

ether extract was dried over sodium sulfate, and concentrated to the sirupy 2,3-O-isopropylidene-D-erythrose. The yield was 4.4 g. (77%). The substance did not reduce hot Fehling solution, but gave the theoretical oxidation equivalent in the Willstätter-Schudel titration.

A solution of 3.9 g. of 2,3-O-isopropylidene-D-erythrose in 50 ml. of dry methanol had a rotation of -6.13° , $[\alpha]_D -78^\circ$. Hydrogen chloride gas (0.5 g.) was bubbled into the solution, and the rotation was observed until it became constant in 2 hours, when the α was -9.98° . The solution was neutralized with 5 g. of silver carbonate, the silver chloride was filtered off, and the filtrate was treated with hydrogen sulfide. After filtration to remove silver sulfide, the solution was concentrated to a sirup that was distilled at 7.5 mm. The main fraction had b.p. 66–67°, and weighed 2.0 g. It showed $[\alpha]_D -137^\circ$ (*c* 1, chloroform). The analysis agrees with that of methyl isopropylidene-erythrosidate.

Anal. Calcd. for $C_8H_{14}O_4$ (174): C, 55.1; H, 8.0; OCH_3 , 17.8. Found: C, 55.0; H, 8.2; OCH_3 , 20.1.

The product did not react with periodate. It was non-reducing to Fehling solution even after a long period of

heating. This is contrary to the result found by Overend, Stacy and Wiggins,⁶ who report that the methyl isopropylidene-erythrosidate prepared by the action of methanol, acetone and sulfuric acid on D-erythrose suddenly reduced Fehling solution after prolonged heating. Their product showed $[\alpha]_D -55^\circ$ (chloroform), and is probably an α,β -mixture. The substance described here may represent the pure β -form.

2,3-Di-O-acetyl-4-O-trityl-D-erythrose Diethyl Mercaptal.—A preparation of crude 2,3-O-isopropylidene-D-erythrose (2.1 g.) was mercaptalated, as described for the mercaptalation of 2,4-O-ethylidene-D-erythrose,³ to give 2.0 g. of a mercaptal. Tritylation followed by acetylation, yielded 3.8 g. of the desired product with m.p. 102–103° after recrystallization from methanol. The melting point was not depressed on admixture with authentic 2,3-di-O-acetyl-4-O-trityl-D-erythrose diethyl mercaptal.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Senecio Alkaloids: Mikanoidine, the Alkaloid from *Senecio mikanoides*

BY ROGER ADAMS AND MAURIZIO GIANTURCO

RECEIVED JUNE 29, 1956

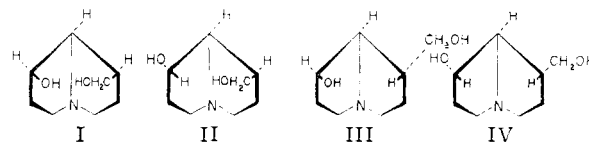
Mikanoidine, the alkaloid in *Senecio mikanoides* (Walp) Otto, is hydrolyzed to the base mikanecine, now identified as platynecine, and to mikanecic acid which proved to be a dehydrated seneciphylic acid.

Manske¹ reported the isolation from *Senecio mikanoides* (Walp), Otto, of an amorphous alkaloid, mikanoidine. This yielded upon alkaline hydrolysis a base, mikanecine ($C_8H_{15}NO_2$), characterized as its picrate, and mikanecic acid which gave a poor analysis for $C_{13}H_{16}O_5$. This empirical formula for the acid was supported by molecular weight values of 254 and 260 in comparison with the theoretical value of 252. Manske deduced from the data that the alkaloid should have the formula $C_{21}H_{29}NO_6$. Since the great majority of the alkaloids obtained from *Senecio* species contain 18 carbon atoms and the corresponding acid moieties ten carbon atoms, mikanecine picrate and mikanecic acid were reinvestigated in this Laboratory. The materials for this work were kindly supplied by Dr. Manske.

It was suggested by Leonard² in his review article on *Senecio* alkaloids that mikanecine picrate might be identical with platynecine picrate. This suggestion has been tested experimentally and by determination of the melting point, melting point of a mixture, and comparison of the infrared spectra the identity of the two compounds was established.

