flask was equipped with a condenser, a thermometer (not necessary unless it is desired to maintain a low temperature), a stirrer and a 500-ml. dropping funnel. The solution of the ester was added to the stirred Grignard solution at such a rate that gentle refluxing of the ether occurred. Cooling of the mixture with an ice-bath was sometimes necessary. After the addition was complete (about one hour), stirring was continued at room temperature for two hours. The mixture was hydrolyzed by pouring it onto cracked ice and sufficient dilute sulfuric acid was added to dissolve the precipitated magnesium hydroxide. The ether layer was separated, washed with a saturated sodium carbonate solution, and dried over anhydrous sodium sulfate. Removal of the ether and chloroform by distillation left a solid–liquid mixture. Petroleum ether (50 ml. 65–95° range) was added to the mixture to throw out of solution any dissolved solid. The solid was removed by filtration and washed with a little petroleum ether and the washings were added to the filtrate. Distillation of the filtrate gave 16.1 g. (81%) of crude product. Further fractionation gave 10.2 g. (51%) of 5-methyl-5-nonanol b. p. 91–92° (15 mm.).

The solid was recrystallized from ethyl alcohol. Recovery of pure glucose pentaacetate (identified by m. p. and mixed m. p. with an authentic sample) was 33.3 g. (87.5%). The same recovery of pentaacetate, but only 20% of carbinol, was isolated if reaction conditions were 0–5° and if the mixture was hydrolyzed immediately after the ester was all added (omit the two-hour stirring). Only 19 g. of crude pentaacetate was isolated if the Grignard reagent was added to the ester, but the yield of carbinol was 50%.

When a molar ratio of Grignard reagent (from methyl iodide, ethyl bromide, bromobenzene to β-D-glucose pentaacetate of 10:1) was used the procedure was the same except for the use of a 2 M Grignard diethyl ether solution. No pentaacetate was recovered nor was any sucrose octaacetate recovered when it reacted similarly with 10 moles of ethylmagnesium bromide. In these experiments 55–69% yields of tertiary alcohols were formed.

When an effort was made to duplicate the work of Fischer[2] with 5.0 g. of methyl iodide as the starting material, no carbinol was found and the recovery of pentaacetate was 60%.

When α- and β-D-glucose pentaacetate were compared in a reaction with ethylmagnesium bromide both gave the same result.

Formation of Glucosazone.—The aqueous layer from the preparation of 3-methyl-3-pentanol (a 10:1 ratio of Grignard reagent to ester was used) was treated with phenylhydrazine. The osazone formed had a m. p. of 205°. A mixed m. p. with glucosazone gave the same value.

Summary

The Grignard reagent reacts with β-D-glucose pentaacetate to form tertiary alcohols. No evidence was obtained for the formation of previously reported simple addition products which on hydrolysis would return the ester in its original form.

The Grignard reagent and β-D-glucose pentaacetate react in a molar ratio of 10:1 when the ester is added to the Grignard solution regardless of the ratio of reagents used.

NEW ORLEANS, LA. RECEIVED MAY 8, 1948

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MISSOURI]

The Bitter Principle of *Helenium Tenuifolium*

BY HERBERT E. UNGNADE AND EDWARD C. HENDLEY[1]

The common sneezeweed, *Helenium tenuifolium*[2] contains a colorless crystalline material with an intensely bitter taste which has been the subject of a number of investigations.[3,4,5]

The bitter principle can be obtained from the dried plant material by extraction with water,[4] chloroform[5] or benzene. The highest yields have been obtained by use of benzene and the product is easier to purify in this case.

A comparison by means of a standardized benzene extraction procedure shows that the leaves and flowers of the mature flowering plant contain the largest quantity of the bitter material which amounts to about 3% on a dry weight basis. Stems and roots contain only small amounts of the same material. Immature plants or second growth contain less than mature plants but proportionally more gum.

Purification of the plant extracts yields three substances melting at 152.3–153.3°, 155.3–156.3° and 192–195°. The first two of these are interconvertible. They possess identical absorption spectra and crystallographic constants which agree with those reported by Clark.[5] They must be regarded as crystalline modifications of isotenulin (I).

The high-melting material, m. p. 192–195°, is a benzene complex of Clark's tenulin (II). It is converted to (I) by refluxing with water. While this isomerization undoubtedly occurs when aqueous or wet solvents are used for extracting the plant, some isotenulin has been isolated even from extractions with dry benzene. It is therefore assumed that both (I) and (II) occur in the plant.

