4-*Methoxy-2,5-xylyl)-1-butanol* (XIV)

A solution containing 43·7 g (0·185 mole) ester (XIII) in 50 ml of freshly distilled tetrahydrofuran was added dropwise under an atm. of N_2 to a solution of 6·0 g (0·632 mole) LAH in 100 ml tetrahydrofuran, and the resulting mixture stirred at room temp for 42 hr. Isolation of the product by the general procedure of Idelson and Becker[19] followed by distillation of the crude product through an 18-in. spinning band column gave 31·4 g of a colourless liquid, b.p. 105–106° at 0·2 mm, n_D^{25} 1·5262. Gas chromatographic analysis indicated that this material was a 3·8:1 mixture of the desired alcohol (XIV) and unreacted ester (XIII) respectively. Separation of a pure specimen of XIV by preparative gas chromatography gave a colourless liquid, λ_{max} 2·75 μ; NMR spectrum: 3·10 and 3·38 (2s, 2, CH-6 and -3), 6·22 (s, 3, —OCH_3) and 7·72 and 7·82τ (2s, 6, CH_3-2 and -5). (Found: C, 75.2; H, 9·6 $C_{13}H_{20}O_2$ requires: C, 75·0; H, 9·7%.)

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[16] UV spectra were determined in absolute EtOH with a Cary model 14 spectrophotometer, and the IR spectra were obtained in 5% CH_2Cl_2 solution with a Perkin–Elmer Infracord spectrophotometer. M.ps were determined on a micro hot stage and are calibrated and corrected; NMR spectra were obtained in $CDCl_3$ solution with a Varian model A-60 spectrometer, using tetramethylsilane as an internal standard. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

[17] L. F. Fieser, *Experiments in Organic Chemistry* p. 77. D. C. Heath, Boston (1957).

[18] Indicates multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = unresolved multiplet), integration, and assignment. Coupling constants given in c/s.

[19] M. Idelson and E. I. Becker, *J. Amer. Chem. Soc.* **80**, 908 (1958).

4-(*4-Hydroxy-2,5-xylyl*)-1-*butanol* (XV)

The general procedure of Gates and Tschudi[20] was employed. A solution of 24·5 g alcohol (XIV) in 55 ml of triethylene glycol was added dropwise to a solution of 77·5 g KOH and 6 ml hydrazine hydrate in 400 ml triethylene glycol which had been heated to 205° and was stirred vigorously with a stream of N_2. The resulting solution was maintained at 205–225° for 4 hr. The solution was then cooled to room temp, diluted with 500 ml water and extracted with four 200-ml portions of ether. The combined ether extracts were washed with 200 ml portions of sat. NaCl aq and dried over Na_2SO_4. Removal of the solvent gave 5·40 g of a colourless liquid.

The aqueous layer was acidified with 135 ml conc. HCl aq and extracted with five 200-ml portions of ether. The combined ether fractions were extracted with three 200-ml portions of sat. $NaHCO_3$ aq and then four 100-ml portions of 10% NaOH aq. The combined NaOH-extracts were neutralized with conc. HCl aq and re-extracted with ether as described above. The combined ethereal extracts were dried over two 200-ml portions of sat. NaCl aq and then over Na_2SO_4. Removal of the solvent on a rotary evaporator gave 20·1 g (88% yield) of an amber oil which crystallized on standing. Repeated recrystallization of an equivalent sample from acetone—hexane gave colourless prisms, m.p. 83–84°, λ_{max} 2·75 μ; λ_{max} 282 (ϵ 2000) and 217 mμ (infl., ϵ 7200). (Found: C, 73·8; H, 9·3. $C_{12}H_{18}O_2$ requires: C, 74.2; H, 9·3%.)

6,9-*Dimethylspiro*[4·5]*deca*-6,9-*dien*-8-*one* (VIII)

A. *Preparation.* The general procedure of Baird and Winstein[6] as modified by Masamune[21] was adopted. A solution of 1·94 g (10·0 mmoles) XV and 1·91 g (10·0 mmoles) *p*-toluenesulphonyl chloride in a mixture containing 30 ml each of pyridine (distilled from BaO) and $CHCl_3$ was allowed to stand at 0° for 17 hr. It was then poured over 250 ml iced sat. $NaHCO_3$ aq and extracted with three 50-ml portions $CHCl_3$. The combined $CHCl_3$-extracts were washed with six 50-ml portions 5% HCl aq and two 50-ml portions sat. NaCl aq. Drying over Na_2SO_4, removal of the solvent on a rotary evaporator, and removal of the last traces of pyridine by codistillation with 100 ml toluene gave 2·44 g of an almost colourless oil.