With the stereochemical formulas of platynecine and dihydroxyheliotridane³ definite (I and II), it was proposed that mikanecine from *Senecio mikanoides* and hastanecine from *Cacalia hastata*⁴ were probably two stereoisomeric forms of 1-hydroxy-

methyl-7-hydroxypyrrolizidine, III and IV. Since mikanecine is identical with platynecine, the fourth isomeric form may be turneforcidine,⁵ m.p. 118.5–



120°, $[\alpha]_D -10.5^\circ$ (MeOH), obtained from *Turneforcicia sibirica*. Turneforcidine⁵ was shown not to be identical with hastanecine, m.p. 113–114°, $[\alpha]_D -9.1^\circ$ (MeOH), by determination of the melting point of a mixture; depression was observed. The paper describing turneforcidine was overlooked at the time the Communication on the stereochemistry of pyrrolizidine bases³ was written.

Upon reinvestigation of mikanecic acid it was observed that the analytical values for carbon and hydrogen reported by Manske and checked in this Laboratory agree closely with the formula $C_{10}H_{12}O_4$ and only poorly with the one previously proposed $C_{13}H_{16}O_5$.¹ The infrared spectrum of the acid and its dimethyl ester showed the presence of two conjugated carboxylic acid and ester groups, respectively, 1690 and 1680 cm^{-1} (Nujol mull) for the acid; 1735, 1730 cm^{-1} and importantly 1260 cm^{-1} (very strong) for the ester ($CHCl_3$), two or more carbon-carbon double bonds, (1650 cm^{-1} (strong) and 1638 cm^{-1} (shoulder) and carbon-methyl groups. The determination of the neutralization equivalent gave consistently the value 100 ± 2 , which, in the light of the infrared spectral data, corresponds to a molecular weight of

(5) G. P. Menshikov, S. O. Denisova and P. G. Massagetov, *ibid.*, **22**, 1465 (1952).

(1) R. H. F. Manske, *Can. J. Research*, **14B**, 6 (1936).

(2) N. J. Leonard in "The Alkaloids" by R. H. F. Manske and H. L. Holmes, Vol. I, Academic Press, Inc., New York, N. Y., 1949, p. 137.

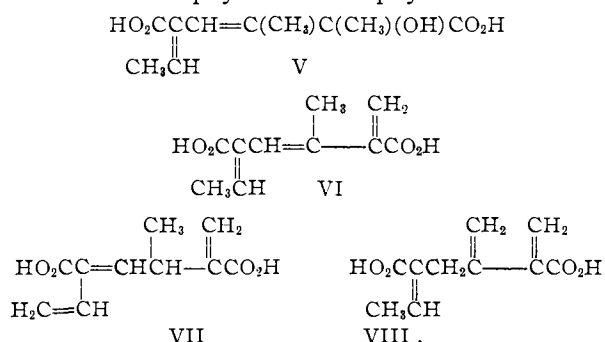
(3) R. Adams and B. L. Van Duuren, *THIS JOURNAL*, **76**, 6379 (1954).

(4) V. S. Kononov and G. P. Menshikov, *J. Gen. Chem. U.S.S.R.*, **15**, 328 (1945).

200 \pm 4. This value is in excellent agreement with the formula $C_{10}H_{12}O_4$, mol. wt. 196, which is therefore, assigned to mikanecic acid. This formula requires that mikanecic acid be either an acyclic dicarboxylic acid containing three carbon-carbon double bonds or a mono- or dicyclic dicarboxylic acid with two or one carbon-carbon double bond, respectively. These latter types of acids have never been encountered in the pyrrolizidine alkaloids and were not further considered after quantitative hydrogenation experiments clearly indicated the presence of three carbon-carbon double bonds in the molecule of mikanecic acid.⁶

The ultraviolet absorption spectrum of this acid showed absorption only at 216 $m\mu$ (95% EtOH), typical of α,β -unsaturated acids and thus excluded the presence of a 1,3-diene system in complete conjugation with a carbonyl group as in sorbic acid. In going from crotonic to sorbic acid a shift of the maximum from approximately 210 to 260 $m\mu$ is encountered.⁷

These facts make it appear likely that mikanecic acid is closely related to one of the most commonly occurring Senecio acids, isoseneciphyllic acid ($C_{10}H_{14}O_5$) (V), and that it may actually be a dehydrated isoseneciphyllic or seneciphyllic acid.