Isotenulin (I) is neutral, the *p*H of the saturated solution is 6.7. It consumes two moles of alkali on heating with aqueous alcoholic sodium hydroxide solution. One mole of alkali is accounted for by the acetoxyl group.[5] The product of the alkaline hydrolysis, desacetylisotenulin, isolated by Clark, allows for the loss of one mole of acetic acid. The function which reacts with the second mole of alkali is regenerated on acidification without isomerization because the hydrolysis product

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[1] From the Ph.D. Thesis of E. C. Hendley.

[2] The authors are indebted to Prof. W. E. Maneval of the Botany Department of the University of Missouri for the botanical identification of the plant.

[3] Weathers, *J. Dairy Sci.*, **16**, 401 (1933); MacDonald and Glaser, *Tenn. Agr. Exptl. Sta. Circ.*, **26**, 2 (1929); Herzer, *Proc. Assoc. Southern Agr. Workers*, **43**, 112 (1942).

[4] Buehler, Whitehead and Goodge, THIS JOURNAL, **59**, 2299 (1937).

[5] Clark, *ibid.*, **61**, 1836 (1939); **62**, 597, 2154 (1940).

can be converted back to isotenulin by acetylation.[5] The behavior of this second grouping is suggestive of a saturated lactone.

The ultraviolet absorption spectra of tenulin (II) and isotenulin (I) (Fig. 1) are indicative of an α,β-unsaturated carbonyl group with one α or one β-substituent.[6]

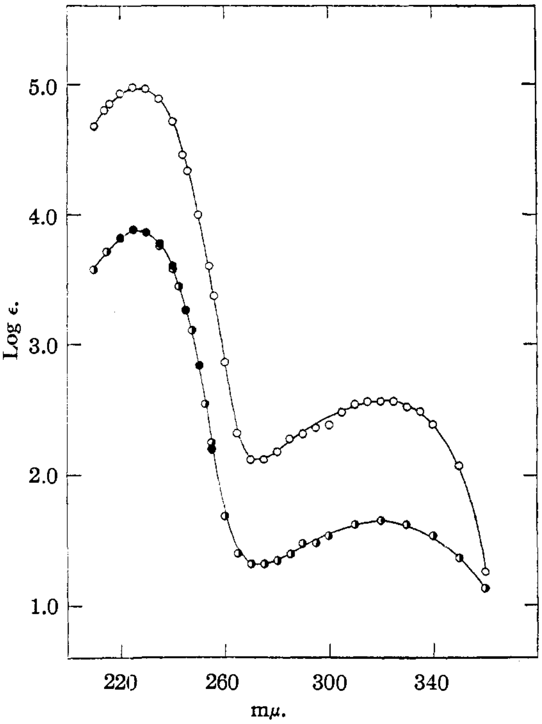

Fig. 1.—Ultraviolet absorption spectra: O, tenulin, m. p. 194–196°; ●, isotenulin, m. p. 152.3–153.5°; ◑, isotenulin, m. p. 155.3–156.3°.

It is not likely that isotenulin contains a hydroxyl group. It does not react with 3,5-dinitrobenzoyl chloride in pyridine and the infrared spectrum fails to show any appreciable absorption in the OH region (Fig. 2). Enol tests are negative.

Experimental[7,8]

Isolation of the Bitter Principle.—The leaves and flowers stripped from the air-dried plants were ground in a mill. The extraction with water was carried out essentially as described by Buehler, *et al.*[4] The dry product from 225 g. of plant material weighed 7.76 g. Chromatographic adsorption of this extract on aluminum oxide (General Chemical Co. Reagent) from benzene solution gave 4.62 g. of crystalline fractions on elution with benzene. Recrystallization and decolorization with Nuchar yielded 1.65 g. of isotenulin, m. p. 152.3–153.3°, and 0.4 g. of the higher melting modification, m. p. 155.3–156.3°.

The chloroform extract of the same plant material (17.73 g.) yielded 0.3 g. of product, melting at 153–154.5°, and 0.32 g., m. p. 182–192°, after crystallization from benzene–Skellysolve C.

Benzene extraction of 18 g. of pulverized plant tissue (leaves and flowers) gave 0.33 g. of crystalline product melting at 150–154° and 0.34 g. melting at 154–157° (total yield 3.72%).

Benzene extraction of ground up stems and roots of the plant by the same method gave only 0.25% of isotenulin, m. p. 150–165°.

Second growth plants (leaves and flowers) yielded 1.18% of crystalline product, m. p. 170–182°, which represents a mixture of substances (I) and (II).