A solution of the above crude product in 200 ml of *t*-butyl alcohol was added dropwise to a solution containing 0·43 g (11 mmoles) K in 750 ml *t*-butyl alcohol, and the resulting mixture was heated under reflux in an atm. of N_2 for 5·5 hr. The reaction mixture was then cooled to room temp, diluted with 1·2 l. ice water and extracted with four 250-ml portions ether. The combined organic extracts were dried over 250 ml sat. NaCl aq and over Na_2SO_4. Removal of solvent under red. press. gave an amber oil which was chromatographed on 53 g silica gel. Elution with 13·5 l. benzene gave 1·41 g of a colourless oil which was shown by gas chromatography to consist principally of VIII (60% yield) and a phenolic ether assumed to have the structure XVII (13% yield). Separation by gas chromatography and final purification by short-path distillation gave VIII as a colourless oil, b.p. 123° at 0·2 mm, λ_{max} 6·00 and 6·16 μ; λ_{max} 246 mμ (ϵ 15,600); NMR spectrum: 3·28 (q, 1, J_{AB} 1·4, CH-10), 3·90 (q, 1, J_{AB} 1·0, CH-7), 8·04 (d, J_{AB} 1·2, CH_3-6) and 8·12 τ (d, J_{AB} 1·4, CH_3-9); m/e: 135, 163, and 222. (Found: C, 82·1; H, 9·3. $C_{12}H_{16}O$ requires: C, 81·8; H, 9·2%.)

Also obtained from the larger gas chromatographic separations was the phenol (X) m.p. 105–105·5° unchanged on admixture with an authentic specimen.[9,10]

The ether (XVII)[7] was obtained from the gas chromatographic separations as a colourless oil, b.p. 138–140° at 0·15 mm, λ_{max} 2·75, 6·20, and 11·22 μ; 282 (ϵ 2250) and 287 mμ (ϵ 2100); NMR spectrum: 3·10 and 3·40 (2s, 2, aromatic CH), 6·02 (q, 2, J_{AB} 7, $-\mathrm{O\underline{CH_2}CH_3}$), 6·38 (t, 2, J_{AB} 6·5, $-\mathrm{CH_2\underline{CH_2}O}$-), 7·76 and 7·82 (2s, 6, aromatic CH_3), and 8·60τ (t, 3, J_{AB} 7, $-\mathrm{OCH_2\underline{CH_3}}$.) (Found: C, 75·7; H, 10·1. $C_{14}H_{22}O_2$ requires: 75·6; H, 10·0%.)

Finally, elution with 1 l. ethyl acetate gave 464 mg (24% recovery) XV as compact prisms, m.p. 82·5–83·5°.

B. *Irradiation.* In a typical run, a solution containing 399 mg spiro dienone VIII (contaminated with 3% of the ether XVII) in 125 ml MeOH was irradiated for 1 hr with a Hanau NK 6/20 low-press. Hg-lamp. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of N_2 through a jet opening in the bottom of the reaction vessel. Gas chromatographic analysis of the reaction mixture revealed the presence of 3 components in yields of 63, 16 and 10%.

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[20] M. Gates and G. Tschudi, *J. Amer. Chem. Soc.* **78**, 1380 (1956).

[21] S. Masamune, *J. Amer. Chem. Soc.* **83**, 1009 (1961).

In addition, broad complex absorption accounting for 11% of the material was seen. Isolation of pure specimens from the three major peaks by gas chromatography and direct comparison of their IR and NMR spectra and retention times with those of authentic samples revealed them to be the cyclopropyl ketone (IV),[3] the linear dienone (IX)[2] and the phenol (X).[9,10]

In a similar experiment a solution containing 228 mg spiro dienone VIII in 100 ml dioxane was irradiated for 225 min. The reaction mixture was concentrated on a rotary evaporator under red. press. and the residue was chromatographed on 12·5 g silica gel. Elution with 840 ml 1:1 benzene–hexane gave 45 mg of an oil which exhibited six peaks on gas chromatographic analysis, including one corresponding to (X)[9,10] (2% yield). Further elution with 3 l. benzene gave 143 mg (63% yield) of colourless oil which was identified as the linear dienone (IX) by direct comparison of its gas-chromatographic retention time and IR and NMR spectra with that of an authentic specimen.[2]

Acknowledgment—The able technical assistance of Mr. T. R. Walker is gratefully acknowledged.