The identity of the skeleton of mikanecic acid with that of isoseneciphyllic or seneciphyllic acid and therefore with those of the other commonly occurring Senecio acids was established by a comparison of the infrared spectra of the diethyl ester of hexahydromikanecic acid and of synthetic diethyl 2,3-dimethyl-5-carbomethoxyheptanoate (XIX). The spectra were identical. With the skeleton of the molecule certain, the introduction of the three double bonds can be achieved in three ways. To satisfy the infrared and ultraviolet spectral data mentioned above, three carbon-carbon double bonds must be so arranged that each of two of the double bonds must be conjugated with one of the

(6) The hypothesis that a carbon-carbon triple bond could be present in the molecule of mikanecic acid was rejected. This was justified on the basis of the infrared spectrum of the compound.

(7) E. A. Braude, *Ann. Repts. Progr. Chem. (Chem. Soc. London)*, **42**, 114 (1945), cites references which report that the ultraviolet absorption spectrum of crotonic acid (solvent, water) has a maximum at 200 $m\mu$ and sorbic acid (solvent *n*-hexane) at 261 $m\mu$. For purposes of comparison, the spectra were determined in 95% ethanol as solvent; crotonic acid exhibited a maximum at 211–213 $m\mu$ and sorbic acid at 256–257 $m\mu$. The maximum of crotonic acid shifted 1–3 $m\mu$ depending on the concentration. Senecic acid with one double bond in crossed conjugation with the carboxyl group has a maximum at 215 $m\mu$, [R. Adams and B. L. Van Duuren, *THIS JOURNAL*, **75**, 4631 (1953)] while isoseneciphyllic acid with two double bonds has a maximum at 214 $m\mu$ [R. Adams, T. R. Govindachari, J. H. Looker and J. D. Edwards, *ibid.*, **74**, 700 (1952)].

two carboxyl groups and no two of the double bonds may be at the same time conjugated with each other and with a carboxyl group. Such structures are represented by VI, VII and VIII.

Structure VII can be rejected since the infrared spectrum of mikanecic acid does not show any absorption at 995–985 cm^{-1} , characteristic of the $\text{CH}_2=\text{CHR}$ grouping.⁸ The infrared spectrum of mikanecic acid shows instead a band at 835 cm^{-1} for the CH out-of-the-plane deformation of the $\text{R}_1\text{R}_2\text{C}=\text{CHR}_3$ grouping and also a very strong, sharp band at 920 cm^{-1} (overtone at 1840 cm^{-1}), which is distinct from the broad band corresponding to the hydroxyl deformation vibration of the carboxyl group appearing at 960 cm^{-1} . In the infrared spectrum of the methyl ester of mikanecic acid, this band occurs at 935 cm^{-1} (overtone at 1850 cm^{-1}). The absorption for the CH out-of-the-plane deformation of a $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ grouping is reported as a strong band at 895–885 cm^{-1} (overtone of medium intensity at 1800–1700 cm^{-1}).⁹ However, when the methylene group is also conjugated with a carboxyl or cyano group, the absorption occurs at higher frequencies; in methyl methacrylate and in α -ethylacrylonitrile the band corresponding to the CH out-of-plane deformation occurs at 935 cm^{-1} (overtone at 1870 cm^{-1}); in α -methylacrylic acid the band appears at 950 cm^{-1} (overtone at 1900 cm^{-1}). The infrared spectral data are thus in agreement with structure VI or VIII for mikanecic acid. Because of the facility with which the conversion of structure VIII to structure VI could be expected to occur under the alkaline conditions employed for the hydrolysis of the alkaloid, structure VI is indicated as the most probable one for mikanecic acid.

If it is assumed that mikanoidine is derived from seneciphylline by dehydration in the acid moiety and reduction in the basic moiety, the probable structure of mikanoidine is shown in IX.