For large scale operation the plant material (300 g., leaves and flowers of mature plants) was refluxed with 2.5 liters of dry benzene for five hours. The extract was filtered and the filtrate was concentrated to a volume of 225 cc. by distillation. On standing at room temperature, 9.32 g. (3.1%) of green-yellow solid separated. Crystallization from benzene and decolorization with Nuchar gave 0.65 g. of colorless product melting at 192–195° for each gram of crude. Chromatographic adsorption of the crude (1.0 g.) yielded 0.20 g. of isotenulin (m. p. 152–154°).

The high melting material (m. p. 192–195°) differed from Clark's tenulin in its crystallographic constants, α, 1.548; β, 1.565; γ, 1.612; $2V$, 65–70°; extinction parallel; $r > v$; optical sign (+) and was found to contain $^3/_4$ mole of benzene of crystallization.

Anal. Calcd. for $C_{17}H_{22}O_5\cdot{}^3/_4C_6H_6$: C, 70.75; H, 7.41. Found: C, 71.02; H, 7.58.

Further crystallizations from benzene gave a constant melting point of 183–185°. This material varied only slightly in composition from the first complex.

Anal. Found: C, 71.21; H, 7.57.

Analytically pure tenulin was obtained from the complexes by heating for six to eight hours at 150° (1×10^{-4} mm.) over paraffin shavings. The solvent-free substance melted at 194–196°.

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.58; H, 7.32.

Tenulin was found to be much more strongly adsorbed on alumina than isotenulin. This difference in behavior has been utilized for the separation of the two substances. Pure tenulin failed to isomerize when adsorbed on aluminum oxide.

Isotenulin (I).—Pure crystalline material, m. p. 152.3–153.3° was obtained either directly from the plant or by conversion of the high melting substance (II) (m.p. 192–195°) by refluxing with water for fifteen minutes. It was crystallized from water or from benzene–Skellysolve C mixtures.

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.63; H, 7.21; mol. wt., 306.35. Found: C, 67.04; H, 7.74; mol. wt., 314.14 (Rast).

The solubility of the pure substance in distilled water at 25° was 0.20 g. per 100 cc. The *p*H of the saturated solution as determined with a standard Beckman instrument was 6.7 (28°).

Repeated crystallizations from benzene–Skellysolve C effected a conversion to the higher melting form, m. p. 155.3–156.3°. Mixed melting points of the two forms were found to be between the values for the melting points of the pure substances (154–155°). On the Kofler hot-stage the two forms showed melting points of 154 and 158°, respectively. The high melting modificaton is undoubtedly identical with the product of Buehler, *et al.*[4] (m. p. 158°).

Optical crystallographic properties of the crystalline modifications:

Low melting form: α, 1.521; β, 1.548; γ, 1.559; optical sign (−); $2V$, 70° ± 5°, extinction parallel, $r > v$ strong.

High melting form: α, 1.520; β, 1.550; γ, 1.558; optical sign (−); $2V$, 70° ± 5°, extinction parallel, $r > v$ strong.[9]

A sample of purified isotenulin made available by Professor Roger Adams of the University of Illinois melted at

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(6) Woodward, *ibid.*, **64**, 76 (1942).

(7) All temperatures except micromelting points uncorrected.

(8) Analyses by Karl T. Zilch and R. A. Carpenter.

(9) The authors are indebted to Dr. W. D. Keller of the University of Missouri Geology Department for the determination of the constants.

