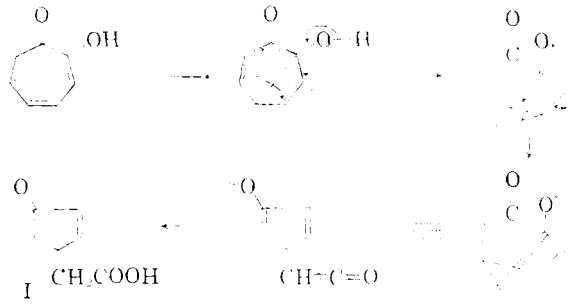
acids. The latter acid has been reported by Farmer[6] (semicarbazone, m.p. 199°) but the material employed in the present study was prepared by Arndt–Eistert chain elongation of 3-oxocyclopentane-1-carboxylic acid.[7] The infrared spectrum of the 2-oxo- derivative possessed bands at 1010 and 1118 cm.$^{-1}$ not shown by the 3-oxo-isomer and the spectrum of the dihydro irradiation material was identical with that of the 3-oxo-derivative. Furthermore, the semicarbazones of the dihydro material and the 3-oxo- isomer melt at 203.0–203.4° and show no depression upon admixture while the same derivative of the 2-oxo-isomer melts at 192.0–192.4° and upon admixture with either of the foregoing materials shows a m.p. depression. With the placement of the carbonyl group at C-3, in respect to the acetic acid side-chain, it follows that in the original irradiation product the only position for the olefinic linkage which gives rise to an unsubstituted cyclopentenone chromophore is between C-4 and C-5, thus forming structure I.

The formation of this material is viewed (shown below) as proceeding via an initial "photo" product of the 3,2,0-bicycloheptadiene type. In line with this postulate of a ketene intermediate, it is found that when α-tropolone is irradiated in ethanol, the ethyl ester of *I* is obtained.



I

(6) E. H. Farmer, *J. Chem. Soc.*, **123**, 3324 (1923).

(7) E. Hope, *ibid.*, 892 (1912); kindly supplied by Professor D. S. Noyce.

(8) National Science Foundation Predoctoral Fellow, 1959–1960.

(9) National Science Foundation Predoctoral Fellow, 1958–1959.

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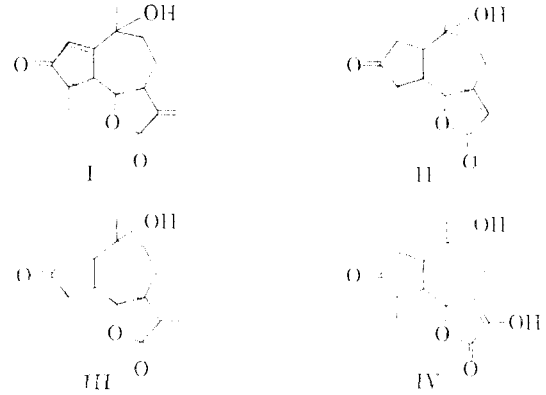
RECEIVED SEPTEMBER 8, 1959

PARTHENIN, A NEW GUAIANOLIDE

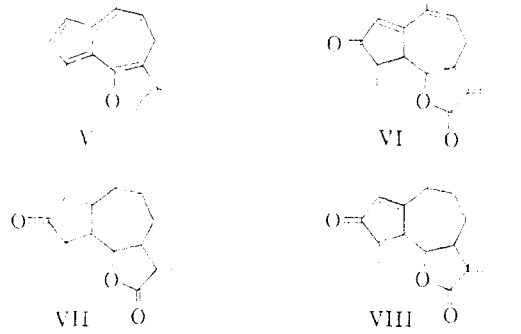
Sir:

The structure of parthenin,[1] the bitter principle of *Parthenium hysterophorus* L., may be represented as I.

Parthenin, isolated in 0.14% yield, has the formula $C_{15}H_{18}O_4$, mol. wt. (Rast) 270, (C, 68.80; H, 7.13) m.p. 163–166°, $[\alpha]^{25}D$ + 7.02°, infrared bands ($CHCl_3$) at 3450 (–OH), 1755 and 1658 (α,β-unsaturated γ-lactone), 1718 and 1592 cm.$^{-1}$ (cyclopentenone), λ_{max} (ethanol) 215 and 340 mμ (ϵ 15100 and 22). Catalytic hydrogenation gave dihydroparthenin (II, C, 68.24; H, 7.24), m.p. 142–144°, $[\alpha]$ + 16.6, infrared bands at 3450 (–OH), 1745 (combination of conjugated lactone and cyclopentanone) and 1668 cm.$^{-1}$ (strong, conjugated C=C), λ_{max} 220 and 261 mμ (ϵ 14000 and 70), and tetrahydroparthenin (III, C, 67.44; H, 8.26), m.p. 140–144°, $[\alpha]$ + 78.4, infrared bands at 3450 and (in acetonitrile) 1760 (γ-lactone) and 1742 cm.$^{-1}$ (cyclopentanone), λ_{max} 277 mμ (ϵ 71).[2]



