

H, 3.74; N, 14.95; OCH₃, 8.3. Found: C, 51.0; H, 4.2; N, 14.85; OCH₃, 8.4.

Acknowledgment.—Thanks are due to the Spruce Falls Power and Paper Company for the award of a Scholarship to one of us (L. B.).

Summary

1. The bisulfite-soluble fraction obtained from the ethanolysis of spruce wood has been shown to contain vanillin and a hitherto unknown dicarbonyl compound, vanilloyl methyl ketone.

2. Two new dicarbonyl compounds, veratroyl-acetaldehyde and vanilloyl methyl ketone have

been synthesized and the latter shown to be identical with the naturally occurring material.

3. A quantitative separation of the components present in the bisulfite fraction has been effected by means of their 2,4-dinitrophenylhydrazones.

4. The amounts of vanillin and vanilloyl methyl ketone have been shown to vary in different ethanolysis experiments.

5. The possibility that vanilloyl methyl ketone may form one member of an oxidation-reduction system functioning in plant respiration is pointed out.

MONTREAL, CANADA

RECEIVED MAY 6, 1940

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, UNITED STATES DEPARTMENT OF AGRICULTURE]

Constituents of Certain Species of Helenium. IV. Concerning the Compound Melting at 233–234° Obtained from Helenium tenuifolium¹

By E. P. CLARK

As incidental information in the second paper of this series^{1a} a report was made upon a compound assigned the formula C₁₆H₂₂O₅ which melted at 233–234°. This substance was thought to be a constituent of the plant from which it was obtained, but further work has shown that it is an ether, C₁₉H₂₆O₆, formed as a result of a reaction between tenulin and ethylene glycol, the solvent used in its preparation.

The history of the material is interesting and instructive but it will suffice to say that while the analytical data obtained upon the substance and several of its derivatives indicated the C₁₆ formula, the Rast molecular weight values were unreliable, and led to erroneous conclusions. The first indication of this appeared when, in the course of degradation experiments, acetyltenuinic acid, a C₁₇ compound, was obtained.

The error is one that should be corrected and as the experiments which led to its discovery are pertinent to the tenulin problem, the work involved is now presented.

Because of the unreliability of the Rast method of determining molecular weights on this series of compounds a new value on the mother substance was sought that left no doubt as to its accuracy. This was done by introducing into the compound an accurately determinable alkoxy group in the

form of an ethoxy acetate. Upon analysis this was shown to have 15.04% of ethoxyl. When, however, the alkyl value (calculated as ethoxyl) given under identical conditions by the corresponding quantity of mother substance was subtracted from the above figure, the result was 10.3% of ethoxyl. This corresponds to a molecular weight of 437 for the acyl compound, and hence the molecular weight of the mother substance is 351. The calculated molecular weight for C₁₉H₂₆O₆ is 350.4. Attention is directed to the analytical data for this compound which has carbon and hydrogen values agreeing equally well for an ethoxy acetate of the formerly proposed C₁₆ compound.

Attempts at degradation led to the formation of a monocarboxylic acid, C₁₉H₂₆O₉. This compound was obtained by two methods, alkaline hydrogen peroxide oxidation and permanganate oxidation. The acid obtained was purified readily and melted at 239°. It was found, however, that when an effort was made to recrystallize the acid from a boiling solution, by adding an excess of mineral acid to its sodium salt, a new material separated which melted at 319°. When an attempt was made to recrystallize this product, it changed to ordinary acetyltenuinic acid, m. p. 238–239°. Analysis of the acid melting at 319° gave a titration value corresponding to a molecular weight of 360, although carbon and hydrogen values were

(1) Not subject to copyright.

(1a) Clark, *THIS JOURNAL*, **61**, 1836 (1939).

somewhat high for anhydrous acetyltenuinic acid.

The conversion of the C_{19} acid to acetyltenuinic acid by mild acidic hydrolysis involved the loss of C_2H_4O , which led to the suspicion that the original material was an acid labile ether formed by the elimination of water from tenulin and ethylene glycol, since the latter was used as the solvent in its preparation. Upon this hypothesis mild acidic hydrolysis of the original compound (m. p. 233°) was tried, and as expected the reaction yielded tenulin and ethylene glycol. Tenulin was identified by its melting point, mixed melting point, and optical characteristics. The ethylene glycol was isolated as a dibenzoyl derivative and identified by comparison with an authentic sample.

The nature of the material melting at 233° was thus definitely identified as a derivative formed by the loss of a molecule of water from ethylene glycol and tenulin. It, therefore, did not occur in the plant, but was formed during the crystallizing process, in which the glycol was used as a solvent.