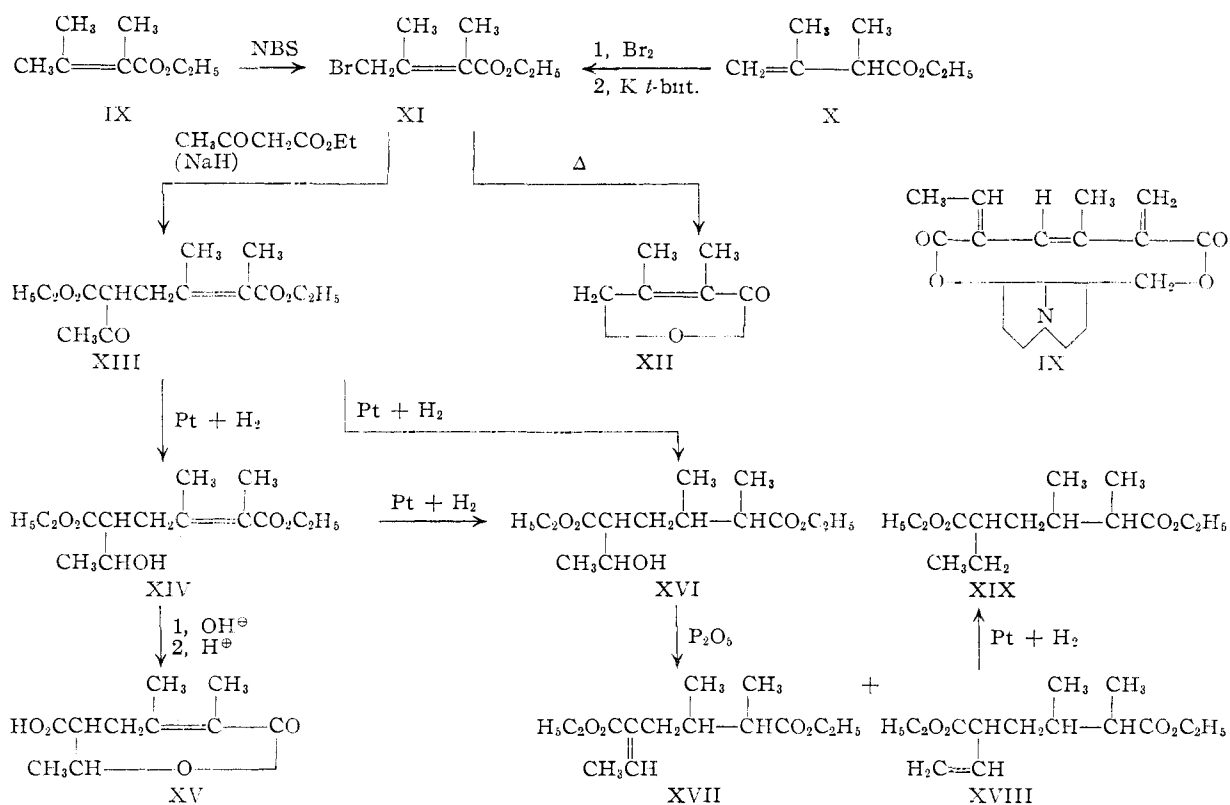
The synthesis of ethyl 2,3-dimethyl-5-carbomethoxyheptanoate is shown by the series of transformations in IX–XIX.

Compounds IX and X¹⁰ were used as starting materials. Compound XI was obtained either by bromination of X followed by dehydrobromination or by treatment of IX with *N*-bromosuccinimide. A by-product XII always accompanied XI and actually could be synthesized from XI merely by heating. Condensation of XI with ethyl acetoacetate gave XIII in good yield. Reduction of the ketonic group of XIII to an alcoholic group with formation of XIV could be achieved readily without reduction of the carbon-carbon double bond. Alkaline hydrolysis of XIV followed by acidification yielded the 7-membered lactonic acid XV. Absorption of a second mole of hydrogen converted compound XIV to XVI which was easily dehy-

(8) Compounds containing the $\text{CH}_2=\text{CHR}$ grouping absorb strongly in this region. The absorption corresponds to the CH out-of-plane deformation. See (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1956, p. 31; (b) E. A. Braude and E. S. Waigant in "Progress in Stereochemistry" by N. Kline, Academic Press, Inc., New York, N. Y., 1954, p. 158.

(9) See ref. in footnote 8.

(10) R. C. Huston and G. L. Goerner, *THIS JOURNAL*, **68**, 2504 (1946).



drated to a mixture of XVII and XVIII. These were not separated but the mixture was directly hydrogenated to yield compound XIX.