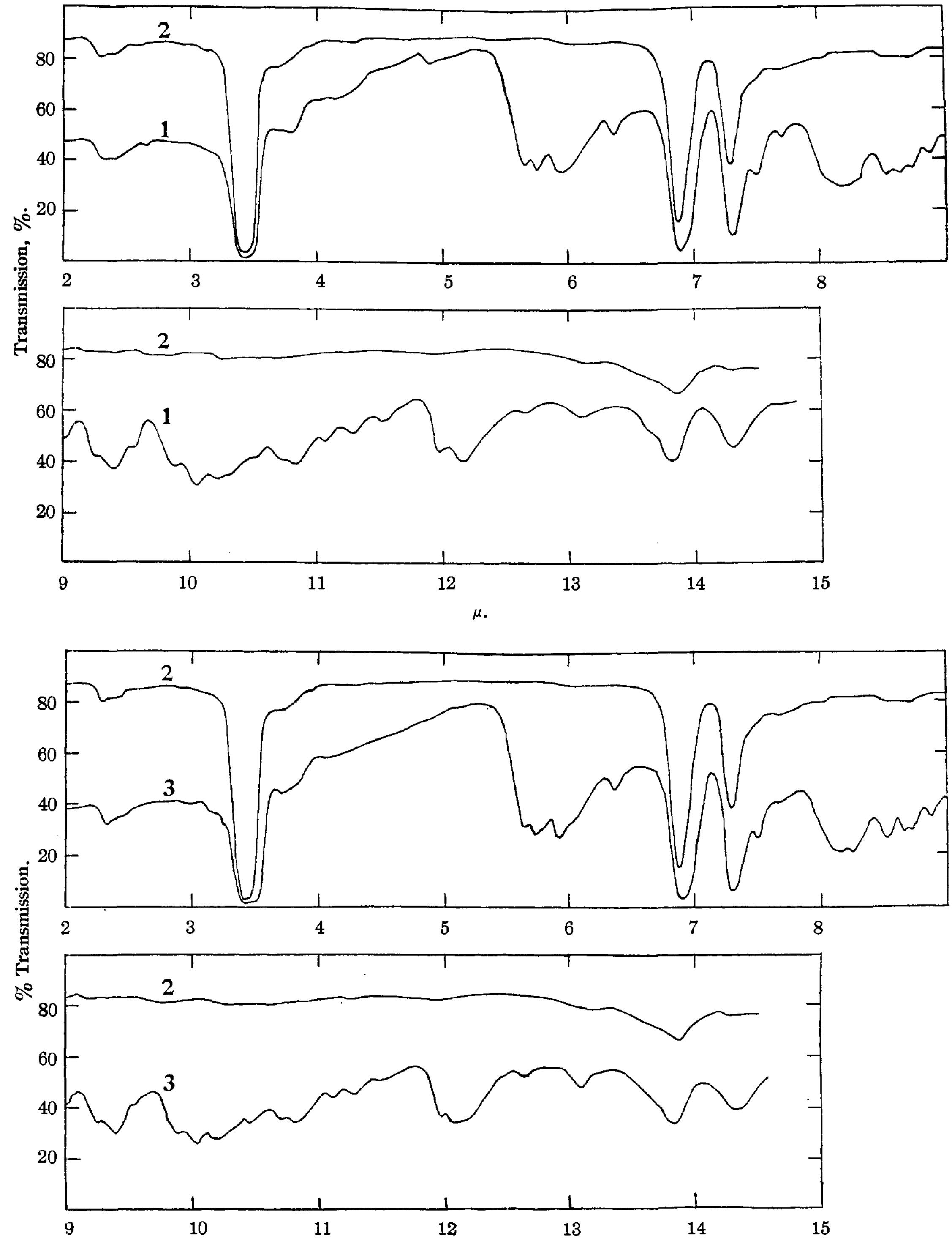

Fig. 2.—Infrared absorption spectra: 1, isotenulin, m. p. 157.5° (micro) of Dr. Adams; 2, Nujol; 3, isotenulin, m. p. 152.3–153.5°.

157.5° (micro). The mixture with the high melting modification obtained in the present investigation melted at 158° (micro). The crystallographic constants of Dr. Adams' sample were: α, 1.520; β, 1.549; γ, 1.559; optical sign (−), extinction parallel, $2V$, 65–70°, $r > v$ strong.[10]

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[10] The authors are indebted to Professor Adams for the sample of isotenulin and for his valuable suggestions.

Absorption Spectra.—The ultraviolet absorption spectra of the two polymorphic forms of isotenulin and of tenulin (Fig. 1) were determined in 95% alcohol with a Beckman spectrophotometer.[11] The concentration was 0.0000709 mole per liter.

The infrared spectra (Fig. 2) of isotenulin, m. p. 152.3–153.5°, and the sample of Dr. Adams were determined with a Beckman IR2 spectrophotometer as Nujol mulls in a 0.050-mm. cell against air as reference.[11] The spectra agreed in virtually every significant band.

The Action of Alkali on Isotenulin.—The pure compound (0.1 g.) (m. p. 152.3–153.3°) was dissolved in a solution of 10 cc. of 0.1247 N aqueous sodium hydroxide and 20 cc. of ethyl alcohol. The resulting solution was refluxed for one hour in an atmosphere of nitrogen. Titration with 0.1058 *N* hydrochloric acid against phenolphthalein showed a consumption of 2.09 moles of alkali. When an identical mixture was allowed to stand for twenty-four hours at room temperature, 1.7 moles of alkali was used.