That the methylene group is conjugated with the lactone carbonyl is shown by the spectra, the preparation of a pyrazoline,[3] a comparison of the C-methyl values of I and III and low temperature ozonolysis which resulted in formaldehyde and a compound $C_{14}H_{16}O_4$ (IV, C, 63.62; H, 5.88). Lithium aluminum hydride reduction of parthenin followed by dehydrogenation over palladium charcoal gave artemazulene (V). This determines the carbon skeleton and the point of attachment of the lactone ring.



The hydroxyl group is tertiary (resistance of I to chromic acid oxidation and acetylation). Its placement at C_{10} of the guaianolide skeleton is dictated, *inter alia*, by the results of periodate titration of II and III (negative in neutral and alkaline solution) and dehydration of parthenin with formic acid which led to a dienone (VI, C, 74.08; H, 6.74), m.p. 125–126°, infrared bands at 1758, 1700, 1650 and 1550 cm.$^{-1}$, λ_{max} 210 and 296 mμ (ϵ 14300 and 12500).

The cyclopentanone carbonyl is placed at C_3 as in helenalin,[4] tenulin[5] and balduilin.[6] None of

(1) H. V. Arny, *J. Pharm.*, 121 (1890); 169 (1897).

(2) *Cf.* the hydrogenation of ambrosin L. Bernardi and G. Büchi, *Experientia*, **13**, 466 (1957); F. Šorm, M. Suchý and V. Herout, *Coll. Czechoslov. Chem. Commun.*, **24**, 1548 (1959).

(3) P. G. Deuel and T. A. Geissman, THIS JOURNAL, **79**, 3778 (1957).

(4) G. Büchi and D. Rosenthal, *ibid.* **78**, 3860 (1956).

(5) D. H. R. Barton and P. de Mayo, *J. Chem. Soc.*, 142 (1956); C. Djerassi, J. Osiecki and W. Herz, *J. Org. Chem.*, **22**, 1361 (1957); W. Herz and R. B. Mitra, THIS JOURNAL, **80**, 4876 (1958).

(6) W. Herz, R. B. Mitra and P. Jayaraman, *ibid.*, **81**, 6061 (1959).

the fractions obtained by ozonolysis of parthenin at room temperature, which also results in the formation of formic acid, gave a positive iodoform test and the n.m.r. spectrum of parthenin had no signal corresponding to the $=C-CH_3$ peaks present, for example, in the n.m.r. spectra of dihydroparthenin (II), anhydroparthenin (VI), neotenulin and santonin.

One of the several reduction products of VI, hexahydroanhydroparthenin (VII), proved to be identical with tetrahydroambrosin.[7,8] This provides proof for the previously assumed structure of ambrosin (VIII)[7] and shows that I and VIII have the same stereochemistry at C_4, C_5, C_6 and C_7. The rotatory dispersion curve[9] of III is almost superimposable on that of tetrahydrohelenalin which suggests the absolute configuration at C_1, C_4 and C_5.

Acknowledgment.—This investigation was supported by a grant from the United States Public Health Service (RG-5814).

(7) (a) H. Abu-Shady and T. D Soine, *J. Am. Pharm. Assoc.*, **42**, 387 (1953); **43**, 365 (1954); (b) L. Bernardi and G. Büchi, *Experientia*, **13**, 466 (1957); (c) F. Šorm, M. Suchý and V. Herout, *Coll. Czechoslov. Chem Commun.*, **24**, 1548 (1959).

(8) We wish to thank Dr. V. Herout for carrying out the comparison.

(9) Kindly determined by Professor C. Djerassi.

(10) Recipient of a Fulbright Travel Grant 1958–1959.