Acknowledgment.—The authors are indebted to Mr. J. Nemeth and Mrs. M. Benassi for the microanalyses and to Mr. J. Brader for the infrared spectra. They are particularly appreciative of the help provided by Mr. E. L. Shelberg and Mr. O. Kolslo of the Abbott Laboratories, North Chicago, who performed the microhydrogenation experiments.

Experimental

All melting points are corrected.

Retronecine.—The base was obtained by the alkaline hydrolysis of monocrotaline and isolated by the usual method.¹¹

Platynecine.—Retronecine was hydrogenated over a Raney nickel catalyst.¹²

Platynecine Picrate.—The picrate was prepared from equimolecular amounts of platynecine and picric acid in methanol and recrystallized from the same solvent; m.p. 184–185° (lit.¹³ m.p. 184–185°).

Mikanecine Picrate.—The sample obtained from Dr. Manske melted after one crystallization from methanol at 184–185° (lit.¹ m.p. 186°).

Anal. Calcd. for $\text{C}_9\text{H}_{15}\text{NO}_5 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$: C, 43.52; H, 4.70; N, 14.50. Found: C, 43.26; H, 4.63; N, 14.39.

The melting point was the same as that of platynecine picrate, the melting point of the mixture was not lowered and the infrared spectra indicated the identity of mikanecine and platynecine picrates.

Mikanecic Acid.—The sample, m.p. 238–240°, optically inactive, obtained from Dr. Manske was subjected to analysis and a neutral equivalent¹⁴ determination; neut. equiv.: 9.2 mg. required 9.2 ml. of 0.01 *N* aqueous sodium hydrox-

ide; found 100 ± 2 . The molecular weight would be 200 ± 4 on the basis of two carboxyl groups deduced from the infrared spectrum. Ultraviolet spectrum (95% EtOH), $\lambda_{\text{max}} 216$, $\epsilon_{\text{max}} 8541$.

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_4$: C, 61.21; H, 6.17. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_5$: C, 61.89; H, 6.39. Found: C, 61.11; H, 6.27.

Hydrogenation of Mikanecic Acid.—Two microhydrogenation experiments of mikanecic acid indicated the absorption of three moles of hydrogen per mole of acid. 1. 3.549 mg. of acid absorbed 1.27 ml. of H_2 at 27° and 756.6 mm.: 2.84 moles of hydrogen per mole of acid. 2. 3.458 mg. of acid absorbed 1.24 ml. of H_2 at 27.5° and 758.0 mm.: 2.85 moles of hydrogen per mole of acid.

Diethyl Hexahydromikanecate.—A suspension of 10 mg. of platinum oxide catalyst in 5 ml. of ethanol was shaken with hydrogen at room temperature and atmospheric pressure until absorption was complete. A solution of 12 mg. of mikanecic acid in 5 ml. of the same solvent was then added and the shaking with hydrogen continued. Three mole-equivalents of hydrogen were absorbed in one hour. After filtering from the catalyst, the solvent was removed at reduced pressure. The residue was dissolved in anhydrous ether and treated with an excess of a solution of diazoethane in the same solvent.¹⁵ When the reaction was complete, the solvent was eliminated and the residue was kept in a desiccator at reduced pressure during 12 hours before the determination of its infrared spectrum.

Ethyl 2,3-Dimethyl-2-butenoate (IX) and Ethyl 2,3-Dimethyl-3-butenoate (X).—These compounds were prepared according to Huston and Goerner¹⁰ and separated by fractional distillation through a 100-cm. spinning band column: ethyl 2,3-dimethyl-2-butenoate, b.p. 98–101° (83 mm.), $n_{\text{D}}^{23.5}$ 1.4421 (lit.¹⁰ b.p. 99–99.5° (81.5 mm.), n_{D}^{20} 1.4430); ethyl 2,3-dimethyl-3-butenoate, b.p. 81–84° (81 mm.), $n_{\text{D}}^{23.5}$ 1.4230 (lit.¹⁰ b.p. 84.5–85.5° (83 mm.), n_{D}^{20} 1.4210).