As indicated before, these reactions have a bearing upon the structure of tenulin. The formation of the ether can conceivably be only by the loss of water from a hydroxyl group in tenulin and one in the glycol. This is further confirmation of the suggestion made in the third communication of this series,² namely, that a hydroxyl group is present in tenulin. Another consideration is that in the formation of the C_{19} acid with alkaline hydrogen peroxide, the acetyl group, which has been shown to be present in tenulin, was not removed, as it is under identical conditions in the formation of tenuinic acid from tenulin. The inference is that the glycol residue, presumably replacing hydrogen in the hydroxyl group of tenulin, hinders the activity of the acetyl group and prevents its hydrolysis. This is in harmony with previous findings that the hydroxyl group and the acetyl group are sterically hindered, and therefore, because of the added hindering effect of the glycol ether, undoubtedly both acetoxy and hydroxyl groups are in close proximity, probably adjacent to each other.

Experimental

Ethoxyacetyl Derivative of the 233° -Melting Substance.—A solution of 0.5 g. of the 233° -melting substance in 3 cc. of pyridine and 1.5 cc. of ethoxyacetic anhydride was allowed to react for fifteen hours. It was then diluted with water, and the solution was distilled under reduced

pressure until a white product separated. After a short time this substance was removed and dissolved in a small volume of methanol, and 5 volumes of water was added. The liquid crystallized and yielded 350 mg. of colorless massive prismatic crystals, m. p. 119° . Upon recrystallization there was no change in the melting point.

Anal. Calcd. for $C_{23}H_{32}O_8$: C, 63.28; H, 7.39; OC_2H_5 , 10.32. Found: C, 63.44; H, 7.40; OC_2H_5 (after subtraction of the alkoxy calculated to ethoxy formed under identical conditions from an equivalent weight of mother substance), 10.33.

Acid Formed by Alkaline Hydrogen Peroxide Oxidation of the 233° Compound.—A solution of 1 g. of the 233° -melting compound in 75 cc. of acetone was treated with 8 cc. of 30% hydrogen peroxide, 25 cc. of water and 5 cc. of 10% sodium hydroxide. The mixture was concentrated by boiling until it had a volume of approximately 20 cc. It was then cooled, acidified with acetic acid, and treated with 10 *N* sulfuric acid until the liquid was acid to congo red. Colorless rods (0.77 g.) with notched ends, which melted at 237° , separated. This material was recrystallized by treating an aqueous solution of its sodium salt with acetic and sulfuric acids as indicated above. It then melted at 239° , and further purification did not change its melting point.

Anal. Calcd. for $C_{19}H_{26}O_9$: mol. wt., 398.4; C, 57.28; H, 6.58. Found: C, 57.24; H, 6.64; mol. wt. (titration calcd. to 1 COOH group), 401.

Methyl Ester of the C_{19} Acid.—An acetone solution of the C_{19} acid was treated with an excess of diazomethane. A quantitative yield of the ester, m. p. 283° , was obtained. As recrystallization of the product did not alter its melting point, it was analyzed as first obtained.

Anal. Calcd. for $C_{20}H_{28}O_9$: C, 58.24; H, 6.84; OCH_3 , 7.52. Found: C, 58.57; H, 6.99; methoxyl (after subtracting the alkoxy calcd. to OCH_3 formed under identical conditions from an equivalent weight of mother substance), 7.8.

Acetyltenuinic Acid by Hydrolysis of the C_{19} Acid.—When the recrystallization process applied to the foregoing C_{19} acid was conducted at the temperature of the boiling solution, an acid resulted consisting of thick trapezoidal plates that melted at 319° . Upon recrystallization these crystals separated as fern-like aggregates of small rods, m. p. 238° . Another recrystallization of the substance brought its melting point to a constant value of 239° . In this condition it was identified as acetyltenuinic acid by comparison with an authentic sample (melting point, mixed melting point, and optical characteristics). Analysis of the acid, which melted at 319° , gave values that agree best for anhydrous acetyltenuinic acid but are not entirely satisfactory.

Anal. Calcd. for $C_{17}H_{22}O_8$: C, 57.62; H, 6.26; mol. wt., 354.4. Found: C, 58.04, 58.09; H, 6.51, 6.42; mol. wt. (titration calcd. to 1 COOH group), 360.

Permanganate Oxidation of the 233° -Melting Substance.—A well-stirred solution of 1 g. of the 233° -melting compound in 200 cc. of 50% aqueous acetone was treated portionwise with 100 cc. of 1% aqueous potassium permanganate solution. The resulting manganese dioxide was reduced with sodium bisulfite and acetic acid, and the

(2) Clark, *THIS JOURNAL*, **62**, 597 (1940).

clear solution was evaporated, under reduced pressure, to about 30 cc. The solution was then acidified with sulfuric acid (congo red). The liquid yielded 0.4 g. of colorless crystals, m. p. 230–233°. They were recrystallized by the procedure given before for the acid obtained by alkaline hydrogen peroxide oxidation of the 233°-melting compound. When pure, the acid melted at 239° and was identical with the acid obtained with hydrogen peroxide (the mixed melting point was not depressed). Titration and carbon and hydrogen determinations gave the following results: C, 57.15; H, 6.72; mol. wt. (titration calcd. as 1 COOH group), 461.