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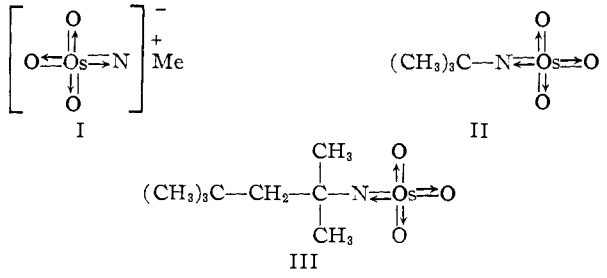
RECEIVED OCTOBER 2, 1959

ORGANIC OSMIAMATES[1]

Sir:

Osmiamates (I)[2] in which the osmium is octovalent are not known in Organic Chemistry. We wish to report the synthesis of two organic osmiamates: *t*-butyl osmiamate (II) and 1,1,3,3-tetramethylbutyl osmiamate (III) which were obtained as a result of our general studies on the reaction of osmium tetroxide with various groups of organic compounds.[3,4] *t*-Butyl osmiamate was prepared by allowing osmium tetroxide (1.0 g.) in 50 cc. of pure ligroin to drop slowly with stirring at 0° and preferably in a nitrogen atmosphere into a ligroin solution (25 cc.) of excess (7.0 g.) of *t*-butylamine. Stirring was continued for 24 hours whereby an orange precipitate separated out and was removed by filtration. This was recrystallized several times from hot pure *n*-pentane at −10° into hair-like, orange-yellow crystals which agglomerated like cotton fibers; yield, 65%; m.p. 110°. This compound also can be prepared in aqueous solutions.



I

II

III

(1) Supported by NIH Contract B-1493(C1).

(2) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, 1950, p. 1507.

(3) N. A. Milas, J. H. Trepagnier, J. T. Nolan, Jr., and M. I. Iliopulos, THIS JOURNAL, **81**, 4730 (1959).

(4) N. A. Milas and M. I. Iliopulos, NIH Report, March (1959).

Anal. Calcd. for $C_4H_9NO_3Os$: N, 4.53; Os, 61.48; mol. wt., 309. Found: N, 4.68; Os,[5,6] 60.08; mol. wt., 303 (cryoscopic in benzene).

With the thiourea reagent[3] *t*-butyl osmiamate gave an immediate pink coloration characteristic for octovalent osmium. A paper chromatogram developed with ligroin–*t*-butyl alcohol mixture, 90:10 v./v., gave an R_f of 0.68 (32°). An infrared spectrum 10% in $CHCl_3$ showed a strong band, absent in the infrared spectrum of the amine, at 910–915 cm.$^{-1}$ compared with that of osmium tetroxide at 951 cm.$^{-1}$. Bands usually attributed to the amino or hydroxyl hydrogens were absent. An ultraviolet spectrum in *t*-butyl alcohol gave a maximum at 323 mμ; ϵ, 4066.

1,1,3,3-Tetramethylbutyl osmiamate (III) was prepared in exactly the same way as the *t*-butyl osmiamate; yield, 69%; m.p. 51.5° (*n*-pentane).

Anal. Calcd. for $C_8H_{17}NO_3Os$: N, 3.83; Os, 52.04. Found: N, 3.80; Os, 51.89.

This osmiamate also gave an immediate pink color with the thiourea reagent and on a paper chromatogram an R_f value of 0.87 (32°). The infrared spectrum 10% in $CHCl_3$ showed a strong band at 910–915 cm.$^{-1}$ with the amino and hydroxyl hydrogen bands absent. The ultraviolet spectrum in *t*-butyl alcohol showed a strong band with a maximum at 323 mμ; ϵ, 3650.

Both osmiamates react with dilute sulfuric acid to give osmium tetroxide and the sulfates of the original amines. They deflagrate spontaneously on a hot plate and show strong oxidizing properties; they react with olefins in the same manner as osmium tetroxide. These and other reactions of osmiamates are now being investigated and will be reported later.

Acknowledgment.—The authors are indebted to Dr. Shin-ichi Sasaki and Mrs. J. A. Hilton for technical assistance, to Dr. S. Nagy for the nitrogen analysis and to Rohm and Haas for a supply of 1,1,3,3-tetramethylbutylamine.

(5) W. Geilmann and R. Neeb, *Z. anal. Chem.*, **156**, 420 (1957).

(6) R. Criegee, *Ann.*, **522**, 75 (1936); R. Criegee, B. Marchand and H. Wannowius, *ibid.*, **550**, 99 (1942). Criegee, *et al.*, indicated that osmium analyses gave always low values.

(7) NIH Postdoctorate Research Associate, Fulbright Traveling Fellow.

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RECEIVED OCTOBER 13, 1959

THE BIOLOGICAL CONVERSION OF SYNTHETIC METHOSTENOL-4-C^{14} TO CHOLESTEROL[1]

Sir:

We have reported recently that sodium acetate-1-C^{14} injected into rats intracardially becomes incorporated into the methostenol (4α-methyl-Δ^7-cholesten-3β-ol) of the skin and liver–small in-

(1) This investigation was supported by a research grant (H-2458-C3) from the National Institutes of Health, Public Health Service.