Ethyl α,β -Dimethyl- γ -bromocrotonate (XI). **Procedure A.**—A solution of 25.5 g. of ethyl 2,3-dimethyl-2-butenoate (IX) in 55 ml. of pure carbon tetrachloride was treated with 32.7 g. of *N*-bromosuccinimide and 0.01 g. of benzoyl peroxide. After the initial reaction had subsided, the mixture was heated under reflux for 12 hours, allowed to come to room temperature and filtered. After washing the solid

(15) E. Müller and W. Rundel, *Ber.*, **89**, 1065 (1956).

(11) R. Adams and E. F. Rogers, *THIS JOURNAL*, **61**, 2815 (1939).

(12) R. Adams and E. F. Rogers, *ibid.*, **63**, 537 (1941).

(13) A. E. Orekhov, R. A. Konovalova and V. Tiedebel, *Ber.*, **58**, 1886 (1935).

(14) A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Co., 1951, New York, N. Y., p. 226.

with two 25-ml. portions of carbon tetrachloride, the combined solvents were eliminated through a short Vigreux column at reduced pressure, and the residue was rapidly distilled. A second distillation through a Holzman column yielded 17.8 g. of product, b.p. 61–63.5° (0.9 mm.). Care must be taken in controlling the vigor of the reaction at the beginning and in handling the product which is a strong lachrymator.

Procedure B.—To a well-stirred solution of 28.4 g. of ethyl 2,3-dimethyl-3-butenate (X) in 90 ml. of *t*-butyl alcohol cooled to 25°, was added dropwise 32 g. of bromine in 90 ml. of *t*-butyl alcohol. The mixture was allowed to stand at room temperature for 45 minutes to ensure complete absorption of bromine and then it was added, dropwise and with stirring, a solution of sodium ethoxide, prepared from 4 g. of sodium and 87 ml. of absolute ethanol. As soon as the ethanol content became high enough to prevent freezing, the mixture was cooled to 0°. After filtration the solvent was removed under reduced pressure at a maximum temperature of 45°. The residue was distilled through an Holzman column to yield 22 g. of product, b.p. 61–63° (0.9 mm.).

The analysis of this product made either by method A or B gave low analytical values for bromine due to the presence of an impurity of α,β -dimethylbutenolide (XII) which always solidified in the water-cooled condenser during the distillation. This lactone was characterized. It was extracted from the condenser, freed from halogen-compounds by repeated freezing and melting, and distilled, b.p. 64° (0.2 mm.). The product thus obtained melts at about 30°. The bromo compound was converted to the lactone in essentially quantitative yield by boiling at ordinary pressure and then distilling.

Anal. Calcd. for C₆H₈O₂: C, 64.27; H, 7.19. Found: C, 64.54; H, 7.53.

The infrared spectrum shows a band at 1755 cm.⁻¹ for a conjugated 5-membered lactone carbonyl group.

Ethyl 2,3-Dimethyl-5-carbethoxy-6-one-2-heptenoate (XIII).—A suspension of 2 g. of sodium hydride in 20 ml. of purified, dry dioxane was added slowly to 12 g. of ethyl acetoacetate in 20 ml. of the same solvent. After all the sodium hydride had dissolved, the solution was cooled to -10° with a Dry Ice-bath causing separation of the sodium compound. A solution of 19 g. of ethyl α,β -dimethyl- γ -bromocrotonate (XI) in 15 ml. of dioxane was added at once and the reaction mixture allowed to come to room temperature and then heated under reflux for 4 hours. The reaction mixture was then cooled, treated with a few milliliters of glacial acetic acid to bring it to neutrality, and filtered. The solvent was eliminated through a short Vigreux column and the residue distilled. After a small head-fraction, 12.6 g. (55% based on somewhat impure halogen compound) of ethyl 2,3-dimethyl-5-carbethoxy-6-one-2-heptenoate (XIII) was collected, b.p. 130–132° (3.5 mm.), *n*²⁰_D 1.4640.

Anal. Calcd. for C₁₄H₂₂O₅: C, 62.20; H, 8.20. Found: C, 62.21; H, 8.01.