Hydrolysis of the 233°-Melting Compound.—A suspension of 0.5 g. of the 233°-melting compound in 5 cc. of 0.4% hydrochloric acid was boiled for approximately one minute. The suspended material quickly dissolved, and at the same time a new material separated. The mixture was cooled and allowed to crystallize for an hour. The resulting white crystals were separated and the compound was identified as tenulin by its melting point (194–195°), its failure to depress the melting point of an authentic sample of tenulin, and its optical crystallographic properties.

The mother liquors were neutralized and evaporated under reduced pressure to about 1 cc. and then treated by shaking with 0.4 cc. of benzoyl chloride and 10 cc. of 10%

sodium hydroxide. The resulting benzoyl derivative was recrystallized from 50% ethanol. It melted at 73° and did not depress the melting point of an authentic sample of dibenzoyl ethylene glycol.

Summary

The compound, m. p. 233°, obtained from a certain lot of *Helenium tenuifolium* and reported as having the composition $C_{16}H_{22}O_5$ has now been shown to have the molecular formula $C_{19}H_{26}O_6$. It is an ether with properties characteristic of an acetal and is formed by a reaction involving the elimination of a molecule of water from ethylene glycol (used as a solvent in its preparation) and tenulin.

The formation of this compound further substantiates the suggestion that tenulin contains a sterically hindered hydroxyl group, and that this group and the acetoxy group of tenulin are probably adjacent to each other.

WASHINGTON, D. C.

RECEIVED MAY 29, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

The Bromination of 2-Naphthyl Benzoate

BY STEWART E. HAZLET

In previous studies on esters containing diphenyl groups it has been shown that hydroxy and acetoxy groups direct an entering bromine atom to the same position,¹ but that benzoyloxy² or benzenesulfonyloxy³ groups in place of the smaller ones cause the bromine atom to enter the molecule at a more remote position.

These results suggested that 2-naphthyl benzoate might brominate in the ring not bearing the benzoyloxy group. It was found, however, that bromination of this ester took place in position 1. The product was definitely proved to be 1-bromo-2-naphthyl benzoate by its hydrolysis to 1-bromo-2-naphthol.

Experimental Part

2-Naphthyl Benzoate.⁴—This compound was prepared by the action of benzoyl chloride on 2-naphthol in pyridine as in similar syntheses.⁵ After recrystallizations from methanol, the yield of material melting at 105°⁴ was 81%.

The Bromination of 2-Naphthyl Benzoate.—Ten grams of 2-naphthyl benzoate was dissolved in 100 ml. of glacial acetic acid with vigorous stirring on a steam-bath. Bromine (3.2 ml., approximately 1.5 molecular proportions) dissolved in glacial acetic acid (10 ml.) was added slowly, and then a trace of iron powder was introduced into the reaction flask. After the vigorous reaction which followed the introduction of the iron had subsided, the stirring and heating were continued for three hours. At the end of this period the reaction mixture was poured into 1000 ml. of water. The product represented only a 40% yield of a monobromo-2-naphthyl benzoate; no other products were recovered. Recrystallizations from methanol resulted in considerable loss, but yielded a product which melted between 98 and 99°.

Anal. Calcd. for $C_{17}H_{11}O_2Br$: Br, 24.41. Found: Br, 24.35, 24.46.

Hydrolysis of the Monobromo-2-naphthyl Benzoate.—One gram of the purified monobromo ester was refluxed gently in a solution which contained 25 ml. of ethanol, 25 ml. of water, and 3 g. of potassium hydroxide. After fourteen hours of refluxing, the ethanol was removed by distillation, more water was added, and the alkaline solution was extracted with ether. Next, carbon dioxide was passed into the aqueous solution. The precipitated phenolic component was extracted with ether and the ethereal solution was dried with anhydrous sodium sulfate in the presence of Norite. The yield of crude bromonaph-

(1) Hazlet and Kornberg, *THIS JOURNAL*, **61**, 3037 (1939).

(2) Hazlet, Alliger and Tiede, *ibid.*, **61**, 1447 (1939).

(3) Hazlet, *ibid.*, **59**, 1087 (1937).

(4) Koenigs and Carl, *Ber.*, **24**, 3900 (1891).

(5) Hazlet, *THIS JOURNAL*, **59**, 287 (1937).