Summary

The bitter principle of *Helenium tenuifolium*, tenulin, has been isolated from the dried plant by an improved method of extraction. It probably occurs in the plant together with the isomeric isotenulin.

Isotenulin contains besides the previously established acetoxyl group probably an α,β-unsaturated carbonyl group and a group which consumes one mole of alkali and is tentatively assigned a lactone structure.

COLUMBIA, MISSOURI RECEIVED APRIL 12, 1948

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(11) Absorption spectra by Dr. E. E. Pickett, University of Missouri.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BENARES HINDU UNIVERSITY]

Production of *Joshi-Effect* in Bromine Vapor under Silent Electric Discharge

BY G. S. DESHMUKH AND S. SIRSIKAR

Previous work[1,2,3] reported occurrence of the above *effect* Δi an instantaneous and reversible photo-decrease of the discharge current i in chlorine, bromine, iodine, oxygen, air, nitrogen and hydrogen. Results[1,4,5,9,10] of detailed investigation in these laboratories in the case of the chlorine gas, in which Δi is apparently most pronounced and easiest to study, have shown that under favorable conditions, it can be as high as 93% current suppression employing but ordinary light.[4] Preliminary work[3] with the last six of the above gases showed that under arbitrary conditions Δi varied from 7% in bromine vapor to about 0.1% in hydrogen. Using improved technique and Joshi's deduction[5,6,7,8] of the maximizing influence on Δi of the gas pressure, excitation near "threshold potential," and a moderately low temperature, the present work has revealed that remarkably enough, the *Joshi-effect* in bromine vapor reaches almost a 100% current decrease (*vide infra*).

Experimental

The general experimental procedure and apparatus used were essentially the same as described elsewhere.[3] Bromine vapor purified carefully by fractionation over liquid air, and freed from uncondensable impurities by pumping off with a Töpler, was frozen in a small bulb sealed serially with the annular space of a Siemens type (glass) ozonizer (Fig. 1). The amount of bromine introduced in the system was such that at even the highest temperature (about 75°) employed during these experiments, some liquid phase remained. The bromine (vapor) pressures for these temperatures were obtained by interpolation from a log p–t curve, using Ramsay and Young's data[11] (*cf.* inset curve A, Fig. 3).

Joshi[1,6,7] has shown that relatively, Δi may be enhanced by increasing the area of the excited surface. A large size ozonizer (about 100 cm. long and 4 cm. in diameter) was therefore, employed. This proved to be a marked advantage in increasing greatly the magnitude of Δi compared with earlier results[2,3]; also, it enabled a study over a wider range of exciting potentials, the general influence of the gas pressure and temperature on the production of Δi considered in Joshi's theory.[8]

The ozonizer was surrounded by a large-size glass jacket filled with water (Fig. 1); this served to reduce any temperature fluctuations during a given series of observations and also minimize any heating effects due to the discharge; and irradiation used for the production of Δi. The entire system was enclosed in an electrically heated asbestos chamber (Fig. 1). It had a glass window of about the ozonizer size fitted with an asbestos shutter worked by a pulley. The inner tube of the ozonizer filled with salt solution and forming one electrode, was connected through a 20,000-ohm Dubilier type stabilizing resistance to one of the secondaries of a H.T. transformer; its other terminal was earthed. The outer electrode of the ozonizer (L.T. in Fig. 1) formed with salt solution was also earthed through a Cambridge a.c. microammeter (μ_A in Fig. 1) of the double wave, metal oxide, rectifier type, which served to measure the

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(1) Joshi, Presi. Addr. Chem. Sec., Indian Sci. Cong. (1943).

(2) Joshi and Deshmukh, *Nature*, **147**, 806 (1941).

(3) Deshmukh, *J. Indian Chem. Soc.*, **24**, 211 (1947).

(4) Joshi and Deo, *Nature*, **153**, 434 (1944).

(5) Joshi, *Proc. Indian Acad. Sci.*, **A22**, 225, 293, 389 (1945).

(6) Joshi, *Curr. Sci.*, **15**, 281 (1946); **8**, 548 (1939).

(7) Joshi, *ibid.*, **16**, 19–21 (1947).

(8) Joshi, *Proc. Indian Sci. Cong., Phys. Sec.*, Abst. 26 (1946); *ibid.* (1947).

(9) Deo, *Proc. Indian Acad. Sci.*, **A21**, 76 (1945).

(10) Joshi, *Nature*, **154**, 147 (1944).

(11) *Cf.* Kaye and Laby, "Physical and Chemical Constants," Longmans, 1936, p. 44.