Ethyl 2,3-Dimethyl-5-carbethoxy-6-ol-2-heptenoate (XIV).—A solution of 12.6 g. of ethyl 2,3-dimethyl-5-carbethoxy-6-one-2-heptenoate (XIII) in 100 ml. of ethanol was subjected to hydrogenation in the presence of 0.5 g. of platinum oxide catalyst at room temperature and ordinary pressure. After the rapid absorption of one mole-equivalent of hydrogen, the reaction was interrupted. The product in ethanol solution gave no color reaction with ferric chloride, thus indicating that essentially all of the keto-carbonyl present in the molecule had been hydrogenated and that the carbon-carbon double bond had consequently not been attacked. The solution was filtered from the catalyst and the

solvent eliminated through a short Vigreux column. The residue was distilled through a Holzman column to give 12.0 g. of product (94%), b.p. 125° (0.7 mm.), *n*²⁰_D 1.4668.

Anal. Calcd. for C₁₄H₂₄O₅: C, 61.74; H, 8.88. Found: C, 62.02; H, 8.80.

2,3-Dimethyl-5-carboxy-6-ol-2-heptenoic Acid Lactone (XV).—A mixture of 1 g. of ethyl 2,3-dimethyl-5-carbethoxy-6-ol-2-heptenoate (XIV) was boiled under reflux with 1:1 aqueous ethanolic potassium hydroxide for 3 hours. On acidification and cooling 0.5 g. (68%) of white crystals separated and were recrystallized from hot water, m.p. 192–193°.

Anal. Calcd. for C₁₀H₁₄O₄: C, 60.59; H, 7.12. Found: C, 60.57; H, 7.39.

The infrared spectrum of this compound (Nujol mull) indicated the presence of a carbon-carbon double bond (1643 cm.⁻¹), acid carbonyl (1677 cm.⁻¹) and of a conjugated lactonic carbonyl belonging to a ring of more than 5-members (1699 cm.⁻¹). This lactonic carbonyl band shifted to 1715 cm.⁻¹ when the infrared spectrum was determined in tetrahydrofuran.

Other extraction of the acidic solution yielded 0.1 g. of oily material which could not be induced to crystallize and was not further investigated.

Preparation and Dehydration of Ethyl 2,3-Dimethyl-5-carbethoxy-6-ol-heptanoate (XVI).—A solution of 10 g. of ethyl 2,3-dimethyl-5-carbethoxy-6-one-2-heptenoate (XIII) in 100 ml. of ethanol was hydrogenated at room temperature and at a pressure of 3 atm. over 2 g. of platinum oxide catalyst. After the rapid absorption of 1.3 mole-equivalents of hydrogen, 1 g. of fresh catalyst was added to aid in completion of the reaction (5 hr.). The solution was filtered from the catalyst, the catalyst washed with 50 ml. of ethanol, the combined solvents eliminated at reduced pressure through a short Vigreux column and the residue distilled through a Holzman column. The yield was 8.5 g. (85%) of ethyl 2,3-dimethyl-5-carbethoxy-6-ol-heptanoate (XVI), b.p. 135–137.5° (3.5 mm.), *n*²⁰_D 1.4481.

Anal. Calcd. for C₁₄H₂₆O₅: C, 61.31; H, 9.55. Found: C, 61.78; H, 9.51.

The slightly high analytical value for carbon content was probably due to the presence of a small amount of dehydrated product.

A solution of 7 g. of XVI in 15 ml. of dry benzene and 6 g. of phosphoric anhydride was heated under reflux for 4 hours. The solution was cooled and filtered and the residue was extracted with two 15-ml. portions of hot benzene. The combined solvents were eliminated at ordinary pressure and the residue was distilled through a Holzman column. The yield was 3.9 g. (60%) of a mixture of XVII and XVIII, b.p. 90–93° (0.3 mm.), *n*^{21.5}_D 1.4490.

Anal. Calcd. for C₁₄H₂₄O₄: C, 65.59; H, 9.44. Found: C, 65.83; H, 9.57.

Ethyl 2,3-Dimethyl-5-carbethoxyheptanoate (XIX).—A solution of 2 g. of the mixture of the above-described unsaturated esters in 50 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure over 0.2 g. of a platinum oxide catalyst. One mole-equivalent of hydrogen was absorbed in 15 minutes and absorption then stopped. After removal of the catalyst and distillation of the solvent at reduced pressure through a short Vigreux column, the residue was distilled in a Kugelrohr at 0.7 mm. (pot temperature 170°). The yield was 1.75 g. (87%), *n*²⁵_D 1.4350.

Anal. Calcd. for C₁₄H₂₆O₄: C, 65.11; H, 10.07. Found: C, 65.41; H, 10.10.

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